CALCULATIONS IN
CHEMISTRY

John Olusina Obimakinde
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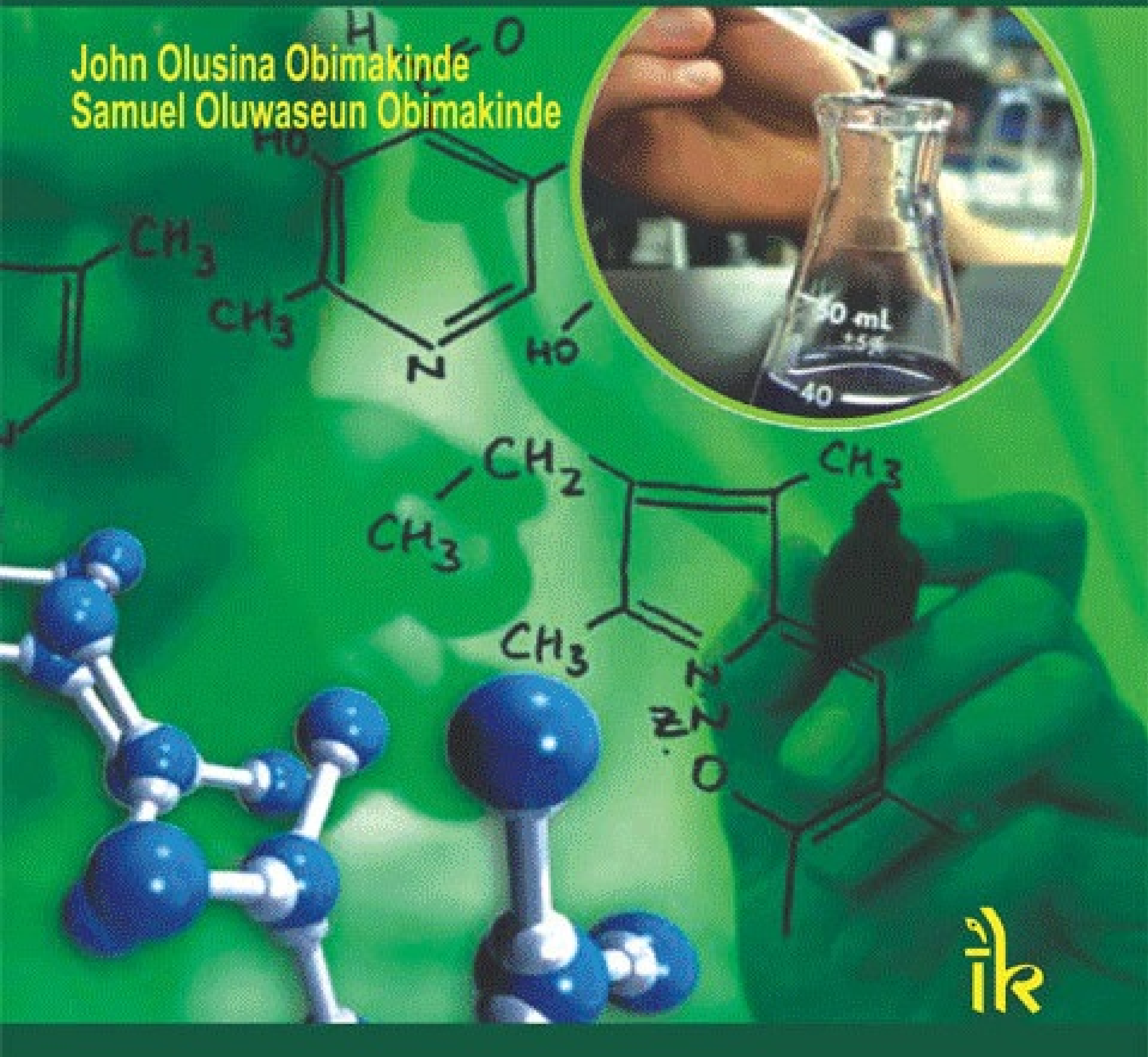

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Dedication

To our wives and children

Preface

We have written this book to help students overcome the challenges posed by the numerical problems in chemistry. 'Calculations in Chemistry' presents the numerical problems of chemistry in a simple, logical and down-to-earth manner that conveys enthusiasm and facilitates learning.

This book has been deliberately structured to make teaching and learning easy. To start with, each chapter or section begins with a clear, concise introduction that explains fundamental concepts and the theoretical basis of each type of calculation. This is directly followed by numerous representative examples that are presented in step-wise manner and simple language. The solved examples are followed by one or more practice problems, to which answers are supplied, to test what has been treated earlier on. In addition, we have provided a comprehensive summary at the end of each chapter as a checklist of key terms and concepts that you are expected to know and remember. At the end of each chapter are numerous exercises, including objective questions, to practise with and boost your confidence. Answers are supplied to all numerical problems.

One of our cardinal guidelines, during the course of writing this book, was to include the entire range of problems you will encounter at this level. However, if you think there is something we ought to have included, then feel free to write us; we will be more than happy to hear from you. We hope you will find this book useful and, above all, be the best you can be!

We regret that we have not been able to locate, despite all attempts, to locate the copyright holders of Figures 1.1, 2.2, 4.1, 4.2, 4.3, 4.5, 4.8, 4.9, 4.10, 4.12, 4.13, 4.14, 5.2, 5.4, 5.5, 5.6, 5.7, 6.3, 6.4, 6.5, 6.6, 6.7, 7.1, 7.2, 7.3, 9.1, 9.2, 9.3, 9.4, 10.4, 10.6, 11.1, 11.2, 12.1, 12.2, 12.3, 12.4, 14.1 and 14.2. We will appreciate any information that will enable us do so.

We express our profound gratitude to God, the source of knowledge, for giving us the wherewithal to undertake a project of this magnitude successfully. Acknowledgements and thanks are, also, due to the many wonderful people, too numerous to mention, who contributed to the successful publication of this book. Lastly, we thank our wives, who had to take the second place during the years of writing this book, for their understanding, patience and support.

Lagos,
Nigeria **John Olusina**
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April 2014 **Samuel**
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Contents

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Chapter Masses and Formulae

Chemistry is the study of the nature, composition and properties of matter,[1] and the changes it undergoes. Matter is classified into elements, compounds and mixtures. An element is a simple substance that cannot be split into simpler substances by ordinary chemical means. Examples of elements include hydrogen, chlorine, sodium, mercury, oxygen, uranium, neon manganese, cobalt, etc.

Elements are represented by means of chemical symbols. The symbols of elements comprise one to three letters which are derived as follows:

- Using the first letter of the name of the element. Examples are given in Table 1.1.

Table 1.1: Symbols of elements

Element	*Symbol*
Hydrogen	H
Carbon	C
Fluorine	F
Iodine	I
Yttrium	Y

Nitrogen	N
Oxygen	O
Sulphur	S
Uranium	U

- Using the first two letters of the name of the element. Examples are given in Table 1.2.

Table 1.2: Symbols of elements

Element	*Symbol*
Tellurium	Te
Radium	Ra
Polonium	Po
Aluminium	Al
Calcium	Ca
Cobalt	Co
Indium	In
Argon	Ar

- Using the first and any other letter of the name of the element. Examples are given in Table 1.3.

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[1] Matter is anything that has mass and occupies space.

Table 1.3: Symbols of elements

Element	*Symbol*
Chlorine	Cl
Magnesium	Mg
Mendelevium	Md
Neptunium	Np
Zinc	Zn
Niobium	Nb
Platinum	Pt
Palladium	Pd

- Using letter(s) from the Latin name of the element. Examples are given in Table 1.4.

Table 1.4: Symbols of elements

Element	*Latin name*	*Symbol*
Gold	Aurum	Au
Potassium	Kalium	K
Silver	Argentum	Ag
Mercury	Hydrargyrum	Hg

Sodium	Natrium	Na
Copper	Cuprum	Cu
Tin	Stannum	Sn
Iron	Ferrum	Fe
Lead	Plumbum	Pb

- Using the first and any other two letter from the name of the element. Examples are given in Table 1.5.

Table 1.5: Symbols of elements

Element	*Symbol*
Ununbium	Uub
Ununtrium	Uut
Ununhexium	Uuh
Ununquadium	Uuq
Ununoctium	Uuo
Ununpentium	Uup
Ununseptium	Uus

- The symbol of tungsten, W, is derived from its German name, *wolfram*.

Figure 1.1 Jöns Jacob Berzelius (1779–1848), the Swedish chemist who introduced the chemical symbol in 1814.

A compound consists of two or more elements that are chemically combined together. Examples include water, H_2O; sucrose, $C_{12}H_{12}O_{22}$; sodium chloride, NaCl; sodium carbonate, Na_2CO_3; sodium hydroxide, NaOH; ammonia, NH_3; etc.

A mixture consists of two or more substances that are physically combined together. The constituents of a mixture could be elements, compounds, or a combination of both. Examples of mixtures and their constituents are given in Table 1.6. The differences between compounds and mixtures are given in Table 1.7.

Table 1.6: Mixtures and their constituents

Mixture	*Normal state*	*Constituents*
Air	Gaseous	Oxygen, nitrogen, water vapour, carbon dioxide and rare gases
Blood	Liquid	Plasma, white blood cells, red blood cells, platelets, hormones, etc.
Brass*	Solid	Copper and zinc
Bronze*	Solid	Copper and tin
Steel*	Solid	Iron and carbon
Urine	Liquid	Water, urea and mineral
		Salts

Crude oil	Liquid	Gas, petrol, kerosene, bitumen, gas oil, etc.

* These metals are called alloys. An alloy is obtained by adding one or more elements to a metal. Alloys usually have much more desirable properties over their base metals.

Table 1.7: Differences between mixture and compound

Mixture	*Compound*
Constituents are mixed in any ratio of masses	Constituents are mixed in a definite ratio of masses
Constituents retain their identities	Constituents lose their identities
Can either be homogeneous or heterogeneous	It is always homogeneous
Constituents can be separated by chemical means like electrolysis	Constituents can be separated by physical means like filtration, chromatography, decantation, etc.

1.1 RELATIVE ATOMIC AND MOLECULAR MASSES

The relative atomic mass A_r of an element is the number of times the average mass of one mole of its atoms is as heavy as one-twelfth the mass of one atom of carbon-12. While approximate values are often used in calculations, it should be well noted that the actual values of relative atomic masses are not usually whole numbers due to the existence of isotopes. The relative atomic masses of elements are listed in Appendix 6.

The relative molecular mass M_r of a substance is the number of times the average mass of one mole or molecule of that substance is as heavy as one-twelfth the mass of one atom of carbon-12. It has no units since it is only a ratio. The relative molecular mass of a substance is obtained by summing up the masses of the elements appearing in its chemical formula. The total mass of an element in a substance is obtained by multiplying its relative atomic mass by its subscript as it appears in the molecular formula of the substance. If, for example, the chemical formula of a substance is $A_xB_yC_z$, it then follows that

$$M_r = (A_{rA} \times x) + (A_{rB} \times y) + (A_{rc} \times z)$$

The molar mass M of a substance, measured in g mol^{-1}, is defined as the mass of one mole of that substance. The molar mass of a substance is its relative molecular mass expressed in g mol^{-1}, while that of an element is its relative atomic mass expressed in g mol^{-1}.

Example 1 Calculate the relative molecular mass and molar mass of hydrogen gas, H_2.

(H = 1)

Solution Since the relative atomic mass of hydrogen is 1, then

$M_r = 1 \times 2 = 2$
So $M = 2$ g mol^{-1}

Example 2 Calculate the relative molecular mass and molar mass of water, H_2O.

(H = 1, O = 16)

Solution
$M_r = (1 \times 2) + (16 \times 1) = 18$
Thus $M = 18$ g mol^{-1}

Example 3 Determine the molar mass of calcium hydroxide, $Ca(OH)_2$.

(H = 1, O = 16, Ca = 40)

Solution We approach this problem in much the same way as we did above, i.e.

$M = [(40 \times 1) + (16 \times 2) + (1 \times 2)]$ g mol^{-1}
$= [40 + 32 + 2]$ g $mol^{-1} = 74$ g mol^{-1}

Example 4 Determine the molar mass of iron(III) sulphate, $Fe_2(SO_4)_3$.

(O = 16, S = 16, S = 32, Fe = 56)

Solution
$M = [(56 \times 2) + 3\{32 + (16 \times 4)\}]$ g mol^{-1}
$= [112 + (3 \times 96)]$ g $mol^{-1} = 400$ g mol^{-1}

Example 5 Determine the molar mass of copper(II) sulphate-5-water, $CuSO_4.5H_2O$.

(O = 16.0, S = 32.1, Cu = 63.5)

Solution

M = [63.5 + 32.1 + (16.0 × 4) + 5{(1.0 × 2) + 16.0}] g mol^{-1}
= [95.6 + 64.0 + 90.0] g mol^{-1} = 249.6 g mol^{-1}

Practice Problems

1. Determine the molar mass of oxygen gas, O_2.
   (O = 16) [*Answer:* 32 g mol^{-1}]
2. Calculate the molar mass of sodium carbonate, Na_2CO_3.
   (C = 12, O = 16, Na = 23) [*Answer:* 106 g mol^{-1}]
3. What is the relative molecular mass of iron(II) sulphate-7-water, $FeSO_4.7H_2O$?
   (H = 1, O = 16, S = 32, Fe = 56) [*Answer:* 278]

1.2 MASS PERCENTAGE COMPOSITION

The percentage composition by mass of an element in a substance is its percentage contribution to the overall mass of that substance. The percentage composition of an element X in the compound X_xY_y is given as

$$\% \text{ composition} = \frac{xA_{r,X}}{M_r} \times 100\%$$

The percentage composition of an element in a pure substance is constant, regardless of the mass of the substance under consideration.

A commonly used method of elemental analysis is combustion analysis. Combustion analysis involves the complete combustion of a substance, and weighing the products. The mass compositions of the elements in the sample can be obtained from the masses of the products obtained by using the relation

$$x = \frac{n \times A_r}{M_r} \times m$$

where x = Mass composition of an element.
M_r = Relative molecular mass of the product of combustion containing the

element.

m = Mass of the product.
n = Number of atoms of the element present in the product.

The combustion of organic compounds produces carbon dioxide and water vapour. The combustion of hydrocarbons is given by the equation

$$C_xH_y + (x + y/4)O_2(g) \rightarrow xCO_2(g) + y/2H_2O(g)$$

The combustion of organic compounds containing hydrogen, carbon and oxygen is given by the equation

$$C_xH_yO_z + (x + y/4 - z/2)O_2(g) \rightarrow xCO_2(g) + y/2H_2O(g)$$

Example 1 Calculate the percentage composition by mass of each element in Na_2CO_3.

(C = 12, O = 16, Na = 23)

Solution The very first step is to determine the relative molecular mass of the compound.

$M_r = (23 \times 2) + 12 + (16 \times 3)$
$= 46 + 12 + 48 = 106$

For sodium we have

% composition $= \frac{23 \times 2}{106} \times 100\%$

So % composition $= \frac{46}{106} \times 100\% = 43.4\%$

For carbon we have

% composition $= \frac{12}{106} \times 100\% = 11.3\%$

For oxygen we have

% composition $= \frac{16 \times 3}{106} \times 100\%$

Then % composition $= \frac{48}{106} \times 100\% = 45.3\%$

All this should add up to 100%: 43.4% + 11.3% + 45.3% = 100%.

Example 2 Calculate the percentage composition by mass of each element in $CaCO_3$.

(C = 12, O = 16, Ca = 40)

Solution We have to begin by calculating the relative molecular mass of $CaCO_3$.

$M_r = 40 + 12 + (16 \times 3)$
$= 52 + 48 = 100$

For calcium we have

$$\% \text{ composition} = \frac{40}{100} \times 100\% = 40\%$$

For carbon we have

$$\% \text{ composition} = \frac{12}{100} \times 100\% = 12\%$$

For oxygen we have

$$\% \text{ composition} = \frac{16 \times 3}{100} \times 100\%$$

Then $\% \text{ composition} = \frac{48}{100} \times 100\% = 48\%$

This should add up to exactly 100%: 40% + 12% + 48% = 100%

Example 3 A sample of brass contains 60% copper and 40% zinc. What mass of brass would contain 100.0 g of copper?

Solution Let the mass of brass that will contain 100.0 g of copper be *m*. Since brass contains 60% copper, then

$$100.0 \text{ g} = \frac{60}{100} \times m$$

So $100.0 \text{ g} = 0.60m$

Thus $m = \frac{100.0 \text{g}}{0.60} = 170 \text{ g}$

Example 4 The complete combustion of 1 cm^3 of a hydrocarbon requires 5 cm^3 of oxygen. Identify the compound and write the balanced equation for the reaction, given that 3 cm^3 of carbon dioxide is produced.

Solution We start by writing the general equation for the combustion of hydrocarbons, i.e.

$$C_xH_y + (x + y/4)O_2(g) \rightarrow xCO_2(g) + y/2H_2O(g)$$

The number of moles of substances in gas phase reactions correspond to their volumes at constant conditions of temperature and pressure. Since 5 cm^3 of oxygen is required for complete combustion, then

$(x + y/4)$ mol of O_2 = 5 mol of O_2
So $x + y/4 = 5$

Similarly, 3 cm^3 of CO_2 is produced. Thus

x mol of CO_2 = 3 mol of CO_2
So $x = 3$

We now substitute the value of x into the above equation to obtain

$3 + y/4 = 5$
Then $y/4 = 5 – 3 = 2$

Cross-multiplying we obtain
$y = 4 \times 2 = 8$

Example 5 The complete combustion of a hydrocarbon sample produced 9.07 g of carbon dioxide and 1.86 g of water vapour. Determine the mass compositions of the elements in the hydrocarbon

(H = 1, C = 12, O = 16)

Solution First, we have to determine the mass composition of carbon and hydrogen in the organic compound, using the relation

$$x = \frac{n \times A_r}{M_r} \times m$$

Carbon is produced as part of CO_2. Thus

$A_r = 12$
$M_r = 12 + (16 \times 2) = 44$
$m = 9.07$ g
C = ?
Substituting we have

$$H = \frac{12}{44} \times 9.07 \text{ g} = 2.5 \text{ g}$$

Hydrogen is produced as part of H_2O. Thus

$A_r = 16$
$M_r = (1 \times 2) + 16 = 18$
$m = 1.86$ g
C = ?
Substituting we have

$H = \frac{2 \times 1}{18} \times 1.86\ \text{g} = 0.21\ \text{g}$

Example 6 An organic compound consists of carbon, hydrogen and oxygen. On combustion, a 9.5-g sample of the compound produces 18.2 g and 11.2 g of carbon dioxide and water vapour respectively. If 1.5 g of the sample occupies a volume of 750 cm^3 when vaporized at 28°C and 108.4 kPa, determine:

(a) The mass composition of each element;
(b) The molar mass of the compound.

($R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$)

Solution

(a) The mass compositions of carbon and hydrogen can be obtained from the relation

$$x = \frac{n \times A_r}{M_r} \times m$$

For carbon we have

$A_r = 12$
$M_r = 44$
$m = 18.2$ g
C = ?

So $C = \frac{12}{44} \times 18.2\ \text{g} = 5.0\ \text{g}$

For hydrogen we have

$A_r = 1$
$M_r = 18$
$m = 11.2$ g
H = ?

So $H = \frac{1 \times 2}{18} \times 11.2\ \text{g} = 1.2\ \text{g}$

The mass composition of oxygen is obtained by subtracting the sum of the masses of carbon and hydrogen from the mass of the sample of the compound, i.e.

$O = 9.5\ \text{g} - (5.0 + 1.2)\ \text{g}$
So $O = 9.5\ \text{g} - 6.2\ \text{g} = 3.3\ \text{g}$

Thus the compositions of the element are C = 5.0 g, H = 1.2 g, O = 3.3 g.

(b) We can only determine the relative molecular mass of the compound by using the ideal gas law.[2]

$$PV = nRT$$

Our interest is the relative molecular mass of the compound. We can obtain this by substituting $n = m/M$ into the relation to obtain

$$PV = \frac{m}{M} RT$$

$$M = \frac{mRT}{PV}$$

$m = 1.5$ g
$T = 273 + 28°\text{C} = 301$ K
$R = 8.314 \text{ J K}^{-1} \text{ mo1}^{-1} = 8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mo1}^{-1}$
$P = 108.4$ kPa
$V = 750 \text{ cm}^3 = 0.75 \text{ dm}^3$
$M = ?$

Substituting all the parameters into the equation gives

$$M = \frac{1.5\text{ g} \times 8.314\ \cancel{\text{kPa}}\ \cancel{\text{dm}^3}\ \text{mol}^{-1} \times 301\ \cancel{\text{K}}}{108.4\ \cancel{\text{kPa}} \times 0.75\ \cancel{\text{dm}^3} \times 1\ \cancel{\text{K}}} = 46 \text{ g mol}^{-1}$$

Alternatively, we can apply the general gas law

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

So $V_1 = \dfrac{P_2V_2T_1}{P_1T_2}$

Defining the initial properties at standard temperature and pressure (STP), we have

$P_1 = 101.325$ kPa
$T_1 = 273$ K
$P_2 = 108.4$ kPa
$V_2 = 0.75 \text{ dm}^3$
$T_2 = 301$ K

---

[2] The gas laws are treated in Chapter 5.

V_1 = ?

Substituting all parameters into the equation gives

$$V_2 = \frac{108.4\ \cancel{\text{kPa}} \times 0.75\ \text{dm}^3 \times 273\ \cancel{\text{K}}}{101.325\ \cancel{\text{kPa}} \times 301\ \cancel{\text{K}}} = 0.73\ \text{dm}^3$$

Thus 1.5 g of the compound occupies a volume of 0.75 dm^3 at STP The rest of the working is easy since 1 mol (equivalent to molar mass) of the gas would occupy a volume of 22.4 dm^3 (molar volume[3] of gases at STP). So

1.5 g = 0.73 dm^3
M = 22.4 $\text{dm}^3\ \text{mol}^{-1}$

Then 1.5 g × 22.4 $\text{dm}^3\ \text{mol}^{-1}$ = M × 0.73 dm^3

$$\text{Thus } M = \frac{1.5\ \text{g} \times 22.4\ \cancel{\text{dm}^3}\ \text{mol}^{-1}}{0.73\ \cancel{\text{dm}^3}}$$

$= 46\ \text{g mol}^{-1}$

Example 7 10 cm^3 of a gaseous hydrocarbon was added to 100 cm^3 of oxygen, which was in excess. The mixture was exploded at 120°C, giving a residual volume of 115 cm^3, which was further reduced to 85 cm^3 after cooling. The resulting mixture was then passed through a concentrated potassium hydroxide solution, and the residual volume was found to have further reduced to 65 cm^3. Determine the molar mass of the compound, hence write the balanced equation of the reaction.

Solution As usual, the very first step in solving this problem is to write the equation for the combustion of hydrocarbons:

$$C_xH_y + (x + y/4)O_2(g) \rightarrow xCO_2(g) + y/2H_2O(g)$$

Since oxygen was supplied in excess, then all of the hydrocarbon sample would undergo combustion. The original residual volume of 115 cm^3 contains carbon dioxide, water vapour and excess oxygen, i.e.

$CO_2 + H_2O + O_2 = 115\ \text{cm}^3$ (1)

After cooling, only carbon dioxide and the excess oxygen remain in the gas phase. In other words, the residual volume of 85 cm^3 contains only CO_2 and O_2, i.e.

---

[3] The molar volume of a gas is the volume occupied by 1 mol of the gas at STP. See Chapter 5 for more details.

$CO_2 + O_2 = 85\text{ cm}^3 \quad (2)$

On passing this residual volume through a concentrated KOH solution, the CO_2 in the mixture is absorbed; leaving only oxygen. Thus

$$O_2 = 65\text{ cm}^3$$

Using the volume of the excess O_2 in equation (2) gives the volume of CO_2 produced, i.e.

$$CO_2 = 85\text{ cm}^3 - 65\text{ cm}^3 = 20\text{ cm}^3$$

According to the equation, 10 cm^3 of the hydrocarbon produces 20 cm^3 of CO_2, then 1 cm^3 of the hydrocarbon would produce x, i.e.

$1\text{ cm}^3 = x\text{ cm}^3$
$10\text{ cm}^3 = 20\text{ cm}^3$
Then $20\text{ cm}^3 \times 1\text{ cm}^3 = x \times 10\text{ cm}^3$

So $x = \dfrac{20\,\cancel{\text{cm}^3} \times 1\,\cancel{\text{cm}^3}}{10\,\cancel{\text{cm}^3} \times 1\,\cancel{\text{cm}^3}} = 2$

The volume of oxygen consumed is obtained by subtracting the volume of the reacting O_2 from volume of supplied, i.e.

$$O_2 = 100\text{ cm}^3 - 65\text{ cm}^3 = 35\text{ cm}^3$$

From the equation, 1 cm^3 of the compound reacts with $(x + y/4)\text{ cm}^3$ of oxygen, whereas 10 cm^3 reacts with 35 cm^3, i.e.

$1\text{ cm}^3 = (x + y/4)\text{ cm}^3 = (2 + y/4)\text{ cm}^3$
$10\text{ cm}^3 = 35\text{ cm}^3$
So $35\text{ cm}^3 \times 1\text{ cm}^3 = 10\text{ cm}^3 \times (2 + y/4)\text{ cm}^3$
Then $35\text{ cm}^6 = (20 + 10y/4)\text{ cm}^6$
So $35 = 20 + 10y/4$

We can as well multiply throughout by 4 to obtain

$140 = 80 + 10y$
So $10y = 140 - 80 = 60$

Thus $y = \dfrac{60}{10} = 6$

Inserting the values of x and y into C_xH_y yields C_2H_6, which is ethane.

The balanced equation of reaction is

$$C_2H_6(g) + (2 + 6/4)O_2(g) \rightarrow 2CO_2(g) + 6/2H_2O(g)$$

So $C_6H_6(g) + 7/2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

Example 8 An unknown organic compound with the relative molecular mass of 31 contains carbon, hydrogen and nitrogen. An analysis of a 0.15-g sample of the compound produces 0.213 g and 0.216 g of ammonia and carbon dioxide respectively. The ammonia produced was then absorbed in 24.8 cm^3 of a 0.25-M hydrochloric acid, which was in excess. If the excess acid requires 26.8 cm^3 of 0.050-M potassium hydroxide solution for complete neutralization, determine the mass compositions of the elements.

(H = 1, N = 14)

Solution The mass compositions of the elements are obtained from the relation

$$x = \frac{n \times A_r}{M_r} \times m$$

For carbon we have

$A_r = 12$
$M_r = 44$
$m = 0.213$ g
C = ?

So $C = \frac{12}{44} \times 0.213$ g

= 0.058 g

The mass of nitrogen in the sample can be obtained by employing the knowledge of back titration.[4] The first step to determine the amount of the acid into which the ammonia was originally absorbed, using the relation

$n = C \times V$
C = 0.25 mol dm^3
V = 24.8 cm^3 = 0.0248 dm^3
n = ?

$$n = \frac{0.25 \text{ mol}}{1 \cancel{\text{dm}^3}} \times 0.0248 \cancel{\text{dm}^3}$$

= 0.0062 mol

The next step is to determine the amount of the excess acid from the amount of KOH needed for its neutralization.

C = 0.050 mol dm^{-3}

$V = 26.8\ \text{cm}^3 = 0.0268\ \text{dm}^3$

$n = ?$

Substituting we have

$$n = \frac{0.050\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 0.0268\ \cancel{\text{dm}^3}$$

$$= 0.0013\ \text{mol}$$

We can now determine the amount of excess acid from stoichiometry. The equation of reaction is

$$\text{KOH}(aq) + \text{HCl}(aq) \rightarrow \text{KCl}(aq) + \text{H}_2\text{O}(l)$$

Since 1 mol of KOH requires 1 mol of HCl, then 0.013 mol of KOH also requires 0.0013 mol of HCl. Thus, the amount of excess acid is 0.0013 mol. Consequently, the amount of the acid that reacted with NH_3 is obtained by subtracting the amount of excess acid from the original amount of the acid, i.e.

$$n = 0.0062\ \text{mol} - 0.0013\ \text{mol}$$
$$= 0.0049\ \text{mol}$$

The amount of ammonia produced can now be determined from stoichiometry. The equation of reaction is

$$\text{NH}_3(aq) + \text{HCl}(aq) \rightarrow \text{NH}_4\text{Cl}(aq)$$

Since 1 mol of HCl requires 1 mol of NH_3, then 0.0049 mol of HCl also requires 0.0049 mol of NH_3. Thus the amount of NH_3 produced during the analysis of the organic compound is 0.0049 mol. This can be converted to mass using the relation

$$n = \frac{m}{M}$$

$$m = n \times M$$

$M = [14 + (1 + 3)]\ \text{g mol}^{-1} = 17\ \text{g mol}^{-1}$

$m = ?$

Substituting we have

$$m = 0.0049\ \cancel{\text{mol}} \times \frac{17\ \text{g}}{1\ \cancel{\text{mol}}}$$

$$= 0.083\ \text{g of NH}_3$$

---

[4] Back titration is treated in Chapter 10.

We can now determine the mass composition of nitrogen in the usual manner, i.e.

$$N = \frac{14}{17} \times 0.083\ \text{g}$$

$$= 0.068\ \text{g}$$

The mass composition of hydrogen can now be obtained by deduction, i.e

$H = 0.15\ \text{g} – (0.058\ \text{g} + 0.068\ \text{g})$

So $H = 0.15\ \text{g} – 0.126\ \text{g}$

$= 0.024\ \text{g}$

Practice Problems

1. Calculate the mass percentage of each element in the compound $NaNO_3$.

   (N = 14, O = 16, Na = 23)
   N = 16.5%, O = 56.5%]
2. Soft solder contains 70% lead and 30% tin. What mass of solder would conta
3. 0.225 g of an organic compound containing carbon, hydrogen, oxygen and 42.3 cm^3 (at STP) of carbon dioxide, water and nitrogen, respectively. Dete elements.

   (H = 1, C = 12, O = 16)

   [*Answers:* C = 0.093 g, H
4. The ammonia obtained during the analysis of 0.35 g of an organic compour M hydrochloric acid solution. The excess acid requires 56 cm^3 of a 0.10-l complete neutralization. Calculate the percentage composition of nitrogen in

   (H = 1,
   14)
   [*Answer:* 34%]
5. An organic compound contains carbon, hydrogen and bromine. The analysi yielded 0.48 g and 2.00 g of carbon dioxide and silver bromide respectively. the compound occupies a volume of 474 cm^3 at 27°C and 0.70 kPa, determin

(a) the mass composition of each element;
(b) the molar mass of the compound.

(C = 1, C = 12, Br = 80, Ag = 108, R = 8.314 J K

[*Answers:* (a)

1.3 VALENCY AND CHEMICAL FORMULA

Valency is the combining power or capacity of an element or radical.[5] Valencies are whole numbers representing the numbers of hydrogen atoms required to combine with an atom for it to attain the stable electronic configuration.

Elements having a single valency are said to be monovalent, while those with two valencies are said to be divalent. Elements with more than two valencies are said to be multivalent. Copper, for example, is a divalent element with valencies of 1 and 2. This accounts for the reason why it can form two different compounds with the same element. Examples are copper(I) oxide and copper(II) oxide. The valencies of different substances are given in Table 1.8.

A chemical formula is a short way of writing the name of substance using only chemical symbols of its constituent elements. For example, the chemical formulae of nitric acid and hydrogen chloride are HNO_3 and HCl respectively.

The chemical formulae of a compound can easily be deduced from the valencies of its constituent elements by adhering to the following rules:

- Write the symbols of the constituent elements and radicals of the compound, with the valency of each denoted as its superscript to the right. The charges of radicals should be ignored.
- If the valencies are not equal, they should be balanced by interchanging the superscripts are using them as the subscripts of the right of the chemical symbols. You should then omit the valencies to obtain the chemical formula of the compound.
- If a radical is involved, then it must be treated as a unit by enclosing it in parentheses before the subscript is added.

Table 1.8: Valencies of some substances

Substance	*Valency*
Aluminium	3
Hydrogen	1

---

[5] A radical (or polyatomic ion) is a group of atoms that reacts as a unit.

Lead	2 and 4
Silver	1
Chlorine	1
Zinc	2
Sulphur	2, 4 and 6
Sodium	1
OH^-	1
CO_3^{2-}	2
NO_3^-	1
PO_4^{3-}	3
SO_4^{2-}	2
HCO_3^-	1
NH_4^+	1
$Cr_2O_7^{2-}$	2

Example 1 Deduce the chemical formula of hydrogen chloride.

Solution The constituent elements are hydrogen and chlorine, both of which have a valency of 1. Thus we should write H^1Cl^1.

Since the valencies are equal, then we omit them and write the chemical formula of hydrogen chloride as HCl.

Example 2 Deduce the chemical formula of sulphuric acid.

Solution The acid contains hydrogen and sulphate (a radical). We should then write $H^1SO_4^2$.

Since the valencies are not equal, then we interchange the valencies and use them as subscripts to obtain

$$H_2^1 SO_4^2$$

Since the valencies are now balanced, then we can omit them to obtain H_2SO_4. Note that we SO_4^2 is not enclosed in parentheses because it has a subscript of 1.

Example 3 Deduce the chemical formula of iron(III) sulphate.

Solution The constituent element and radical are iron and sulphate respectively. The Roman numeral of 3 appearing in the name of the compound shows that the applicable valency of iron is 3. Thus we write $Fe^3SO^2_4$.

The valencies are obviously not balanced. As usual, we now interchange the valencies and use them as subscripts to obtain

$$Fe^2_3(SO^2_4)_3$$

We can now cancel out the charges to obtain $Fe_2(SO_4)_3$. Note that SO^2_4 is enclosed in parentheses because its subscript is greater than 1.

Practice Problems

1. Deduce the chemical formula of potassium permanganate. [*Answer:* $KMnO_4$]
2. Deduce the chemical formula of aluminium oxide. [*Answer:* Al_2O_3]
3. Deduce the chemical formula of calcium hydroxide. [*Answer:* $Ca(OH)_2$]
4. Deduce the chemical formula of tin (II) chloride. [*Answer:* $SnCl_2$]
5. Deduce the chemical formula of lead (II) nitrate. [*Answer:* $Pb(NO_3)_2$]

1.4 EMPIRICAL AND MOLECULAR FORMULAE

The empirical formula of compound is its simplest formula that shows its constituent elements and the whole-number ratio in which they are combined. The empirical formulae of two or more compounds are the same if they contain the same elements combined in the same ratio. For example, the empirical formula of benzene and ethyne is CH because the compounds contain carbon and hydrogen in the ratio 1 : 1.

On the other hand, the molecular formula of a compound is a formula that shows its constituent elements and the actual number of the atoms of each element present in a mole or molecule of that compound. Empirical formula corresponds to the formula unit or chemical formula of a compound. Unlike empirical formula, every compound has a unique molecular formula. The molecular formulae of benzene and ethyne, for example, are C_6H_6 and C_2H_2 respectively. It should, however, be noted that some compounds have the same empirical and molecular formulae. A typical example of such compounds is sodium nitrate, $NaNO_3$. Examples of empirical and molecular formulae and a summary of the differences between them are given in Table 1.9 and 1.10 respectively.

The empirical formula of a compound can be obtained from its molecular formula by dividing the number of atoms of by their highest common factor. It can also be determined from mass or percentage compositions as follows:

- Calculate the number of moles of each element from the relation

$$n = \frac{m}{M}$$

where m = The mass composition of an element.
M = The molar mass of an element.

A mass of 100 g should be assumed if percentage compositions are given. In this case the percentage composition of each element is taken as its mass.

- Obtain the number mole ratio by dividing the number of moles of each element by the smallest value. Values obtained should be rounded to the nearest whole number provided they are within 5% of the whole number. If a value cannot be rounded, then the fraction should be cleared by multiplying all values by an integer that results in the lowest possible mole ratio.
- Write out the empirical formula by writing the mole ratio as subscripts of the elements.

The molecular formula of a compound can be obtained from its empirical formula by multiplying the number of atoms in the empirical formula by the number of empirical formula units in the molecular formula. This number is obtained from the relation

$$(\text{E.F.})\text{n} = M_r$$

where n number of empirical formula units in the molecular formula.

Table 1.9: Empirical and molecular formula

Compound	*Empirical formula*	*Molecular formula*
Glucose	CH_2O	$C_6H_{12}O_6$
Ethyne	C_2H_2	CH
Sodium carbonate	Na_2CO_3	Na_2CO_3
Water	H_2O	H_2O
Hydrogen peroxide	HO	H_2O_2
Benzene	CH	C_6H_6
Ethanoic acid	CH_2O	$C_2H_4O_2$

Table 1.10: Differences between empirical and molecular formula

Empirical formula	*Molecular formula*
It only shows the ratio in which elements are combined.	It shows the actual number of the atoms of each element present.
It is not unique to a compound, i.e., more than one compound can have the same empirical formula.	It is unique to compound, i.e., no two compounds can have the same molecular formula.

It does not correspond to the formula unit of a compound, and cannot be used to obtain molar.	It corresponds to the formula unit of a compound, and can be used to obtain molar mass.

Example 1 What is the empirical formula of acetic acid if its molecular formula is $C_2H_4O_2$?

Solution All we have to do is to divide the number of atoms by 2, their highest common factor, to obtain CH_2O.

Example 2 On analysis, a sample of a hydrocarbon yields 18.5 g of carbon and 1.5 g of hydrogen. Determine the empirical formula of the compound.

(H = 1, C = 12)

Solution We start by calculating the number of moles of carbon and hydrogen in the sample, using the relation

$$n = \frac{m}{M}$$

For carbon we have

m = 18.5 g

M = 12 g mol^{-1}

n = ?

Substituting we have

$$n = \frac{18.5\,\cancel{g} \times 1\text{ mol}}{12\,\cancel{g}}$$

$$= 1.5\text{ mol}$$

For hydrogen we have

m = 1.5 g

M = 1 g mol^{-1}

n = ?

Substituting we have

$$n = \frac{1.5\,\cancel{g} \times 1\text{ mol}}{1\,\cancel{g}}$$

$$= 1.5\text{ mol}$$

We now determine the mole ratio by dividing through by 1.5 mol, the smaller of the values

$$C = \frac{1.5\ \cancel{\text{mol}}}{1.5\ \cancel{\text{mol}}} = 1$$

$$H = \frac{1.5\ \cancel{\text{mol}}}{1.5\ \cancel{\text{mol}}} = 1$$

Thus the empirical formula of the compound is CH.

Example 3 Given that the sample of a compound contains 8.0 g of carbon, 1.3 g of hydrogen and 10.7 g of oxygen, determine its empirical formula.

(H = 1, C = 12, O = 16)

Solution We first determine the number of mole of each element in the compound, using the relation

$$n = \frac{m}{M}$$

For carbon we have

$m = 8.0$ g

$M = 12$ g mol^{-1}

$n = ?$

Substituting we have

$$n = \frac{8.0\ \cancel{\text{g}} \times 1\ \text{mol}}{12\ \cancel{\text{g}}}$$

$= 0.67$ mol

For hydrogen we have

$m = 1.3$ g

$M = 1$ g mol^{-1}

$n = ?$

Substituting we have

$$n = \frac{1.3\ \cancel{\text{g}} \times 1\ \text{mol}}{1\ \cancel{\text{g}}}$$

$= 1.3$ mol

For oxygen we have

$m = 10.7$ g

$M = 16\ \text{g mol}^{-1}$

$n = ?$

Substituting we have

$$n = \frac{10.7\ \cancel{\text{g}} \times 1\ \text{mol}}{16\ \cancel{\text{g}}}$$

$= 0.67\ \text{mol}$

The least number of moles is 0.67 mol. Thus the mole ratio is:

$$\text{C} = \frac{0.67\ \cancel{\text{mol}}}{0.67\ \cancel{\text{mol}}} = 1$$

$$\text{H} = \frac{1.3\ \cancel{\text{mol}}}{0.67\ \cancel{\text{mol}}} = 2$$

$$\text{O} = \frac{0.67\ \cancel{\text{mol}}}{0.67\ \cancel{\text{mol}}} = 1$$

Thus the empirical formula of the compound is CH_2O.

Example 4 The percentage compositions of sodium, carbon and oxygen in a compound are 43.4%, 11.3% and 48.3% respectively. What is empirical formula of the compound?

(C = 12, O = 16, Na = 23)

Solution As usual, we start by calculating the number of mole of each element from the relation

$$n = \frac{m}{M}$$

Since percentage compositions are given, then we should assume a mass of 100 g of the compound such that the percentage compositions become masses.

For sodium we have

$m = 43.4\ \text{g}$

$M = 23\ \text{g mol}^{-1}$

$n = ?$

Substituting we have

$$n = \frac{43.4\ \cancel{\text{g}} \times 1\ \text{mol}}{23\ \cancel{\text{g}}} = 1.9\ \text{mol}$$

For carbon we have

$m = 11.3$ g
$M_r = 12$ g mol^{-1}
$n = ?$

Substituting we have

$$n = \frac{11.3\,\cancel{g} \times 1\,\text{mol}}{12\,\cancel{g}} = 0.94\ \text{mol}$$

For oxygen we have

m = 48.3 g
$M = 16$ g mol^{-1}
$n = ?$

Substituting we have

$$n = \frac{48.3\,g \times 1\,\text{mol}}{16\,g} = 3.0\ \text{mol}$$

Since the smallest number of moles is 0.94 mol, then the mole ratio is

$$\text{Na} = \frac{1.9\,\cancel{\text{mol}}}{0.94\,\cancel{\text{mol}}} = 2$$

$$\text{C} = \frac{0.94\,\cancel{\text{mol}}}{0.94\,\cancel{\text{mol}}} = 1$$

$$\text{O} = \frac{3.0\,\cancel{\text{mol}}}{0.94\,\cancel{\text{mol}}} = 3$$

Thus the empirical formula of the compound is Na_2CO_3, which is both the empirical and molecular formulae of sodium carbonate.

Example 5 Determine the molecular formula of the compound whose empirical formula is CH_2O, given that its relative molecular mass is 174.

(H = 1, C = 12, O = 16)

Solution We have to apply the relation

$(CH_2O)n = M_r$
$M_r = 174$
C = 12
H = 1

$O = 16$

$n = ?$

Substituting we have

$(CH_2O)n = 174$

Thus $[12 + (1 \times 2) + 16]n = 174$

So $30n = 174$

Then $n = \frac{174}{30} = 6$

Finally, we can now multiply the empirical formula by 6 to obtain $C_6H_{12}O_6$, which is the molecular formula of glucose, or its isomer fructose.

Example 6 Determine the molecular formula of the compound with the empirical formula HO, given that its relative molecular mass is 34.

(H = 1, O = 16)

Solution We have to start from the relation

$(HO)n = M_r$

$M_r = 34$

$H = 1$

$O = 16$

$n = ?$

Substituting we have

$(1 + 16)n = 34$

Then $17n = 34$

So $n = \frac{34}{2} = 2$

We now multiply the empirical formula by 2 to obtain H_2O_2, which is the molecular formula of hydrogen peroxide.

Example 7 The molar mass of lycopene, a hydrocarbon responsible for the red colour of ripe tomatoes, is 536 g mol^{-1}. If the percentage composition of carbon in the compound is 89.6%, determine the empirical and molecular formulae of the compound.

(H = 1, C = 12)

Solution As usual, the very first step is to calculate the number of moles of each element:

$$n = \frac{m}{M}$$

For carbon we have

m = 89.6 g
M = 12 g mol^{-1}
n = ?

Substituting we have

$$n = \frac{89.6\,\cancel{g} \times 1\,\text{mol}}{12\,\cancel{g}} = 7.47\ \text{mol}$$

For hydrogen we have

m = 100 g – 89.6 g = 10.4 g
M = 1 g mol^{-1}
n = ?

Substituting we have

$$n = \frac{10.4\,\cancel{g} \times 1\,\text{mol}}{1\,\cancel{g}} = 10.4\ \text{mol}$$

Next, we work out the mole ratio:

$\text{C} = \frac{7.47\,\cancel{\text{mol}}}{7.47\,\cancel{\text{mol}}} = 1$

$\text{H} = \frac{10.4\,\cancel{\text{mol}}}{7.47\,\cancel{\text{mol}}} = 1.4 = \frac{7}{5}$

Since we cannot round 1.4 to 1, then we have to multiply the above mole ratio by 5 to obtain

$$\text{C} = 5$$
$$\text{H} = 7$$

Thus the empirical formula of lycopene is C_5H_7.

As usual, the molecular formula of the compound is obtained as follows:

$(C_5H_7)n = M_r$
$M_r = 536$
C = 12

H = 1

n = ?

Substituting we have

$[(12 \times 5) + (1 \times 7)]\, n = 536$

So $(60 + 7)\, n = 536$

Thus $67\, n = 536$

$\therefore\ n = \frac{536}{67} = 8$

Finally, we now multiply the empirical formula by 8 to obtain the molecular formula of lycopene as $C_{40}H_{56}$.

Example 8 The relative molecular mass of aspartame, an artificial sweetener containing carbon, hydrogen, oxygen and nitrogen, is 294. If the percentage compositions of the constituent elements are 57%, 6 g, 27.3% and 9.7% respectively, determine the empirical and molecular formulae of the compound.

(H = 1, C = 12, N = 14, O = 16)

Solution We must first work out the number of moles of the constituent elements:

$$n = \frac{m}{M}$$

For carbon we have

m = 57 g

M = 12 g mol^{-1}

n = ?

Substituting we have

$$n = \frac{57\,\cancel{g} \times 1\ \text{mol}}{12\,\cancel{g}} = 4.75\ \text{mol}$$

For hydrogen we have

m = 6 g

M = 1 g mol^{-1}

n = ?

Substituting we have

$$n = \frac{6\,\cancel{g} \times 1\ \text{mol}}{1\,\cancel{g}} = 6\ \text{mol}$$

For oxygen we have

$m = 27.3$ g
$M = 16$ g mol^{-1}
$n = ?$

Substituting we have

$$n = \frac{27.3\,\cancel{g} \times 1\,\text{mol}}{16\,\cancel{g}} = 1.71\ \text{mol}$$

For nitrogen we have

$m = 9.7$ g
$M = 14$ g mol^{-1}
$n = ?$

Substituting we have

$$n = \frac{9.7\,\cancel{g} \times 1\,\text{mol}}{14\,\cancel{g}} = 0.693\ \text{mol}$$

We can now determine the mole ratio by dividing each number of moles by 0.693 mol:

$\text{C} = \frac{4.75\,\cancel{\text{mol}}}{0.693\,\cancel{\text{mol}}} = 7$

$\text{H} = \frac{6\,\cancel{\text{mol}}}{0.693\,\cancel{\text{mol}}} = 9$

$\text{N} = \frac{0.693\,\cancel{\text{mol}}}{0.693\,\cancel{\text{mol}}} = 1$

$\text{O} = \frac{1.71\,\cancel{\text{mol}}}{0.693\,\cancel{\text{mol}}} = 2.5 = \frac{5}{2}$

Since we cannot round 2.5 to 3, we have to multiply each number by 2 to obtain

C = 14
H = 18
N = 2
O = 16

Thus the empirical formula of aspartame is $C_{14}H_{18}N_2O_5$.

Finally, we now determine the molecular formula as follows:

$(C_{14}H_{18}N_2O_5)\ n = M_r$
$M_r = 294$
$C = 12$
$H = 1$
$N = 14$
$O = 16$
$n = ?$

Substituting we have

$$[(14 \times 7) + (1 + 18) + (2 \times 14) + (16 \times 5)\ n = 294]$$

So $(168 + 18 + 28 + 80)\ n = 294$
Thus $294n = 294$

$\therefore\ n = \frac{294}{294} = 1$

Thus the molecular formula of aspartame is the same as its empirical formula of $C_{14}H_{18}N_2O_5$.

Practice Problems

1. The analysis of a compound yields 18.5 g and 1.5 g of carbon and hydr
formula of the compound.

12)
[*Answer:* CH]

2. The percentage compositions of carbon, hydrogen and oxygen in a
respectively. Determine the empirical formula of the compound.

12, O = 16)
[*Answer:* C_2H_6O]

3. Determine the molecular formula of the compound with the empirical form
mass is 60.

12, O = 16)

[Answer: $C_2H_4O_2$]

4. Determine the molecular formula of the compound whose empirical formu
relative molecular mass is 46.
$C_2H_4O_2$]
5. Determine the molecular formula of the compound in Question 1, give

[*Answer:* C_6H_6]
6. Determine the molecular formula of the compound in Question 1, give

[*Answer:* C_2H_2]

1.5 REDUCED MASS

Reduced mass m is the effective inertia mass of a two-body system. This quantity, which is commonly used in quantum mechanics, is given by the relation

$$\mu = \frac{M_A M_B}{M_A + M_B}$$

where M_A and M_B are the molar masses of the elements in a binary compound. The SI unit of reduced mass is the kilogram, kg. We can obtain our result directly in kilogram without first converting the molar masses to kilogram by multiplying the above equation by the mass of an atom in kg, i.e.

$$\frac{10^{-3}\,\text{kg}}{N_A} = \frac{10^{-3}\,\text{kg}}{6.02 \times 10^{23}} = 1.66054 \times 10^{-7}\,\text{kg}$$

This value is called 1 atomic mass unit (a.m.u.).
We now substitute to obtain

$$\mu = \frac{10^{-3}\,\text{kg}}{N_A}\left(\frac{M_{rA} M_{rB}}{M_{rA} + M_{rB}}\right)$$

where M_{rA} and M_{rB} are the relative molecular masses of the two elements in a binary compound.

Example 1 Calculate the reduced mass of NaCl.

(Na = 23, Cl = 35.5, $N_A = 6.02 \times 10^{23}$)

Solution We have to apply the relation

$$\mu = \frac{10^{-3}\,\text{kg}}{N_A}\left(\frac{M_{rA}\,M_{rB}}{M_{rA}+M_{rB}}\right)$$

M_{rA} = 23

M_{rB} = 35.5

$N_A = 6.02 \times 10^{23}$

μ = ?

Substituting we obtain

$$\mu = \frac{10^{-3}\,\text{kg}}{6.02\times 10^{23}}\left(\frac{23\times 35.5}{23+35.5}\right)$$

So $\mu = 1.66 \times 10^{27}$ kg × 13.96

$= 2.3 \times 10^{-26}$ kg

Example 2 Calculate the reduced mass of NaH.

(H = 1.0, Na = 23)

Solution We have to apply the relation

$$\mu = \frac{10^{-3}\,\text{kg}}{N_A}\left(\frac{M_{rA}\,M_{rB}}{M_{rA}+M_{rB}}\right)$$

M_{rA} = 23

M_{rB} = 1.0

$N_A = 6.02 \times 10^{23}$

μ = ?

Substituting we obtain

$$\mu = \frac{10^{-3}\,\text{kg}}{6.02\times 10^{23}}\left(\frac{23\times 1.0}{23+1.0}\right)$$

So $m = 1.66 \times 10^{-27}$ kg × 0.96

$= 1.6 \times 10^{-27}$ kg

Practice Problem

Calculate the reduced masses of $CaCl_2$.

(Cl = 35.5, Ca = 40.0)

[*Answer:* 4.3×10^{-26} kg]

SUMMARY

- Matter is anything that has mass and occupies space.
- An element is a simple substance that cannot be split into simpler substances by ordinary chemical means.
- A chemical symbol is a short way of writing the name of an element.
- A compound consists of two or more elements that are chemically combined together.
- A mixture consists of two or more substances that are physically combined together.
- A radical is a group of atoms that reacts as a unit.
- The relative atomic mass, A_r of an element is the number of times the average mass of one of its atoms is as heavy as one-twelfth the mass of one atom of carbon-12.
- The relative molecular mass, M_r of a substance is the number of times the average mass of one mole or molecule of the substance is as heavy as one-twelfth the mass of one atom of carbon-12.
- The molar mass of a substance is the mass of one mole of that substance.
- The percentage composition by mass of an element in a compound is its percentage contribution to the total mass of a substance.
- The general formula for the combustion of a hydrocarbon is

$$C_xH_y + (x + y/4)O_2(g) \rightarrow xCO_2(g) + y/2H_2O(g)$$

- The general formula for the combustion of an organic compound containing carbon, hydrogen and oxygen is

$$C_xH_yO_z + (x + y/4 - z/2)O_2(g) \rightarrow xCO_2(g) + y/2H_2O(g)$$

- Valency is the combining power or capacity of an element.
- Chemical formula is the short way of writing of the name of substance using only chemical symbols of its constituent elements.
- The empirical formula of a substance is its simplest formula that shows its constituent elements and the ratio in which they are combined.
- The molecular formula of a substance is the formula that shows its constituent elements and the actual number of atoms of each element present in a mole or molecule of that compound.
- Reduced mass m is the effective inertial mass of a two-body system. It is given by the relation

$$\mu = \frac{10^{-3}\,\text{kg}}{N_A}\left(\frac{M_{rA} M_{rB}}{M_{rA} + M_{rB}}\right)$$

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. Which of the following is not an element?
   A. Hydrogen B. Sulphur
   C. Blood D. Calcium
   E. Uranium
2. Which of the following is the symbol of silver?
   A. Hg B. Ag
   C. Cu D. K
   E. Ca
3. Which of the following substance is a compound?
   A. Blood B. Soap
   C. Air D. Manganese
   E. Cobalt
4. What is the composition of carbon dioxide?
   A. Carbon and oxygen B. Oxygen and calcium
   C. Calcium and lead D. Oxygen and uranium
   E. None of the above
5. Which of these is **NOT** a constituent of air?
   A. Hydrogen B. Nitrogen
   C. Oxygen D. Rare gases
   E. Carbon dioxide
6. Which of the following quantities have no units?
   A. Weight B. Mass
   C. Molar mass D. Density
   E. Relative atomic mass
7. Which of the following compounds have the same empirical and molecular formulae?
   i. H_2O_2 ii. Na_2O iii. $Na_2S_2O_3$ iv. Na_2O_2 v. CH_3CH_2COOH

A. i and ii B. ii and iv

C. ii only D. iii and iv

E. iv and v

8. Which of these can be obtained from an empirical formula of a compound that differs from its molecular formula?

A. Molar mass

B. The identity of the compound

C. The constituent elements of the compound

D. The number of atoms of its constituent elements

E. None of the above

9. Which of the following chemical formulae is **NOT** well written?

A. Na_2O B. K_2SO_4

C. $Zn(OH)_2$ D. NaCl

E. $H_3(PO_4)_2$

10. 250 mg of silver chloride was obtained during the analysis of an organic compound. What is the mass composition of chlorine?

A. 0.062 g B. 0.080 g

C. 0.082 g D. 0.094 g

E. 0.098 g

(Cl = 35.5, Ag = 108)

11. The analysis of 0.245-g sample of a hydrocarbon produced 0.77 g of carbon dioxide. Determine the percentage composition of hydrogen in the compound.

A. 14.3% B. 27.6%

C. 30.1% D. 32.2%

E. 41.7%

(H = 1, C = 12)

12. What is the empirical formula of the compound described in Question 3 above?

A. C_2H_3 B. CH_2

C. C_2H D. C_2H_5

E. CH_3

ESSAY TYPE QUESTIONS

Matter

13. (a) Explain the basic difference between a compound and an element.
    (b) In which ways do mixtures differ from compounds?
14. (a) Define the following terms:
    (i) element (ii) compound (iii) mixture
15. (a) What are radicals? Give four examples.
    (b) What is valency? List the valencies of ten elements.
16. (a) What is chemical symbol?
    (b) Write the symbols of the following elements:
    (i) sodium (ii) mercury (iii) cobalt (iv) manganese (v) platinum (vi) silver
    (vii) aluminium (viii) gold (ix) tungsten (x) molybdenum

Relative atomic and molecular masses

17. Calculate the molar masses of the following elements:
    (i) Na_2SO_3 (ii) $CaSiO_3$ (iii) $K_4Fe(CN)_6$ (iv) $Cu(NO_3)_2$ (v) Na_2HPO_4
    (H = 1, C = 12, N = 14, O = 16, Na = 23, Si = 28, P = 31, S = 32, Cl = 35.5, Ca = 40, Fe = 56, Co = 59, Cu = 65.5)

Mass composition of elements

18. Given below are some compounds. Calculate the mass and percentage compositions of the elements in each compound.
    (i) $CuSO_4$ (ii) $K2SO_3$ (iii) $Pb(C_2H_5)_4$ (iv) $KHCO_3$ (v) Pb_3O_4 (vi) Hg_2SO_4
    (H = 1, C = 12, N = 14, O = 16, Si = 28, S = 32, K = 39, Fe = 56, Hg = 201, Pb = 207)
19. The analysis of 0.10-g sample of a compound containing carbon, hydrogen and oxygen produced 0.20 g of carbon dioxide and 0.082 g of water. If the vapour of 150 mg of the compound occupies a volume of 277 cm^3 at 27°C and 0.373 atm, determine
    (a) the mass composition of each element;
    (b) the empirical formula of the compound;
    (c) the relative molecular mass of the compound;
    (d) the molecular formula of the compound.
    (H = 1, C = 12, O = 16, $R = 0.082$ atm dm^3 K^{-1} mol^{-1})
20. 20.0 cm^3 of a hydrocarbon was ignited with 200.0 cm^3 of oxygen which was in excess to produce 250.0 cm^3 of residual gas. After cooling, the volume reduced to 150.0 cm^3, after which the remaining gaseous mixture was passed

through a concentrated sodium hydroxide solution. If the final volume of residual gas is 70.0 cm^3, determine the molecular formula of the compound, hence write the balanced equation of reaction.

21. An organic compound contains carbon, hydrogen and oxygen. 10.0 cm^3 of the compound was ignited with 100.0 cm^3 of oxygen which was in excess to produce 120.0 cm^3 of residual gases which was later reduced to 90.0 cm^3 after cooling. If the volume of the residual gases further reduced to 70.0 cm^3 after it was passed through a concentrated potassium hydroxide solution, determine

(a) the molecular formula of the compound and the equation of the reaction;

(b) the molar mass of the compound.

22. An unknown organic compound contains carbon, hydrogen and nitrogen. On analysis, 250-mg sample of the compound yielded 0.30 g of water and 28.3 cm^3 of nitrogen at STP Determine

(a) the mass and percentage compositions of each element;

(b) the empirical formula of the compound;

(c) the molecular formula of the compound, given that its relative molecular mass is 99.

(H =1, C = 12, N = 14, O = 16)

23. The ammonia obtained during the analysis of a 150-mg sample of a compound containing carbon, hydrogen, nitrogen and oxygen was absorbed into 50.0 cm^3 of 0.10-M hydrochloric acid solution which was in excess. The excess acid requires 30.0 cm^3 of 0.10-M potassium hydroxide for its complete neutralization. If 0.31 g of carbon dioxide and 0.11 g of water vapour were also obtained, determine

(a) the mass composition of each element;

(b) the empirical formula of the compound.

(H = 1, C = 12, N = 14, O = 16)

24. The analysis of 0.022 g of an unknown organic compound containing carbon, hydrogen and nitrogen produced 0.033 g of carbon dioxide. The ammonia obtained was absorbed into 50.0 cm^3 of 0.020-M hydrochloric acid solution which was in excess. The excess acid requires 75.0 cm^3 of 0.0013-M sodium carbonate for complete neutralization. A further analysis showed that the vapour of 0.050-g sample of the compound occupies a volume of 700.0 cm^3 at 27°C and 3.30 kPa. Determine

(a) the mass composition of each element;

(b) the empirical formula of the compound;

(c) the molar mass of the compound;

(d) the molecular formula of the compound.

(H = 1, C = 12, N = 14, O = 16)

25. The analysis of 0.268 g of a hydrocarbon yielded 0.84 g of carbon dioxide. Determine

(a) the mass and percentage compositions of carbon and hydrogen;

(b) the empirical formula of the compound;

(c) the molecular formula of the compound if it has a relative molecular mass of 84.

(H = 1, C = 12)

26. The analysis of 0.193 g of phenylhydrazine, a compound containing carbon, hydrogen and nitrogen yielded 0.48 g and 0.060 g of carbon dioxide and ammonia respectively. If the relative molecular mass of the compound is 108, determine

(a) the mass and percentage compositions of each element;

(b) the empirical formula of the compound;

(c) the molecular formula of the compound.

(H = 1, C = 12, N = 14)

27. The analysis of 0.50-g sample of a compound containing carbon, hydrogen and chlorine produced 0.90 g and 1.5 g of water and silver chloride respectively. Determine

(a) the mass compositions of the elements;

(b) the empirical formula of the compound;

(c) the molecular formula of the compound if its relative molecular mass is 99.

(H = 1.0, C = 12.0, Cl = 35.5, Ag = 107.8)

28. An organic compound with a molar mass of 126 g mol^{-1} contains carbon, hydrogen, oxygen and sulphur. On analysis, 1.5 g of the compound yielded 2.8 g, 0.63 g and 1.1 g of barium sulphate, water and carbon dioxide respectively. Determine

(a) the percentage composition of each element;

(b) the empirical formula of the compound;

(c) the molecular formula of the compound.

(H = 1, C = 12, S = 32, Ba = 137)

29. An organic compound with the same empirical and molecular formulae

contains carbon, hydrogen and oxygen. If 1.2-g sample of the compound yielded 1.3 g of carbon dioxide and 0.54 g of water, determine

(a) the percentage composition of each element;

(b) the molecular formula of the compound, hence give the name of the group to which the compound belongs.

(H = 1, C = 12, O = 16)

30. A chemist performs the qualitative analysis of glycine and found out that its molecular formula is $C_2H_5O_2N$. If he worked with 0.225 g of the compound, calculate

(a) the mass composition of each of the element in 0.225 g of glycine;

(b) the masses of carbon dioxide, ammonia and water produced during the experiment.

(H = 1, C = 12, O = 16, N = 14)

31. The complete combustion of 1 mol of a hydrocarbon requires 5 mol of oxygen. If 4 mol of water is produced, write

(a) the molecular formula of the compound;

(b) the balanced equation of reaction.

32. 1 cm^3 of an organic compound containing carbon, hydrogen and oxygen requires 3 cm^3 of oxygen for complete combustion. If the process yields 2 cm^3 of carbon dioxide and 3 cm^3 of water, determine the molecular formula of the compound.

33. A compound contains carbon, hydrogen and chlorine. On analysis, 5.0 g sample of the compound produced 3.3 g and 16.3 g of carbon dioxide and silver chloride respectively. If the vapour of 200.0 mg of the compound occupies a volume of 680.0 cm^3 at 25°C and 7.5 kPa, determine

(a) the mass and percentage composition of each element;

(c) the molar mass of the compound;

(d) the molecular formula of the compound.

(H = 1.0, C = 12, O = 16.0, Cl = 35.5)

Valency and chemical formula

34. Deduce the chemical formulae of the following compounds:

(a) Copper(II) chloride

(b) Calcium hypochlorite

(c) Iron(III) nitrate

(d) Manganese(IV) sulphate

35. Deduce the chemical formulae of the following compounds:

(a) Iron(II) silicate
(b) Iron(II) sulphate
(c) Potassium and hydrogen carbonate
(d) Magnesium and hydroxide
(e) Calcium carbonate

Empirical and molecular formulae

36. Find the empirical formulae of the compounds whose percentage compositions are given below.

(a) Ca = 62.5%, C = 37.5%
(b) Ca = 33%, S = 27%, O = 53%
(c) K = 25%, Mn = 35%, O = 41%
(d) K = 27%, Mn = 35%, O = 41%
(e) K = 39%, H = 1%, C = 12%

(H = 1, C = 12, O = 16, S = 32, K = 39, Ca = 40, Mn = 55)

37. Find the empirical formulae of the compounds whose mass compositions are given below.

(a) P = 17.5 g, O = 22.5 g
(b) Pb = 27.3 g, S = 4.2 g, O = 8.5 g
(c) Na = 12.2 g, Si = 4.2 g, O = 8.5 g
(d) Na = 7.5 g, Cl = 11.6 g, O = 20.9 g

(O = 16, Na = 23, P = 31, S = 32, Cl = 35.5, Pb = 207)

38. Find the molecular formulae of the compounds whose empirical formulae and relative molecular masses are given below.

(a) CH, 78 (b) CH_2O, 60
(c) C_2H_6O, 46 (d) NaO, 78
(e) $C_3H_6O_2$, 74 (f) C_2H_4O, 88
(g) CH_2O, 60 (h) CH_2 = 42
(i) CH_2, 56 (j) CH_2, 70 CH_2, 28

(H = 1, C = 12, O = 16)

39. Vitamin C (ascorbic acid) contains carbon, hydrogen and oxygen. The percentage compositions of carbon and hydrogen are 40.9% and 4.5% respectively. Given that a
10.0-g sample of the compound contains 0.0568 mol, determine

(a) the empirical formula of the compound;
(b) the molar mass of the compound;
(c) the molecular formula of the compound.

(H = 1, C = 12, O = 16)

40. Glycine, with a relative molecular mass of 75, is an amino acid derived from ethanoic acid. When a 1.52-g sample of the compound was burnt, 1.78 g of carbon dioxide, 0.91 g of water and 0.28 g of nitrogen were produced. Determine

(a) the percentage compositions of the constituent elements;
(b) the empirical formula of glycine;
(c) the molecular formula of glycine.

(H = 1, C = 12, N = 14, O = 16)

Reduced mass

41. Calculate the reduced mass of the following compounds:

(a) CaC_2 (b) AgCl
(c) H_2O (d) NaF
(e) HBr

(H = 1, C = 12, O = 16, F = 19, Na = 32, Cl 35.5, Ca = 40, Ag = 107.9, Br = 137)

Answers

----

1. C 2. B 3. B 4. A 5. A 6. E
7. C 8. C 9. E 10. A 11. A 12. B

16. (b) (i) Na (ii) Hg (iii) Co (iv) Mn (v) Pt (vi) Ag (vii) Al (viii) Au (ix) W (x) Md

17. (a) 126 g mol^{-1} (b) 116 g mol^{-1} (c) 368 g mol^{-1} (d) 189.5 g mol^{-1} (e) 142 g mol^{-1}

18. (a) Cu: 65.5 g, 40.6%; S: 32 g, 19.8%; O: 64 g, 39.6%
(b) K: 78 g, 49.4%; S: 32 g, 20.3%; O: 48 g, 30.4%
(c) Pb: 207 g, 64.1%; C: 24 g, 29.7%; H: 20 g, 6.2%

(d) K: 39 g, 39%; H: 1 g, 1% ; C: 12 g, 12%; O: 48 g, 48%

(e) Pb: 621 g, 90.7%; O: 64 g, 9.3%

(f) Hg: 402 g; 80.7%; S: 32 g, 6.4%; O: 64 g, 12.9%

19. (a) C: 0.055 g, H: 0.0091 g O: 0.036 g (b) C_2H_4O

(c) 44 g mol^{-1} (d) C_2H_4O

20. C_4H_{10}, $C_4H_{10}(g) + 13/2O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$

21. (a) C_2H_6O, $C_2H_6O(g) + 3O_2(g) \rightarrow$rarr; $2CO_2(g) + 3H_2O(g)$ (b) 46 g mol^{-1}

22. (a) C: 0.18 g, 72%; H: 0.033 g, 13%; N: 0.035 g, 14% (b) $C_6H_{13}N$

(c) $C_6H_{13}N$

23. (a) C: 0.085 g, H: 0.012 g, O: 0.025 g, N: 0.028 g (b) C_4H_8ON

24. (a) C: 0.0090 g, H: 0.0010 g, N: 0.012 g (b) CHN

(c) 54 g mol^{-1} (d) $C_2H_2N_2$

25. (a) C: 0.23 g, 85.8%; H: 0.038 g, 14.2%; (b) CH_2

(c) C_6H_{12}

26. (a) C: 0.131 g, 65%; H: 0.021 g, 10.5%; N: 0.0494 g, 24.5% (b) C_3H_4N

(c) $C_6H_8N_2$

27. (a) C: 0.10 g, H: 0.028 g, Cl: 0.372 g (b) CH_2Cl

(c) $C_2H_4Cl_2$

28. (a) C: 20%, H: 4.7%, O: 50%, S: 25.3% (b) $C_2H_6O_4S$

(c) $C_2H_6O_4S$

29. (a) C: 0.35 g, 29.2%; H: 0.060 g, 5%; O: 0.79 g, 65.8%

(b) CH_2O_2 (HCOOH), carboxylic acid

30. (a) C: 0.072 g, H: 0.015 g, O: 0.096 g, N: 0.042 g

(b) CO_2: 0.264 g, NH_3: 0.0510 g, H_2O: 0.135 g

31. (a) C_3H_8

(b) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

32. C_2H_6O

33. (a) C: 0.90 g, 18%; H: 0.10 g, 2%; Cl: 4.0 g, 80% (b) 97 g mol^{-1}

(c) $C_2H_2Cl_2$

34. (a) $CuCl_2$ (b) $Ca(OCl)_2$ (c) $Fe(NO_3)_3$ (d) $Mn(SO_4)_2$

35. (a) $FeSiO_3$ (b) $FeSO_4$ (c) $KHCO_3$ (d) $Mg(OH)_2$

(e) $CaCO_3$

36. (a) CaC_2 (b) $CaSO_4$ (c) $KMnO_4$ (d) KHC

37. (a) PO_3 (b) $PbSO_4$ (c) Na_4SO_4 (d) $NaClO_4$

38. (a) C_6H_6 (b) $C_2H_4O_2$ (c) C_2H_6O (d) Na_2O_2
(e) $C_3H_6O_2$ (f) $C_4H_8O_2$ (g) $C_4H_4O_2$ (h) C_3H_6
(i) C_4H_8 (j) C_5H_{10} (k) C_2H_4

39. (a) $C_3H_4O_3$ (b) 176 g mol^{-1} (c) $C_6H_8O_6$

40. (a) C = 32.2%, H = 6.6%, N = 18.4%, O = 42.8% (b) $C_2H_5NO_2$ (c) $C_2H_5NO_2$

41. (a) 2.5×10^{-26} kg (b) 4.4×10^{-26} kg (c) 3.0 (c) 3.0×10^{-27} kg
(d) 1.7×10^{-26} kg (e) 1.6×10^{-27} kg

2

Chapter Chemical Reaction and Stoichiometry

Figure 2.1 Lorenzo Romano Avogadro, count of Quaregna and Cerreto (1776–1856). He is famous for the Avogadro's law and Avogadro's number.

2.1 THE MOLE

The mole (abbreviated to mol) is the unit for measuring the amount of substances, based on the number of their constituent particles. One mole of a substance is defined as the amount of that substance containing as many elemental entities as exactly 12 g of carbon-12. An elemental entity could be atom, molecule or ion. A mol of a substance is numerically equal to 6.02 × 10^{23} particles. This value, called Avogadro's number N_A, has the unit of per mole (mol^{-1}).

The number of moles n of a substance can be determined as follows:

- From the mass of given sample, using the relation

$$n = \frac{m}{M}$$

where

m = Mass of the sample.

M = Molar mass of the substance.

- From the number of atoms in a sample, using the relation

$$n = \frac{N}{N_A}$$

where

N = The number of atoms in a sample.

N_A = Avogadro’s number.

- From molarity (molar concentration) and volume of a solution, using the relation

$$n = C \times V$$

where

C = The concentration of solution in M(mol dm^{-3}).

V = The volume of solution in dm^3.

[Note: The number of moles of a gas at STP can be determined from its volume at STP This is explained fully in Chapter 5]

Example 1 Calculate the number of moles of sulphuric acid, H_2SO_4, in 30.0 g of the acid.

(H = 1, O = 16, S = 32)

Solution We have to apply the relation

$$n = \frac{m}{M}$$

$$m = 30.0 \text{ g}$$

$$M = [(2 \times 1) + 32 + (16 \times 4)] \text{ g mol}^{-1} = 98 \text{ g mol}^{-1}$$

$$n = ?$$

Substituting we obtain

$$n = \frac{30.0 \cancel{\text{g}} \times 1 \text{mol}}{98 \cancel{\text{g}}}$$

$$= 0.31 \text{ mol}$$

Example 2 What is the mass of 0.15 mol of sodium hydrogen carbonate, $NaHCO_3$?

(H = 1, C = 12, O = 16, Na = 23)

Solution As usual, we have to apply the relation

$$n = \frac{m}{M}$$

$$\therefore \quad m = n \times M$$

$$M = [23 + 1 + 12 + (16 \times 3)] = 84 \text{ g mol}^{-1}$$

$$n = 0.15 \text{ mol}$$

$$m = ?$$

We now substitute to obtain

$$n = 0.15 \cancel{\text{mol}} \times \frac{84 \text{ g}}{1 \cancel{\text{mol}}}$$

$$= 13 \text{ g}$$

Example 3 Calculate the molar mass of a compound if 5.3 g of the compound contains 0.13 mol.

Solution We have to apply the equation

$$n = \frac{m}{M}$$

$$\therefore \; M = \frac{m}{n}$$

$$n = 0.13 \text{ mol}$$

$$m = 5.3 \text{ g}$$

$$M = ?$$

Substituting we obtain

$$M = \frac{5.3 \text{ g}}{0.13 \text{ mol}}$$

$$= 41 \text{ g mol}^{-1}$$

Example 4 Calculate the mass of a sample of sodium chloride containing 6.20×10^{22} atoms.

(Na = 23.0, Cl = 35.5, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)

Solution We must first determine the number of moles of the sample, usin the relation

$$n = \frac{N}{N_A}$$

$$N = 6.2 \times 10^{22}$$
$$N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$$
$$n = ?$$

Substituting we obtain

$$n = \frac{6.20 \times 10^{22} \times 1\ \text{mol}}{6.02 \times 10^{23}}$$

$$= 0.103\ \text{mol}$$

The mass can now be determined from the relation

$$m = n \times M$$
$$M = (23.0 + 35.5)\ \text{g mol}^{-1} = 58.5\ \text{g mol}^{-1}$$
$$m = ?$$

Finally, we now substitute to obtain

$$m = 0.103\ \cancel{\text{mol}} \times \frac{58.5\ g}{1\ \cancel{\text{mol}}}$$

$$= 5.9\ \text{g}$$

Example 5 Calculate the number of atoms in 0.23 mol of nitric acid, HNO_3.

Solution We have to apply the relation

$$n = \frac{N}{N_A}$$

$$\therefore\ N = n \times N_A$$
$$n = 0.23\ \text{mol}$$
$$N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$$
$$N = ?$$

Substituting we have

$$N = 0.23\ \cancel{\text{mol}} \times \frac{6.02 \times 10^{23}}{1\ \cancel{\text{mol}}}$$

$$= 1.4 \times 10^{23}$$

Example 6 Calculate the amount, in mol, of hydrochloric acid present in 200.0 cm^3 of 0.15-M solution of the acid.

Solution We have to apply the relation

$$n = C \times V$$

$$C = 0.15 \text{ mol dm}^{-3}$$

$$V = 200.0 \text{ cm}^3 = 0.20 \text{ dm}^3$$

$$n = ?$$

Substituting we obtain

$$n = \frac{0.15 \text{ mol}}{\cancel{\text{dm}^3}} \times 0.20 \cancel{\text{dm}^3}$$

$$= 0.030 \text{ mol}$$

We must always ensure that the volume is in dm^3!

Practice Problems

1. Calculate the number of moles in 2.5 g of oxygen gas. (O = 16) [*Answer:* 0.078 mol]
2. Calculate the mass of 0.32 mol of calcium chloride, $CaCl_2$. (Ca = 40, Cl = 35.5) [*Answer:* 36 g]
3. What is the number of atoms in 0.21 mol of calcium carbide, CaC_2? [*Answer:* 1.3×10^{23}]
4. Calculate the number of moles of a substance in 20.0 cm^3 of a 0.22-M solution of the substance. [*Answer:* 0.0044 mol]

2.2 CHEMICAL EQUATIONS

A chemical equation is a short way of writing a chemical reaction, using only chemical formulae and symbols to represent the reactants and products. The reactants are written on the left-hand side of the equation, while the products are written on the right. An arrow (→) points from the reactants to the products. A reversible reaction is denoted with double arrows (⇔).

In addition, the physical states or nature of reactants and products are denoted in parentheses beside their formulae or symbols, as follows:

- (*s*), if the specie is in the solid state.
- (*l*), if the specie is in the liquid state.
- (*g*), if the specie is in the gaseous state.
- (*aq*), if the specie is in aqueous solution, i.e., dissolved in water.

So if a liquid A reacts with a solid B to produce a solid C and another substance D (that is dissolved in solution), then the equation is written as

$$A(l) + B(s) \rightarrow C(s) + D(aq)$$

Some examples of chemical equation are:

- The irreversible reaction between hydrogen and oxygen to produce water vapour:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

- The reversible reaction between nitrogen and hydrogen to produce ammonia gas:

$$N_2(\mathrm{g}) + H_2(\mathrm{g}) \Leftrightarrow 2NH_3(g)$$

- The reaction between zinc granules and hydrochloric acid to produce zinc chloride and hydrogen:

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(s) + H_2(g)$$

An equation should be written in such a way that the number of atoms of each element on either sides of the equation are equal. This is based on the law of conservation of mass, which is treated later in this chapter. An equation that falls short of this requirement should be balanced by multiplying the reactants and products by the appropriate numbers, which could be fractions or whole numbers.

Example 1 Balance the following equation:

$$H_2(g) + O_2(g) \rightarrow H_2O(g)$$

Solution This equation is not balanced because two atoms of O are present on the LHS, while just one is on the RHS. The equation is balanced by multiplying H_2 and H_2O by 2, i.e.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

This brings the number of H and O atoms on each side to 4 and 2 respectively.

Note that $2H_2$ denotes four atoms of hydrogen, and $2H_2O$ denotes four atoms of hydrogen and 2 atoms of oxygen.

Example 2 Balance the equation $N_2(g) + H_2(g) \Leftrightarrow NH_3(g)$.

Solution The equation is not balanced because there are two atoms of N on the LHS, while there is only one on the RHS. Besides, there are two atoms of H on the LHS, while there are three on the RHS. The equation is be balanced by multiplying H_2 by 3, and NH_3 by 2, i.e.

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$$

This brings the number of N and H atoms on each side to 2 and 6 respectively.

Example 3 Balance the equation $Zn(s) + HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$.

Solution This equation is not balanced because there is one atom each of Cl and H on the LHS, while each has two on the RHS. The equation is balanced by multipling HCl by 2, i.e.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(s) + H_2(g)$$

We now have two atoms each of H and Cl on both sides and, of course, the number of Zn atoms on each side remains unaleterd.

Practice Problems

Balance the following equations:

1. $SO_2(g) + H_2(g) \rightarrow SO_3(g)$

[Answer: $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$]

2. $N_2(g) + H_2(g) \Leftrightarrow NH_3(g)$

[Answer: $2N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$]

3. $KClO_3(s) \rightarrow KCl(s) + O_2(g)$

[Answer: $2KClO_3(s) \rightarrow KCl(s) + O_2(g)$]

4. $H_2SO_4(aq) + NaOH(aq) \rightarrow N_2SO_4(aq) + H_2O(l)$

[Answer: $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$]

2.2.1 Ionic Equations

Reactions involving aqueous ionic compounds can be written in terms of their ions. Such equations are called ionic equations. The following rules are followed in writing ionic equations:

- Break up all the aqueous ionic compounds (or other aqueous species) into their constituent ions.
- Cancel out any ions that appear on both sides of the equation. Such ions are

called spectator ions.

- Balance oxygen atoms with water when necessary.
- Ensure that the charges as well as the number of atoms on both sides of the equation are balanced.

These rules are illustrated with the following examples.

Example 1 Write the ionic equation for the reaction between sodium hydroxide and hydrochloric acid.

Solution The first step is to write the balanced equation of reaction:

$$\mathrm{NaOH}(aq) + \mathrm{HCl}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

We now break up the ionic substances into their ions, and cancel out the spectator ions:

$$\cancel{\mathrm{Na}^+(aq)} + \mathrm{OH}^-(aq) + \mathrm{H}^+(aq) + \cancel{\mathrm{Cl}^-(aq)} \rightarrow \cancel{\mathrm{Na}^+(aq)} + \cancel{\mathrm{Cl}^-(aq)} + \mathrm{H_2O}(l)$$

Thus the net ionic equation is

$$\mathrm{OH}^-(aq) + \mathrm{H}^+(aq) \rightarrow \mathrm{H_2O}(l)$$

The equation is balanced because both sides contain the same number of atoms of each element and the net charges on both sides are equal.

When an acid is dissolved in water, each hydrogen ion (proton) reacts with a water molecule to form hydronium ion $\mathrm{H_3O^+}$, as follows:

$$\mathrm{H}^+(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{H_3O}^+(aq)$$

Thus we can write $\mathrm{H_3O^+}$ instead of $\mathrm{H^+}$ in the above ionic equation, i.e.

$$\mathrm{H_3O}^+(aq) + \mathrm{OH}^-(aq) \rightarrow \mathrm{H_2O}(l)$$

The net charges on both sides are equal. However, we need to balance the atoms by multiplying $\mathrm{H_2O}$ by 2 to obtain the net ionic equation

$$\mathrm{H_3O}^+(aq) + \mathrm{OH}^-(aq) \rightarrow 2\mathrm{H_2O}(aq)$$

Example 2 Write the balanced ionic equation for the reaction between sulphuric acid, $\mathrm{H_2SO_4}$ and calcium hydroxide, $\mathrm{Ca(OH)_2}$.

Solution The equation of reaction is

$$\mathrm{H_2SO_4}(aq) + \mathrm{Ca(OH)_2}(aq) \rightarrow \mathrm{CaSO_4}(aq) + 2\mathrm{H_2O}(l)$$

Then $2\mathrm{H}^+(aq) + \cancel{\mathrm{SO_4^{2-}}(aq)} + \cancel{\mathrm{Ca}^{2+}(aq)} + 2\mathrm{OH}^-(aq) \rightarrow \cancel{\mathrm{Ca}^{2+}(aq)} + \cancel{\mathrm{SO_4^{2-}}(aq)} + 2\mathrm{H_2O}(l)$

Thus $2\mathrm{H}^+(aq) + 2\mathrm{OH}^-(aq) \rightarrow 2\mathrm{H_2O}(l)$

As usual, we can write H_3O^+ in place of H^+, and balance the equation to obtain

$$2H_3O^+(aq) + 2OH^-(aq) \rightarrow 4H_2O(l)$$

Example 3 Write the ionic equation for the reaction

$$H_2SO_4(aq) + NaCl(aq) \rightarrow NaHSO_4(aq) + HCl(g)$$

Solution We start by breaking up the appropriate species into their ions, as follows:

$$2H_3O^+(aq) + \cancel{SO_4^{2-}}(aq) + \cancel{Na^+}(aq) + Cl^-(aq) \rightarrow \cancel{Na^+}(aq) + H_3O^+(aq) + \cancel{SO_4^{2-}}(aq) + HCl(g)$$

So, $H_3O^+(aq) + Cl^-(aq) \rightarrow HCl(g)$

The equation is not balanced because H_3O^+ has introduced an O atom to the LHS. Also, the LHS now contains three H atoms; wheras there is only one H atom on the RHS. We can take care of this by introducing H_2O to the RHS to obtain the net ionic equation

$$H_3O^+(aq) + Cl^-(aq) \rightarrow HCl(g) + H_2O(l)$$

Note that we have not broken up hydrogen chloride, $HCl(g)$, into its ions because it is a molecular compound existing in the gaseous state.

Example 4 Write the ionic equation form of the equation:

$$Na_2CO_3(aq) + CaCl_2(aq) \rightarrow CaCO_3(s) + 2NaCl(aq)$$

Solution We begin by breaking all substances in aqueous solution into their ions:

$$\cancel{2Na^+}(aq) + CO_3^{2-}(aq) + Ca^{2+}(aq) + \cancel{2Cl^-}(aq) \rightarrow CaCO_3(s) + \cancel{2Na^+}(aq) + \cancel{2Cl^-}(aq)$$

Then $CO_3^{2-}(aq) + Ca^{2+}(aq) \rightarrow CaCO_3(s)$

Note that we have not broken up $CaCO_3(s)$ into its ions because it is an insoluble compound, although it is ionic.

Practice Problems

Write the ionic forms of the following equations:

1. $NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

   [*Answer:* $Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$]
2. $2NaHCO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) + 2CO_2(g)$

   [*Answer:* $2HCO_3^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l) + 2CO_2(g)$]

2.2.2 Information from Chemical Equation

The following useful information can be obtained from a balanced chemical equation:

- The reactants and products of the reaction.
- The number of moles of the reactants and products. This is represented by the stoichiometric coefficients of the reactants and products, i.e., the numbers multiplying the species in the equation. This is illustrated with the following equation:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

This equation is another way of saying two moles of hydrogen react with one mole of oxygen to produce two moles of water vapour.

- The total charge on each ion in the equation (ionic equations). This is obtained by multiplying the charge on each ion by its stoichiometric coefficient. This is illustrated with the following equation:

$$2H^+(aq) + 2OH^-(aq) \rightarrow 2H_2O(l)$$

The total charge on $OH^- = 2 \times (-1) = -2$

The total charge on H^+ is $2 \times 1 = 2$

Thus the net charge on the LHS = 2 − 2 = 0

This shows that the net charge on the LHS is the same as the net charge on the RHS, since H_2O is a neutral molecule.

- The elements and radicals involved in the reaction.
- The physical states of the reactants and products.
- The direction of reaction. An arrow (→) indicates a reaction proceeding only in the forward reaction, i.e., the reaction is irreversible. Double arrows (⇔) indicate a reaction proceeding in both directions, i.e., the reaction is reversible.
- It shows how radicals or elements are exchanged during a reaction.
- The enthalpy[1] or heat change of the reaction, provided this is specified along with the equation, e.g.

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -408 \text{ kJ mol}^{-1}$$

This tells us that the heat of formation of carbon dioxide is 408 kJ mol^{-1}. The negative sign indicates that heat is lost, i.e., the reaction is exothermic.

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[1] Heat of reaction is treated in Chapter 11.

The following information cannot be obtained from a chemical equation:

- The pH of any of the species in the equation.
- The rate of reaction.
- The enthalpy or heat change of the reaction, unless this is specified along with the equation.
- The colour of any of the species in the equation.

Practice Problems

1. What is the number of mole each specie in the following reaction?

$K_2CO_3(aq) + 2HCl(aq) \rightarrow KCl(aq) + H_2O(l) + CO_2(g)$

[*Answers:* $K_2CO_3 = 1$, $HCl = 2$, $KCl = 1$, $H_2O = 1$, $CO_2 = 1$]

2. What is the total charge on each of the following reactants and products?

$2H_3O^+(aq) + 2OH^-(aq) \rightarrow 4H_2O(l)$ [*Answers:* $H_3O^+ = +2$, $OH^- = -2$, $H_2O = 0$]

2.3 REACTION STOICHIOMETRY

Unlike physical changes, chemical reactions occur between fixed amounts of reactants to form fixed amounts of the products. The relationship which exists between the amounts of the reactants and products in a chemical reaction is called stoichiometry.

The stoichiometry of a reaction is given by a well-balanced equation of the reaction. As we said earlier, the coefficient of each specie occurring in the equation is called its stoichiometric coefficient, which denotes the number of moles of that substance in the reaction. For example, calcium carbonate, $CaCO_3$, decomposes when heated, as follows:

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Amount (mol) 1 1 1

Mole ratio 1 : 1 : 1

This equation shows that 1 mol of $CaCO_3$ decomposes to produce 1 mol each of CaO and CO_2.

For gas phase reactions, the stoichiometric coefficients of the species also indicate their volumes. This is illustrated with the reaction

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

Amount (mol) 2 1 2

Volume (cm^3) 2 1 2

The equation shows that 2 mol or 2 cm^3 of hydrogen reacts with 1 mol or 1 cm^3 of oxygen to produce 2 mol or 2 cm^3 of water vapour.

Stoichiometry is very important as it forms the basis of the calculations involving chemical equations. In the industry, such calculations help to know the right amounts of reactants that should be mixed to obtain a desired amount of the product. The stoichiometric amounts of reactants are the amounts of such reactants that will just react with each other completely as specified by the equation of reaction. On the other hand, if the amount of a reactant exceeds the stoichiometric amount, then it is said to be in excess. The exess reactant remains unreacted.

The maximum amount of a product which can be formed in a chemical reaction is always governed by a particular reactant, unless the reactants are supplied in stoichiometric amounts. Such a reactant which governs the maximum amount of a product that can be formed in a chemical reaction is called a limiting reagent. A limiting reagent is always the reactant which produces the smallest yield of a particular product.

The examples given below illustrate the typical calculations that are encountered in chemical equations.

Example 1 Determine the limiting reagent when 2.5 mol of nitrogen is mixed with 4.0 mol of hydrogen to produce ammonia.

Solution The very first step is to write the balanced equation of reaction:

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$$

As we noted above, the limiting reagent is the reactant which produces the smallest amount of the product. Thus we have to calculate the amount of the product that would be produced from the given amount of each reactant.

According to the equation, 1 mol of N_2 produces 2 mol of NH_3, then 2.5 mol of N_2 would produce x, i.e.

1 mol = 2 mol

2.5 mol = x

Thus 1 mol × x = 2 mol × 2.5 mol

So $x = \frac{2\text{ mol} \times 2.5 \cancel{\text{ mol}}}{1 \cancel{\text{ mol}}}$

= 5 mol

Similarly, 3 mol of H_2 produces 2 mol of NH_3, then 4.0 mol of H_2 would produce x, i.e.

3 mol = 2 mol
4 mol = x
Then 3 mol × x = 4 mol × 2 mol

So $x = \frac{4 \text{ mol} \times 2 \cancel{\text{mol}}}{3 \cancel{\text{mol}}}$
= 2.7 mol

Since the given amount of hydrogen produces the smaller amount of the product, then hydrogen is the limiting reagent.

Example 2 Sodium nitrate, $NaNO_3$, decomposes according to the equation

$$NaNO_3(s) \rightarrow 2NaNO_2(s) + O_2(g)$$

Calculate the number of moles of oxygen that would be produced from 20.0 g of sodium nitrate.

(N = 14, O = 16, Na = 23)

Solution Since stoichiometry provides direct information on the number of moles, then we have to convert the given mass of $NaNO_3$ to moles by using the relation

$n = \frac{m}{M}$

m = 20.0 g
M = [23 + 14 + (16 × 3)] g mol^{-1} = 85 $gmol^{-1}$
n = ?

Substituting we have

$n = \frac{\cancel{20.0 \text{ g}} \times 1 \text{ mol}}{\cancel{85 \text{ g}}}$

= 0.24 mol

According to the equation, 1 mol of $NaNO_3$ yields 1 mol of O_2, then 0.24 mol of $NaNO_3$ would equally yield 0.24 mol of O_2, or

1 mol = 1 mol
0.24 mol = x
So 1 mol × x = 1 mol × 0.24 mol

Thus $x = \frac{1\text{ mol} \times 0.24\ \cancel{\text{mol}}}{1\ \cancel{\text{mol}}}$

$= 0.24$ mol

Example 3 What mass of potassium chloride, KCl, will be produced when 40.8 g of barium chloride, $BaCl_2$, reacts with 50.7 g of potassium sulphate, K_2SO_4. The equation of reaction is

$$BaCl_2(s) + K_2SO_4(aq) \rightarrow B_2SO_4(s) + 2KCl(aq)$$

(O = 16.0, Cl = 35.5, S = 32.0, K = 39.0, Ba = 137.3)

Solution The maximum amount of KCl that would be obtained is that produced by the limiting reagent. Thus we have to calculate the amount of the product that would be produced from the given mass of each reactant, and choose the smaller of the two values. In the meanwhile we have to first convert the masses of the two reactants to moles:

$$n = \frac{m}{M}$$

For $BaCl_2$ we have:

$$M = [137.3 + (35.5 \times 2)]\text{ g mol}^{-1} = 208.3\text{ g mol}^{-1}$$

$$m = 40.8\text{ g}$$

$$n = ?$$

Substituting we have

$$n = \frac{\cancel{40.8\text{ g}} \times 1\text{ mol}}{\cancel{208.3\text{ g}}}$$

$$= 0.196\text{ mol}$$

For K_2SO_4 we have:

$$M = [(39.0 \times 2) + 32.0 + (16.0 \times 4)]\text{ g mol}^{-1} = 174.0\text{ g mol}^{-1}$$

$$m = 50.7\text{ g}$$

$$n = ?$$

Substituting we have

$$n = \frac{50.7\ \cancel{\text{g}} \times 1\text{ mol}}{174.0\ \cancel{\text{g}}}$$

$$= 0.291\text{ mol}$$

According to the equation, 1 mol of $BaCl_2$ yields 2 mol of KCl, then 0.196 mol would also produce 0.392 mol of KCl, or

$$1 \text{ mol} = 2 \text{ mol}$$
$$0.196 \text{ mol} = x$$

Thus $1 \text{ mol} \times x = 2 \text{ mol} \times 0.196 \text{ mol}$

Then $x = \frac{2 \cancel{\text{mol}} \times 0.196 \text{ mol}}{1 \cancel{\text{mol}}}$

$= 0.392 \text{ mol}$

Similarly, 1 mol of K_2SO_4 yields 2 mol of KCl, then 0.291 mol would also produce 0.582 mol of KCl, or

$1 \text{ mol} = 2 \text{ mol}$
$0.291 \text{ mol} = x$

Thus $1 \text{ mol} \times x = 2 \text{ mol} \times 0.291 \text{ mol}$

So $x = \frac{2 \cancel{\text{mol}} \times 0.291 \text{ mol}}{1 \cancel{\text{mol}}}$

$= 0.582 \text{ mol}$

$BaCl_2$ is the limiting reagent because it produces the smaller amount of KCl. Thus the maximum amount of KCl that could be produced is 0.392 mol. Finally, we have to convert this to mass by using the relation

$n = \frac{m}{M}$

$\therefore \; m = M \times n$
$M = (39.0 + 35.5) \text{ g mol}^{-1} = 74.5 \text{ g mol}^{-1}$
$m = ?$

Substituting we obtain

$m = \frac{74.5 \text{ g}}{1 \cancel{\text{mol}}} \times 0.392 \cancel{\text{mol}}$

$= 29.2 \text{ g}$

Practice Problems

1. Calculate the limiting reagent when 5.5 g of oxygen is mixed with 1.4 g of

hydrogen to produce water vapour.

(H = 1, O = 16) [*Answer:* Oxygen]

2. Calculate the mass of water that will be produced when 10.0 g of dilute hydrochloric acid is added to 20.0 g of sodium carbonate. The equation of reaction is

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

(H = 1.0, C = 12.0, O = 16.0, Na = 23.0, Cl = 35.5) [*Answer:* 5.00 g]

2.3.1 Percentage Yield

Due to some factors like loss of reactants and presence of impurities, the actual amount of a product obtained usually differs from that obtained from calculations. The amount obtained from calculations is called the theoretical yield *T*; that obtained in practice is called the actual yield *A*. The percentage of the theoretical yield obtained in practice is called percentage yield, i.e.

$$\text{Percentage yield} = \frac{A}{T} \times 100\%$$

Example 1 20.0 g of calcium carbonate was heated vigorously to produce calcium oxide and carbon dioxide. Calculate the percentage yield of the decomposition if the volume of carbon dioxide obtained at STP is 4.0 dm^3.

(O = 16.0, Ca = 40.0)

Solution We must first obtain the theoretical volume of CO_2 produced at STP from the equation of reaction:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

The amount of $CaCO_3$ decomposing can be obtained from the relation

$$n = \frac{m}{M}$$

$$m = 20.0 \text{ g}$$

$$M = [40 + 12 + (10 \times 3)] \text{ g mol}^{-1} = 100 \text{ g mol}^{-1}$$

$$n = ?$$

Substituting we have

$$n = \frac{20.0 \cancel{\text{g}} \times 1 \text{ mol}}{100.0 \cancel{\text{g}}}$$

$$= 0.200 \text{ mol}$$

According to the equation, 1 mol of $CaCO_3$ yields 1 mol of CO_2, then 0.200 mol of $CaCO_3$ would equally yield 0.200 mol of CO_2 at STP, or

$$1\ \text{mol} = 1\ \text{mol}$$
$$x = 0.200\ \text{mol}$$

Then

$1\ \text{mol} \times x = 1\ \text{mol} \times 0.200\ \text{mol}$

Thus

$$x = \frac{1\,\cancel{\text{mol}} \times 0.200\ \text{mol}}{1\,\cancel{\text{mol}}}$$

$= 0.200$ mol at STP

Since the volume of gas was measured at STP, then the theoretical volume can now be obtained from molar volume[2], i.e.

$$V = n \times 22.4\ \text{dm}^3\,\text{mol}^{-1}$$
$$V = ?$$

Substituting we obtain

$$V = 0.200\,\cancel{\text{mol}} \times \frac{22.4\ \text{dm}^2}{1\,\cancel{\text{mol}}}$$
$$= 4.48\ \text{dm}^3$$

Alternatively, 1 mol of CO_2 occupies a volume of 22.4 dm^3 at STP, then 0.200 mol would occupy x, i.e.

$$1\ \text{mol} = 22.4\ \text{dm}^3$$
$$0.200\ \text{mol} = x$$
$$\text{So } x \times 1\ \text{mol} = 22.4\ \text{dm}^3 \times 0.200\ \text{mol}$$

Thus

$$x = \frac{22.4\ \text{dm}^3 \times 0.200\,\cancel{\text{mol}}}{1\,\cancel{\text{mol}}}$$

$$= 4.48\ \text{dm}^3$$

Finally, we can now obtain the percentage yield from the relation

$$\text{Percentage yield} = \frac{A}{T} \times 100$$

$$A = 4.0\ \text{dm}^3$$

$$\text{Percentage yield} = ?$$

Substituting we have

$$\text{Percentage yield} = \frac{4.0\ \cancel{\text{dm}^3}}{4.48\ \cancel{\text{dm}^3}} \times 100\%$$

$$= 89\%$$

Example 2 Carbon reacts with zinc oxide according to the following equation:

$$C(s) + ZnO(s) \rightarrow CO(g) + Zn(s)$$

What mass of zinc is obtained from 25.5 g of zinc oxide if the percentage yield is 98%?

(C = 12, O = 16, Zn = 65.4)

Solution Since the percentage yield is 98%, then 98% of theoretical yield would be obtained in practice. The theoretical yield is obtained as follows:

$$n = \frac{m}{M}$$

$$m = 25.5\ \text{g}$$

$$M = (65.4 + 16.0)\ \text{g mol}^{-1} = 81.4\ \text{g mol}^{-1}$$

$$n = ?$$

Substituting we obtain

$$n = \frac{25.5\ \cancel{\text{g}} \times 1\ \text{mol}}{81.4\ \cancel{\text{g}}}$$

$$= 0.313\ \text{mol}$$

According to the equation, 1 mol of ZnO yields 1 mol of Zn, then 0.313 mol of ZnO would also yield 0.313 mol, or

$$1\ \text{mol} = 1\ \text{mol}$$

$$x = 0.313\ \text{mol}$$

Thus

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[2] The molar volume of a gas is 22.4 $\text{dm}^3\ \text{mol}^{-1}$ at STP This is treated in details in Chapter 5.

$x \times 1\ \text{mol} = 0.313\ \text{mol} \times 1\ \text{mol}$

So

$x = \frac{0.313\ \cancel{\text{mol}} \times 1\ \text{mol}}{1\ \cancel{\text{mol}}}$

$= 0.313\ \text{mol}$

We must now convert this amount of Zn to mass, using the relation

$$m = n \times M$$

$$M = 65.4\ \text{g mol}^{-1}$$

$$m = ?$$

We now substitute to obtain

$$m = 0.313\ \cancel{\text{mol}} \times \frac{65.4\ \text{g}}{1\ \cancel{\text{mol}}}$$

$$= 20.5\ \text{g}$$

Since the actual yield is 98% of the theoretical yield, then

$$A = \frac{98}{100} \times 20.5\ \text{g}$$

$$= 20\ \text{g}$$

Practice Problems

1. During the laboratory preparation of hydrogen, dilute hydrochloric acid was added to 5.2 g of zinc granules until all the zinc granules were used up. The remaining solution was then evaporated to dryness and weighed. What is the percentage yield of $ZnCl_2$ if the mass of the residue is 7.0 g? The equation of reaction is

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

(H = 1.0, Cl = 35.5, Zn = 65.4) [*Answer:* 64%]

2. 20.0 g of sodium hydroxide was added to excess dilute hydrochloric acid. Calculate the mass of sodium chloride obtained if the percentage yield is 92%.

(H = 1.0, O = 16.0, Na = 23.0, Cl = 35.5) [*Answer:* 27 g]

2.4 CHEMICAL LAWS

Chemical laws are the laws governing chemical reactions. These include:

The law of conservation mass: The law of conservation of mass states that matter is neither created nor destroyed during a chemical reaction, but only changes from one form to another. Thus the total mass of all the reactants, if weighed, would be found to be equal to that of the products. However, this law is only applicable to ordinary chemical reactions because mass is destroyed in nuclear reactions as energy is produced.

The law of definite proportion: The law of definite proportion states that all pure samples of a particular chemical compound contain similar elements combined in the same proportion by mass. For example, all pure samples of water, H_2O, will always contain hydrogen and oxygen combined in ratio 2:1, regardless of the source or method of preparation.

The law of multiple proportions: The law of multiple proportions states that if two elements, A and B, combine to form more than one chemical compound, then the various masses of the element A which combines separately with a fixed mass of the other elements B, are in a simple multiple ratio. For example, iron combines with chlorine to form two compounds: iron(II) chloride, $FeCl_2$ and iron(III) chloride, $FeCl_3$. It is obvious that the masses of chlorine in the two compounds are in a simple ratio of 2:3.

The law of reciprocal proportion: The law of reciprocal proportion states that the masses of several elements, A, B, C, which combine separately with a fixed mass of another element, D, are the same as, or simple multiples of, the masses in which A, B, C, themselves combine with one another.

Example 1 The analysis of two different samples of copper(II) oxide, CuO yields the following data:

	Sample A	Sample B
Mass of CuO	20.0 g	15.0 g
Mass of Cu	16.0 g	11.9 g

Calculate the percentage of copper in each sample, and state the law of chemical combination which your results verify.

Solution The percentage composition of copper in each sample is calculated from the relation

$$\% \text{ composition} = \frac{\text{Mass of element}}{\text{Mass of compound}}$$

For sample A:

Mass of copper = 20.0 g
Mass of compound = 16.0 g
% composition = ?

Substituting we obtain

$$\% \text{ composition} = \frac{16.0\ \cancel{g}}{20.0\ \cancel{g}} \times 100\%$$

$$= 80.0\%$$

For sample B:

Mass of copper = 11.9 g
Mass of compound = 15.0 g
% composition = ?

Substituting we obtain

$$\% \text{ of composition} = \frac{11.9\ g}{15.0\ g} \times 100\%$$

$$= 79.3\%$$

Since the amounts of copper in the two samples are approximately equal, then the results confirms the law of definite proportions.

Example 2 4.50 g of copper(I) oxide, Cu_2O, and 3.80 g of copper(II) oxide, CuO, were reduced to constant masses of 4.00 g and 3.04 g respectively. Find the ratio of the masses of copper that will react separately with 5.00 g of oxygen in both cases, hence state which chemical law your result confirms.

Solution Oxygen has been removed from the two samples by reduction. Thus the masses of the residues are the masses of copper. The mass of oxygen in each sample can be calculated by subtracting the mass of copper from the mass of its oxide, as follows:

	Cu_2O	CuO
Mass of oxide	4.50 g	3.80 g
Mass of copper	4.00 g	3.04 g
So Mass of oxygen	0.500 g	0.76 g

For Cu_2O:

4.00 g of copper combines with 0.500 g of oxygen, then x would react with 5.00 g of oxygen, i.e.

4.00 g = 0.500 g
x = 5.00 g

Then 0.500 g × x = 5.00 g × 4.00 g

Thus $x = \frac{5.00\ \cancel{g} \times 4.00\,g}{0.500\ \cancel{g}}$

= 40.0 g

For CuO:

3.04 g of copper reacts with 0.76 g of oxygen, then x would react with 5.00 g of oxygen, i.e.

3.04 g = 0.76 g
x = 5.00 g

So 0.76 g × x = 3.04 g × 5.00 g

Then $x = \frac{3.04\ \cancel{g} \times 5.00\,g}{0.76\ \cancel{g}}$

= 20 g

Thus the different masses of copper that react with a fixed mass of oxygen are in the ratio 2:1, i.e.

	Cu_2O	CuO
Mass of copper	40 g	20 g
Mass ratio	$\frac{40.0}{20} = 2$:	$\frac{20}{20} = 1$

The inference we can draw from this result is that the separate masses of copper which combine with a fixed mass of oxygen to form the two oxides are in a simple ratio of 2:1, which confirms the law of multiple proportions.

Practice Problems

1. The analysis of two samples of sodium chloride obtained from different sources yields the following data:

	A	B
Mass of sodium chloride	2.50 g	1.80 g
Mass of sodium	0.98 g	0.71 g

Calculate the percentage by mass of chlorine in each sample, hence state which chemical law your results support. [*Answer:* (A) 60.8% (B) 60.6%; the law of definite proportions]

2. 3.02 g of copper(I) oxide and 2.55 g of copper(II) oxide were reduced by coke. The masses of copper obtained from the two oxides are 2.68 g and 2.04 g respectively. Calculate the mass of copper that would react with 1 g of oxygen in each case, and comment on your result.
[*Answers:* (A) 7.9 g (B) 4.0 g; the results supports the law of multiple proportions]

SUMMARY

- The mole is the amount of a substance that contains as many elementary entities as exactly 12 g of carbon-12. It is calculated as follows:

$$n = \frac{m}{M},\ n = \frac{N}{N_A} \text{ and } n = C \times V$$

- A chemical equation is a short way of writing a chemical reaction using only chemical formulae and symbols to represent the reactants and products.
- An ionic equation is an equation in which the ions taking part in the reaction are clearly shown.
- Stoichiometry is the relationship between the amounts of reactants and products in a chemical reaction.
- A limiting reagent is the reactant governing the maximum amount of a product that can be formed in a chemical reaction. It corresponds to the reactant which produces the smallest amount of the product.
- The percentage yield of a reaction is the percentage of the expected or theoretical yield of the product that is obtained in practice, i.e.

$$\text{Percentage yield} = \frac{A}{T} \times 100\%$$

- Chemical laws are the laws governing chemical reactions.
- The law of conservation of mass states that matter is neither created nor destroyed in a chemical reaction, but changes from one form to another.
- The law of definite proportion states that all pure samples of a particular chemical compound contain similar elements combined in the same proportion by mass.
- The law of multiple proportions states that if two elements, A and B, combine to form more than one chemical compound, then the various masses of the element A which combines separately with a fixed mass of the other elements B, are in a simple multiple ratio.
- The law of reciprocal proportion states that the masses of several elements, A, B, C, which combine separately with a fixed mass of another element, D, are the same as, or simple multiples of, the masses in which A, B, C, themselves combine with one another.

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. Which of these is the standard for defining the mole?
   A. Carbon-13 B. Carbon-12
   C. Carbon-14 D. Carbon-10
   E. Uranium-235
2. Which of these denotes Avogadro’s number?
   A. 6.02×10^{22} mol^{-1} B. 6.02×10^{23} mol^{-1}
   C. 6.02×10^{24} mol^{-1} D. 6.20×10^{25} mol^{-1}
   E. 6.01×10^{30} mol^{-1}
3. What is the mass of 0.37 mol of sodium chloride?
   A. 13 g B. 15 g
   C. 21 g D. 22 g
   E. 51 g

(Na = 23.0, Cl = 35.5)

4. Which of these has/have the least mass?

i. 0.2 mol of CaC_2 ii. 0.15 mol of HCl iii. 0.2 mol of CaO
   A. i B. i and ii
   C. ii D. iii

E. i and iii

(H = 1.0, C = 12.0, O = 16.0, Cl = 35.5, Ca = 40.1)

5. Which of the following is correct about the reaction $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$?

A. More volume of nitrogen will always be required than hydrogen.

B. The volume of the reactants will not affect that of the product.

C. The reaction is irreversible.

D. More volume of hydrogen will always be required than nitrogen.

E. None of the above.

6. Sulphuric acid dissociates in solution, as follows:

$H_2SO_4(aq)$⇔$2H^+(aq) + SO_4^{2-}(aq)$

How many moles of hydrogen ions, H^+, are produced from the dissociation of every mole of the acid?

A. 1 B. 1.5

C. 2 D. 2.5

E. 3

7. Which of these will not dissociate in solution?

A. CO_2 B. H_2SO_4

C. NaCl D. $MgSO_4$

E. HCl

8. What is the net charge on 3 mol of iron(II) ion?

A. −8 B. −6

C. +5 D. +6

E. +8

9. Which of these following can be obtained directly from a chemical equation?

A. The pH of the products.

B. The colour of the reactants.

C. The rate of reaction.

D. The equilibrium constant of the reaction.

E. None of the above.

10. What volume would 2.72 mol of oxygen occupy at STP?

A. 50.5 cm^3 B. 60.1 cm^3

C. 60.5 cm^3 D. 60.9 cm^3

E. 62.0 cm^3

(Molar volume of gases = 22.4 $dm^3 mol^{-1}$)

11. What volume of 0.15-M solution of an acid would contain 0.35 mol of the acid?

A. 2.3 cm^3 B. 2.4 cm^3

C. 2.7 cm^3 D. 2.9 cm^3

E. 3.2 cm^3

12. What mass of carbon dioxide would be produced from the decomposition of 20.0 g of zinc carbonate? The equation of reaction is $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

A. 6.0 g B. 6.2 g

C. 6.7 g D. 7.0 g

E. 8.2 g

(C = 12, O = 16, Zn = 65)

13. Which of these equations is/are not balanced?

i. $2C(s) + O_2(g) \rightarrow 2CO(g)$ ii. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ iii. $KClO_3(s) \rightarrow KCl(s) + O_2(g)$ iv. $H_2SO_4(aq) + KOH(aq) \rightarrow K_2SO_4(aq) + H_2O(1)$

A. i B. i and ii

C. iii and iv D. iv

E. iii

ESSAY TYPE QUESTIONS

The mole

14. (a) Define the mole.

(b) Which relation connects the mole and mass?

15. Calculate the number of moles of sodium hydroxide in 22.7 g of the compound.

(H = 1, O = 16, Na = 23)

16. What is the mass of 0.102 mol of calcium hydroxide?

(H = 1, O = 16, Ca = 40)

17. 0.0427 mol of the compound $Na_2CO_3.xH_2O$ has a mass of 12.2 g. Find the value of x.

(H = 1, C = 12, O = 16, Na = 23)

18. How many atoms are there in 0.25 mol of lead?

$(N_A = 6.02 \times 10^{23} \text{ mol}^{-1})$

19. A certain sample of lead(II) oxide contains 7.80×10^{23} atoms. What is the number of moles of the oxide?

$(N_A = 6.02 \times 10^{23} \text{ mol}^{-1})$

Chemical equations

20. (a) What is a chemical equation?

(b) State all the possible information you can obtain from a chemical equation.

21. Balance each of the following equations:

(a) $CH_4(g) + O_2(g) \rightarrow H_2O(g) + O_2(g)$

(b) $Ag_2CO_3(s) \rightarrow Ag(s) + CO_2(g) + O_2(g)$

(c) $Pb(NO_3)_2(s) \rightarrow PbO(s) + O_2(g)$

(d) $Fe_2O_3(s) + H_2(g) \rightarrow Fe(s) + H_2O(g)$

(e) $MnO_2(s) + HCl(aq) \rightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$

22. Balance the equations given below and, if possible, write the ionic form of each.

(a) $Zn(s) + HNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + H_2O(1) + NO(g)$

(b) $Fe_2O_3(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$

(c) $CuO(s) + HN_3(g) \rightarrow Cu(g) + H_2O(l) + N_2(g)$

(d) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

(e) $Mg_3N_2(s) + H_2O(l) \rightarrow Mg(OH)_2(s) + NH_3(g)$

Reaction stoichiometry

23. (a) What do you understand by stoichiometry? State its importance.

(b) Explain what is meant by a limiting reagent.

24. Zinc chloride is to be produced from 25.2 g of hydrochloric acid and 32.7 g of zinc. Identify the limiting reagent.

(H = 1.0, Cl = 35.5, Zn = 65.4)

25. Consider the reaction:

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

Identify the limiting reagent for the production of chloromethane when 105.6

g of methane is mixed with 88.2 g of oxygen.

26. Ethylene burns in air according to the following equation:

$$2C_2H_2(g) + 5O_2(g) \rightarrow 2H_2O(l) + 4CO_2(g)$$

What mass of oxygen is required to burn 200.0 g of ethyne completely?

(H = 1, C= 12, O = 16)

27. 50.0 g of calcium carbonate, $CaCO_3$, was heated vigorously until a constant mass of the residue was obtained. The residue was then treated with excess dilute sulphuric acid to obtain calcium sulphate, $CaSO_4$. Determine the mass of calcium sulphate produced

(H = 1.0, O = 16.0, S = 32.1, Cl = 35.5, Ca = 40.1)

28. Hydrogen peroxide decomposes to liberate oxygen gas, as follows:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

From what mass of hydrogen peroxide would you expect a yield 150.0 g of oxygen?

(H = 1, O = 16)

29. Determine the maximum amount of sodium carbonate that would be produced by mixing 32.4 g of sodium chloride and 50.5 g of calcium carbonate. The equation of reaction is

$$2NaCl(aq) + CaCO_3(s) \rightarrow Na_2CO_3(s) + CaCl_2(s)$$

(C = 12.0, O = 16.0, Na = 23.0, Ca = 40.1)

30. (a) What is percentage yield?

(b) 22.2 g of a compound was obtained instead of the 23.5 g expected from calculations. Calculate the percentage yield of the compound?

31. 1.5 kg of propane was mixed with 1.8 kg of hydrogen in an experiment on the combustion of propane. What is the percentage yield of water if the mass of water obtained is 750.0 g? The equation of reaction is

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

(H = 1, C = 12, O = 16)

32. 22.2 g of potassium hydroxide was added to excess dilute nitric acid. Calculate the mass of potassium nitrate obtained if the percentage yield is 88%.

(H = 1.0, N = 14.0, O = 16.0, K = 39.1)

Chemical laws

33. Explain the following chemical laws:

(a) The law of conservation of mass. (b) The law of multiple proportions. (c) The law of definite proportions.

34. The analysis of two samples of calcium oxide produces the following data:

	A	B
Mass of calcium oxide	5.50 g	3.80 g
Mass of oxygen	1.57 g	1.08 g

Calculate the percentage by mass of calcium in each sample, hence state which chemical law your results support.

35. 2.60 g of copper(I) oxide and 4.20 g of copper(II) oxide were reduced by coke. The masses of copper obtained from the two oxides were 2.30 g and 3.40 g, respectively. Calculate the masses of copper that would react with 2.50 g of oxygen in each case, and state which chemical law your results support.

Answers

1. B 2. B 3. D 4. C 5. D 6. C
7. A 8. D 9. E 10. D 11. A 12. D
13. C 15. 0.57 mol 16. 4.1 g
17. 10 18. 1.5×10^{23} 19. 1.30 mol

20. (a) $CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g)$ (b) $Ag_2CO_3(s) \rightarrow Ag_2O(s) + CO_2(g)$

(c) $2Pb(NO_3)_2(s) \rightarrow 2PbO(s)\ 4NO_2(g) + O_2(g)$ (d) $Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$

(e) $MnO_2(s) + 4HCl(aq) \rightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$

21. (a) $3Zn(s) + 8HNO_3(aq) \rightarrow 3Zn(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$

$3Zn(s) + 8H^+(aq) + 2NO_3^-(aq) \rightarrow 3Zn^{3+}(aq) + 4H_2O(l) + 2NO(g)$

(b) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO(g)$

(c) $3CuO(s) + 2NH_3(g) \rightarrow 3Cu(s) + 3H_2O(l) + N_2(g)$

(d) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

(e) $Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(s) + 2NH_3(g)$

24. HCl 25. Cl_2 26. 615.4 g

27. 68 g 28. 79.7 g 29. 29.4 g

30. (b) 94.5% 31. 92.6% 32. 35.2 g

34. A: 71.5%, B: 71.6%; the law of definite proportions

35. CU_2O: 19.2 g of Cu, CUO: 10.6 g of Cu; the law of multiple proportions

3

Chapter Redox Reactions and IUPAC Nomenclature

The term redox reaction is the short form of reduction-oxidation reaction. Reduction and oxidation are complimentary processes because the reduction of a substance is always accompanied by the oxidation of another substance, and vice versa.

A substance that is reduced in a redox reaction is called an oxidizing agent, while that which is oxidized is called a reducing agent. Examples of oxidizing agents include acidified potassium permanganate, $KMnO_4$; acidified potassium dichromate, $K_2Cr_2O_7$; hot concentrated sulphuric acid, H_2SO_4; sodium hypochlorite, NaClO; concentrated nitric acid, HNO_3; iron(III) chloride; $FeCl_3$; etc. Examples of reducing agents include iron(II) chloride, $FeCl_2$, iron(II) sulphate, $FeSO_4$; hydrogen sulphide, H_2S; ammonia, NH_3; potassium iodide, KI; sulphur dioxide, SO_2; carbon monoxide, CO; etc.

Oxidation and reduction can be defined in the following ways:

In terms of oxygen transfer: Oxidation is the addition of oxygen to a substance, while reduction is the removal of oxygen, e.g.

$$CuO(s) + Zn(s) \rightarrow ZnO(s) + Cu(s)$$

In the above reaction, CuO has been reduced to Cu, while Zn has been oxidized to ZnO. The oxidizing and reducing agents are CuO and Zn respectively.

In terms of the transfer of electronegative and electropositive elements: Oxidation is the addition of an electronegative element to a substance, while reduction is the removal of an electronegative element. Conversely, oxidation is the removal of an electropositive element from a substance, while reduction is the addition of an electropositive element, e.g.

$$2KI(aq) + Cl_2(g) \rightarrow 2KCl(aq) + I_2(g)$$

In the above reaction, KI has been oxidized to I_2, while Cl_2 has been reduced to KCl. The oxidizing agent is Cl_2, while the reducing agent is KI.

In terms of hydrogen transfer: Oxidaton is the removal of hydrogen from a substance, while reduction is the addition of hydrogen, e.g.

$$H_2S(g) + I_2(g) \rightarrow 2HI(g) + S(s)$$

In the above reaction, H_2S has been oxidized to S, while I_2 has been reduced to HI. The oxidizing agent is I_2, while the reducing agent is H_2S.

In terms of electron transfer: Oxidation is the removal of electron(s) from a substance, while reduction is the addition of electron(s). This form of definition encapsulates all other forms of definition of oxidation and reduction. In the first reaction, for example, zinc has been oxidized to Zn^{2+} by the removal of two electrons, while Cu^{2+} has been reduced to Cu by the addition of two electrons. As we shall see shortly, this reaction can be represented as follows:

$$Cu^{2+}(s) + Zn(s) \rightarrow Zn^{2+}(s) + Cu(s)$$

The modern form of definition of oxidation and reduction is in terms of electron transfer. Thus you should always define oxidation and reduction in this way unless you are told to do otherwise.

3.1 OXIDATION NUMBER

Oxidation number is the effective charge of an atom in a substance as determined by a set of arbitrary rules. The important information that can be obtained from oxidation number are:

- Identification of redox reactions. A reaction is a redox reaction only if there is a change in the oxidation number of the atoms involved in the reaction.
- Oxidized and reduced species. Oxidation corresponds to an increase in oxidation number, while reduction corresponds to a decrease in oxidation number. Thus an oxidized specie is the atom whose oxidation number increases, while a reduced specie is the atom whose oxidation number reduces. An oxidizing agent is the atom whose oxidation number decreases, while a reducing agent is the atom whose oxidation number increases.

Oxidation number is determined as follows:

- The oxidation numbers of an atom in its uncombined state or in a molecule of its element is zero. For example, the oxidation number of oxygen atom in O_2 is zero.

- The sum of the oxidation numbers of the atoms in a neutral molecule is zero. For example, the sum of the oxidation numbers of hydrogen and oxygen atoms in H_2O is zero.
- The sum of the oxidation numbers of the atoms in a radical equals the charge on that radical. The sum of the oxidation number of the atoms in HCO_3^-, for example, is −1.
- The oxidation numbers of all Groups I and II elements are +1 and +2 respectively. That of hydrogen is +1, except in hydrides in which it is −1. That of oxygen is −2, except in peroxides in which it is −1.
- With the exception of boron, the oxidation numbers of Group III elements are equal to their valencies of +1, +3 or +1. For example, the oxidation number of aluminium is always +3 because it has a single valency of +3.
- The oxidation number of halogens is always –1, except when bonded to oxygen or more electronegative elements. Since fluorine is the most negative of all elements, its oxidation number is always –1.

Example 1 Calculate the oxidation number of carbon in HCO_3^-.

Solution We have to add the oxidation numbers of all the elements and equate this to −1, which is the net charge on the radical. Let the oxidation number of carbon be x. The oxidation numbers of hydrogen and oxygen are +1 and −2 respectively. Thus

$+1 + x + 3(-2) = -1$

So $+1 + x - 6 = -1$

Collecting like terms we have

$x = -1 + 6 - 1$

$= +4$

Thus the ON of carbon is +4.

Example 2 Calculate the oxidation number of manganese in MnO_4^-.

Solution The sum of the oxidation numbers of the constituent elements must be equal to −1, the net charge on the radical.

We denote the oxidation number of manganese by x, and proceed as follows:

$x + 4(-2) = -1$

So $x - 8 = -1$

Collection like terms we have

$x = -1 + 8$

$= +7$

Thus ON of manganese is +7.

Example 3 Calculate the oxidation number of chromium in $K_2Cr_2O_7$.

Solution The sum of the oxidation numbers of the constituent elements of $K_2Cr_2O_7$ must be equal to zero, since it is neutral. If the oxidation number of chromium is x, then

$2(+1) + 2x + 7(-2) = 0$

So $+2 + 2x - 14 = 0$

Collecting like terms we have

$2x = +14 - 2$

Thus $2x = +12$

Then $x = +6$

Thus the ON of chromium is +6.

Example 4 Calculate the oxidation number of iron in $[Fe(OH_2)_6]^{3+}$.

Solution The sum of the oxidation numbers of all constituent atoms must be equal to +3. Also, the oxidation number of OH_2 is 0 since it is neutral. If the oxidation number of iron is x then

$x + (6 \times 0) = +3$

$\therefore\ x = +3$

Example 5 Determine the oxidation number of platinum in $[Pt(NH_3)_2Cl_4]$.

Solution Let the oxidation number of platinum be x. Since NH_3 is a neutral molecule, then

$x + (2 \times 0) + (4 \times \{-1\}) = 0$

So $x - 4 = 0$

$\therefore\ x = +4$

Example 6 Determine the oxidation number of chromium in the compound $[Cr(NH_3)_3(H_2O)_3]Cl_3$.

Solution The oxidation number of NH_3 and H_2O is 0 because they are neutral molecules. If the oxidation number of chromium is denoted by x, then

$x + (3 \times 0) + (3 \times 0)\ (3 \times \{-1\}) = 0$

So $x - 3 = 0$
$\therefore\ x = +3$

Example 7 Which of the following reactions is/are redox reaction(s)?

i. $4FeO(s) + O_2(g) \rightarrow 2Fe_2O_3(g)$

ii. $3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$

iii. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(1)$

Solution We will have to check if the oxidation numbers of the atoms have changed on forming the products. This is done by calculating the oxidation number of each atom in the reactants and products. We will simply specify the result below each atom, as follows:

For the first equation we have

$4FeO(s) + O_2(g) \rightarrow 2Fe_2O_3(g)$

(+2)(−2) 0 (+3)(−2)

We can see, here, that the oxidation number of iron has changed from +2 on the LHS to +3 on the RHS. Also, the oxidation number of oxygen changed from 0 on the LHS to –2 on the RHS. The first equation, therefore, is a redox reaction.

For the second equation we have

$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$

0 (+1)(−2) (+2)(+5)(−2) (+1)(−2) (+2)(−2)

The oxidation number of copper has increased from 0 on the LHS to +2 on the RHS. Thus the equation is a redox reaction.

For the third equation we have

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(1)$

(+1)(+5)(−2) (+1)(−1) (+1)(−1) (+1)(+5)(−2)

Unlike the two previous reactions, no change has occurred in the oxidation number of any of the elements. Thus the reaction is not a redox reaction.

Example 8 Identify the oxidizing and reducing agents in the following redox reaction:

$$3Cu(s) + 8HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$

Solution We need to assign oxidation number to each of the elements involved in the reaction, and see which has undergone an increase or decrease in oxidation number from the LHS to the RHS. Since oxidation and reduction are complimentary, then the reducing agent becomes obvious once the oxidizing agent is known, and vice versa.

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$

0 (+1)(+5)(−2) (+2)(+5)(−2) (+1)(−2) (+2)(−2)

The ON of copper has increased from 0 in Cu to +2 in $Cu(NO_3)_2$. This is an oxidation process, involving the change of Cu atom to Cu^{2+} by the loss of electron to HNO_3. Thus Cu is the reducing agent and HNO_3 is the oxidizing agent.

Example 9 Identify the oxidizing and reducing agents in the reaction

$$2FeCl_2(s) + 2Cl_2(g) \rightarrow 2FeCl_3(aq)$$

Solution As usual, the ON of each atom is specified below:

$$2FeCl_2(s) + 2Cl_2(g) \rightarrow 2FeCl_3(aq)$$

(+2)(−1) 0 (+3)(−1)

The ON of Fe has increased from +2 in $FeCl_2$ to +3 in $FeCl_3$. Thus $FeCl_2$ (or Fe^{2+}) is the reducing agent, while chlorine gas (Cl_2) is the oxidizing agent.

Example 10 Identify the oxidizing and reducing agents in the reaction

$$MnO_2(s) + 4HCl(aq) \rightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$$

Solution As usual, we have

$$MnO_2(s) + 4HCl(aq) \rightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$$

(+4)(−2) (+1)(−1) (+2)(−1) (+1)(−2) 0

The ON of Mn has decreased from +4 in MnO_2 to +2 in $MnCl_{2.}$ Thus, MnO_2 (or Mn^{4+}) is the oxidizing agent, while HCl (or Cl^-) is the reducing agent. (Note that the change of ON of Cl from −1 is an increase in ON because all negative numbers are smaller than 0).

Practice Problems

1. Calculate the oxidation number of nitrogen in $Mg(NO_3)_2$. [*Answer:* +5]
2. What is the oxidation number of sulphur in H_2SO_4? [*Answer:* +5]
3. Calculate the oxidation number of nitrogen in each of the following:
   (a) NO (b) NO_2 (C) N_2O [*Answers:* (a) +2 (b) +4 (c) +1]

4. Identify which of the following is/are redox reaction(s).

i. $ZnO(s) \rightarrow CO(g) + Zn(s)$ ii. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ iii. $H_3O(aq)\ OH^-(aq) \rightarrow 2H_2O(l)$

iv. $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$ [*Answer:* i and ii only]

5. Identify the oxidizing and reducing agents in the following reactions:

(a) $CuO(s) + Zn(s) \rightarrow ZnO(s) + Cu(s)$

(b) $3CuO(s) + 2NH_3(g) \rightarrow 3Cu(s) + 3H_2O(s) + N_2(g)$

[*Answers:* (a) OA = CuO, RA = Zn (b) OA = CuO, RA = CuO]

3.2 REDOX EQUATIONS

Redox reactions can be written in ionic form to show how substances have been oxidized and reduced. Such equations are called redox equations.

Like other chemical equations, a redox equation must be balanced. An easy way of writing and balancing redox equations is by the method of half-equation. A half-equation is obtained by splitting a redox reaction into two, each representing the process of oxidation or reduction. The half-equation that represents oxidation is called oxidation half-equation, while that representing reduction is termed reduction half-equation. A combination of the two half-equations gives the net or overall equation. The rules involved are as follows:

- Write the half-equations for the reaction.
- Balance each half-equation. Charges are balanced with electron(s), e^-, and oxygen atoms with equal number of water molecules, nH_2O.
- Hydrogen atoms are balanced with hydrogen ions, H^+, when the reaction occurs in acidic medium.
- To balance an equation occurring in a basic medium, first balance the reaction like that in an acidic medium. Finally, add the number of hydroxide ions, OH^-, equivalent to the number of hydrogen atoms to both sides of the equation, and simplify.
- Combine both half-equations by adding the substances on the corresponding sides of each equation, and cancel any substance appearing on both sides.

Example 1 Write the balanced redox equation for the reaction

$$Cu(s) + 2AgCl(aq) \rightarrow CuCl_2(aq) + 2Ag(s)$$

Solution We start by writing the half-equations. The reducing agent is copper because its oxidation number has changed from 0 to +2 in copper(II) chloride

($CuCl_2$). Thus the oxidation half-equation is

$$Cu(s) \rightarrow Cu^{2+}(aq)$$

We have one atom each of copper on both sides. To balance the charge, we add two electrons to the RHS to obtain

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

The oxidation number of silver, the reducing agent, has reduced from +1 in AgCl to 0. Thus the reduction half-equation is

$$Ag^+(aq) \rightarrow Ag(s)$$

We have one atom each of silver on both sides. To balance the charge we add an electron to the LHS to obtain

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

The number of electrons in both half-equations must be the same. Thus we multiply the equation by 2 to obtain

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$

Finally, we now combine the two half-equations to obtain

$$Cu(s) + 2Ag^+(aq) + \cancel{2e} \rightarrow Cu^{2+}(aq) + 2Ag(s) + \cancel{2e}$$

Thus the overall equation is

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

The equation shows explicitly that Cu has been oxidized to Cu^{2+}, and Ag^+ reduced to Ag.

Example 2 Balance the following ionic equation occurring acidic medium

$$MnO_4^-(aq) + SO_2(g) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq)$$

Solution We start by splitting the equation into half-equations. The oxidizing agent is MnO_4^- which has been reduced to Mn^{2+}. Thus the reduction half-reaction is

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$$

Mn atoms are balanced. The 4 O atoms must be balanced by adding $4H_2O$ molecules to the RHS to obtain

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(1)$$

The addition of $4H_2O$ molecules has left us with a deficient of 8 H atoms on the LHS. Since the reaction is in an acidic medium, then we balance the 8 H atoms by adding 8 H^+ to the LHS, i.e.

$$MnO_4^-(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(1)$$

We are now to balance the charges on both sides. The total charge on the LHS is +7 or (−1 + 8), while that on the RHS is +2. Thus we balance the charges by adding five electrons to the LHS to obtain

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(1)$$

SO_2 has been oxidized to SO_4^{2-}. Thus the oxidation half-equation is

$$SO_2(g) \rightarrow SO_4^{2-}(aq)$$

As usual, we balance the 2 extra O atoms on the RHS by adding $2H_2O$ molecules to the LHS, i.e.

$$SO_2(g) + 2H_2O(1) \rightarrow SO_4^{2-}(aq)$$

Next, we balance the 4 H atoms on the LHS by adding 4 H^+ to the RHS, i.e.

$$SO_2(g) + 2H_2O(1) \rightarrow SO_4^{2-}(aq) + 4H^+(aq)$$

The net charge on the LHS is 0, while that of the RHS is +2, i.e. −2 + 4. Thus we balance the charges by adding 2 electrons to the RHS to obtain

$$SO_2(g) + 2H_2O(1) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$$

The electrons in both half-equations are not the same. We can balance the electrons by multiplying each half-equation by the number of electrons in the other half-equation. In other words, we have to multiply the reduction half-equation by 2, and the oxidation half-equation by 5. With this we obtain

$$2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(1)$$

$$5SO_2(g) + 10H_2O(1) \rightarrow 5SO_4^{2-}(aq) + 20H^+(aq) + 10e^-$$

Finally, we can now combine the half-equations to obtain

$$5SO_2(g) + 10H_2O(1) + 2MnO_4^-(aq) + 16H^+(aq) + \cancel{10e^-}$$

$$\rightarrow 2Mn^{2+}(aq) + 8H_2O(1) + 5SO_4^{2-}(aq) + 20H^+(aq) + \cancel{10e^-}$$

Thus the overall redox equation is

$$5SO_2(g) + 2H_2O(l) + 2MnO_4^-(aq) \rightarrow 2Mn^{2+}(aq) + 4H^+(aq) + 5SO_4^{2-}(aq)$$

Example 3 Write the balanced redox equation for the reaction between acidified potassium dichromate, $K_2Cr_2O_7$, and iron(II) chloride, $FeCl_2$.

Solution We are provided with no equation. However, this should pose no problem provided we are able to identify the reducing and oxidizing agents. Acidified $K_2Cr_2O_7$ is a common oxidizing agent that dissociates as follows:

$$K_2Cr_2O_7(aq) \rightarrow 2K^+(aq) + Cr_2O_7^{2-}(aq)$$

The reduction of dichromate, $Cr_2O_7^{2-}$, to chromate(III) ions, Cr^{3+}, is responsible for the oxidizing property of $K_2Cr_2O_7$. Thus the reduction half-equation is

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$

This reaction is responsible for the change in colour of $K_2Cr_2O_7$ from orange to colourless in the presence of a reducing agent.

To balance the Cr atom, we multiply the RHS by 2 to obtain

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$$

The 7 O atoms on the LHS is balanced by adding $7H_2O$ molecules to the RHS to obtain

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

This has introduced 14 H atoms to the RHS. Since the reaction occurs in an acidic medium, we balance the 14 H atoms by adding 14 H^+ to the LHS to obtain

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

The net charge on the LHS is +12 or (−2 + 14), while that on the RHS is +6 or (2 × 3). To balance the charges, we add six electrons to the LHS, i.e.

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

Iron(II) chloride, $FeCl_2$, is a reducing agent. The oxidation of iron(II) ions, Fe^{2+}, to iron(III) ions, Fe^{3+}, is responsible for the reducing property of $FeCl_2$. Thus the oxidation half-equation is

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$$

The Fe atoms are balanced. The net charge on the LHS is +2, while that on the RHS is +3. The charges are balanced by adding an electron to the RHS, to obtain

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

To balance the number of electrons in both half-equations, we multiply the reduction half-equation by 1, and the oxidation half-equation by 6 to obtain

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$6Fe^{2+}(aq) \rightarrow 6Fe^{3+}(aq) + 6e^-$$

Finally, we now combine the two equations to obtain

$$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) + \cancel{6e} \rightarrow 6Fe^{3+}(aq) + \cancel{6e} + 2Cr^{3+}(aq) + 7H_2O(l)$$

Thus the overall equation is

$$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

Example 4 Write a balanced redox equation for the reaction between sodium tetrahydroxoplumbate(II), $Na_2[Pb(OH)_4]$, and potassium hypochlorite, KClO, in a basic medium.

Solution The oxidizing agent is KClO. The effective reduction change of the compound is the conversion of hypochlorite, ClO^-, to chloride ions, Cl^-. Thus the reduction half-equation is

$$ClO^-(aq) \rightarrow Cl^-(aq)$$

As usual, the oxygen atom on the LHS is balanced by adding a water molecule to the RHS to obtain

$$ClO^-(aq) \rightarrow Cl^-(aq) + H_2O(l)$$

The addition of water to the RHS has left the LHS deficient in 2 H atoms, which are balanced by adding 2 H^+ to the LHS, i.e.

$$ClO^-(aq) + 2H^+ \rightarrow Cl^-(aq) + H_2O(l)$$

The net charge of the LHS is +1, while that of the RHS is −1. The two charges are balanced by adding 2 electrons to the LHS to obtain

$$ClO^-(aq) + 2H^+(aq) + 2e^- \rightarrow Cl^-(aq) + H_2O(l)$$

The reducing agent is $Na_2[Pb(OH)_4]$ whose effective oxidation change is the conversion of tetrahydroxoplumbate(II) ions, $[Pb(OH)_4]^{2-}$, to lead(IV) oxide, PbO_2. Thus the oxidation half-equation is

$$[Pb(OH)_4]^{2-}(aq) \rightarrow PbO_2(aq)$$

We balance the 4 extra O atoms on the LHS by adding $2H_2O$ to the RHS to obtain

$$[Pb(OH)_4]^{2-}(aq) \rightarrow PbO_2(aq) + 2H_2O(l)$$

The addition of the $2H_2O$ has also balanced the 4 H atoms on the LHS. The net charge on the LHS is −2, while that on the RHS is 0. The charges are balanced by adding 2 electrons to the RHS to obtain

$$[Pb(OH)_4]^{2-}(aq) \rightarrow PbO_2(aq) + 2H_2O(l) + 2e^-$$

Since the two half-equations contain the same number of electrons, we can now combine them to obtain

$[Pb(OH)_4]^{2-}(aq) + ClO^-(aq) + 2H^+(aq) + \cancel{2e} \rightarrow PbO_2(aq) + 2H_2O(l) + \cancel{2e} + Cl^-(aq) + H_2O(l)$

So $[Pb(OH)_4]^{2-}(aq) + ClO^-(aq) + 2H^+(aq) \rightarrow PbO_2(aq) + Cl^-(aq) + 3H_2O(l)$

Since the reaction is in a basic medium, we have to had 2 OH^- to both sides of the equation to obtain

$[Pb(OH)_4]^{2-}(aq) + ClO^-(aq) + 2H^+(aq) + 2OH^-(aq) \rightarrow PbO_2(aq) + Cl^-(aq) + 3H_2O(l) + 2OH^-(aq)$

Thus $[Pb(OH)_4]^{2-}(aq) + ClO^-(aq) + 2H_2O(aq) \rightarrow PbO_2(aq) + Cl^-(aq) + 3H_2O(l) + 2OH^-(aq)$

So $[Pb(OH)_4]^{2-}(aq) + ClO^-(aq) \rightarrow PbO_2(aq) + Cl^-(aq) + H_2O(l) + 2OH^-(aq)$

Practice Problems

1. Split the following redox equation into half-equations:

   $$Fe(s) + Ag^+(aq) \rightarrow Fe^{2+}(aq) + Ag(s)$$

   [*Answer:* Oxidation half-equation, $Fe(s) \rightarrow Fe^{2+}(aq) + e^-$, Reduction half-equation, $Ag^+(aq) + e^- \rightarrow Ag(s)$]

2. Balance the redox equation $2I^-(aq) + MnO_4^{2-}(aq) \rightarrow Mn^{2+}(aq) + I_2(g)$, given that reaction occurred in an acidic medium.

   [*Answer:* $8I^-(aq) + MnO_4^{2-}(aq) + 16H^+(aq) \rightarrow 4I_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$]

3.3 IUPAC NOMENCLATURE OF INORGANIC SUBSTANCES

IUPAC nomenclature is a system of naming chemical substances based on the rules stipulated by the International Union of Pure and Applied Chemistry (IUPAC). These rules are used for generating the systematic names of chemical substances. A systematic name is a name that reflects the constituent elements or composition of a chemical substance. For example, calcium oxide and sodium hydroxide are the systematic names of CaO and NaOH respectively. Unlike systematic names, a common name is the name that is traditionally associated with a chemical substance, and is not based on any rules. Such a name gives little or no information about the composition of a substance. For example, lime and caustic soda are the common names of CaO and NaOH respectively. Another example is sodium carbonate-10-water, $Na_2CO_3.10H_2O$, which is commonly called washing soda.

The systematic naming of inorganic compounds is based on the following rules:

3.3.1 Binary Compounds of a Metal and Nonmetal

A binary compound consisting of a metal and nonmetal is named by first naming the metal, which is usually the first element in the formula of the compound. This should be followed by the oxidation number, in Roman numeral, of the metal in parentheses, except when the metal has only one possible oxidation state. Finally, name the second element (the nonmetal) by modifying its name such that it ends with ‘-ide.’ This rule should also be applied to compounds containing the anionic radical ammonium, NH^+_4, and hydrogen. This rule is illustrated in Table 3.1.

Table 3.1: IUPAC names of binary compounds

Compound	*ON**	*ON* •	*IUPAC name*
$FeCl_2$	+2, +3	+2	Iron(II) chloride
$FeCl_3$	+2, +3	+3	Iron(III) chloride
CuO	+1, +2	+2	Copper(II) oxide
Cu_2O	+1, +2	+1	Copper(I) oxide
NaCl	+1	+1	Sodium chloride
NH_4Cl	+1	+1	Ammonium chloride
CaC_2	+2	+2	Calcium carbide
HCl	+1	+1	Hydrogen chloride
HF			

	+1	+1	Hydrogen fluoride
NaH	+1	+1	Sodium hydride

- Possible oxidation number(s) of the first element.
- Oxidation number of the first element in the specified compound.

3.3.2 Binary Compounds of Nonmetals (Covalent Compounds or Molecules)

Compounds formed between two nonmetals are named by first naming the first element, followed by the name of the second element which is modified to end with ‘-ide’. Moreover, the number of atoms of an element is indicated as a prefix in Greek as follows: ‘mono-’(1), ‘di-’(2), ‘tri-’(3), ‘tetra-’(4), ‘penta-’(5), ‘hexa-’(6), ‘hepta-’(7), ‘octa-’(8), etc. Note, however, that ‘mono-’ is never used before the first element. Examples are given in Table 3.2.

Exceptions to the above rules are compounds like ammonia, NH_3, and water, H_2O, whose common names are retained in the IUPAC system of naming.

Table 3.2: IUPAC names of molecules

Compound	*IUPAC Name*
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
N_2O	Dinitrogen monoxide
N_2O_5	Dinitrogen pentoxide
CO	Carbon monoxide
CO_2	Carbon dioxide
CCl_4•	Carbon tetrachloride
BF_3	Boron trifluoride

SF_4	Sulphur tetrafluoride
P_4O_{10}*	Diphosphorus pentoxide

- This compound is also called tetrachloromethane.

* This compound is also called phosphorus pentoxide. The name of the compound stems from its empirical formula of P_2O_5 because chemists used to believe that this formula is its molecular formula. This name is still retained in the IUPAC system of naming for historical reasons.

3.3.3 Compounds of Metals and Cationic Radicals

Compounds of metals and cationic radicals are named like binary compounds of metals and nonmetals, except that the name of the radical is unchanged. Examples are given in Table 3.3.

Table 3.3: IUPAC names of metals and cationic radicals

Compound	*ON**	*ON•*	*Radical*	*IUPAC Name*
$Al_2(SO_4)_3$	+3	+3	SO^{2-}_4	Aluminium sulphate
$NaHCO_3$	+1	+1	HCO^{-}_3	Sodium hydrogen carbonate
$NaClO$	+1	+1	ClO^{-}	Sodium chlorate
$KMnO_4$	+1	+1	MnO^{-}_4	Potassium permanganate
$K_2Cr_2O_7$	+1	+1	$Cr_2O^{2-}_7$	Potassium dichromate
$FeSO_4$	+2, +3	+2	SO^{2-}_4	Iron(II) sulphate
$Fe_2(SO)_3$	+2, +3	+3	SO^{2-}_4	Iron(III) sulphate
KH_2PO_4	+1	+1	$H_2PO^{-}_4$	Potassium dihydrogen phosphate
$NaClO_4$	+1	+1	ClO^{-}_4	Sodium chlorate

NaS_2O_3	+1	+1	$S_2O^{2-}_3$	Sodium thiosulphate
Na_2O_2	+1	+1	O^{2-}_2	Sodium peroxide
H_2O_2	+1	+1	O^{2-}_2	Hydrogen peroxide
$Ca(OH)_2$	+2	+2	OH^-	Calcium hydroxide
KCN	+1	+1	CN^-	Potassium cyanide

* Possible oxidation number(s) of the first element.

• Oxidation number of the first element in the specified compound.

3.3.4 Aqueous Solutions of Hydrogen Halides

Hydrogen halides are binary compounds formed between hydrogen and the halogens. These compounds have the general formula HX, where X is the halogen. Hydrogen halides dissolve in water to form acids. These acids are named by adding the prefix ‘hydro-’ to the name of the halogen, which is modified to end in ‘-ic’. Finally, the word acid is added. Examples are given in Table 3.4.

Table 3.4: IUPAC names of aqueous solutions of hydrogen halides

Acid	*IUPAC name*
HCl	Hydrochloric acid
HBr	Hydrobromic acid
HF	Hydofluoric acid

3.3.5 Oxoacids

Oxoacids are acids containing oxygen atoms, which usually come last in their radicals. Examples are H_3PO_4, HNO_3, H_2SO_4, etc. An oxoacid is named by modifying the name of its constituent radical to end with ‘-ic’ and ‘-ous’ if it ends with ‘-ate’ and ‘-ite’ respectively. Finally, the word acid is added. Examples are given in Table 3.5.

Table 3.5: IUPAC names of oxoacids

Acid	*Radical*	*IUPAC name*
H_2SO_4	SO^{2-}_{4}	Sulphuric acid
H_3PO_4	PO^{3-}_{4}	Phosphoric acid
H_2CO_3	PO^{2-}_{3}	Carbonic acid
$HClO_3$	ClO^{-}_{3}	Chloric acid
$HClO$	ClO^{-}	Hypochlorous acid
HNO_3	NO^{-}_{3}	Nitric acid
H_2SO_3	SO^{2-}_{3}	Sulphurous acid
HIO_3	IO^{-}_{3}	Iodic acid
HIO_2	IO^{-}_{2}	Iodous acid

3.3.6 Hydrated Salts

A hydrated salt is a salt containing water of crystallization. To name a hydrated salt, name the salt as usual. This should be followed by a hyphen (-), the number of molecules of water of crystallization, a hyphen and, finally, water. Examples are given in Table 3.6.

Table 3.6: IUPAC names of hydrated salts

Salt	*N*[*]	*IUPAC Name*
$CuSO_4.5H_2O$	5	Copper(II) sulphate-5-water
$Na_2CO_3.10H_2O$	10	Sodium carbonate-10-water
$Na_2CO_3.H_2O$	1	Sodium carbonate-1-water
$FeSO_4.7H_2O$	7	Iron(II) sulphate-7-water
$Al_2(SO_4)_3.18H_2O$	18	Aluminium sulphate-18-water
$CoCl_2.6H_2O$	6	Cobalt(II) chloride-6-water

* Number of molecules of water of crystallization

3.3.7 Double Salts

To name a double salt[1], first name the less electropositive cation, followed by the second cation. In addition, the oxidation number, in Roman numeral, of a cation should be specified in parentheses if it has more than one possible oxidation state. Finally, name the radical and water of crystallization. Examples are given in Table 3.7.

Table 3.7: IUPAC names of double salts

Salt	*IUPAC name*
$KCr(SO_4)_2.12H_2O$	Chromium(III) potassium sulphate-12-water
$(NH_4)_2Fe(SO_4)_2.6H_2O$	Ammonium iron(II) sulphate-6-water
$KAl(SO_4)_2.12H_2O$	Aluminium potassium sulphate-12-water

3.3.8 Complexes

A complex consists of a central metallic ion surrounded by several anions or molecules called ligands. A complex could be an anion, cation or a neutral molecule. Complex ions are usually enclosed in square brackets, [ ], for easy identification. Examples include $[Ag(NH_3)_2]^+$,$[Fe(H_2O)_6]^{2+}$, $[Zn(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$, $[Zn(OH)_4]^{2-}$, $[CoCl_4]^{2-}$, $[Pb(OH)_6]^{2-}$, $[Fe(ON)_6]^{2-}$, $[P_t(NH_3)_2Cl_4]$, etc. The formation of complexes is characteristic of transition metals like iron, copper, zinc, lead, etc.

A complex is named by first naming the ligands. A ligand is named by modifying its name as given in Table 3.8. In addition, the number of atoms of the ligand should be indicated as a prefix in Greek.

Table 3.8: Names of ligands

Ligand	*Name*
Br^-	Bromo
Cl^-	Chloro
F^-	Fluoro
I^-	Iodo
CN^-	Cyano (when bonded through carbon)
CN^-	Isocyano (when bonded through nitrogen)
OH^-	Hydroxo
H^-	Hydrido
O^{2-}	Oxo
$Cr_2O_7^{2-}$	Oxalato
NO_2^-	Nitro (when bonded through nitrogen)

NO_2^-	Nitrito (when bonded through oxygen)
H_2O	Aqua
NH_3	Ammine
NO	Nitrosyl
CO	Carbonyl

[1] A double salt is a salt containing two cations. See Chapter 12 for details.

When two or more ligands are present, they should be named in alphabetical order. The prefixes should be ignored in the alphabetical arrangement. Finally, the central metallic atom is named as follows:

- If the complex is an anion, the name of the metal should be modified to end with '-ate'. With the exception of mercury, the Latin names of elements whose symbols are derived from their Latin names are used. Thus iron is named ferrate (from ferrum); lead is plumbate (from plumbum); tin is stannate (from stannum); copper is cuprate (from cuprum); gold is aurate (from aurum), while silver is argentate (from argentum). The name of the metal is followed by its oxidation number in Roman numeral in parentheses.
- The name of the metal is unchanged if the complex is a cation or neutral molecule.

Examples of some complexes are given in Table 3.9.

Table 3.9: IUPAC Names of complex

Complex	*Ligand(s)*	*IUPAC name*
$[Fe(CN)_6]^{3-}$	CN^-	Hexacyanoferrate(III) ion
$[Fe(CN)_6]^{2-}$	CN^-	Hexacyanoferrate(II) ion
$[Zn(NH_3)_4]^{2+}$	NH_3	Tetraamminezinc(II) ion

$[Al(H_2O)_2(OH)_4]^-$	H_2O, OH^-	Tetrahydroxodiaquaaluminate(III) ion
$[Cr(NH_3)_4Cl_2]^+$	NH_3, Cl^-	Tetraamminedichlorochromium(III) ion
$[AlH_4]^-$	H^-	Tetrahydridoaluminate(III) ion
$[Pb(OH)_4]^{2-}$	OH^-	Hexahydroxoplumbate(II) ion
$[Fe(OH_2)_6]^{3+}$	OH^-	Hexahydroxoiron(III) ion
$[BH_4]^-$	H^-	Tetrahydroxoborate(III) ion
$[Cu(NH_3)_4]^{2+}$	NH_3	Tetraamminecopper(II) ion
$[P_t(NH_3)_2Cl_4]$	NH_3, Cl^-	Diamminetetrachloroplatinum(IV)
$[CuCl_4]^{2-}$	Cl^-	Tetrachlorocuprate(II) ion
$[Al(H_2O)_2(OH)_4]^-$	H_2O, OH^-	Diaquatetrahydroxoaluminate(III) ion
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	H_2O, NH_3	Tetraamminediaquacopper(II) ion
$[NiCl_4]^{2-}$	Cl^-	Tetrachloronickelate(II) ion
$[Cr(NH_3)_4Cl_2]^+$	NH_3, Cl^-	Tetraamminedichlorochromium(III) ion
$[CoCl(NO_2)(NH_3)_4]^+$	Cl^-, NO^-_2, NH_3	Tetraamminechloronitrocobalt(III) ion
$[CoCl(ONO)(NH_3)_4]^+$	Cl^-, NO^-_2, NH_3	Tetraamminechloronitritocobalt(III) ion
$[Ni(NH_3)_4Cl_4]$	NH_3, Cl^-	Teraamminedichloronickel(II)

3.3.9 Coordination Compounds

A coordination compound is a compound containing a complex ion. Like binary compounds of metals and nonmetals, coordination compounds are named starting with the cation, followed by the anion. Examples are given in Table 3.10.

Table 3.10: IUPAC names of coordination compounds

Compound	*IUPAC name*
$Na_2[Pb(OH)_6]$	Sodium hexahydroxoplumbate(IV)
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$Na[BH_4]$	Sodium tetrahydridoborate(IV)
$[Pt(NH_3)_5Cl]Br_3$	Pentaamminechloroplatinum(IV) bromide
$NH_4[Pt(NH_3)Cl_3]$	Ammonium amminetrichloroplatinate(II)
$K_2[Zn(OH_4)_4]$	Potassium tetrahydroxozincate(II)
$NH_4[Pt(NH_3)Cl_3]$	Ammonium amminetrichloroplatinate(II)
$[Cr(NH_3)_3(H_2O)_3]Cl_3$	Triamminetriaquachromium(III) chloride
$K_2[Ni(CN)_4]$	Potassium tetracyanonickel(II)
$Na_2[Fe(CN)_5NO]$	Sodium pentacyanonitrosylferrate(III)

Practice Problems

1. What is the IUPAC name of $KHSO_4$?

   [*Answer:* Potassium hydrogen sulphate]
2. What is the IUPAC name of PCl_5?

[*Answer:* Phosphorus pentachloride]

3. What is the IUPAC name of the compound $Ca(ClO)_2$?

[*Answer:* Calcium hypochlorite]

4. What is the IUPAC name of $Ag[(NH_3)_2]^+$?

[*Answer:* Diamminesilver(I) ion]

5. What is the IUPAC name of $Na_2[Zn(NH_3)_4]$?

[*Answer:* Sodium tetraamminezincate(II)]

6. What is the IUPAC name of $Na_2[Zn(OH)_4]$?

[*Answer:* Sodium tetrahydroxozincate(II)]

SUMMARY

- Oxidation is electron loss, while reduction is electron gain. Both processes are complementary.
- An oxidizing agent is an electron acceptor, while a reducing agent is an electron donor.
- Redox reactions are reactions involving oxidation and reduction.
- A redox equation is an ionic equation representing a redox reaction.
- A half-equation is an equation depicting oxidation or reduction. Both are combined to get the overall or net equation of the redox reaction.
- Oxidation number is the effective charge of an atom in a substance, as determined by a set of arbitrary rules. A redox reaction is one in which any of the participating atoms undergoes a change in oxidation number.
- An oxidizing agent is also a substance that has undergone an increase in oxidation number, while a reducing agent is a substance that has undergone a decrease in oxidation number.
- IUPAC Nomenclature is the system of naming compounds based on the International Union of Pure and Applied Chemistry (IUPAC) rules. Oxidation numbers are employed in the naming of many inorganic substances.

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. Consider the reaction:

$$2KI(aq) + Cl_2(g) \rightarrow 2KCl(aq) + I_2(g)$$

What is the oxidizing agent?

A. KI B. Cl_2

C. KCl D. I_2

E. K

2. Which of these equations is **NOT** a redox reaction?

A. $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

B. $2C(s) + O_2(g) \rightarrow 2CO(g)$

C. $Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$

D. $CuO(s) + Zn(s) \rightarrow ZnO(s) + Cu(s)$

E. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

3. Which of the following is the effective reduction change of permanganate, MnO_4^{2-}?

A. Mn^{2+} B. MnO_2

C. OH^- D. SO_4^{2-}

E. Mn^{4+}

4. Which of the following is the effective oxidation change of iodide ion, I^-?

A. I_2 B. 2I

C. H_2O D. KI

E. OH^-

5. Which of the following substances will change the colour of acidified $K_2Cr_2O_7$?

A. H_2O B. H_2SO_4

C. K D. SO_2

E. Cl_2

6. In which of the following substances does hydrogen possess the oxidation number of –1?

A. H_2O B. H_2O_2

C. NH_3 D. NaH

E. NH_2

7. In which of the following substances is the oxidation number of oxygen –1?

A. N_2O B. K_2O

C. K_2O_2 D. CaO

E. O_3

8. What is the oxidation number of cobalt in $[CoCl_4]^{2-}$?

A. +4 B. +2

C. +3 D. +1

E. +6

9. What is the oxidation number of zinc in $K_2[Zn(OH)_4]$?

A. +5 B. +3

C. +2 D. +1

E. +4

10. What is the IUPAC name of $Ca(IO_3)_2$?

A. Calcium iodite

B. Calcium iodate

C. Calcium oxoiodate

D. Calcium(II) iodate

E. Calcium(I) iodate

11. Which of these is the correct name for Br^- when found in a complex ion?

A. Bromo

B. Bromide

C. Bromide ion

D. Halogen

E. Halide

ESSAY TYPE QUESTIONS

Oxidation number

12. Explain oxidation and reduction in terms of

(a) Oxygen transfer (b) Hydrogen transfer (c) Transfer of electropositive and electronegative elements (d) Electron transfer.

13. (a) What are oxidizing and reducing agents? Write five equations to

illustrate a redox reaction.

(b) Identify the oxidizing and reducing agents in the equations you have written above.

14. (a) Explain how you would use potassium dichromate to test for a reducing agent.

(b) Explain what is meant by a half-equation.

15. Calculate the oxidation number of chlorine in each of the following substances:

(a) $KClO_3$ (b) $KClO$ (c) $NaClO_2$ (d) $NaClO_3$ (e) $NaClO_4$

16. Calculate the oxidation number of chromium in each of the following substances:

(a) CrO (b) Cr_2O_3 (c) CrO_3 (d) K_2CrO_4 (e) CrO_2 (f) Na_2CrO_4 (g) CrO_7^{2-}

17. Calculate the oxidation number of nitrogen in each of the following substances:

(a) NO (b) N_2O (c) HNO_3 (d) N_2O_4 (e) NO_2 (f) $NaNO_2$ (g) N_2O (h) HNO_2

18. Calculate the oxidation number of manganese in each of the following substances:

(a) $KMnO_4$ (b) $MnSO_4$ (c) K_2MnO_4 (d) MnO_4^- (e) MnO_2 (f) MnO

Redox equations

19. Split each of the following redox equations into two half-equations:

(a) $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(g)$

(b) $2Fe(s) + 3Cl_2(g) \rightarrow 2Fe^{3+}(aq) + 6Cl^-(aq)$

(c) $2Ag^+(aq) + Cu(s) \rightarrow 2Ag(aq) + Cu^{2+}(aq)$

(d) $N_2(g) + 3H(g) \rightarrow NH_3(g)$

(e) $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

20. Balance the following redox equations:

(a) $MnO_4^-(aq) + I^-(aq) \rightarrow Mn^{2+}(aq) + I_2(g)$

(b) $2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g)$

(c) $Cr_2O_7^{2-}(aq) + 3H_2S(s) \rightarrow 2Cr^{3+}(aq) + 3S(s)$

(d) $6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq)$

21. Write the balanced redox equations for the following:

(a) The reaction between hydrogen sulphide, H_2S, and sulphur dioxide, SO_2, to produce solid sulphur and water.

(b) The reaction between potassium permanganate, $KMnO_4$, and hydrogen sulphide, H_2S, in a basic medium.

(c) The reaction between potassium dichromate, $K_2Cr_2O_7$, and sulphur dioxide, SO_2, in an acidic medium.

(d) The reaction between potassium permanganate, $KMnO_4$, and hydrogen peroxide, H_2O_2, in an acidic medium.

(e) The reaction between chromium(III) hydroxide, $Cr(OH)_3$, and potassium hypochlorite, KClO, in a basic medium.

IUPAC nomenclature of inorganic substances

22. Give the IUPAC names of the following substances:

(a) $Na[Pb(O_6)_6]$ (b) $Li[AlH_4]$ (c) $Co[(H_2O)_6]^{2+}$ (d) $Zn[(NH_3)_4]^{2+}$ (e) $(NH_4)_2Cr_2O_7$ (f) Hg_2SO_4 (g) $CaHSO_4$ (h) H_2SO_3 (i) HOCl (j) $Ca(H_2PO_4)_2$ (k) $Na_2CO_3.H_2O$ (l) $NaClO_4$ (m) $Mg_3(PO_4)_2$ (n) $(NH_4)_2Fe(SO_4)_2.6H_2O$ (o) $HF(g)$

Answers

1. B 2. E 3. B 4. A 5. D 6. D

7. C 8. B 9. C 10. B 11. A

15. (a) +5 (b) +1 (c) +3 (d) +5 (e) +7

16. (a) +2 (b) +3 (c) +6 (d) +6 (e) +4 (f) +6 (g) +12

17. (a) +2 (b) +1 (c) +5 (d) +4 (e) +4 (f) +3 (g) +5 (h) +12

18. (a) +7 (b) +2 (c) +6 (d) +7 (e) +4 (f) +2

19. (a) OHE: $2I^-(aq) \rightarrow I_2(s) + 2e^-$, RHE: $2Fe^{3+}(aq) + e^- \rightarrow 2Fe^{2+}(aq)$

(b) OHE: $2Fe(s) \rightarrow 2Fe^{3+}(aq) + 6e^-$, RHE: $3Cl_2(g) + 6e^- \rightarrow 6Cl^-(aq)$

(c) OHE: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$, RHE: $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$

(d) OHE: $3H_2(g) \rightarrow 6H^+(aq) + 6e^-$, RHE: $N_2(g) + 6e^- \rightarrow 2N^{3-}(g)$

(e) OHE: $2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2e^-$, RHE: $I_2(aq) + 2e^- \rightarrow 2I^-$

20. (a) $2MnO_4^{2-}(aq) + 16H^+(aq) + 10I^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5I_2(g)$

(b) $2MnO_4^{2-}(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

(c) $Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3H_2S(g) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3S(s)$

(d) $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$

21. (a) $2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(l)$

(b) $2MnO_4^-(aq) + 5H_2S(g) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5S(s)$

(c) $3SO_2(g) + Cr_2O_7^{2-}(aq) + 2H^+(aq) \rightarrow 3SO_4^{2-}(aq) + 2Cr^{3+}(aq) + H_2O(l)$

(d) $2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$

(e) $2Cr(OH)_3(\mathrm{s}) + 3ClO^-(aq) + 4OH^-(aq) \rightarrow 2CrO_4^{2-}(aq) + 3Cl^-(aq) + 5H_2O(l)$

22. (a) Tetraamminediaquacopper(II) ion

(b) Lithium tetrahydridoaluminate(III)

(c) Hexaaquacobalt(II) ion

(d) Tetraamminezinc(II) ion

(e) Ammonium dichromate

(f) Mercury(I) sulphate

(g) Calcium hydrogensulphate

(h) Sulphuric acid

(i) Chloric acid

(j) Calcium dihydrogenphosphate

(k) Sodium carbonate-1-water

(l) Sodium chlorate

(m) Magnesium phosphate

(n) Ammonium iron(II) sulphate-6-water

(o) Hydrogen fluoride

4

Chapter

Atomic Structure and Chemical Bonding

The idea that matter is made up of tiny particles called atoms was proposed by Demecritus (Fig. 4.1), a Greek philosopher, in 400 BC. The word 'atom' is derived from the Greek word meaning 'indivisible' or 'uncuttable'. However, this view of the atom has since been modified to account for subsequent discoveries. An atom is now defined as the smallest particle of an element that can ever exist and still retain its chemical identity. Alternatively, an atom can be defined as the smallest particle of an element that can partake in chemical reaction. An atom consists of three main sub-particles, namely, electron, proton and neutron. The characteristics of these particles are given in Table 4.1.

Figure 4.1 Demecritus
(c. 460 BC – c. 370 BC).

4.1 DALTON'S ATOMIC THEORY

In 1808, John Dalton, came up with the first experimental evidence of the existence of the atom. The result of his work, called the Dalton's atomic theory, is summarized as follows:

1. Matter consists of small indivisible particles called atoms.
2. Atoms of the same element are exactly alike in all respects, but differ from the atoms of other elements.

3. Atoms are neither created nor destroyed in a chemical reaction but exchange partners to be converted to new substances.
4. Chemical combinations take place between small whole number ratios of atoms.

However, subsequent discoveries have given us more insight into the structure of the atom, which have led to the modifications of Dalton theory. Some of these discoveries, which have shaped our current knowledge of the atom are given below.

Figure 4.2 John Dalton, English chemist (1766–1884).

Table 4.1: Subatomic particles

Particle	*Location*	*Symbol*	*Charge (C)*	*Relative charge*	*Mass (kg)*	*Relative mass*
Electron	Outside nucleus	e−	-1.60×10^{-19}	−1	9.11×10^{-31}	Negligible
Proton	Nucleus	p	1.60×10^{-19}	1	1.67×10^{-27}	1
Neutron	Nucleus	n	0	0	1.68×10^{-27}	1

The electron: In 1897, Joseph John Thomson applied a high potential difference (voltage) across the electrodes of a gas tube containing a gas at low pressure. The gas began to glow due to the emission of rays from the cathode (the negatively charged electrode). The properties of these rays, called cathode rays, are as follows:

1. They cast shadow of opaque objects placed in their path on a screen, showing that they travel in a straight line.

2. The manner in which they are deflected by both electric and magnetic fields shows that they are negatively charged.
3. They cause fluorescence in certain materials like zinc sulphide.
4. They have ionizing effect on gases.

Figure 4.3 J.J. Thomson, British physicist (1856–1940). He won the Nobel Prize for Physics in 1906.

Thomson also found that the properties of the cathode rays were the same regardless of the type of metal used as the cathode. Thus it was rightly concluded that all elements or atoms are made up of these particles, which are now called electrons. He later obtained the specific charge (e/m) or the ratio of the electron's charge to its mass to be 1.76×10^{11} C kg^{-1}. In 1910, Robert Millikan, an American scientist, measured the charge of the electron to be -1.60×10^{-19} C in his famous oil drop experiment. This charge is taken to be a unit of negative charge, i.e., −1. The mass of the electron, as obtained from its specific charge is 9.1×10^{-31} kg, which is negligibly small that it is normally assumed that the electron does not contribute towards the overall mass of the atom.

The proton and atomic number: Repeating his earlier experiment with a central perforated cathode, Thomson discovered that the particles emitted at the cathode also travelled in a straight line, but in an opposite direction to those of cathode rays. He concluded that these rays were positively charged. He called these particles protons, and obtained the specific charge to be 9.58×10^{7} C kg^{-1}. This shows that the proton is approximately 1840 times heavier than the electron. Millikan was also able to determine the charge of a proton to be 1.60×10^{-19} C, which is equal but opposite to that of the electron.

Since the atom is electrically neutral, it then follows that an atom must contain the same number of protons and electrons. An atom becomes an ion when there is a surplus of any of the two particles. When an atom loses electron(s), there is a surplus of positive charges. This is called a positively charged ion or cation (cathode- seeking ion). On the other hand, when electron(s) is/are added to an atom, there is a surplus of negative charges. This is referred to as a negatively charged ion or anion (anode-seeking ion).

Atoms of different elements contain different number of protons. The number of protons in the nucleus of an element is called atomic number Z. The term atomic number was introduced by Moseley in 1914. The atomic number is the basis for arranging elements in the Periodic Table. For example, the lightest element known, hydrogen, has an atomic number of 1 and occupies the first position in the Periodic Table. The atomic number of an element is usually written as a subscript to the left of its symbol, i.e. ${}_{Z}X$.

Thomson's model of the atom: Thomson proposed his model of the atom based on the discoveries explained above. The Thomson's atomic model is essentially a sphere of positively charged matter in which negative charges (electrons) are embedded.

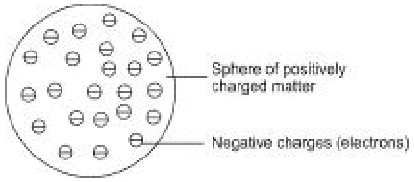

Figure 4.4 Thomson's model of the atom. It is a sphere of positively charged matter in which negative charges are embedded.

The nucleus: The Thomson's model of the atom was later rejected due to the landmark discovery of the New Zealander physicist, Ernest Rutherford, who discovered the atomic nucleus. At the instance of Rutherford, Hans Geiger and Ernest Mardsen, bombarded a thin gold foil with a particles. Based on the Thomson's model of the atom, they had expected the particles to travel through the foil with little or no deflections. However, what they discovered was more than enough proof that the Thomson's model was wrong. Watching through a microscope, they discovered that most of the particles did travelled in a straight line through the foil, while some were deflected or scattered through wide angles. Moreover, some particles bounced back in the opposite direction. It was then concluded that the reflected a particles had been acted upon by some massive positively charged 'obstacle.'

Rutherford proposed his nuclear model of the atom based on the result of this experiment. The Rutherford's model of the atom describes the atom as consisting largely of an empty space with a central, minute nucleus, in which all the positive charge and mass of the atom are concentrated; with electrons revolving around it. The electrons are held in place by electrostatic force of attraction to the positively charged nucleus. The path in which an electron orbits the nucleus is called an orbit. Rutherford's model could be likened to the solar system in which the sun represents the nucleus, and the electrons, the planets.

Rutherford obtained the size of the atom to be 10^{-10} m. This is 10000 times the size of the nucleus.

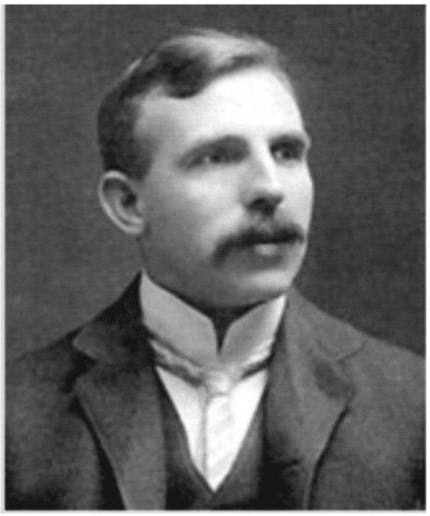

Figure 4.5 Lord Ernest Rutherford (1871–1937), the New Zealand physicist who won the Nobel Prize for Chemistry in 1908.

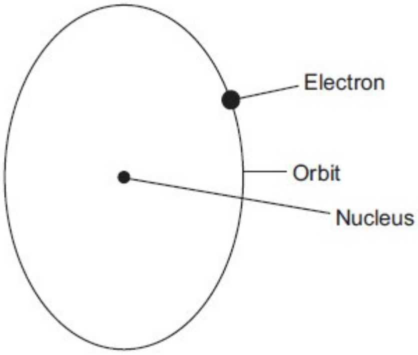

Figure 4.6 Rutherford's model of the atom. Note the electrons orbiting the nucleus.

The neutron and mass number: Based on the mass of the atom, Rutherford also proposed the existence of another atomic article of equal mass to the proton. This confirmed by Chadwick, an English scientist in 1932. These particles, called neutrons, were also found to be electrically neutral. The mass of an atom is determined by the number of protons and neutrons it contains. The total number of protons and neutrons in an atom of an element is called its mass number A, i.e.

$$A = n + Z$$

where n is the number of neutrons. The mass number of an element is usually denoted with a superscript to the left of its symbol, i.e. ^{A}X.

Isotopy: According to Dalton, atoms of the same elements are exactly alike in all respects. In other words, atoms of the same elements must possess exactly the same properties, including the same mass number. However, with the invention of the mass spectrometer by Aston in 1920, it has been discovered that atoms of the same elements differ slightly in mass, though they all possess the same atomic number. This phenomenon, in which atoms of the same element possess different mass numbers, is called isotopy. Each distinct atom of an element is called an isotope. For example, the isotopes of chlorine are Cl-35 and Cl-37 with a relative abundance of 75% and 25% respectively.

Isotopes exist due to the variation in the number of neutrons in atoms of an element, and explains the reason why the relative atomic masses of elements are not usually whole numbers. The relative atomic masses of elements which exhibit isotopy are the average of the relative atomic masses of their isotopes. The relative atomic masses of some radioactive elements are taken to be the relative atomic masses of their most stable isotopes. Examples of such elements include actinium, astatine, francium, etc.

Example 1 An oxygen atom contains 8 neutrons. What is the mass number of the element if it has an atomic number of 6?

Solution We have to apply the relation

$A = n + Z$

$\text{n} = 8$

$Z = 8$

$A = ?$

Substituting we have

$$A = 8 + 8 = 16$$

Example 2 Calculate the number of electrons in an atom of iodine, given that an atom of iodine-134 contains 81 neutrons.

Solution Since an atom is electrically neutral, then it must contain the same number of electrons as protons. Thus calculating the atomic number of an element is a way of obtaining the number of electrons in its atom. So we have to apply the relation

$A = n + Z$

$\therefore\ Z = A - \text{n}$

$A = 134$

$n = 81$

$Z = ?$

Substituting we obtain

$$Z = 134 - 81 = 53$$

Thus an atom of iodine contains 53 electrons. Since all isotopes of an element have the same atomic number, then this must be the number of electrons in all atoms of iodine, regardless of the isotope under consideration.

Example 3 The isotopes of chlorine are ^{35}Cl and ^{37}Cl, with a relative abundance of 75% and 25%, respectively. Calculate the relative atomic mass of the element.

Solution The relative atomic mass of the element is the average of the masses of its two isotopes, which is obtained as follows:

$$A_r = \left(\frac{75}{100}\times 35\right)+\left(\frac{25}{100}\times 37\right)$$

$$= 26.25 + 9.25$$

$$= 35.50$$

Example 4 The isotopes of oxygen are ^{16}O, ^{17}O and ^{18}O, with a relative abundance of 99.76%, 0.040% and 0.20% respectively. What is the relative atomic mass of oxygen?

Solution As usual,

$$A_r = \left(\frac{99.76}{100}\times 16\right)+\left(\frac{0.04}{100}\times 17\right)+\left(\frac{0.20}{100}\times 18\right)$$

$$= 15.96 + 0.0068 + 0.036$$

$$= 16.00$$

Practice Problems

1. Calculate the mass number of an isotope of boron which contains 5 neutrons, given that the atomic number of the element is 5. [*Answer:* 10]
2. The mass number of an isotope of molybdenum is 107. What is the atomic number of the element, given that the isotope contains 65 neutrons. [*Answer:* 42]
3. The two stable isotopes of carbon are ^{12}C and ^{13}C, with a relative abundance of 98.90% and 1.10%, respectively. Calculate its relative atomic mass of the elements.

[*Answer:* 12.01]

4.1.1 Quantum Mechanics

While Rutherford's idea of the nuclear atom is basically correct, a major shortfall of his model of the atom is that of planetary electrons orbiting the nucleus in fixed orbits. Since moving electrons must radiate (or lose) energy, then the electrons would move in a decreasing spiral path until they finally fall into the nucleus, leading to the collapse of the atom. But the fact that this does not happen cannot be explained in terms of classical mechanics (laws of motion) which ought to govern the movement of electrons in their orbits as proposed by Rutherford. Consequently, his idea of planetary electrons was abandoned. An alternative explanation adopted for explaining the motion of electrons around the nucleus is quantum mechanics, which is the analysis of the properties of matter based on the fact that its energy changes by a fixed or discrete value.

The word quantum (quanta in plural) means a packet or parcel of energy. The quanta or packets of energy are called photons. The quantization energy means the restriction of energy to a fixed or discrete value.

Light: Light is an electromagnetic radiation or wave. A wave is a disturbance that travels through a medium and transmits energy from one place to another without causing any permanent displacement of the medium. An electromagnetic wave is a wave that requires no material medium for its propagation. Such waves can travel through vacuum. The energy associated with a wave are determined by its frequency or wavelength.

- *Frequency:* The frequency v of a wave is the number of oscillations or cycles it makes per second. The SI unit of frequency is the hertz (Hz), which means per second (s^{-1}). This unit is named for the German physicist Heinrich Hertz.
- *Wavelength:* The wavelength l of a wave is the distance between two successive crests or troughs. The SI unit of wavelength is the metre (m). Frequency and wavelength are related by the equation

$$v = \frac{c}{\lambda}$$

where c is the velocity of light.

The energy of a photon, as described by quantum mechanics, is given by the Planck's equation

$E = hv$

where v = Frequency of light.

h = Planck's constant = 6.63×10^{-34} J Hz^{-1}.

Atomic emission spectrum of hydrogen: Elements emits lights or radiations of different colours when supplied with energy, such as when heated. This is used in qualitative analysis for identifying certain elements. These radiations also form a powerful tool that helps in understanding the structure of the atom. With a spectrometer, the radiation from an element can be separated into its different wavelengths or colours, and reproduced on a photographic plate as series of lines called a spectrum. The lines in the spectrum are called spectral lines.

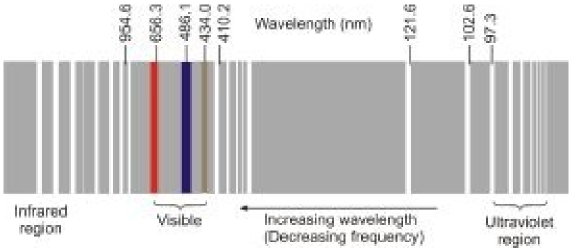

Figure 4.7 The atomic emission spectrum of hydrogen. Each line is produced when an electron moves from one energy level to another. The lines are divided into five series, three of which are shown.

The emission spectrum of hydrogen is divided into five series of lines. The visible lines in the spectrum constitute the Balmer series. The wavelengths of all the lines in the spectrum can be obtained by using the equation developed by Johannes Rydberg:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

where l = The wavelength of a particular line.

R = Rydberg’s constant = 1.097×10^{7} m^{-1}.

n_1 and n_2 are integers whose values depend on the region in which the line lies in the spectrum, as shown in Table 4.2.

Table 4.2: Lines in the hydrogen spectrum

Series	n_2	n_1	*Region*
Lyman	1	2, 3…	Ultraviolet
Balmer	2	3, 4…	Visible

Paschen	3	4, 5…	Infra-red
Brackett	4	5, 6…	Far infra-red
Pfund	5	6, 7…	Far infra-red

Figure 4.8 Johann Jacob Balmer (1825–1898), the Swiss schoolteacher who first recognized the pattern of the lines in the visible region of the hydrogen spectrum in 1885, and the equation describing them.

Figure 4.9 Johannes Rydberg (1854–1919), the Swedish chemist who discovered the full pattern of the hydrogen spectrum, and the equation describing all the lines in it.

Bohr's model of the atom: In 1913, Niels Bohr, a Danish physicist, proposed his model of the atom. This model, which is based on the emission spectrum of hydrogen, is called the Bohr's model of the atom. According to this model, electrons can only exist in fixed circular orbits or energy levels around the nucleus. The energy of each energy level or orbit is quantized or fixed at a particular value, and is given by the relation

$$E_n = -h\frac{cR}{n^2}$$

where h = Planck’s constant.

c = Velocity of light.

R = Rydberg’s constant.

n = Quantum number describing each energy level, i.e. 1, 2, …

The negative sign indicates that an atom must be supplied with energy to unbind or remove an electron from it.

According to Bohr, the emission of radiation is due to the movement of electrons from one orbit to another, and each line in the spectrum is caused by an electron moving from one energy level to another. The decrease in energy as an electron jumps from a higher to a lower energy level or orbit is given by the equation

$$DE = E_2 - E_1 = hcR\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

where n_1 and n_2 are the quantum numbers describing the higher and lower energy levels, respectively. The energy decrease is equal to the energy of the radiation emitted by the atom. Thus

$$DE = E_2 - E_1 = hcR\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = hv$$

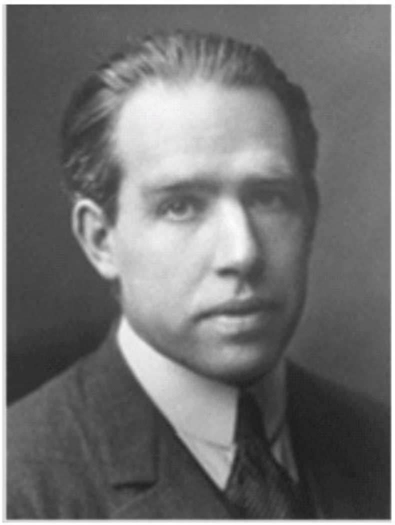

Figure 4.10 Niels Henrik David Bohr, Danish physicist (1885–1962). He won the Nobel Prize for Physics in 1922.

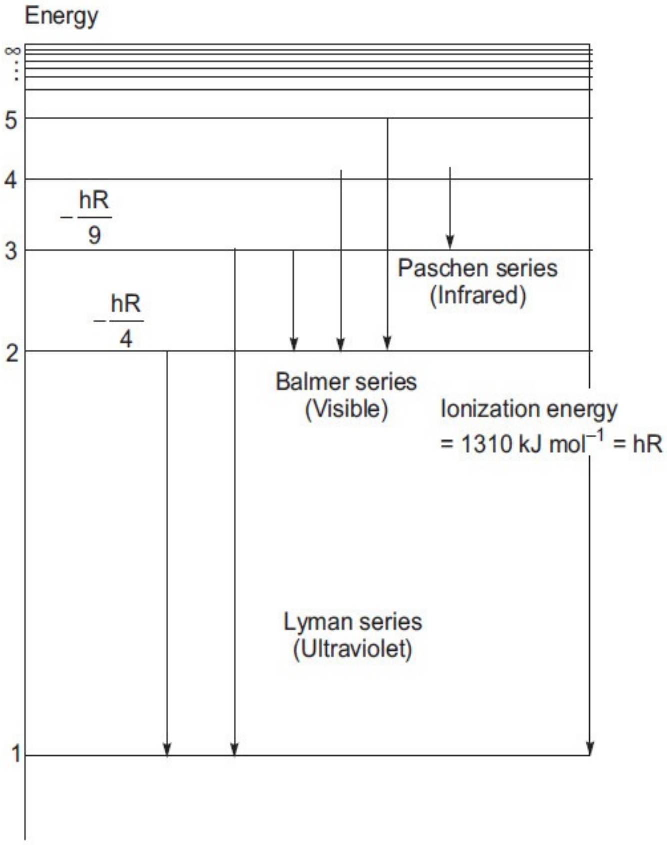

Figure 4.11 The energy levels in the hydrogen atom.

A major limitation of the Bohr's model is that it can only account for the spectrum of the hydrogen atom. In other words, it cannot be applied to atoms that are more complicated than the hydrogen atom. This model has now been replaced by the wave-mechanics model, which does not restrict the electron to a fixed energy level but gives a region around the nucleus where there is a high probability of locating an electron. This region, called an orbital, is described by the Schrödinger's equation. Details of this equation and its derivation can be found in relevant physics and physical chemistry texts.

Example 1 Calculate the energy of each photon of blue light if has a frequency of 6.4×10^{14} Hz.

$$(h = 6.63 \times 10^{-34} \text{ J Hz}^{-1})$$

Solution We have to apply the relation

$$E = hv$$

$$h = 6.63 \times 10^{-34} \text{ J Hz}^{-1} = 6.63 \times 10^{-34} \text{ J s}$$

$$v = 6.4 \times 10^{14} \text{ Hz} = 6.4 \times 10^{14} \text{ s}^{-1}$$

E = ?

Substituting we have

$$E = 6.63 \times 10^{-34}\ \text{J}\ \cancel{\text{s}} \times \frac{6.4 \times 10^{14}}{1\ \cancel{\text{s}}}$$

$$= 4.2 \times 10^{-19}\ \text{J}$$

Figure 4.12 Erwin Schrödinger, Austrian physicist (1887–1961). He won the Nobel Prize for Physics with Paul Adrien Maurice Dirac in 1933.

Example 2 Calculate the wavelength of ultraviolet light, given that it has a frequency of 1.0×10^{15} Hz.

($c = 3.00 \times 10^{8}\ \text{m s}^{-1}$)

Solution We have to apply the relation

$$\lambda = \frac{c}{\nu}$$

$c = 3.00 \times 10^{8}\ \text{m s}^{-1}$

$\nu = 1.0 \times 10^{15}\ \text{s}^{-1}$

λ = ?

Substituting we have

$$\lambda = \frac{3.00 \times 10^{8}\ \text{m}\ \cancel{\text{s}^{-1}}}{1.0 \times 10^{16}\ \cancel{\text{s}^{-1}}}$$

$$= 3.0 \times 10^{-7}\ \text{m} = 300\ \text{nm}$$

Example 3 Calculate the wavelength of the line formed in the spectrum of hydrogen as an electron falls from the second to the first orbit; hence calculate the decrease in energy associated with this transition of electron.

($R = 1.097 \times 10^{7}\ \text{m}^{-1}$, $h = 6.63 \times 10^{-34}\ \text{J Hz}^{-1}$, $c = 3.00 \times 10^{8}\ \text{m s}^{-1}$)

Solution We have to calculate the wavelength of the line from the Rydberg's equation

$$\frac{1}{\lambda} = R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$R = 1.097 \times 10^{7}\ \text{m}^{-1}$

$n_1 = 2$

$n_2 = 1$

$\lambda = ?$

Substituting we obtain

$$\frac{1}{\lambda} = \frac{1.097 \times 10^{7}}{1\,\text{m}}\left(\frac{1}{1} - \frac{1}{2^2}\right)$$

So $\frac{1}{\lambda} = \frac{1.097 \times 10^{7}}{1\,\text{m}}\left(\frac{1}{1} - \frac{1}{4}\right)$

Then $\frac{1}{\lambda} = \frac{1.097 \times 10^{7}}{1\,\text{m}} \times 0.75$

Thus $\frac{1}{\lambda} = \frac{8.2 \times 10^{6}}{1\,\text{m}}$

Cross-multiplying we have

$8.2 \times 10^{6} \times l = 1\ \text{m}$

$\therefore\ \lambda = \frac{8.2 \times 10^{6}}{1\,\text{m}}$

$= 1.2 \times 10^{-7}\ \text{m} = 120\ \text{nm}$

The energy decrease is calculated from the relation

$\Delta E = hv$

$h = 6.63 \times 10^{-34}\ \text{J s}$

The frequency of the light is obtained from the equation

$v = \frac{c}{\lambda}$

$c = 3.00 \times 10^{8}\ \text{m s}^{-1}$

$v = ?$

Substituting we have

$$v = \frac{3.00 \times 10^{8}\ \text{m}\ \cancel{\text{s}^{-1}}}{1.2 \times 10^{-7}\ \cancel{\text{m}}}$$

$$= 2.5 \times 10^{15}\ \text{Hz}\ (\text{s}^{-1})$$

ΔE = ?

Finally, we now substitute to obtain

$$\Delta E = 6.63 \times 10^{-34}\ \text{J}\ \cancel{\text{s}} \times \frac{2.5 \times 10^{15}}{1\ \cancel{\text{s}}}$$

$$= 1.7 \times 10^{-18}\ \text{J}$$

Example 4 Calculate the initial orbit of an electron which emits a blue light as it moves from the energy level to the lowest energy level in a hydrogen atom, given that wavelength of the light is 486 nm.

($R = 1.097 \times 10^{7}\ \text{m}^{-1}$, $c = 3.00 \times 10^{8}\ \text{m s}^{-1}$)

Solution We have to apply the Rydberg's equation

$$\frac{1}{\lambda} = R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

Blue light belongs to the visible region of the hydrogen spectrum. Thus $n_2 = 2$.

$\lambda = 486\ \text{nm} = 4.86 \times 10^{-7}\ \text{m}$

$R = 1.097 \times 10^{7}\ \text{m}^{-1}$

n_1 = ?

Substituting we have

$$\frac{1}{4.86 \times 10^{-7}\ \text{m}} = \frac{1.097 \times 10^{7}}{1\ \text{m}}\left(\frac{1}{2^2} - \frac{1}{n_1^2}\right)$$

Thus $\dfrac{2.06 \times 10^{6}}{1\ \text{m}} = \dfrac{1.097 \times 10^{7}}{1\ \text{m}}\left(\dfrac{1}{4} - \dfrac{1}{n_1^2}\right)$

So $\dfrac{2.06 \times 10^{6}}{1\ \text{m}} = \dfrac{2.74 \times 10^{6}}{1\ \text{m}} - \dfrac{1.097 \times 10^{7}}{1\ \text{m} \times n_1^2}$

Then $\frac{2.06 \times 10^6}{1\,\text{m}} - \frac{2.74 \times 10^6}{1\,\text{m}} = \frac{1.097 \times 10^7}{1\,\text{m} \times n_1^2}$

So $-\frac{6.85 \times 10^5}{1\,\text{m}} = \frac{1.097 \times 10^7}{1\,\text{m} \times n_1^2}$

Cross-multiplying yields

$6.85 \times 10^5\ \text{m} \times n_1^2 = 1.097 \times 10^7\ \text{m}$

Thus $n_1^2 = \frac{1.097 \times 10^7\ \cancel{\text{m}}}{6.85 \times 10^5\ \cancel{\text{m}}} = 16$

Taking the square roots of both sides we obtain

$n_1 = \sqrt{16}$

$= 4$

Example 5 Calculate the frequency of the line with the lowest frequency of the Paschen series.

($R = 1.097 \times 10^7\,\text{m}^{-1}$, $c = 3.00 \times 10^8\ \text{m s}^{-1}$)

Solution Frequency is indirectly proportional to wavelength. Thus the line with the least frequency corresponds to that with the longest wavelength. This line is obtained from the Rydberg's equation

$$\frac{1}{\lambda} = R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

Since frequency is directly proportional to energy, then the line with the lowest frequency corresponds to the lowest energy change, which involves the transition of an electron to the lowest permitted energy level for the region from the next higher one. Since we are dealing with a line in the Paschen series, then

$n_1 = 4$

$n_2 = 3$

$R = 1.097 \times 10^7\,\text{m}^{-1}$

$\lambda = ?$

Substituting we obtain

$\frac{1}{\lambda} = \frac{1.097 \times 10^7}{1\,\text{m}}\left(\frac{1}{3^2} - \frac{1}{4^2}\right)$

So $\frac{1}{\lambda} = \frac{1.097 \times 10^{7}}{1\,\text{m}}\left(\frac{1}{9} - \frac{1}{16}\right)$

Thus $\frac{1}{\lambda} = \frac{1.097 \times 10^{7}}{1\,\text{m}} \times 0.049$

Then $\frac{1}{\lambda} = \frac{5.4 \times 10^{6}}{1\,\text{m}}$

Cross-multiplying we obtain

$\lambda \times 5.4 \times 10^{5} = 1\,\text{m}$

$\therefore \lambda = \frac{1\,\text{m}}{5.4 \times 10^{6}}$

$= 1.9 \times 10^{-6}\,\text{m}$

We can now obtain the frequency from the relation

$v = \frac{c}{\lambda}$

$c = 3.00 \times 10^{8}\,\text{m s}^{-1}$
$v = ?$

Substituting we have

$v = \frac{3.00 \times 10^{8}\,\cancel{\text{m}}\,\text{s}^{-1}}{1.9 \times 10^{-6}\,\cancel{\text{m}}}$

$= 1.6 \times 10^{14}\,\text{Hz}\ (\text{s}^{-1})$

Example 6 Calculate the energy of the second energy level the hydrogen atom.

($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $R = 1.097 \times 10^{7}$ m^{-1}, $c = 3.00 \times 10^{8}$ m s^{-1})

Solution We have to apply the equation

$E_2 = -h\frac{cR}{n^2}$

$h = 6.63 \times 10^{-34}\,\text{J s}$
$R = 1.097 \times 10^{7}\,\text{m}^{-1}$
$c = 3.00 \times 10^{8}\,\text{m s}^{-1}$
$n = 2$
$E_2 = ?$

Substituting we have

$$E_2 = -6.63 \times 10^{-34}\ \mathrm{J}\,\cancel{\mathrm{s}} \times \frac{3.00 \times 10^{8}\ \cancel{\mathrm{m}} \times 1.097 \times 10^{7}}{1\,\cancel{\mathrm{s}} \times 1\,\cancel{\mathrm{m}} \times 2^{2}}$$

Then $E_2 = -6.63 \times 10^{-34}\ \mathrm{J} \times \frac{3.29 \times 10^{16}}{4}$

Thus $E_2 = -6.63 \times 10^{-34}\ \mathrm{J} \times 8.23 \times 10^{14}$
$= -5.46 \times 10^{-19}\ \mathrm{J}$

Example 7 Calculate the energy decrease accompanying the transition of an electron from the third to the second energy level of the hydrogen atom.

($R = 1.097 \times 10^{7}\ \mathrm{m}^{-1}$, $h = 6.63 \times 10^{-34}\ \mathrm{J\ Hz}^{-1}$, $c = 3.00 \times 10^{8}\ \mathrm{m\ s}^{-1}$)

Solution The applicable relation is

$$\Delta E = hcR\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$h = 6.63 \times 10^{-34}\ \mathrm{J\ s}$
$R = 1.097 \times 10^{7}\ \mathrm{m}^{-1}$
$c = 3.00 \times 10^{8}\ \mathrm{m\ s}^{-1}$
$n_1 = 3$
$n_2 = 2$
$\Delta E = ?$

Substituting we have

$$\Delta E = 6.63 \times 10^{-34}\ \mathrm{J}\,\cancel{\mathrm{s}} \times \frac{3.00 \times 10^{8}\ \cancel{\mathrm{m}}}{1\,\cancel{\mathrm{s}}} \times \frac{1.097 \times 10^{7}}{1\,\cancel{\mathrm{m}}} \times \left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

Then $\Delta E = 2.18 \times 10^{-18}\ \mathrm{J} \times \left(\frac{1}{4} - \frac{1}{9}\right)$

Thus $\Delta E = 2.18 \times 10^{-18}\ \mathrm{J} \times 0.139$
$= 3.03 \times 10^{-19}\ \mathrm{J}$

Alternatively, we can calculate the energy of each orbit separately using the relation $E_n = -h\frac{cR}{n^2}$, and then find the difference between the two values, i.e.

$$\Delta E = E_3 - E_2$$

The energy of the second orbit has already been obtained to be -5.46×10^{-19} J in the previous example. Thus

$$E_2 = -5.46 \times 10^{-19} \text{ J}$$

To get E_3 we now substitute into the above relation to obtain

$$E_3 = -6.63 \times 10^{-34} \text{ J}\cancel{\text{s}} \times \frac{3.00 \times 10^8 \cancel{\text{m}} \times 1.097 \times 10^7}{1\cancel{\text{s}} \times 1\cancel{\text{m}} \times 3^2}$$

Then $E_3 = -6.63 \times 10^{-34} \text{ J} \times \frac{3.29 \times 10^{16}}{9}$

Thus $E_3 = -6.63 \times 10^{-34} \text{ J} \times 3.66 \times 10^{14}$

$= -2.43 \times 10^{-19}$ J

$\Delta E = ?$

Finally, we now substitute to obtain

$\Delta E = -2.43 \times 10^{-19} \text{ J} - (-5.46 \times 10^{-19} \text{ J})$

Thus $\Delta E = -2.43 \times 10^{-19} \text{ J} + 5.46 \times 10^{-19}$

$= 3.03 \times 10^{-19}$ J

Practice Problems

1. Calculate the frequency of red light if it has a wavelength of 700 nm.
   ($c = 3.00 \times 10^8$ m s^{-1}) [*Answer:* 4.3×10^{14} Hz]
2. Calculate the decrease in energy when an atom emits a radiation of wavelength 97 nm.
   ($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $c = 3.00 \times 10^8$ m s^{-1}) [*Answer:* 2.1×10^{-18} J]
3. Calculate the energy of the electron occupying the ground state of the hydrogen atom.
   ($R = 1.097 \times 10^7$ m^{-1}, $h = 6.63 \times 10^{-34}$ J Hz^{-1}, 3.00×10^8 m s^{-1})
   [*Answer:* -2.18×10^{-18} J]
4. Calculate the wavelength of the line with the longest-wavelength line of the Pfund series of the hydrogen spectrum, hence determine the energy decrease corresponding to this line.
   ($R = 1.097 \times 10^7$ m^{-1}, $h = 6.63 \times 10^{-34}$ J Hz^{-1}, $c = 3.00 \times 10^8$ m s^{-1})
   [*Answers:* 3.38×10^{-6} m, 5.89×10^{-20} J]

4.2 WAVE-PARTICLE DUALITY OF MATTER

In 1924, Louis de Broglie, a French scientist proposed that matter behaves like a wave and particle. This phenomenon is called the wave-particle duality of matter. The relationship between the wavelength of a particle and its momentum is given by the de Broglie relation:

$$\lambda = \frac{h}{m \times c}$$

where m = The mass of particle.

c = The velocity of particle.

The product of mass and velocity, i.e. $m \times v$ is called momentum p. An important implication of the above relation is that objects of large masses have very small wavelengths.

Figure 4.13 Louis de Broglie, French physicist (1892–1987). He won the Nobel Prize for Physics in 1929.

Example 1 Show that the wavelength of a particle is related to its velocity by the relation

$$l = \frac{h}{m \times c}$$

Solution The energy of a particle is given by the Einstein mass-energy relation

$$E = mc^2 \quad (4.1)$$

The energy of a wave is given by the relation

$$E = hv \quad (4.2)$$

Equating Equation (4.1) to (4.2) yields

$$mc^2 = hv \quad (4.3)$$

Now, we know that $v = c/l$. Substituting into Equation (4.3), we obtain

$mc^2 = h\frac{c}{\lambda}$

So $\lambda = \frac{h}{m \times c}$

Example 2 Determine the wavelength associated with the motion of an electron having a rest mass of 9.1×10^{-28} g moving with a velocity of 500 cm s^{-1}.

($h = 6.63 \times 10^{-34}$ J Hz^{-1})

Solution We have to apply the de Broglie relation

$\lambda = \frac{h}{m \times c}$

$h = 6.63 \times 10^{-34}$ J s $= 6.63 \times 10^{-34}$ kg m^2 s^{-1}
$m = 9.1 \times 10^{-28}$ g $= 9.1 \times 10^{-31}$ kg
$c = 500$ cm $s^{-1} = 0.5$ m s^{-1}
$\lambda = ?$

Substituting yields

l$\lambda = \frac{6.63 \times 10^{-34}\ \cancel{\text{kg}}\ \text{m}^2\ \cancel{\text{s}^{-1}}}{9.1 \times 10^{-31}\ \cancel{\text{kg}}\ 0.5\ \text{m}\ \cancel{\text{s}^{-1}}}$

Thus $\lambda = \frac{6.63 \times 10^{-34}\ \text{m}^2}{4.6 \times 10^{-31}\ \text{m}}$

$= 1.4 \times 10^{-3}$ m = 1.4 mm

Note that 1 J = kg m^2 s^{-1}.

Example 3 A particle has a mass of 3.34×10^{-27} kg. Calculate the speed of the particle if it has an associated wavelength of 0.275 mm.

($h = 6.63 \times 10^{-34}$ J Hz^{-1})

Solution We have to apply the relation

$\lambda = \frac{h}{m \times c}$

$c = \frac{h}{m \times \lambda}$

$h = 6.63 \times 10^{-34}$ kg m^2 s^{-1}

$\lambda = 0.275 \text{ mm} = 2.75 \times 10^{-4} \text{ m}$

$m = 3.34 \times 10^{-27} \text{ kg}$

$c = ?$

Substituting we have

$$c = \frac{6.63 \times 10^{-34} \cancel{\text{kg}} \text{ m}^2 \cancel{\text{s}^{-1}}}{9.1 \times 10^{-27} \cancel{\text{kg}} \times 2.75 \times 10^{-4} \text{ m}}$$

Then $$c = \frac{6.63 \times 10^{-34} \text{ m}^2 \cancel{\text{s}^{-1}}}{9.19 \times 10^{-31} \text{ m}}$$

$= 7.21 \times 10^{-4} \text{ m s}^{-1}$

Example 4 A particle moving with a velocity of 8.0 mi hr^{-1} has a wavelength of 50.0 nm. Calculate the mass of the particle.

($h = 6.63 \times 10^{-34}$ J Hz^{-1})

Solution As usual, we have to apply the relation

$$\lambda = \frac{h}{m \times c}$$

$$\therefore \ m = \frac{h}{c \times \lambda}$$

$c = 8.0 \text{ mi hr}^{-1} = 3.6 \text{ m s}^{-1}$

$h = 6.63 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$

$\lambda = 50.0 \text{ nm} = 50.0 \times 10^{-9} \text{ m}$

$m = ?$

Substituting we obtain

$$m = \frac{6.63 \times 10^{-34} \cancel{\text{kg}} \text{ m}^2 \cancel{\text{s}^{-1}}}{3.6 \times \text{m} \cancel{\text{s}^{-1}} \times 50.0 \times 10^{-9} \text{ m}}$$

Then $$m = \frac{6.63 \times 10^{-34} \text{kg} \cancel{\text{m}^2}}{1.8 \times 10^{-7} \cancel{\text{m}^2}}$$

$= 3.7 \times 10^{-27} \text{ kg}$

Practice Problems

1. Calculate the wavelength of a particle of mass 6.7×10^{-25} g travelling at a velocity of 15.5 m min^{-1}.

   ($h = 6.63 \times 10^{-34}$ J Hz^{-1}) [*Answer:* 0.38 m]
2. Calculate the wavelength of a particle whose wavelength is 420 nm.

   ($h = 6.63 \times 10^{-34}$ J Hz^{-1}) [*Answer:* 1.6×10^{-27} kg m s^{-1}]

4.3 UNCERTAINTY PRINCIPLE

The uncertainty principle was postulated by the German scientist Werner Heisenberg in 1927. It states that the more precisely the speed (or momentum) of an electron is known, the less the accuracy with which its position can be determined, and vice versa. In other words, the speed (or momentum) and the position of an electron cannot be determined with certainty at the same time. This is expressed mathematically as

$$\Delta x \times m \times \Delta v \geq \frac{h}{4\pi} \text{ or } \Delta x \times \Delta p \geq \frac{h}{4\pi}$$

where Δx = Uncertainty in the position of particle.

m = Mass of electron.

Δv = The uncertainty in the speed of the electron.

Δp = The uncertainty in the momentum of the electron.

Figure 4.14 Werner Karl Heisenberg, German physicist (1901–1976). He won the Nobel Prize for Physics in 1932.

Example 1 How uncertain is the position of an electron if the uncertainty in its speed is 2.5 mm s^{-1}?

$$(m_e = 9.11 \times 10^{-31} \text{ kg}, \pi = 3.142)$$

Solution We have to use the relation

$\Delta x \times m \times \Delta v \geq \frac{h}{4\pi}$

$\therefore\ \Delta x \geq \frac{h}{4\pi \times m \times \Delta v}$

$h = 6.63 \times 10^{-34}$ J Hz^{-1} = 6.63×10^{-34} kg m^{2} s^{-1}
$m_e = 9.11 \times 10^{-31}$ kg
$\Delta v \geq 2.5$ mm s^{-1} = 0.0025 m s^{-1}
$\Delta x \geq ?$

Substituting we have

$$\Delta x \geq \frac{6.63 \times 10^{-34}\ \cancel{\text{kg}}\ \text{m}^2\ \cancel{\text{s}^{-1}}}{4 \times 3.192 \times 9.11 \times 10^{-31}\ \cancel{\text{kg}} \times 0.0025\ \text{m}\ \cancel{\text{s}^{-1}}}$$

Thus $\Delta x \geq \frac{6.63 \times 10^{-34}\ \text{m}}{2.9 \times 10^{-32}}$

≥ 0.023 m

The implication of this result is that the position of the electron will be uncertain to at least 0.023 m.

Example 2 Determine the uncertainty in the momentum of an electron if its position is known to be within 220 pm.

($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $\pi = 3.142$)

Solution We have to apply the relation

$\Delta x \times \Delta\pi \geq \frac{h}{4\pi}$

$\therefore\ \Delta\pi \geq \frac{h}{4\pi \times \Delta x}$

$h = 6.63 \times 10^{-34}$ kg m^{2} s^{-1}
$\Delta x \geq 220$ pm = 220×10^{-12} m
$\Delta p \geq ?$

Substituting we obtain

$$\Delta\pi \geq \frac{6.63 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{4 \times 3.142 \times 220 \times 10^{-12}\ \text{m}}$$

Thus $\Delta\pi \geq \frac{6.63 \times 10^{-34}\,\mathrm{kg\,m\,s^{-1}}}{2.8 \times 10^{-9}}$

$\geq 2.54 \times 10^{-25}$ kg m s^{-1}

Example 3 Calculate the uncertainty in the speed of an electron if its position is known to within 140 pm.

($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $m_e = 9.11 \times 10^{-31}$ kg, $\pi = 3.142$)

Solution As usual, we have to apply the relation

$\Delta x \times m \times \Delta v \geq \frac{h}{4\pi}$

$\therefore\ \Delta v \geq \frac{h}{4\pi \times \Delta x \times m}$

$h = 6.63 \times 10^{-34}$ kg m^2 s^{-1}

$m = 9.11 \times 10^{-31}$ kg

$\Delta x \geq 140$ pm $= 140 \times 10^{-12}$ m

$\Delta v \geq$?

Substituting we have

$\Delta v \geq$

Thus $\Delta v \geq \frac{6.63 \times 10^{-34}\,\mathrm{m\,s^{-1}}}{1.6 \times 10^{-39}}$

$\geq 4.1 \times 10^{5}$ m s^{-1}

Practice Problems

1. Determine the uncertainty in the speed of an electron when the uncertainty in its position is at least 200 pm.

   ($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $m_e = 9.11 \times 10^{-31}$ kg, p = 3.142) [*Answer:* 3×10^{5} m s^{-1}]

2. Evaluate the uncertainty in the position of an electron when its speed is known to within 2.1 mm s^{-1}.

   ($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $m_e = 9.11 \times 10^{-31}$ kg, p = 3.142) [*Answer:* 2.8 cm]

4.4 IONIZATION ENERGY

The ionization energy *I* of an element is the minimum energy required to remove an electron from the ground state of its gaseous atom. The minimum energy required to remove a second electron is called the second ionization energy. The unit of ionization energy is joules per mole (J mol^{-1}).

The ionization energy of an element corresponds to the energy of the radiation emitted when an electron falls from infinity, or the highest energy level, to the ground state of its atom. Since this process produces the radiation of the highest frequency (shortest wavelength), then the ionization energy of an element can be obtained from the highest frequency, or the shortest wavelength, in its spectrum.

Example 1 Calculate the ionization energy of hydrogen.

($R = 1.097 \times 10^{7}$ m, $h = 6.63 \times 10^{-34}$ J Hz^{-1}, $c = 3.00 \times 10^{8}$ m s^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1})

Solution Since we are dealing with the hydrogen atom, then we have to apply the relation

$$\Delta E = hcR\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$h = 6.63 \times 10^{-34}$ J s

$R = 1.097 \times 10^{7}$ m^{-1}

$c = 3.00 \times 10^{8}$ m s^{-1}

$n_1 = •$

$n_2 = 1$

$\Delta E = ?$

Substituting we have

$$\Delta E = 6.63 \times 10^{-34}\ \text{J}\,\cancel{\text{s}} \times \frac{3.00 \times 10^{8}\ \cancel{\text{m}}}{1\ \cancel{\text{s}}} \times \frac{1.097 \times 10^{7}}{1\ \cancel{\text{m}}} \times \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)$$

Thus $\Delta E = 2.18 \times 10^{-18}\ \text{J} \times \left(\frac{1}{1}\right)$

$= 2.18 \times 10^{-18}$ J

This is the energy required to remove an electron from the ground state of a gaseous hydrogen atom. Since ionization energy is usually reported per mol, then

$I = 2.18 \times 10^{-18}\ \text{J} \times 6.02 \times 10^{23}\ \text{mol}^{-1}$

$= 1310\ \text{kJ mol}^{-1}$

Example 2 Calculate the ionization enery of lithium if the shortest wavelength of the radiations emitted by its atom is 231 nm.

($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $c = 3.00 \times 10^{8}$ m s^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1})

Solution We have to apply the relation

$$\mathrm{D}E = hv$$

The frequency of the light is obtained from the relation

$$v = \frac{c}{\lambda}$$

$c = 3.00 \times 10^{8}\,\text{m s}^{-1}$

l $= 231\ \text{nm} = 231 \times 10^{-9}\,\text{m}$

$v = ?$

Substituting we have

$$v = \frac{3.00 \times 10^{8}\ \cancel{\text{m}}\,\text{s}^{-1}}{231 \times 10^{-9}\ \cancel{\text{m}}}$$

$= 1.30 \times 10^{15}$ Hz (s^{-1})

$h = 6.63 \times 10^{-34}$ J s

$\Delta E = ?$

We can now substitute into the original equation to obtain

$$\Delta E = 6.63 \times 10^{-34}\,\text{J}\,\cancel{\text{s}} \times \frac{1.30 \times 10^{15}}{1\,\cancel{\text{s}}}$$

$= 8.62 \times 10^{-19}\,\text{J}$

Thus $I = 8.62 \times 10^{-19}\,\text{J} \times 6.02 \times 10^{23}\ \text{mol}^{-1}$

$= 519\ \text{kJ mol}^{-1}$

Example 3 Calculate the frequency of the shortest-wavelength light emitted by potassium atom if its ionization energy is 421 kJ mol^{-1}.

($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $c = 3.00 \times 10^{8}$ m s^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1})

Solution The frequency of the shortest-wavelength light corresponds to the longest frequency of the spectrum. The very first step is to calculate the ionization energy per atom, i.e.

$$\Delta E = \frac{421 \times 10^{3}\ \text{J}\ \cancel{\text{mol}^{-1}}}{6.02 \times 10^{23}\ \cancel{\text{mol}^{-1}}}$$

$= 6.99 \times 10^{-19}$ J

We can now calculate the frequency from the relation

$\Delta E = h\nu$

$$\therefore\ \nu = \frac{\Delta E}{h}$$

$h = 6.63 \times 10^{-34}$ J s

$\nu = ?$

Finally, we now substitute to obtain

$$\nu = \frac{6.99 \times 10^{-19}\ \cancel{\text{J}}}{6.63 \times 10^{-34}\ \cancel{\text{J}}\ \text{s}}$$

$= 1.05 \times 10^{15}$ Hz

Practice Problems

1. The wavelength of the shortest-wavelength light emitted by helium atom is 50.5 nm. What is the ionization energy of the element?

   ($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $c = 3.00 \times 10^{8}$ m s^{-1}, $N_A = 6.02 \times 10^{23}$)

   [*Answer:* 2370 kJ mol^{-1}]

2. The ionization energy of calcium is 590 kJ mol^{-1}. Calculate the frequency and wavelength of the shortest-wavelength light emitted by the atom of the element.

   ($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $c = 3.00 \times 10^{8}$ m s^{-1}, $N_A = 6.02 \times 10^{23}$)

   [*Answers:* 1.5×10^{15} Hz, 2.0 nm]

4.5 IONIC BOND, IONIZATION ENERGY AND LATTICE ENERGY

Ionic or electrovalent compounds consist of oppositely charged ions (cations and anions) held together by electrostatic force of attraction called ionic bond. The formation of an ionic compound could be conceived to take place in a series of hypothetical steps, which can be illustrated with the formation of sodium chloride, as follows:

The first step is the conversion of solid sodium and chlorine gas to l mol of their gaseous atoms, i.e.

$\mathrm{Na}(s) \rightarrow \mathrm{Na}(g) \quad \Delta H = 109 \text{ kJ mol}^{-1}$

$\tfrac{1}{2}\mathrm{Cl}_2(g) \rightarrow \mathrm{Cl}(g) \quad \Delta H = 109 \text{ kJ mol}^{-1}$

The second step involves the formation of gaseous sodium and chloride ions. This process involves the removal of an electron from the ground state of the gaseous sodium atom. As noted earlier, this process is called ionization, and it is denoted as follows:

$\mathrm{Na}(g) \rightarrow \mathrm{Na}^{+}(g) + \mathrm{e}^{-} \quad \Delta H = 502 \text{ kJ mol}^{-1}$

The energy specified is the ionization energy of sodium. The electron removed in this process is attached to the gaseous atom of chlorine to form 1 mol of chloride ions, i.e.

$\mathrm{Cl}(g) + \mathrm{e}^{-} \rightarrow \mathrm{Cl}^{-}(g) \quad \Delta H = -370 \text{ kJ mol}^{-1}$

The energy specified is the minimum energy required to attach an electron to the ground state of the gaseous chlorine atom. This is called the electron affinity of chlorine.

Summing up the above processes, we have

$\mathrm{Na}(s) + \tfrac{1}{2}\mathrm{Cl}_2(g) \rightarrow \mathrm{Na}^{+}(g) + \mathrm{Cl}^{-}(g) \quad \Delta H = 362.3 \text{ kJ mol}^{-1}$

The energy specified is the heat required for the formation of 1 mol of the cations and anions from their standard atoms.

The last step is the formation solid sodium chloride from the cations and anions, i.e.

$\mathrm{Na}^{+}(g) + \mathrm{Cl}^{-}(g) \rightarrow \mathrm{NaCl}(s) \quad \Delta H = -773.5 \text{ kJ mol}^{-1}$

The heat specified is the energy of formation of 1 mol of solid sodium chloride from its gaseous ions. This is called the energy of crystallization, which is always exothermic. An equal amount of energy must be supplied to the solid to reverse this process. This energy is called lattice energy, which is defined as the standard energy required for the separation of 1 mol of the solid into a gas of its ions, i.e.

$\mathrm{NaCl}(s) \rightarrow \mathrm{Na}^{+}(g) + \mathrm{Cl}^{-}(g) \quad \Delta H = -773.5 \text{ kJ mol}^{-1}$

It should be noted that lattice energy is always endothermic since energy has to be supplied to split the solid into it gaseous ions. Thus lattice energy and energy of crystallization are both equal and opposite.

The net equation for the formation of sodium chloride and its heat of formation are obtained by adding all the above equations, i.e.

$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow Na^+(g) + Cl^-(g)$ $\Delta H = 362.3$ kJ mol^{-1}

$+ Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ $\Delta H = -773.5$ kJ mol^{-1}

$Na(s) + \cancel{Na^+(g)} + \frac{1}{2}Cl_2(g) + \cancel{Cl^-(g)} \rightarrow \cancel{Na^+(g)} + \cancel{Cl^-(g)} + NaCl(s)$

So $Na(s) + \frac{1}{2}Cl(g) \rightarrow NaCl(s)$ $DH^o_f = -411.2$ kJ mol^{-1}

The net equation is the equation for the formation of 1 mol of sodium chloride from its standard elements, and the energy required for the process is −411.2 kJ mol^{-1}. In other word, 411.2 kJ of heat must be evolved before 1 mol of sodium chloride could be formed from its standard elements. In general, the formation of ionic compound is always followed by a decrease in energy, i.e., always exothermic. A series of steps leading to a positive heat of formation for an ionic compound means such a reaction is not feasible.

From the information given above, we can easily calculate the enthalpy change for any of the steps using Hess's law[1], provided the data for all the remaining processes are known.

Example 1 Calculate the lattice energy of sodium chloride from information given below:

Reaction	ΔH/kJ mol^{-1}
$Na(s) \rightarrow Na(g)$	109.0
$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$	121.3
$Na(s) + \frac{1}{2}Cl(g) \rightarrow NaCl(s)$	−411.2
$Cl(g) + e^- \rightarrow Cl^-(g)$	−370.0
$Na(g) \rightarrow Na^+(g) + e^-$	502.0

Solution The lattice energy has to be determined from Hess's law. This is done by adding and subtracting equations and their corresponding heats of reaction to obtain the required equation and its heat of reaction. In this case, the required equation is that for the crystallization of the gaseous ions into solid sodium chloride. Once we obtain this, we can always obtain the lattice enthalpy from the crystallization energy by changing its sign from negative to positive.

Now, we know that the sum of all the steps, including the unknown, must be equal to the net equation for the formation of sodium chloride from its standard elements, i.e.

$\mathrm{Na}(s) + \tfrac{1}{2}\mathrm{Cl}_2(g) \rightarrow \mathrm{NaCl}(s)$ $\Delta H = -411.2$ kJ mol^{-1}

Thus we can obtain the required equation and its enthalpy change by adding all the other equations and their heats of reaction and subtracting the results from the net equation for the formation of sodium chloride and its corresponding heat of reaction (heat of formation). We must always remember this basic arithmetic principle: an equation can only be solved if there is only one unknown variable. The sum of the above equations (with the exception of that for the formation of the compound) is:

$\mathrm{Na}(s) \rightarrow \mathrm{Na}(g)$ 109.0 kJ mol^{-1}

$\tfrac{1}{2}\mathrm{Cl}_2(g) \rightarrow \mathrm{Cl}(g)$ 121.3 kJ mol^{-1}

$\mathrm{Cl}(g) + \mathrm{e}^- \rightarrow \mathrm{Cl}^-(g)$ −370.0 kJ mol^{-1}

$+ \mathrm{Na}(g) \rightarrow \mathrm{Na}^+(g) + \mathrm{e}^-$ 502.0 kJ mol^{-1}

$\mathrm{Na}(s) + \tfrac{1}{2}\mathrm{Cl}_2(g) + \cancel{\mathrm{Cl}(g)} + \cancel{\mathrm{e}^-} + \cancel{\mathrm{Na}(g)} \rightarrow \cancel{\mathrm{Na}(g)} + \cancel{\mathrm{Cl}(g)} + \mathrm{Cl}^-(g) + \mathrm{Na}^+(g) + \cancel{\mathrm{e}^-}$

So $\mathrm{Na}(s) + \tfrac{1}{2}\mathrm{Cl}_2(g) \rightarrow \mathrm{Cl}^-(g) + \mathrm{Na}^+(g)$ DH = 362.3 kJ mol^{-1}

Finally, we now subtract this equation from the equation for the formation of NaCl(s) from its standard elements, i.e.

$\mathrm{Na}(s) + \tfrac{1}{2}\mathrm{Cl}_2(g) \rightarrow \mathrm{NaCl}(s)$ −411.2 kJ mol^{-1}

$-\ \mathrm{Na}(s) + \tfrac{1}{2}\mathrm{Cl}_2(g) \rightarrow +\mathrm{Cl}^-(g) + \mathrm{Na}^+(g)$ 362.3 kJ mol^{-}

$\rightarrow \mathrm{NaCl}(s) - \mathrm{Cl}^-(g) - \mathrm{Na}^+(g)$

So $\mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \rightarrow \mathrm{NaCl}(s)$ DH = −773.5 kJ mol^{-1}

Since the heat of crystallization of NaCl is −773.5 kJ mol^{-1}, then we have to change the sign to obtain its lattice energy as 773.5 kJ mol^{-1}.

Example 2 Calculate the electron affinity of bromine from the information given below:

Reaction	ΔH/kJ mol^{-1}
$\mathrm{K}(s) \rightarrow \mathrm{K}(g)$	89.0
$\mathrm{K}(g) \rightarrow \mathrm{K}^-(g) + \mathrm{e}^-$	418.0
$\tfrac{1}{2}\mathrm{Br}_2(g) \rightarrow \mathrm{Br}(g)$	112.0
$\mathrm{K}(s) + \tfrac{1}{2}\mathrm{Br}_2(g) \rightarrow \mathrm{KBr}(s)$	−393.8
$\mathrm{K}^+(g) \rightarrow \mathrm{Br}^-(g) \rightarrow \mathrm{KBr}(s)$	−689.0

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[1] See Chapter 11 for details on Hess's law.

Solution We should know from the definition of electron affinity that the required equation is

$\mathrm{Br}(g) + \mathrm{e}^-(g) \rightarrow \mathrm{Br}^-(g) \quad \Delta H = ?$

Our goal is to obtain this equation and the corresponding enthalpy change (electron affinity or electron gain enthalpy) from the above information. This is done by first summing up the equations (with the exception of that for the formation of potassium bromide from its standard elements), i.e.

$\mathrm{K}(s) \rightarrow \mathrm{K}(g) \quad 89.0\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{K}(g) \rightarrow \mathrm{K}^-(g) + \mathrm{e}^- \quad 418.0\ \mathrm{kJ\ mol^{-1}}$

$\frac{1}{2}\mathrm{Br}_2(g) \rightarrow \mathrm{Br}(g) \quad 112.0\ \mathrm{kJ\ mol^{-1}}$

$+\ \mathrm{K}^+(g) + \mathrm{Br}^-(g) \rightarrow \mathrm{KBr}(s) \quad -689.0\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{K}(s) + \cancel{\mathrm{K}(g)} + \frac{1}{2}\mathrm{Br}_2(g) + \cancel{\mathrm{K}^+(g)} + \mathrm{Br}^-(g) \rightarrow \cancel{\mathrm{K}(g)} + \cancel{\mathrm{K}^+(g)} + \mathrm{e}^- + \mathrm{Br}(g) + \mathrm{KBr}(s)$

So $\mathrm{K}(s) + \frac{1}{2}\mathrm{Br}_2(g) + \mathrm{Br}^-(g) \rightarrow \mathrm{Br}(g) + \mathrm{KBr}(s) + \mathrm{e}^- \quad \Delta H = -70\ \mathrm{kJ\ mol^{-1}}$

Finally, we have to subtract this equation from the equation for the formation of the compound from its standard elements, i.e.

$\mathrm{K}(s) + \frac{1}{2}\mathrm{Br}_2(g) \rightarrow \mathrm{KBr}(s) \quad -393.8\ \mathrm{kJ\ mol^{-1}}$

$-\ \mathrm{K}(s) + \frac{1}{2}\mathrm{Br}_2(g) + \mathrm{Br}^-(g) \rightarrow \mathrm{Br}(g) + \mathrm{KBr}(s) + \mathrm{e}^- \quad -70.0\ \mathrm{kJ\ mol^{-1}}$

$-\mathrm{Br}^-(g) \rightarrow -\mathrm{Br}(g) - \mathrm{e}^-$

So $\mathrm{Br}(g) + \mathrm{e}^- \rightarrow \mathrm{Br}^-(g) \quad \Delta H = -323.8\ \mathrm{kJ\ mol^{-1}}$

Thus the electron affinity of bromine is $-323.8\ \mathrm{kJ\ mol^{-1}}$.

Example 3 Calculate the ionization energy of calcium from the following data.

Reaction	ΔH/kJ
$\mathrm{Ca}(s) \rightarrow \mathrm{Ca}(g)$	178.0
$2\mathrm{F}(g) + 2\mathrm{e}^- \rightarrow 2\mathrm{Fe}^+(g)$	−656.0
$\mathrm{Ca}^{2+}(g) + 2\mathrm{Fe}(g) \rightarrow \mathrm{CaF}_2(s)$	−2628.0
$\mathrm{F}_2(g) \rightarrow 2\mathrm{F}(g)$	159.4
$\mathrm{Ca}(s) + \mathrm{F}_2(g) \rightarrow \mathrm{CaF}_2(s)$	−1219.6
$\mathrm{Ca}^+(g) \rightarrow \mathrm{Ca}^{2+}(g) + \mathrm{e}$	1137.0

Solution We should know from the definition of ionization energy that the required equation is

$\mathrm{Ca}(g) + \mathrm{e}^- \rightarrow \mathrm{Ca}^+(g)$ $\Delta H = ?$

As usual, we first sum up all the equations except that of formation of calcium fluoride from its standard elements, i.e.

$\mathrm{Ca}(s) \rightarrow \mathrm{Ca}(g)$ 178.0 kJ

$2\mathrm{F}(g) + 2\mathrm{e}^- \rightarrow 2\mathrm{Fe}^+(g)$ −656.0 kJ

$\mathrm{Ca}^{2+}(g) + 2\mathrm{F}^-(g) \rightarrow \mathrm{CaF}_2(s)$ −2628.0 kJ

$\mathrm{F}_2(g) \rightarrow 2\mathrm{F}(g)$ 159.4 kJ

$+\ \mathrm{Ca}^+(g) \rightarrow \mathrm{Ca}^{2+}(g) + \mathrm{e}^-$ 1137.0 kJ

$\mathrm{Ca}(s) + \cancel{2\mathrm{F}(g)} + 2\mathrm{e}^- + \cancel{\mathrm{Ca}^{2+}(g) + 2\mathrm{F}^-(g)} + \mathrm{F}_2(g) + \mathrm{Ca}^+(g)$

$\rightarrow \mathrm{Ca}(g) + \cancel{2\mathrm{F}^-(g)} + \mathrm{CaF}_2(s) + \cancel{2\mathrm{F}(g) + \mathrm{Ca}^{2+}(g)} + \mathrm{e}^-$

So $\mathrm{Ca}(s) + \mathrm{F}_2(g) + \mathrm{Ca}^+(g) + \mathrm{e}^- \rightarrow \mathrm{Ca}(g) + \mathrm{CaF}_2(s)$ D$H = -1809.6\ \mathrm{kJ\ mol}^{-1}$

Finally, we subtract this equation from that for the formation of calcium fluoride from its standard elements, i.e.

$\mathrm{Ca}(s) + \mathrm{F}_2(g) \rightarrow \mathrm{CaF}_2(s)$ $-1219.6\ \mathrm{kJ\ mol}^{-1}$

$-\ \mathrm{Ca}(s) + \mathrm{F}_2(g) + \mathrm{Ca}^+(g) + \mathrm{e}^- \rightarrow \mathrm{Ca}(g) + \mathrm{CaF}_2(s)$ $-1809.6\ \mathrm{kJ\ mol}^{-1}$

$\mathrm{Ca}^+(g) - \mathrm{e}^- \rightarrow \mathrm{Ca}(g)$

So $\mathrm{Ca}(g) \rightarrow \mathrm{Ca}^+(g) + \mathrm{e}^-$ $\Delta H = 590\ \mathrm{kJ\ mol}^{-1}$

Thus the ionization energy of calcium is 590 kJ mol^{-1}.

Example 4 Which of the compounds, XCl and XCl_2 is likely to be formed between the element X and chlorine? The lattice energies of XCl and XCl_2 are 900 kJ mol^{-1} and 4500 kJ mol^{-1} respectively. Other relevant data are given below:

Reaction	ΔH/kJ mol^{-1}
$\mathrm{X}(s) \rightarrow \mathrm{X}(g)$	102.0
$\mathrm{X}(g) \rightarrow \mathrm{X}^+(g) + \mathrm{e}^-$	509.0
$\mathrm{X}(g) \rightarrow \mathrm{X}^{2+}(g) + \mathrm{e}^-$	4650.0
$\tfrac{1}{2}\mathrm{Cl}_2(g) \rightarrow \mathrm{Cl}(g)$	121.3
$\mathrm{Cl}(g) + \mathrm{e}^- \rightarrow \mathrm{Cl}^-(g)$	−349.0

Solution The compound with the negative heat of formation will be the one that is more favoured to be formed from its standard elements. Thus we need to calculate the heat of formation of each compound, and see which is negative.

We begin with XCl: Since lattice energy is the opposite of heat of crystallization, then

$X^+(g) + Cl^-(g) \rightarrow XCl(s)$ $\Delta H = -900.0 \text{ kJ mol}^{-1}$

The heat of formation of XCl is obtained by summing this equation and other appropriate equations from those given above, i.e.

$X(s) \rightarrow X(g)$ $102.0 \text{ kJ mol}^{-1}$

$X(g) \rightarrow X^+(g) + e^-$ $509.0 \text{ kJ mol}^{-1}$

$X(g) \rightarrow X^{2+}(g) + e^-$ $4650.0 \text{ kJ mol}^{-1}$

$½Cl_2(g) \rightarrow Cl(g)$ $121.3 \text{ kJ mol}^{-1}$

$Cl(g) + e^- \rightarrow Cl^-(g)$ $-349.0 \text{ kJ mol}^{-1}$

$+ X^+(g) + Cl(g) \rightarrow XCl(s)$ $-900.0 \text{ kJ mol}^{-1}$

$X(s) + \cancel{X(g)} + ½Cl(g) + \cancel{Cl(g)} + \cancel{e^-} + \cancel{X^+(g)} + \cancel{Cl^-(g)}$

$\rightarrow \cancel{X(g)} + \cancel{X^+(g)} + \cancel{e^-} + \cancel{Cl(g)} + \cancel{Cl^-(g)} + XCl(s)$

So $X(s) + ½Cl(g) \rightarrow XCl(s)$ $\Delta H = 516.7 \text{ kJ mol}^{-1}$

Thus the heat of formation of $XCl(s)$ is $-516.7 \text{ kJ mol}^{-1}$.

Now we shift attention to XCl_2. Since the lattice energy is $4500.0 \text{ kJ mol}^{-1}$, then

$X^{2+}(g) + 2Cl^-(g) \rightarrow XCl_2(s)$ $\Delta H = -4500.0 \text{ kJ mol}^{-1}$

We have to add this equation to the other equations given above to obtain the heat of formation of XCl_2, i.e.

$X(s) \rightarrow X(g)$ 102.0 kJ

$X(g) \rightarrow X^+(g) + e^-$ 509.0 kJ

$X(g) \rightarrow X^{2+}(g) + e^-$ 4650.0 kJ

$Cl_2(g) \rightarrow 2Cl(g)$ 242.6 kJ

$2Cl(g) + 2e^- \rightarrow 2Cl^-(g)$ -698.0 kJ

$+ X^{2+}(g) + 2Cl^-(g) \rightarrow XCl_2(s)$ -4500.0 kJ

$X(s) + \cancel{X(g)} + \cancel{X^+(g)} + Cl_2(g) + \cancel{2Cl(g)} + \cancel{2e^-} + \cancel{2Cl(g)} + \cancel{X^{2+}(g)}$

$\rightarrow \cancel{X(g)} + \cancel{X^+(g)} + \cancel{e^-} + \cancel{X^{2+}(g)} + \cancel{e^-} + \cancel{2Cl(g)} + \cancel{2Cl^-(g)} + XCl_2(s)$

So $X(s) + Cl_2(g) \rightarrow XCl_2(s)$ $\Delta H = 215.6 \text{ kJ mol}^{-1}$

Thus the heat of formation of XCl_2 is $215.6 \text{ kJ mol}^{-1}$. Since this heat of formation is positive, then the formation of the compound is not feasible.

Consequently, X and chlorine are likely to form XCl, whose heat of formation is negative.

Practice Problems

1. Calculate the ionizations energy of silver from the information given below, given that the lattice energy of silver chloride is 916 kJ mol^{-1}.

Reaction	ΔH/kJ mol^{-1}
$Ag(s) \rightarrow Ag(g)$	285.0
$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$	122.0
$Cl(g) + e^- \rightarrow Cl^-(g)$	−349.0
$Ag(s) + \frac{1}{2}Cl(g) \rightarrow AgCl(s)$	−127.0

[*Answer:* 731 kJ mol^{-1}]

2. Calculate the lattice energy of magnesium oxide from the information given below:

Reaction	ΔH/kJ mol^{-1}
$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO_2$	−602
$Mg(s) \rightarrow Mg(g)$	111
$Mg(g) \rightarrow Mg^+(g) + e^-$	736
$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$	1450
$\frac{1}{2}O_2(g) \rightarrow O(g)$	249
$O(g) + e^- \rightarrow O^-(g)$	−142
$O^-(g) + e^- \rightarrow O^-(g)$	844

[*Answer:* 3850 kJ mol^{-1}]

3. Which of the compounds XCl and XCl_2 is likely to be formed by an element X and chlorine, given the following information:

Reaction	ΔH/kJ mol^{-1}
$X(s) \rightarrow X(g)$	864
$X(g) \rightarrow X^+(g) + e^-$	900
$X(g) \rightarrow X^{2+}(g) + e^-$	1760
$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$	122
$Cl(g) + e^- \rightarrow Cl^-(g)$	−349

The lattice energies of XCl and XCl_2 are 1637 kJ mol^{-1} and 3017 kJ mol^{-1} respectively.

[*Answer:* XCl_2]

4.6 COVALENT BOND AND HEAT OF REACTION

The type of bond that results from the sharing of valence electrons by atoms is called covalent bond. Unlike ionic bonding, this type of bonding results in the formation of molecules. The formation of oxygen molecule, for example, results when two oxygen atoms share two pairs of electrons. When a pair of electrons is shared between two atoms, the resulting covalent bond is called single covalent bond. When two pairs of electrons are shared, it is called double covalent bond. When three pairs of electrons are shared, it is referred to as triple covalent bond.

A shared pair of electrons is usually donated in Lewis structure by a short horizontal line (−), two shared pairs by two parallel horizontal lines (=), and three shared pairs by three parallel horizontal lines (∫). These can be illustrated by carbon-to-carbon bonds, as follows:

C−C Single covalent bond

C=C Double covalent bond

C∫C Triple covalent bond

Each bond possesses a characteristic energy called bond energy or enthalpy *B*, which is defined as the amount of energy required to dissociate or break the bond between covalently bonded atoms in one mole of a molecule. Bond energies for polyatomic molecules are reported in terms of average values of bond energies due to the slight variation in the values of bond energies of the same bonds in different molecules.

We can always explore the principle of conservation of energy to estimate the heat of reaction from bond or average bond enthalpies, using the relation

$$DH^o = \sum H_r^\circ - \sum H_f^\circ$$

$\sum H_r^\circ$ = Sum of bond breaking energy or the total bond energy.

$\sum H_f^\circ$ = Sum of bond forming energy.

Example 1 Calculate the heat of formation of water vapour, given that the energies of the bond H−H, O−O and O−H are 436 kJ mol^{-1}, 496 kJ mol^{-1} and 463 kJ mol^{-1} respectively.

Solution The heat of formation is given by the relation

$$\mathrm{D}H^\circ_f = \sum H_r^\circ - \sum H_p^\circ$$

We have to write the equation of reaction for the formation of water vapour from its standard elements, i.e.

$$H_2(g) + ½O_2(g) \rightarrow H_2O(g)$$

The next step is to write this equation in terms of Lewis structure, as follows:

$$\mathrm{H{-}H} + 1/2\mathrm{O{=}O} \rightarrow \mathrm{H{-}O{-}H}$$

The bond breaking energy or heat of atomisation of reactants is the sum of the bond energies of the reactants, i.e.

$\sum H_r^\circ$ = B(H−H) + ½B(O=O)

B(H−H) = 436 kJ mol^{-1}

B(O=O) = 496 kJ mol^{-1}

$\sum H_r^\circ$ = ?

Substituting we have

$$\sum H_r^\circ = 436 \text{ kJ mol}^{-1} + ½ \times 496 \text{ kJ mol}^{-1} = 684 \text{ kJ mol}^{-1}$$

The heat released on forming the product is the sum of the bond energies of the product, i.e.

$\sum H_p^\circ$ = B(O−H) + B(O−H) = 2B(O−H)

B(O−H) = 463 kJ mol^{-1}

$\mathrm{D}H^\circ_f$ = ?

Substituting we obtain

$\sum H_p^\circ$ = 2 × 463 kJ mol^{-1} = 926 kJ mol^{-1}

$\sum H_p^\circ$ = ?

Substituting into the original equation, we have

$\mathrm{D}H^\circ_f$ = 684 kJ mol^{-1} – 926 kJ mol^{-1}

= −242 kJ mol^{-1} of water vapour

Example 2 Calculate the heat of combustion of benzene vapour from the information given below:

Bond	B/kJ mol^{-1}
C−C	518
C=C	518
C−H	412
C=O	743
O−H	463
O=O	497

Solution The heat of combustion is obtained from the relation

$$\text{D}H^o_c = \sum H^\circ_r - \sum H^\circ_p$$

As usual, the first step is to write the equation of reaction:

$$C_6H_6(g) + 15/2O_2(g) \rightarrow 6CO_2(g) + 3H_2O(g)$$

The next step is to write this equation in terms of Lewis structure, i.e.

Benzene consists of six C−H bonds, three C−C bonds and three C=C bonds. Thus

$\sum H^\circ_r$ = 6B(C−H) + 3B(C−C) + 3B(C=C) + 15/2B(O=O)

B(C–H) = 512 kJ mol^{-1}
B(C–C) = 518 kJ mol^{-1}
B(C=C) = 518 kJ mol^{-1}
B(O=O) = 49 kJ mol^{-1}
$\sum H^\circ_r$ = ?

Substituting we have

H^o_f = 6 × 412 kJ mol^{-1} + 3 × 518 kJ mol^{-1} + 3 × 518 kJ mol^{-1} + 15/2 × 496 kJ mol^{-1}

= 9300 kJ mol^{-1}

Carbon dioxide contains two C=O bonds, while water contains two O–H bonds. Thus

$\sum H_p^\circ$ = 6 × 2*B*(C=O) + 3 × 2*B*(O–H)

B(C=O) = 743 kJ mol^{-1}

B(O–H) = 463 kJ mol^{-1}

$\sum H_p^\circ$ = ?

Substituting we have

$\sum H_p^\circ$ = 12 × 743 kJ mol^{-1} + 6 × 463 kJ mol^{-1} = 11694 kJ mol^{-1}

ΔH_c^o = ?

Finally, we now substitute into the original equation to obtain

ΔH_c^o = 9300 kJ mol^{-1} – 11694 kJ mol^{-1}

= −2394 kJ mol^{-1} of benzene

The experimental value is −3302 kJ mol^{-1}.

Example 3 Calculate the strength of the single bond N–H from the reaction given below:

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta H^o = -76$ kJ

The dissociation enthalpies of hydrogen and nitrogen are 436 kJ mol^{-1} and 944 kJ mol^{-1}, respectively.

Solution We know that the heat of reaction is given as

$$\Delta H^o = \sum H_r^\circ - \sum H_p^\circ$$

Writing the above reaction in terms of Lewis structure, we have

$$\mathrm{N{-}N} + 3\mathrm{H{-}H} \longrightarrow 2\mathrm{H{-}\overset{\overset{\displaystyle H}{|}}{N}{-}H}$$

$\sum H_r^\circ$ = 1 mol × *B*(N–N) + 3 mol × *B*(H−H)

B(N–N) = 944 kJ mol^{-1}

B(H–H) = 436 kJ mol^{-1}

$\sum H_r^\circ$ = ?

Substituting we have

$$\sum H_r^\circ = 1\,\cancel{\text{mol}}\,\frac{944\text{ kJ}}{1\,\cancel{\text{mol}}} \times 3\,\cancel{\text{mol}} \times \frac{436\text{ kJ}}{1\,\cancel{\text{mol}}} = 2252\text{ kJ}$$

There are three N−H single bonds in ammonia. Thus

$\sum H_p^\circ$ = 3 × 2 mol × B(N–H) = 6 mol × B(N−H)

ΔH^o = −76 kJ

Substituting we have

−76 kJ = 2252 kJ – 6 mol × B(N–H)

Thus 6 mol × B(N–H) = 2252 kJ + 76 kJ

So 6 mol × B(N–H) = 2328 kJ

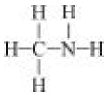
Then B(N–H) = $\frac{2328\text{ kJ}}{6\text{ mol}}$

= 388 kJ mol^{-1}

Example 4 Use the information given below to calculate the heats of atomization of the methylamine, CH_3NH_2.

Bond	B/kJ mol^{-1}
C–N	305
N–H	388
C–H	412

Solution The heat of atomisation is the heat required to dissociate the molecule into its gaseous atoms, which is equivalent to the total energy of all the bonds in the molecule. Thus all we need to do is to identify all the bonds in the molecule, and sum up their energies. To do this we must first write the Lewis structure of the molecule:



The structure shows that the compound contains three C–H bonds, a C–N bond and two N–H bonds. Thus the enthalpy of atomization is given as

ΔH^o_a = 3B(C–H) + B(C–N) + 2B(N–H)

B(C–H) = 412 kJ mol^{-1}

B(C–N) = 305 kJ mol^{-1}

B(N–H) = 388 kJ mol^{-1}

$\Delta H^o{}_a$ = ?

Substituting we obtain

$\Delta H^o{}_a$ = 3 × 412 kJ mol^{-1} + 305 kJ mol^{-1} + 2 × 388 kJ mol^{-1}

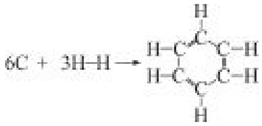
= 2317 kJ mol^{-1}

Example 5 Calculate the heat of formation of liquid benzene, given that the average bond energies of the bonds C–C, C=C, C–H, O=O and C=O are 518 kJ mol^{-1}, 518 kJ mol^{-1}, 412 kJ mol^{-1}, 496 kJ mol^{-1} and 743 kJ mol^{-1} respectively. The heats of vaporisation of benzene, dissociation of hydrogen and sublimation of carbon are 30.8 kJ mol^{-1}, 716.7 kJ mol^{-1} and 436 kJ mol^{-1} respectively.

Solution The heat of formation calculated using mean bond energies is the heat of formation of the compound in the gaseous state. We know that for 1 mol of liquid to translate into the gaseous state, an amount of heat, called the heat of vaporisation has to be supplied to the liquid. To reverse this process, i.e., to effect condensation, the vapour has to lose an amount of heat equivalent to the heat of vaporisation. This heat is referred to as the heat of condensation, which is equal and opposite to the heat of vaporisation. Thus we should calculate the heat of formation of benzene in the gaseous state, and then subtract the heat of condensation from it to obtain its heat of formation in the liquid state. The very first step is to write the equation for the formation of gaseous benzene from its standard elements:

$$6\mathrm{C}(s) + 3\mathrm{H}_2(g) \rightarrow \mathrm{C}_6\mathrm{H}_6(g)$$

In terms of Lewis structure, we have



$\sum H_1^\circ$ = $\Delta H^o{}_s$ [C(s) → C(g)] + 3B(H−H)

D$H^o{}_s$ = 716.7 kJ mol^{-1}

B(H−H) = 436 kJ mol^{-1}

$\sum H_1^\circ$ = ?

So $\sum H^{\circ}_{i}$ = 6 × 716.7 kJ mol^{-1} + 3 × 436 kJ mol^{-1} = 5608.2 kJ mol^{-1}

$\sum H^{\circ}_{i}$ = 6*B*(C–H) + 3(C−C) + 3(C=C)

B(C−H) = 412 kJ mol^{-1}
B(C−C) = 518 kJ mol^{-1}
B(C=C) = 518 kJ mol^{-1}

$\sum H^{\circ}_{i}$ = ?

Thus $\sum H^{\circ}_{i}$ = 6 × 412 kJ mol^{-1} + 3 × 518 kJ mol^{-1} + 3 × 518 kJ mol^{-1} = 5580 kJ mol^{-1}

Substituting we have

ΔH^{o}_{f} = 5608.2 kJ mol^{-1} − 5580 kJ mol^{-1}
= 28.2 kJ mol^{-1}

This is the heat of formation of 1 mol of gaseous benzene. Now, we are interested in the heat of formation of liquid benzene from its vapour, i.e.

$$C_6H_6(g) \rightarrow C_6H_6(l) \quad \Delta H^{o}_{\text{cond.}} = -30.8 \text{ kJ mol}^{-1}$$

Now we know that

$\Delta H^{o}_{\text{cond.}} = \Delta H^{o}_{\text{f}}[C_6H_6(l)] - \Delta H^{o}_{\text{f}}[C_6H_6(g)]$

So –30.8 kJ mol^{-1} = $\Delta H^{o}_{\text{f}}[C_6H_6(l)]$ – 28.2 kJ mol^{-1}

Thus $\Delta H^{o}_{\text{f}}[C_6H_6(l)]$ = −30.8 kJ mol^{-1} + 28.2 kJ mol^{-1}
= −2.6 kJ mol^{-1}

Practice Problems

1. Use the information given below to estimate the amount of heat required to dissociate dibromomethane, CH_2Br_2, into its gaseous atoms.

Bond	*B*/kJ mol^{-1}
C–H	435
C−Br	283

[*Answer:* 1456 kJ mol^{-1}]

2. Calculate the heat of formation of ammonia in its gaseous and liquid states. The heat of vaporisation of ammonia is 23.4 kJ mol^{-1}, while the average bond energy of the bond N−H is 388 kJ mol^{-1}. The dissociation energies of

hydrogen and nitrogen are 436 kJ mol^{-1} and 944 kJ mol^{-1} respectively.

[*Answer:* −76 kJ mol^{-1}, −99.4 kJ mol^{-1}]

3. It requires 164 kJ of heat to dissociate 1 mol of methane into its gaseous atoms. Estimate the energy of the C=C bond in ethane, CH_2CH_2, given that it requires 2347 kJ of heat to dissociate 1 mol of the compound.

[*Answer:* 699 kJ mol^{-1}]

4.7 DIPOLE MOMENT AND FORMAL CHARGE

The formation of a polar molecules arises from the uneven sharing of electrons by atoms of different electronegativities. The more electronegative atom tends to pull the shared pair of electrons towards itself, resulting in the formation of partial positive (δ+) and negative (δ−) charges. Such a molecule is said to be polar or possess a partial ionic charge, while the covalent bond is called polar bond. It exists in such molecules as water, hydrogen chloride, hydrogen fluoride, etc.

The size of a dipole is measured in terms of dipole moment μ, which is defined as the product of the magnitude of a dipole multiplied by the distance between the two partial charges, i.e.

$$\mu = Q \times d$$

where Q = Magnitude of the charge.

d = Separation of the charges or bond length.

The SI unit of dipole moment is coulomb metre (C m), but it is the usual practice to use the debye (D). The debye is named for Peter Debye (1884-1966), the Dutch scientist who won the 1936 Nobel Prize in chemistry for his work on dipole moments. The debye and the SI unit are related as follows:

$$1\ \text{D} = 3.336 \times 10^{-30}\ \text{Cm}$$

It should be noted that no compound possess a purely covalent character. In other words, covalent compounds possess some element of ionic bonding, and vice versa. Dipole moment is an important quantity with which the ionic character of a molecule can be determined. The reference value or standard is usually the dipole moment between a single positive and negative charge separated by a distance of 100 pm, which is numerically equal to 4.80 D. A compound with a dipole moment of 4.80 D is said to possess 100% ionic character. The ionic character of a molecule is calculated by expressing its actual dipole moment as a percentage of its dipole moment if it were purely ionic.

The formal charge FC of an atom in a molecule is the charge assigned to such an atom by assuming an equal sharing of the bonding electrons by the two atoms involved in the bonding. It is determined from the relation

$\text{FC} = V - L - \tfrac{1}{2}S$

where V = Number of valence electrons in the free or unbonded atom.

L = Number of lone-pair electrons, i.e., electrons not involved in bonding.

S = Number of shared electrons.

Example 1 The length of the bond H−Cl is 127 pm. Calculate the dipole moment of HCl if the hydrogen atom possesses a charge of 2.84×10^{-20}C. Hence determine the ironic character of the molecule.

Solution We have to apply the relation

$\mu = Q \times d$

$Q = 2.84 \times 10^{-20}\ \text{C}$

$d = 127 \times 10^{-12}\ \text{m}$

$\mu = ?$

Substituting we have

$$m = 2.84 \times 10^{-20}\ \text{C} \times 127 \times 10^{-12}\ \text{m} = 3.61 \times 10^{-30}\ \text{Cm}$$

Converting to debye we have

$$\mu = \frac{3.61 \times 10^{-30}\ \cancel{\text{C}}\,\cancel{\text{m}}}{3.336 \times 10^{-30}\ \cancel{\text{C}}\,\cancel{\text{m}}} \times 1\ \text{D}$$

$= 1.08\ \text{D}$

However, if the bond were purely ionic, then the dipole moment would be

$$\mu = \frac{127\ \cancel{\text{pm}}}{100\ \cancel{\text{pm}}} \times 4.84\ \text{D}$$

$= 6.15\ \text{D}$

Remember that the reference value is 4.84 D, when an electron and proton are separated by a distance of 100 pm.

Finally, we now have to express 1.08 D as a percentage of 6.20 D to obtain

$$\text{Ionic character} = \frac{1.08\ \cancel{\text{D}}}{6.15\ \cancel{\text{D}}} \times 100\%$$

$= 17.6\%$

We can see from this result that although HCl is predominantly a covalent compound, it is not purely covalent as it has an ionic character of 17.6%, or a covalent character of 82.4%.

Example 2 The length of the bond C–CI responsible for the polarity of chloromethane is 175 pm. Estimate the charge on the carbon atom if the dipole moment of the molecule is 1.87 D.

Solution We have to estimate the charge from the relation

$\mu = Q \times d$

$\mu = 1.87\ \text{D} = 6.24 \times 10^{-30}\ \text{Cm}$

$d = 175 \times 10^{-12}\ \text{m}$

$Q = ?$

Substituting we have

$6.24 \times 10^{-30}\ \text{C m} = Q \times 175 \times 10^{-12}\ \text{m}$

So $Q = \dfrac{6.24 \times 10^{-30}\ \text{C}\cancel{\text{m}}}{175 \times 10^{-12}\ \cancel{\text{m}}}$

$= 3.57 \times 10^{-20}\ \text{C}$

Example 3 An ionic compound possesses an ionic character of 95%. What is the dipole moment of the compound if it has a dipole moment of 3.52 D when treated as a purely ionic compound?

Solution The actual dipole moment of the compound is calculated as follows:

$95\% = \dfrac{\mu}{3.52\ \text{D}} \times 100\%$

Thus $\dfrac{\mu}{3.52\ \text{D}} = \dfrac{95}{100}$

Cross-multiplying we have

$100\text{m} = 334.4\ \text{D}$

$\mu = \dfrac{334.4\ \text{D}}{100}$

$= 3.34\ \text{D}$

Example 4 The electronegativities of hydrogen and fluorine are 2.1 and 4.0. Use this information to estimate the dipole moment of the hydrogen fluoride.

Solution The difference in the electronegativities of the two elements in a molecule is an estimation of its dipole moment, i.e.

$\mu = X_A - X_B$

where X_A = The electronegativity of the more electronegative element.

X_B = The electronegativity of the less electronegative element.

So $X_A = 4.0$

$X_B = 2.1$

$\mu = ?$

Substituting we have

$\mu = 4.0 - 2.1$

$= 1.9$ D

Example 5 Calculate the formal charge of each atom in a water molecule.

Solution We have to apply the relation

$$\text{FC} = V - L - \tfrac{1}{2}S$$

To know the value of each term, we have to draw the Lewis structure of water:

$$\text{H}-\underset{\cdot\cdot}{\text{O}}^{\cdot\cdot}-\text{H}$$

Since the two hydrogen atoms are equivalent, then the formal charge obtained for one equals that of the other. Hydrogen is a group one element. Thus

$$V = 1$$

Since the only valence electron in the hydrogen atom has been used for bonding, then

$$L = \text{O}$$

A single covalent bond exists between oxygen and hydrogen atoms, indicating that only two electrons are shared. Thus

$S = 2$

FC $= ?$

We now substitute to obtain

$F = 1 - 0 - \tfrac{1}{2} \times 2$

$= 0$

We now shift attention to oxygen. Oxygen, a Group 6 element, contains 6 electrons in its valence shell. Thus

$$V = 6$$

Two valence electrons are involved in bonding, one with each hydrogen atom. Thus

$$L = 4$$

Note that the octet rule has to be followed in counting the number of lone-pair electrons. The rule says that each atom is involved in bonding in such a way as to attain the stable octet electronic configuration of the noble gases. In other words, an atom takes part in bonding to make its valence electrons attain the stable value of 8. The number of lone-pair electrons is counted by subtracting the number of bonding electrons from 8. This value is usually indicated by dots on each element in the Lewis structure of molecules.

Oxygen shares two electrons with each hydrogen atom. Thus

$S = 4$

$\text{FC} = ?$

Substituting we have

$\text{FC} = 6 - 4 - ½ \times 4$

$= 0$

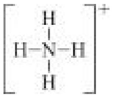
Thus the sum of the formal charges of all the three atoms in the molecule is zero. This is a general rule: the sum of the formal charges of all atoms in a neutral molecule is always zero. For an ion, the sum is usually equal to the charge on the ion, which is centred on the atom that possesses the equivalent formal charge. This is illustrated in the next example.

Example 6 Calculate the formal charge for each of the atoms in ammonium ion, NH_4^+.

Solution As usual, we have to apply the relation

$$\text{FC} = V - L - ½S$$

The Lewis structure of NH_4^+ is



Since the bonding in each hydrogen atom is identical, then for each hydrogen atom

V = 1

L = 0

S = 2

FC = ?

Substituting we have

FC = 1 – 0 – ½ × 2

= 0

For nitrogen (a Group 5 element), we have

V = 5

L = 0

S = 8

FC = ?

Substituting we have

FC = 5 – 0 – ½ × 8

= +1

The sum of the formal charges of the atoms is +1, i.e.

$$4 \times 0 + 1 = +1$$

Thus the ammonium ion possesses a single positive charge, centred on the central nitrogen atom.

Practice Problems

1. The atoms in a molecule are separated by a distance of 178 pm. What is the dipole moment if the magnitude of the charge is 2.81×10^{-20} C? Hence, determine the ionic character of the compound.

[*Answers:* 1.50 D, 17.4%]

2. The electronegativities of hydrogen and bromine are 2.1 and 2.8 respectively. Estimate the dipole moment of hydrogen bromide.

[*Answer:* 0.70 D]

3. Calculate the formal charge of each atom in the ammonia molecule.

[*Answers:* H = 0, N = 0]

SUMMARY

- An atom is the smallest particle of an element that can take part in chemical reaction. It consists of electron, neutron and proton.
- The atomic number Z of an element is the number of proton in the nucleus in of its atom.
- The mass number A of an element is the sum of the protons and neutrons in the nucleus of its atom.
- The Rutherford's model of the atom consists of a hollow sphere with a minute core called the nucleus, in which most of the mass of the atom is concentrated.
- Isotopy is a phenomenon in which atoms of the same element differ in mass number.
- Quantum mechanics describes light as consisting of photons or packets of energy having an amount energy of energy equivalent to

$$E = hv$$

- The Bohr's model of the atom consists of a hollow sphere with a positively charged core called the nucleus, in which most of the mass of the atom is concentrated. Electrons orbit the nucleus in fixed circular orbits. The energy of each orbit of the hydrogen atom is given by the relation

$$E_n = -h\frac{cR}{n^2}$$

- The spectrum of an atom is the series of lines formed by the radiations it emits. The wavelength of a line in the spectrum of hydrogen is calculated from the Rydberg's equation

$$\frac{1}{\lambda} = R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

- The decrease in energy accompanying the movement of an electron from a higher to a lower orbit is given by the energy of emitted light, i.e.

$$\Delta E = hv$$

For the hydrogen atom:

$$\Delta E = hcR\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

- The wave-mechanics model of the atom does not restrict the electron to a fixed orbit, but describes a region or orbital around the nucleus in which there is a high probability of locating an electron.
- The wave-particle duality of matter postulates that matter behaves like a wave as well as a particle. The wavelength of matter is related to its momentum by the de Broglie's relation

$$\lambda = \frac{h}{m \times c}$$

- The uncertainly principle states that the more the certainty in which the momentum of a particle is known, the less the certainty with which its position can be determined, and vice versa. This is given numerically as

$$\Delta x \times m \times \Delta c = \frac{h}{4\pi} = \Delta x \times \Delta p = \frac{h}{4\pi}$$

- The ionization energy *I* of an atom is the minimum energy required to remove an electron from the ground state of its gaseous atom.
- Ionic bond is a type of bond arising from the electrostatic forces of attraction between cations and anions.
- The electron affinity of an element is the minimum energy required to add an electron to its gaseous atom.
- Lattice energy is the minimum energy required to dissociate a solid into a gas of its ions.
- The heat of atomisation is the energy required to dissociate a substance into its gaseous atoms.
- A covalent bond is formed when two atoms share valence electrons.
- Bond energy is the minimum energy required to dissociate the bond between two covalently bonded atoms in 1 mol of a molecule.
- Bond energies are used for estimating the heat of reaction using the relation

$$\Delta H^o_r = \sum H^\circ_r - \sum H^\circ_p$$

- Dipole moment m is the product of the magnitude of the charge in a molecule multiplied by the distance between the two equal and opposite charges, i.e.

$$\lambda = Q \times d$$

- The difference in the electronegativities of the two elements in a molecule is an estimation of its dipole moment, i.e.

$$\lambda = X_A - X_B$$

- The formal charge of an atom in a molecule is the charge assigned to such an atom by assuming that the bonding electrons atre equally shared between the two atoms involved in the bonding. It is given by the relation

$$FC = V - L - \tfrac{1}{2}S$$

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. Which of the following is **NOT** true of an atom?
   A. It consists of neutron, proton and electron.
   B. It is electrically neutral.
   C. It contains as many electrons as protons.
   D. Its number of electrons equals its atomic mass.
   E. It retains the chemical identity of an element.
2. Which of the following occurs when an atom loses electron?
   A. It becomes positively charged.
   B. It becomes negatively charged.
   C. It remains electrically neutral.
   D. It is repelled by a cathode.
   E. It is attracted by an anode.
3. Which of the following is associated with a radiation of very short wavelength?
   A. Low frequency. B. Low colour intensity.
   C. High energy. D. Low energy.
   E. None of the above.
4. The spectral lines of sodium are produced by
   A. The transition of atoms from a higher to a lower energy level.
   B. The agitation of the molecules.
   C. The melting of the sodium.
   D. The increase in the velocity of the atoms.
   E. All of the above.
5. According to the wave-mechanics model of the atom, a region around the nucleus where there is a high possibility of locating an electron is called

A. an orbit B. a path
C. an orbital D. a trajectory
E. a photon

6. What is the wavelength associated with a particle of mass 6.27×10^{-32} kg travelling with a velocity of 1000 cm s^{-1}?

A. 1.11×10^{-5} m B. 1.16×10^{-5} m
C. 1.05×10^{-3} m D. 1.06×10^{-3} m
E. 1.10×10^{-2} m

($h = 6.63 \times 10^{-34}$ J Hz^{-1})

7. Which of the following models of the atom does not incorporate a nucleus?

A. Bohr’s. B. Rutherford’s.
C. Wave-mechanics. D. Thomson’s.
E. None of the above.

8. What is the momentum of a particle if its wavelength is 0.050 m?

A. 1.5×10^{-35} kg m s^{-1} B. 5.7×10^{-33} kg m s^{-1}
C. 1.3×10^{-32} kg m s^{-1} D. 1.3×10^{-32} kg m s^{-1}
E. 0.80×10^{-12} kg m s^{-1}

9. Isotopes of the same element are characterized by

A. equal number of electrons. B. equal mass numbers.
C. equal number of neutrons. D. different atomic numbers.
E. different number of electrons.

10. Which of the following scientists did not contribute to our knowledge of the atom?

A. Chadwick B. Rutherford
C. Millikan D. Boyle
E. Dalton

11. Calculate the energy of an electromagnetic radiation of wavelength 468 nm.

A. 3.10×10^{-19} J B. 4.01×10^{-19} J
C. 4.05×10^{-19} J D. 4.24×10^{-19} J
E. 4.25×10^{-19} J

($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $c = 3.00 \times 10^{-8}$ m s^{-1})

12. Which phenomenon is illustrated by the substances given below?

A. Allotropy B. Ionization
C. Dissociation D. Duplication
E. Isotopy

13. If the momentum of a particle is known precisely, then according to the uncertainty principle its position would be
A. known with certainty.
B. known to a high uncertainty.
C. totally unknown.
D. known to a low uncertainty.
E. decreased.

14. Which of the following is true about ionic compounds?
i. The energy invested in all the steps is much more than recovered when the gaseous ions crystalline to form the solid.
ii. Ionic compounds have an ionic character of 100%.
iii. Ionic compounds consist of oppositely charged ions held together by ionic bonds.
iv. Ionic compounds can be formed between two electronegative elements.
A. i and ii B. ii and iv
C. i and iii D. i and iv
E. ii and iv

15. Which of the following is not an ionic compound?
A. NH_3 B. NaCl
C. CsF D. $CaCl_2$
E. CuCl

16. The minimum energy required to remove two electrons from the valence shell of gaseous atom is its
A. ionization energy.
B. second ionization energy.
C. sum of the first and second ionizations energies.
D. electron affinity.
E. heat of crystallization.

17. The sum of the enthalpy changes for the formation of gaseous ions of magnesium and oxygen from the standard elements is 3214.9 kJ. What is the heat of formation of magnesium oxide if the lattice enthalpy of the compound is 3850.0 kJ mol^{-1}?

A. −3250 kJ mol^{-1} B. –3214.9 kJ mol^{-1}

C. –635.1 kJ mol^{-1} D. −635.8 kJ mol^{-1}

E. 3214.9 kJ mol^{-1}

18. The total energy required for the formation of 1 mol of Ca^+ from 1 mol of its element in its standard state is 768.2 kJ mol^{-1}. What is the heat of sublimation of calcium if its first ionization energy is 590 kJ mol^{-1}?

A. 178.2 kJ mol^{-1} B. 500.5 kJ mol^{-1}

C. 600 kJ mol^{-1} D. 780.2 kJ mol^{-1}

E. 820.5 kJ mol^{-1}

19. The line in the bond C–N indicates that

A. an electron is shared between the two atoms.

B. an electron is equally shared between the two atoms.

C. two electrons are shared between the two atoms.

D. two electrons are equally shared between the two electrons.

E. none of the above.

20. Which of the following is **NOT** a covalent compound?

A. PCl_5 B. HCl

C. CF_4 D. MgO

E. C_6H_6

21. Which of the following best favours the formation of a covalent bond?

A. Large difference in atomic radii.

B. Close electropositivities.

C. Close molecular diameter.

D. Octet structure.

E. Close electronegativities.

22. It required 2858 kJ of heat to dissociate 1 mol of ethane, C_2H_6. What is the average energy associated with the bond C−H if the average energy of the bond C−C is 368 kJ mol^{-1}?

A. 250 kJ mol^{-1} B. 412 kJ mol^{-1}

C. 415 kJ mol^{-1} D. 500 kJ mol^{-1}

E. 2490 kJ mol^{-1}

23. Which of the following favours the formation of a dipole between two atoms?

A. Very close electronegativities

B. Difference in electronegativities

C. Very close electropositivities

D. Difference of atomic radii

E. Close atomic radii

24. A student reported the result of his calculation of the dipole moment of a molecule as 8.61×10^{-30} C m. What is his result in debye?

A. 1.12 D B. 2.15 D

C. 2.58 D D. 2.84 D

E. 3.25 D

25. What is the dipole moment of a molecule with two equal and opposite charges of magnitude 6.50×10^{-20} C separated by a distance of 180 pm?

A. 1.21 D B. 2.51 D

C. 3.21 D D. 3.40 D

E. 3.51 D

26. The sum of the formal charges of nitrogen and oxygen in NO^- is

A. −2 B. −1

C. 0 D. +1

E. +2

ESSAY TYPE QUESTIONS

Atomic theory

27. State Dalton's atomic theory.

28. Describe the following models of the atom:

(i) Thomson's (ii) Rutherford's (iii) Bohr's (iv) Wave-mechanics

29. Briefly describe the experiment that led to the discovery of the atomic nucleus.

30. State the three main fundamental sub-particles of the atom and give their properties.

31. (a) What is isotopy?

(b) The isotopes of uranium are U-235 and U-238 with a relative abundance of 0.72% and 99.28% respectively. Calculate the relative atomic mass of the element.

32. What is an atomic spectrum? Explain how it is formed.

33. Calculate the wavelength and energy of a radiation having the frequency of 5.2×10^{14} Hz.

($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $c = 3.00 \times 10^{8}$ m s^{-1})

34. Calculate the frequency and energy of the light emitted when an electron falls from the fourth to the second orbit of the hydrogen atom.

($R = 1.097 \times 10^{7}$ m, $h = 6.63 \times 10^{-34}$ J Hz^{-1}, $c = 3.00 \times 10^{8}$ m s^{-1})

35. An electron in a hydrogen atom jumps to the third orbit, emitting a radiation of 1.6×10^{14} Hz. What is the original orbit of the electron?

($R = 1.097 \times 10^{7}$ m, $c = 3.00 \times 10^{8}$ m s^{-1})

36. Calculate the energy of an electron in the fourth energy level of the hydrogen atom.

($R = 1.097 \times 10^{7}$ Hz, $c = 3.00 \times 10^{8}$ m s^{-1})

Wave-particle duality of matter

37. (a) Explain the wave-particle duality of matter.

(b) A particle of mass 10.0 g moves with a speed of 20 cm s^{-1}. What is the frequency of the particle?

(c) Calculate the wavelength associated with a particle of mass 3.2×10^{-11} kg moving with a velocity of 100 cm hr^{-1}.

($h = 6.63 \times 10^{-34}$ J Hz^{-1})

Uncertainty principle

38. (a) State the uncertainty principle.

(b) Calculate the uncertainty in the position of a particle of mass 0.10 g if its speed is known to within 10.0 cm s^{-1}.

(c) Calculate the minimum uncertainty in the velocity of a body of mass 2.5 tonnes if its location is known to within 10 cm.

($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $\pi = 3.142$)

Ionization energy

39. (a) What is ionization energy?

(b) The longest-frequency light emitted by lead atom has a frequency of 1.79×10^{15} Hz. Calculate the ionization energy of the metal.

($h = 6.63 \times 10^{-34}$ J Hz^{-1}, $c = 3.00 \times 10^{8}$ m s^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1})

40. Calculate the ionization energy of tin if the wavelength of the shortest-wavelength light emitted by its atom is 169 nm.

(h = 6.63 × 10^{-34} J Hz^{-1}, c = 3.00 × 10^{8} m s^{-1}, N_A = 6.02 × 10^{23} mol^{-1})

41. The ionization energy of fluorine is 1680 kJ mol^{-1}. What is the wavelength of the shortest-wavelength light emitted by a fluorine atom?

(h = 6.63 × 10^{-34} J Hz^{-1}, c = 3.00 × 10^{8} m s^{-1}, N_A = 6.02 × 10^{23} mol^{-1})

Ionic bond and lattice energy

42. (a) What is an ionic compound?

(b) List five examples of ionic compounds.

43. Briefly explain the following:

(a) Lattice energy (b) Heat of atomisation (c) Electron affinity

44. Calculate the lattice energy of sodium iodide from the information given below:

Heat of sublimation of sodium, 108 kJ mol^{-1}
Ionization energy of sodium, 494 kJ mol^{-1}
Heat of formation of sodium iodide, −288 kJ mol^{-1}
Heat of dissociation of iodine, 151 kJ mol^{-1}
Electron-gain enthalpy of iodine, −295 kJ mol^{-1}
Heat of sublimation of iodine, 62.44 kJ mol^{-1}

45. Calculate the lattice energy of lithium bromide from the information given below:

Heat of formation of lithium bromide, −352.7 kJ mol^{-1}
Heat of atomisation of lithium, 159.3 kJ mol^{-1}
Electron affinity of bromine, −325 kJ mol^{-1}
Ionization energy of lithium, 519 kJ mol^{-1}
Heat of vaporisation of bromine, 30.91 kJ mol^{-1}
Heat of dissociation of bromine, 193 kJ mol^{-1}

46. Calculate the heat required to sublime 332.3 g of caesium, given the following information:

Heat of formation of caesium chloride, −443 kJ mol^{-1}
Dissociation energy of chlorine, 244 kJ mol^{-1}
Electron-gain enthalpy of chlorine, −349 kJ mol^{-1}
Lattice enthalpy of caesium chloride, 668.6 kJ mol^{-1}
Ionization energy of caesium, 376 kJ mol^{-1}

(Cs = 132.91)

47. Calculate the heat of atomisation of aluminium from the data given below:

Heat of formation of aluminium chloride, −704.1 kJ mol^{-1}

First ionization energy of aluminium, 577 kJ mol^{-1}

Second ionization energy of aluminium, 1820 kJ mol^{-1}

Third ionization energy of aluminium, 2740 kJ mol^{-1}

Electron affinity of chlorine, −349 kJ mol^{-1}

Heat of formation of Cl(*g*), 122 kJ mol^{-1}

Heat of crystallization of AI^{3+}(*g*) and $3CI^{-}$(*g*), −5490 kJ mol^{-1}

48. Calculate the second ionization energy of magnesium from the data given below:

Heat of formation of magnesium oxide, −601.7 kJ mol^{-1}

Lattice enthalpy of magnesium oxide, 3850 kJ mol^{-1}

Heat of dissociation of oxygen, 498.4 kJ mol^{-1}

Heat of formation of O^{-}(*g*), −142 kJ mol^{-1}

Heat of formation of O^{2-} (*g*), 844 kJ mol^{-1}

Heat of atomization of magnesium, 111.1 kJ mol^{-1}

First ionization energy of magnesium, 736 kJ mol^{-1}

49. Calculate the electron affinity of fluorine from the information given below:

Heat of formation of potassium fluoride, −567.3 kJ mol^{-1}

Heat of sublimation of potassium, 89 kJ mol^{-1}

Ionization energy of potassium, 418 kJ mol^{-1}

Heat of dissociation of fluorine, 79.7 kJ mol^{-1}

Lattice enthalpy of potassium fluoride, 826 kJ mol^{-1}

50. From the information given below, assess the minimum heat required to vaporise 799.1 g of bromine completely.

Heat of formation of silver bromide, −100.4 kJ mol^{-1}

Heat of sublimation of silver, 284.9 kJ mol^{-1}

Heat of crystallization of Ag^{+}(*g*) and Br^{-}(*g*), −903 kJ mol^{-1}

Electron affinity of bromine, −325 kJ mol^{-1}

Ionization energy of silver, 731 kJ mol^{-1}

The heat of the reaction Br(*g*) → ½Br_2(*g*) is −96.54 kJ.

(Br = 79.91)

Covalent bond and heat of reaction

51. Briefly explain the following:
    - (a) Covalent bond and compounds.
    - (b) Bond dissociation energy.
    - (c) Single, double and triple covalent bonds.

52. From the values of average bond energies given below, calculate the heat required to dissociate each of the following substances into their ions.

    (a) CO_2 (b) CH_3OH (c) C_2H_4 (d) H_2O (d) N_2O

Bond	*B*/kJ mol^{-1}
C=O	743
C–H	412
C–O	360
O–H	463
N=O	600
C=C	612
N−N	409

53. Calculate the heat of formation of each of the following compounds:

    (a) Methane, CH_4 (b) Hydrazine, N_2H_4

    The heats of dissociation of nitrogen and sublimation of carbon are 944 kJ mol^{-1} and 716.7 kJ mol^{-1} respectively.

    [*B*(C–H) = 412 kJ mol^{-1}, *B*(N–H) = 388 kJ mol^{-1}, *B*(N–N) = 163 kJ mol^{-1}, *B*(H–H) = 436 kJ mol^{-1}]

54. Calculate heat of formation of liquid ammonia if its heat of vaporisation is 23.4 kJ mol^{-1}. The average strength of the bond N–H is 388 kJ mol^{-1}. The enthalpy of atomization of hydrogen and nitrogen are 436 kJ mol^{-1} and 944 kJ mol^{-1} respectively.

55. What quantity of enthalpy change is expected to accompany the formation of 45.0 g of water, given that the heat of dissociation of oxygen and hydrogen are 496 kJ mol^{-1} and 436 kJ mol^{-1} respectively. The heat of vaporisation of water is 44 kJ mol^{-1}.

    [H = 1, O = 16, *B*(O–H) = 463 kJ mol^{-1}]

56. Use the average bond energies and reactions given below to estimate the heat of formation of ethanol, given that the heats of sublimation of carbon and vaporisation of ethanol are 717 kJ mol^{-1} and 43.5 kJ mol^{-1} respectively.

$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$

$2C(g) + 2H_2(g) \rightarrow C_2H_4(g)$

$H_2(g) + ½O_2(g) \rightarrow H_2O(g)$

B(C–H) = 412 kJ mol^{-1}, B(C=C) = 612 kJ mol^{-1}

B(O–H) = 463 kJ mol^{-1}, B(C−C) = 348 kJ mol^{-1}

B(H–H) = 436 kJ mol^{-1}, B(O=O) = 496 kJ mol^{-1}

B(C−O) = 360 kJ mol^{-1}

57. Estimate the heat of combustion of ethene, C_2H_4, from the average values of bond energy given below:

[B(C=C) = 612 kJ mol^{-1}, B(C–H) 412 kJ mol^{-1}, B(O=O) = 496 kJ mol^{-1}, B(C=O) = 743 kJ mol^{-1}, B(O–H) = 463 kJ mol^{-1}]

58. The average energies of the bonds C=O, C−C and C=C are 743 kJ mol^{-1}, 518 kJ mol^{-1}and 518 kJ mol^{-1}. Use this information and the data given above to estimate the heat of combustion of benzene vapour.

59. Estimate the heat of dissociation of bromine if 95 kJ of heat is released in the reaction $Br_2 + C_2H_4 \rightarrow C_2H_4Br_2$.

[B(C=C) = 612 kJ mol^{-1}, B(C−C) = 348 kJ mol^{-1}, B(C–H) = 412 kJ mol^{-1}, B(C–Br) = 276 kJ mol^{-1}]

The heat of sublimation of carbon is 717 kJ mol^{-1}, and the average strength of the bond Br–C is 293 kJ mol^{-1}.

60. It requires 1788 kJ of heat to dissociate 1 mol of chloromethane. Calculate the heat of atomisation of chlorobenzene, given that the average values of the bonds C=C, C–C and C–H are 612 kJ mol^{-1}, 348 kJ mol^{-1} and 412 kJ mol^{-1} respectively.

61. The two processes involved in the industrial manufacture of hydrogen are:

$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$ DH^o = 206.1 kJ

$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ DH^o = −41.2 kJ

Use the information to estimate the strength of the bond C–H, given that B(C=O) = 743 kJ mol^{-1}, B(H–H) = 436 kJ mol^{-1} and B(O–H) = 463 kJ mol^{-1}.

Dipole moment and formal charge

62. Briefly explain the following:

(i) Electric dipole (ii) Dipole moment (iii) Formal charge

63. The dipole moment of water is measured to be 1.85 D. Given that the

length of the O−H bond is 95.7 pm, and that the angle between the O−H bonds is 104.5°, calculate the magnitude of the partial positive charge on the hydrogen atom.

(Hint: The dipole moment of water is the vector sum of the dipole moments of the two O−H bonds; which is given by m = 2mcos½q)

64. Two equal and opposite charges are estimated to be separated by a distance of 1.51 Å. Calculate the dipole moment and ionic character of the molecule. The magnitude of the positive charge is 1.8×10^{-20} C.

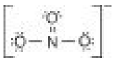
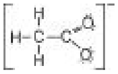
65. The dipole moment of a molecule is estimated to be 1.58 D. What is the distance between the atoms if the magnitude of the positive charge is 3.56×10^{-20} C?

66. A compound has an ionic character of 20.5%. What is its actual dipole moment if its dipole moment when considered a pure ionic compound is 21.56 D?

67. The dipole moment of a molecule is 1.78 D. What is the magnitude of the positive charge if the two atoms are separated by a distance of 1.75 Å?

68. Calculate the formal charge of each atom, and the sum of the formal charges of the atoms in the following molecules:

(a) NH_3 (b)  (c) CH_3OH (d) C_2H_4

(d)  (e) CH_3COOH (f) 

(g) PCl_3 (h) BF_3 (i) BrO^+

Answers

1. D 2. A 3. C 4. A 5. C 6. E

7. A 8. E 9. A 10. D 11. B 12. A

13. C 14. C 15. A 16. C 17. A 18. C

19. E 20. D 21. E 22. C 23. A 24. C

25. E 26. B 31. (b) 238

33. Wavelength: 580 nm; energy: 3.4×10^{-19} J

34. 6.17×10^{14} J Hz, 4.09×10^{-19} J

35. 4 36. -1.36×10^{-19} J

37. (b) 9.0×10^{38} Hz (c) 7.0×10^{-20} m

38. (b) $\geq 5.3 \times 10^{-30}$ m (c) 2.0×10^{-37} ms^{-1}

39. (b) 714 kJ 40. 708 kJ 41. 7.13×10^{-5} m

44. 702 kJ mol^{-1} 45. 818 kJ mol^{-1} 46. 192 kJ

47. 330 kJ mol^{-1} 48. 1450 kJ mol^{-1} 49. 328 kJ mol^{-1}

50. 303 kJ

52. (a) 1486 kJ mol^{-1} (b) 2059 kJ mol^{-1} (c) 2260 kJ mol^{-1}
(d) 926 kJ mol^{-1} (e) 1009 kJ mol^{-1}

53. (a) −59.3 kJ mol^{-1} (b) 101 kJ mol^{-1}

54. −61.4 kJ mol^{-1} 55. −715 kJ 56. −285 kJ mol^{-1}

57. −1076 kJ mol^{-1} 58. −2394 kJ mol^{-1} 59. 193 kJ mol^{-1}

60. 5492 kJ mol^{-1} 61. 386 kJ mol^{-1} 63. 5.26×10^{-20} C, 39.5%

64. 0.815 D, 11.2% 65. 1.48 Ǻ 66. 4.31 D

67. 3.39×10^{-20} C

68. (a) N: 0, H: 0

(b) S: +1, singly bonded O atom: −1, doubly bonded O atoms: 0

(c) C: 0, H: 0, O: 0

(d) H: 0, C: 0 (e) N: +1, singly bonded O atoms: −1, doubly bonded O atom: 0

(e) H: 0, C: 0, O: 0

(f) H: 0, C: 0, singly bonded O atom: −1, doubly bonded O atom: 0

(g) P: 0, Cl: 0 (h) F: 0, B: 0

(i) Br: +1, O: 0

5

Chapter

The Gaseous State

A gas is a substance that fills the volume of a vessel in which it is confined. In molecular terms, a gas can be defined as a substance whose molecules are widely separated from each other due to extremely low cohesive forces.

5.1 GAS PRESSURE

Gas pressure P is the force exerted by the molecules of a gas per unit area of the vessel in which it is confined, i.e.

$$P = \frac{\text{force}}{\text{area}}$$

The SI unit of pressure is N m^{-2} or Pa (pascal). Other units are the atmosphere (atm), millimetre of mercury (mm Hg) and Torr. These units are related as follows:

$$1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ Torr} = 101325 \text{ N m}^{-2} \text{(Pa)}$$

Example 1 Convert 200 mmHg to pascal.

Solution Let the value of 200 mmHg be x in Pa. Using this and the relationship given above, we have

$760 \text{ mmHg} = 101325 \text{ Pa}$

$200 \text{ mmHg} = x$

Thus $760 \text{ mmHg} \times x = 200 \text{ mmHg} \times 101325 \text{ Pa}$

$$\therefore\ x = \frac{200\ \cancel{\text{mmHg}} \times 101325 \text{ Pa}}{760\ \cancel{\text{mmHg}}}$$

= 30000 Pa (N m^{-2})

Example 2 Convert 0.30 atm to mmHg.

Solution Let 0.30 atm be *x* in mmHg. Then

1 atm = 760 mmHg

0.30 atm = x

Thus 1 atm × x = 760 mmHg × 0.30 atm

$$\therefore\ x = \frac{760\ \text{mmHg} \times 0.30\ \cancel{\text{atm}}}{1\ \cancel{\text{atm}}}$$

= 230 mmHg

Practice Problems

1. Convert 2005 Pa to atm. [*Answer:* 0.02 atm]
2. Convert 2.5 atm to mmHg. [*Answer:* 1900 mmHg]
3. Convert 12108.5 Pa to mmHg. [Answer: 90.8 mmHg]

5.1.1 Dalton's Law of Partial Pressures

Dalton's law of partial pressures states that the total pressure exerted by a mixture of gases that do not react chemically together is the sum of the partial pressures of its constituent gases. The pressure of each of the gases is called partial pressure. If we have a mixture of *n* gases, then the total pressure of the mixture will be

$$P_t = P_1 + P_2 + \dots + P_n$$

where P_1, P_2, etc. are the partial pressures of the constituent gases.

The saturated vapour pressure of water has to be taken into consideration when measuring the pressure of a gas collected over water. The actual pressure of the gas is the total pressure exerted by the gas minus the saturated vapour pressure of water at the prevailing temperature, i.e.

$$P_t = P + P_{sv}$$

Example 1 A mixture of gases containing nitrogen, carbon dioxide, water vapour, oxygen and neon stored over water has a pressure of 900 mmHg at 10°C. Calculate the pressure exerted by oxygen if the actual pressures exerted by nitrogen, carbon dioxide and neon are 330 mmHg, 250 mmHg and 150 mmHg respectively.

(SVP of water at 10°C = 9.2 mmHg)

Solution

$$P_t = P_1 + P_2 + P_3 + P_4 + P_5$$

The mixture is stored over water at 10°C, then the partial pressure of water vapour is the saturated vapour pressure of water at this temperature. Thus

P_t = 900 mmHg

P_1 = 9.2 mmHg

P_2 = 250 mmHg

P_3 = 300 mmHg

P_4 =150 mmHg

P_5 = ?

Substituting we have

900 mmHg = 9.2 mmHg + P_5 + 150 mmHg + 250 mmHg + 300 mmHg

900 mmHg = 709.2 mmHg + P_5

$\therefore$ P_5 = 900 mmHg – 709.2 mmHg

= 190.8 mmHg

Example 2 Hydrogen peroxide was decomposed in the presence of manganese (IV) oxide during the laboratory preparation of oxygen. The resulting gas was collected over water at a temperature and pressure of 15°C and 720 mmHg respectively. What is the actual pressure of oxygen?

(SVP of water at 15°C = 12.7 mmHg)

Solution There are two gases: oxygen and water vapour. Thus we have to apply the relation

$$P_t = P + P_{SV}$$

The total pressure of oxygen and that of the saturated vapour of water at 15°C is 720 mmHg.
Thus

P_t = 720 mmHg

$P_{S.V.}$ = 12.7 mmHg

P = ?

Substituting the data above, we have

$720\ \text{mmHg} = P + 12.7\ \text{mmHg}$

Thus $P = 720\ \text{mmHg} - 12.7\ \text{mmHg}$

$= 707.3\ \text{mmHg}$

Practice Problem

A mixture of hydrocarbons containing methane, butane and ethane has a pressure of 1000 mmHg. The pressure exerted by ethane is twice that of methane. Calculate the partial pressure of butane in atm if the pressure exerted by methane is 0.21 atm. [*Answer*: 0.69 atm]

5.1.2 Barometric Formula

The atmosphere exerts pressure on everything on Earth. This pressure is called atmospheric pressure. The atmospheric pressure at the sea level is 1 atm (or 1.10325 kPa). Atmospheric pressure decreases with altitude. This is given by the barometric formula

$$\ln\left(\frac{P_h}{P_0}\right) = -\frac{Mgh}{RT}$$

where P_h = Pressure at above sea level.

P_0 = Pressure at sea level = 1 atm.

h = Height above sea level.

g = Acceleration due to gravity.

M = Molar mass of air = 29 g mol^{-1}.

R = Universal gas constant.

T = Absolute temperature.

Example 1 Prove the barometric formula.

Solution We know that gas pressure is the force exerted by the gas per unit area, i.e.

$$P = \frac{F}{A} \quad (5.1)$$

The force (or weight) exerted by the air of mass *m* is given by

$$F = mg \quad (5.2)$$

Since volume is area times length, then the area of a gas of length h is given as

$$A = \frac{V}{h} \quad (5.3)$$

Substituting Equations (5.2) and (5.3) into (5.1) yields

$$P = \frac{mgh}{V} \quad (5.4)$$

Now, we know that the density of any substance is defined as

$$\rho = \frac{m}{V} \quad (5.5)$$

Substituting Equation (5.5) into (5.4) yields

$$P = \mathrm{r}gh$$

We can write this equation in the differential form as

$$\mathrm{d}P = -\rho g \mathrm{d}h \quad (5.6)$$

The negative sign indicates that pressure decreases with altitude. Now the density of a gas is given by

$$\mathrm{r} = \frac{PM}{RT}$$

Substituting this into Equation (5.6) yields

$$\mathrm{d}P = -\frac{PMg}{RT}\mathrm{d}h \quad (5.7)$$

We now rearrange Equation (5.7) by dividing throughout by P to obtain

$$\frac{\mathrm{d}P}{P} = -\frac{Mg}{RT}\mathrm{d}h \quad (5.8)$$

We can now integrate Equation (5.8) within the limits $P = P_0$, $P = P_h$ and $h = 0$, $h = h$, i.e

$$\int_{P_0}^{P_h}\frac{\mathrm{d}P}{P} = \int_0^h \frac{Mg}{RT}\mathrm{d}h$$

Since M, g, R and T are constants, then we can bring out the term Mg/RT out of the integral to obtain

$$\int_{P_0}^{P_h} \frac{\mathrm{d}P}{P} = -\frac{Mg}{RT}\int_0^h \mathrm{d}h$$

Thus $|\ln P|_{P_0}^{P_h} = -\frac{Mg}{RT}|h|_0^h$

So $\ln\left(\frac{P_h}{P_0}\right) = -\frac{Mgh}{RT}$

or $\ln\left(\frac{P_h}{P_0}\right) = \frac{Mgh}{RT}$

Example 2 What is the atmospheric pressure at 15°C on a mountain that stands 2500 m above the sea level, given that the pressure on the ground level is 1 atm, and that other conditions are negligible?

($g = 9.8$ m s^{-2}, $M = 29$ g mol^{-1}, $R = 8.314$ J K^{-1} mol^{-1})

Solution The key to solving this problem is the barometric formula

$$\ln\left(\frac{P_h}{P_0}\right) = -\frac{Mgh}{RT}$$

$P_0 = 1$ atm
$M = 29$ g mol^{-1} = 0.029 kg mol^{-1}
$g = 9.8$ m s^{-2}
$h = 2500$ m
$R = 8.314$ J K^{-1} mol^{-1} = 8.314 kg m^2 s^{-2} K^{-1} mol^{-1})
$T = 273$ K + 15°C = 288 K
$P_h = ?$

Substituting we have

$$\ln\left(\frac{P_h}{1\ \text{atm}}\right) = -\frac{0.029\ \cancel{\text{kg}}\ \cancel{\text{mol}^{-1}} \times 9.8\ \cancel{\text{m}}\ \cancel{\text{s}^{-2}} \times 2500\ \cancel{\text{m}} \times 1\cancel{\text{K}}}{8.314\ \cancel{\text{kg}}\ \cancel{\text{m}^2}\ \cancel{\text{s}^{-2}}\ \cancel{\text{mol}^{-1}} \times 288\ \cancel{\text{K}}}$$

Thus $\ln\left(\frac{P_h}{1\ \text{atm}}\right) = -0.30$

Taking the natural antilogarithms of both sides yields

$$\frac{P_h}{1\ \text{atm}} = e^{-0.30} = 0.74$$

Cross-multiplying we have

So P_h = 1 atm × 0.74

= 0.74 atm

Example 3 At what height would the atmospheric pressure at 25°C be half the value at the sea level, given that the atmospheric pressure on the earth's surface is 1 atm, and that the effects of other factors are negligible?

(g = 9.8 m s^{-2}, M = 29 g mol^{-1}, R = 8.314 J K^{-1} mol^{-1})

Solution We have to apply the relation

$$\ln\left(\frac{P_h}{P_0}\right) = -\frac{Mgh}{RT}$$

P_h = 1 atm/2 = 0.5 atm

P_0 = 1 atm

M = 29 g mol^{-1} = 0.029 kg mol^{-1}

R = 8.314 J K^{-1} mol^{-1} = 8.314 kg m^2 s^{-2} K^{-1} mol^{-1})

T = 273 K + 15°C = 288 K

g = 9.8 m s^{-2}

h = ?

We now substitute to obtain

$$\ln\left(\frac{0.5\ \cancel{\text{atm}}}{1\ \cancel{\text{atm}}}\right) = -\frac{0.029\ \cancel{\text{kg}}\ \cancel{\text{mol}^{-1}} \times 9.8\ \cancel{\text{m s}^{-2}} \times h \times \cancel{1}\cancel{\text{K}}}{8.314\ \cancel{\text{kg}}\ \text{m}^2\ s^{-2}\ \cancel{\text{mol}^{-1}} \times 298\ \cancel{\text{K}}}$$

So $-0.69 = \frac{0.28\ \text{m} \times h}{2477.6\ \text{m}^2}$

Cross-multiplying yields

0.28 m × h = –1709.5 m^2

Thus $h = \frac{1709.5\ \text{m}^2}{2477.6\ \text{m}^2}$

= 6100 m

Practice Problems

1. Calculate the atmospheric pressure on a hill that stands 1500 m above sea level, given that the atmospheric pressure at the sea level is 1 atm, and that the effects of other conditions are negligible.

   (g = 9.8 m s^{-2}, M = 29 g mol^{-1}, R = 8.314 J K^{-1} mol^{-1}) [*Answer:* 0.83 atm]

2. The atmospheric pressure at a town was measured to be 0.70 atm at 25°C. What is its altitude above the sea if the effects of other factors are negligible?

   (g = 9.8 m s^{-2}, M = 29 g mol^{-1}, R = 8.314 J K^{-1} mol^{-1}) [*Answer:* 2900 m]

5.2 GAS LAWS

Gas laws are principles governing the behaviours of gases under different conditions. These include:

Boyle's law: Boyle's law describes the relationship between the volume and pressure of an ideal or perfect gas at constant temperature. It states that at constant temperature, the volume of given mass of a gas is inversely proportional to its pressure, and vice versa, provided the temperature remains constant.

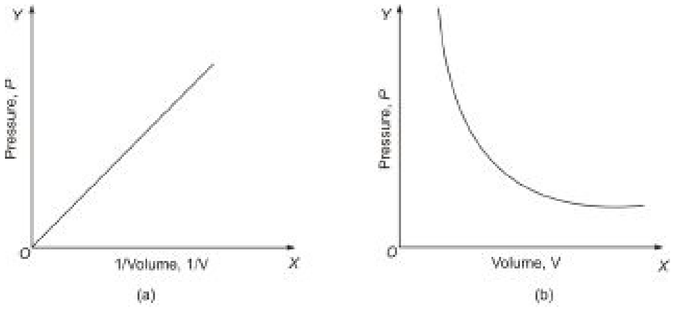


Figure 5.1 Graphs of Boyle's law.

Boyle's law is an example of inverse variation, a type of relationship between two quantities in which one decreases as the other increases, and vice versa. Boyle's law is expressed mathematically as

$$V \mu \frac{1}{P}$$

Introducing the constant of proportionality, we obtain

$$V = \frac{k}{P}$$

Thus PV = constant or $P_1V_1 = P_2V_2$, etc.

The subscripts 1 and 2 denote the initial and final properties of the gas.

Figure 5.2 Robert Boyle, Irish chemist and physicist (1627–1691).

Example 1 300 cm^3 of a gas has a pressure of 725 mmHg. Calculate the new volume of the gas if its pressure is reduced to 600 mmHg at constant temperature.

Solution This is an isothermal compression, i.e., reduction in volume. Thus we have to apply Boyle's law, i.e.

$$P_1V_1 = P_2V_2$$

$$\therefore\ V_2 = \frac{P_1V_1}{P_2}$$

P_1 = 725 mmHg

V_1 = 300 cm^3

P_2 = 600 mmHg

V_2 = ?

Substituting we now obtain

$$V_2 = \frac{725\ \cancel{\text{mmHg}} \times 300\ \text{cm}^3}{600\ \cancel{\text{mmHg}}}$$

$$= 400\ \text{cm}^3$$

Example 2 250 cm^3 of a gas has a pressure of 2.5 atm. Calculate its new pressure when its volume is reduced to 1.5 cm^3 at constant temperature.

Solution We have to apply the relation

$$P_1V_1 = P_2V_2$$

$$\therefore\ P_2 = \frac{P_1V_1}{V_2}$$

$V_1 = 250\ \text{cm}^3$

$P_1 = 2.5\ \text{atm}$

$V_2 = 1.5\ \text{cm}^3$

$P_2 = ?$

Substituting we have

$$P_2 = \frac{250\ \cancel{\text{cm}^3} \times 2.5\ \text{atm}}{1.5\ \cancel{\text{cm}^3}}$$

$$= 420\ \text{atm}$$

Practice Problems

1. A gas has a volume of 150 cm^3 at normal atmospheric pressure (101.3 kPa). Calculate its new pressure if the volume is increased by 225 cm^3 at constant temperature.

   [*Answer:* 53 kPa]
2. A gas has a pressure of 30.5 kPa when its volume is 310 cm^3. Calculate the volume of the gas at 45 kPa if the temperature remains constant. [*Answer*: 210 cm^3]

Charles's law: Charles's law describes the relationship between the volume and temperature of an ideal gas at constant pressure. Charles's law states that the volume of an ideal gas is proportional to its absolute temperature at constant pressure, and vice versa.

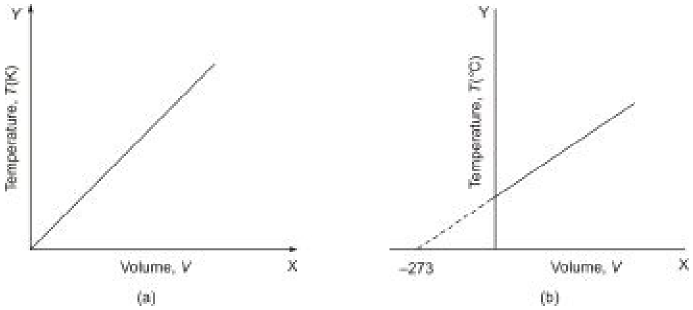


Figure 5.3 Graphs of Charles's law.

Charles's law is a case of direct variation, and is expressed mathematically as

$$V \mu T$$

Introducing the constant of proportionality, we have

$$V = kT$$

So $\frac{V}{T}$ = constant or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$, etc.

The subscripts 1 and 2 denote the initial and final properties of a gas.

Figure 5.4 Jacques Alexandre Charles, French physicist (1746–1823).

Example 1 What would be the volume of 500.0 cm^3 of a gas at 25°C if its temperature is reduced to 19°C at constant pressure?

Solution We have to apply Charles's law, i.e.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$\therefore\ V_2 = \frac{T_2 V_1}{T_1}$

We must not forget to convert the temperature to kelvin. Thus

$V_1 = 500.0\ \text{cm}^3$

$T_1 = 25°\text{C} + 273\ \text{K} = 298\ \text{K}$

$T_2 = 19°\text{C} + 273\ \text{K} = 292\ \text{K}$

$V_2 = ?$

Substituting we have

$$V_2 = \frac{500.0\ \text{cm}^3 \times 292\ \cancel{\text{K}}}{298\ \cancel{\text{K}}}$$

$= 490\ \text{cm}^3$

Example 2 250 cm^3 of a gas at 27°C has its volume increased by 50 cm^3 at constant pressure. What is the new temperature of the gas?

Solution We have to apply the relation

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$\therefore\ T_2 = \frac{T_1 V_2}{V_1}$

$V_1 = 250\ \text{cm}^3$

$V_2 = 250\ \text{cm}^3 + 50\ \text{cm}^3 = 300\ \text{cm}^3$

$T_1 = 27°\text{C} + 273\ \text{K} = 300\ \text{K}$

$T_2 = ?$

We now substitute to obtain

$$T_2 = \frac{300\ \cancel{\text{cm}^3} \times 300\ \text{K}}{250\ \cancel{\text{cm}^3}}$$

$= 400\ \text{K}$

Practice Problems

1. Find the volume of a gas at 57°C if it occupies a volume of 5.21 dm^3 at 30°C and at the same pressure. [*Answer:* 5.7 dm^3]
2. By what value must the temperature of 550 cm^3 of an ideal gas at 80°C be reduced in order to obtain a volume of 450 cm^3 at the same pressure? [*Answer*: 64°C or 64 K]

The general gas equation: The general gas equation is obtained by combining Boyle's and Charles's laws, i.e.

V µ $\frac{1}{P}$ Boyle's law

V µ T Charles's law

We now combine the two laws to obtain

$$V \text{ µ } \frac{T}{P}$$

Introducing the constant of proportionality, we obtain

$V = \frac{kT}{P}$

$\therefore \frac{PV}{T} = k$ or $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$, etc.

Example 1 300.0 cm^3 of an ideal gas has a pressure of 842 mmHg at 15°C. What is the volume of the gas at 28°C and 505 mmHg?

Solution We have to apply the general gas equation, i.e.

$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$\therefore V_2 = \frac{P_1V_1T_2}{P_2T_1}$

P_1 = 842 mmHg

V_1 = 300.0 cm^3

T_1 = 273 K + 15°C = 288 K

P_2 = 505 mmHg

T_2 = 273 K + 28°C = 301 K

V_2 = ?

Substituting we have

$$V_2 = \frac{842\ \cancel{\text{mmHg}} \times 300.0\ \text{cm}^3 \times 301\ \cancel{\text{K}}}{505\ \cancel{\text{mmHg}} \times 288\ \cancel{\text{K}}}$$

= 523 cm^3

Example 2 A given mass of a gas occupies a volume of 1000 cm^3 at 15°C and 927 cm^3 when its pressure is doubled. What is its new temperature?

Solution As usual, the applicable relation is

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore\ T_2 = \frac{P_2V_2T_1}{P_1V_1}$$

Let us represent the initial pressure P_1 with x. Then

V_1 = 1000.0 cm^3

T_1 = 273 K + 15°C = 288 K

$P_2 = 2x$

V_2 = 927 cm^3

T_2 = ?

Substituting we have

$$T_2 = \frac{2\cancel{x} \times 927\ \cancel{\text{cm}^3} \times 288\ \text{K}}{\cancel{x} \times 1000.0\ \cancel{\text{cm}^3}}$$

= 534 K

Example 3 800 cm^3 of a gas was collected over water at STP. Calculate the pressure of the dry gas at 200 K if it occupies a volume of 395 cm^3 at this temperature.

(S.V.P. of water at 0°C = 4.6 mmHg)

Solution We start by stating the equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore\ P_2 = \frac{P_1V_1T_2}{T_1V_2}$$

We will define all initial properties at STP, i.e., at 273 K and 760 mmHg. Since 0°C is equivalent to 273 K, then the saturated vapour pressure of water at 0°C is the same as that at 273 K. Thus

P_1 = 760 mmHg – 4.6 mmHg = 755.4 mmHg

T_1 = 273 K

V_1 = 800 cm^3

V_2 = 395 cm^3

T_2 = 200 K

P_2 = ?

Substituting we obtain

$$P_2 = \frac{755.4 \text{ mmHg} \times 800 \cancel{\text{cm}^3} \times 200 \cancel{\text{K}}}{395 \cancel{\text{cm}^3} \times 273 \cancel{\text{K}}}$$

= 1000 mmHg

Practice Problems

1. The volume of an ideal gas was halved when its pressure was reduced by 250 mmHg at STP. Calculate the new temperature of the gas. [*Answer:* 92 K]
2. An ideal gas occupies a volume of 15.7 dm^3 at 1.52×10^3 Pa and 57°C. Calculate its volume at STP. [*Answer:* 0.20 dm^3]

The ideal gas law: The ideal gas law given by the relation

$PV = nRT$

where P = Pressure.

V = Volume in dm^3.

n = Number of moles.

T = Absolute temperature.

R = Universal gas constant = 0.082 dm^3 atm K^{-1} mol^{-1} = 8.314 J K^{-1} mol^{-1} = 62.4

$\text{dm}^3\,\text{Torr K}^{-1}\,\text{mol}^{-1}$.

The ideal gas law is an example of equation of state. An equation of state shows the relationship between the four properties of a gas—pressure, amount, volume and temperature.

Example 1 A gas occupies a volume of 1500 cm^3 at 2500 kPa and 27°C. What is the amount, in moles, of the gas present at these temperature and pressure?

$$(R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1})$$

Solution We must apply the ideal gas law, i.e.

$$PV = nRT$$

$$\therefore\ n = \frac{PV}{RT}$$

We have to convert the volume to dm^3. Since 1000 cm^3 is equivalent to 1 dm^3, then

$V = 1.5\ \text{dm}^3$

$T = 273\ \text{K} + 27°\text{C} = 300\ \text{K}$

$P = 2500\ \text{kPa}$

$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} = 8.314\ \text{kPa dm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$

$n = ?$

Substituting into the equation, we have

$$n = \frac{2500\ \cancel{\text{kPa}} \times 1.5\ \cancel{\text{dm}^3} \times 1\ \text{mol} \times 1\ \cancel{\text{K}}}{8.314\ \cancel{\text{kPa}}\ \cancel{\text{dm}^3} \times 300\ \cancel{\text{K}}}$$

$$= 2\ \text{mol}$$

Example 2 What is the volume occupied by 0.27 mol of a gas at 10°C and 2.5 atm?

$$(R = 0.082\ \text{atm dm}^3\ \text{K}^{-1}\ \text{mol}^{-1})$$

Solution We must use the ideal gas equation

$$PV = nRT$$

$$\therefore\ V = \frac{nRT}{P}$$

$P = 2.5\ \text{atm}$

n = 0.27 mol

T = 273 K +10°C = 283 K

R = 0.082 atm $\text{dm}^3\,\text{K}^{-1}\,\text{mol}^{-1}$

V = ?

Substituting we have

$$V = \frac{0.27\ \cancel{\text{mol}} \times 0.082\ \cancel{\text{atm}}\ \text{dm}^3 \times 283\ \cancel{\text{K}}}{2.5\ \cancel{\text{atm}} \times 1\ \cancel{\text{K}} \times 1\ \cancel{\text{mol}}}$$

$= 2.5\ \text{dm}^3$

Example 3 An ideal gas occupies a volume of 2725 cm^3 at 800 mmHg and −15°C. Calculate the amount, in moles, of the gas if its volume is reduced to 1927 cm^3 at −20°C?

(R = 62.4 mmHg $\text{dm}^3\,\text{K}^{-1}\,\text{mol}^{-1}$)

Solution The amount of the gas must be calculated at the final conditions of pressure and temperature. The final pressure can be obtained from the equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore\ P_2 = \frac{P_1V_1T_2}{T_1V_2}$$

P_1 = 800 mmHg

V_1 = 2725 cm^3

T_1 = 273 – 15°C = 258 K

V_2 = 1927 cm^3

T_2 = 273 K – 20°C = 253 K

P_2 = ?

Substituting we obtain

$$P_2 = \frac{800\ \text{mmHg} \times 2725\ \cancel{\text{cm}^3} \times 253\ \cancel{\text{K}}}{925\ \cancel{\text{cm}^3} \times 258\ \cancel{\text{K}}}$$

$= 1109.4$ mmHg

We can now obtain the amount of the gas from the ideal gas equation

$PV = nRT$

$$\therefore\ n = \frac{PV}{RT}$$

V = 1.927 dm^3
P = 1109.4 mmHg
T = 253 K
R = 62.4 mmHg dm^3 K^{-1} mol^{-1}
n = ?

Finally, we now substitute to obtain

$$n = \frac{1109.4\ \cancel{mmHg} \times 1.927\ \cancel{dm^3} \times 1\ mol \times 1\ \cancel{K}}{62.4\ \cancel{mmHg}\ \cancel{dm^3} \times 263\ \cancel{K}}$$

= 0.140 mol

Practice Problems

1. 0.421 mol of a gas occupies a volume of 5.00 dm^3 at 0°C. What is the pressure of the gas in Torr?
   (R = 62.4 L Torr K^{-1} mol^{-1}) [*Answer*: 1430 Torr]
2. What is the volume of 0.283 mol of a gas at STP?
   (R = 0.082 atm dm^3 K^{-1} mol^{-1}) [*Answer*: 6.3 dm^3]
3. A given amount of a gas was collected over water at 283 K and 1.50 atm. Calculate the number of moles of the gas if it occupies a volume of 5.00 dm^3.
   (R = 0.082 atm dm^3 K^{-1} mol^{-1}, S.V.P. of water at 285 K = 10.5 mmHg)
   [*Answer:* 0.32 mol]

5.3 CRITICAL CONSTANTS OF GASES AND EQUATIONS OF STATE FOR REAL GASES

Gases can be liquefied by compression, i.e., by increase in pressure. However, whether an increase in pressure would be enough to liquefy a gas depends on its temperature. The temperature of a gas, above which an increase in pressure cannot be used to effect its liquefaction, is called critical temperature T_c. Thus a gas must be cooled below its critical temperature in order to liquefy it by compression. Every gas has its unique critical temperature. The critical temperature of oxygen, for example, is –118°C. Above this temperature, the application of pressure, no matter how large; cannot be used to liquefy the gas, except it is first cooled to below –188°C.

The corresponding properties of a gas at its critical temperature constitute its other critical constants. These include critical pressure P_c, critical molar volume $V_{m,c}$ and critical compressibility factor Z_c. These constants are defined as follows:

$$P_c = \frac{a}{3V_{m,c}^2} = \frac{a}{27b^2}$$

$$T_c = \frac{8P_cV_{m,c}}{3R} = \frac{8a}{27Rb}$$

$$Z_c = \frac{P_cV_c}{RT_c} = \frac{3}{8} \text{ (For a van der Waals gas)}$$

where a and b = van der Waals constants.

R = Universal gas constant.

Gases which obey the gas laws without exception are called ideal or perfect gases. However, no such gases exist in practice. Gases only obey the gas equations under the conditions of low pressure and high temperature, under which the effect of intermolecular forces of attractions become negligible. However, at high pressure and low temperature, the behaviour of gases deviates markedly from that given by the gas equations. The reason for this is the presence of intermolecular forces of attraction and repulsion, which become very pronounced under these conditions, and which were ignored in the kinetic theory of gases upon which the gas laws are based.

The attempt to account for the intermolecular forces of attraction and repulsion has led to different modifications of the ideal gas equation to produce different equations of state that are applied to real gases. These include:

The virial equation of state: We know that the ideal gas equation for 1 mol of a gas is given as

$$PV_m = RT$$

where V_m = Molar volume.

We can introduce a term called the compressibility factor Z, such that the equation now becomes

$PV_m = RTZ$

where $Z = 1$ for ideal gases.

Z is usually expressed in power series in reciprocal of volume (1/V) or pressure (1/P). These series, called virial expansions, lead to the following virial equations of state:

$PV_m = RT\,(1 + BP + CP^2 + \ldots)$

$PV_m = RT\left(1 + B/V + C/V^2 + \ldots\right)$

For n mol of a gas we have

$PV = nRT\,(1 + BP + CP^2 + \ldots)$

$PV = nRT\left(1 + B/V + C/V^2 + \ldots\right)$

V is the volume of the gas; and RT the first virial coefficient. The terms B, C, etc. are the temperature dependent second, third, etc. virial coefficients of the gas respectively. The significance of the virial coefficients reduces with the power of the series. It is also important to note that each of the virial coefficients is different for the two forms of the above virial equations.

The second virial coefficient is always negative at low temperatures. It increases with increase in temperature and falls to zero at a particular temperature before assuming a positive value. The temperature at which this virial coefficient becomes zero (other virial coefficients become negligible) is called Boyle temperature T_B. At this temperature, the gas is almost perfect, i.e., it obeys the ideal gas equation to a very high degree. In other words, a virial equation almost reduces to the ideal gas equation (the compressibility factor tends to 1) at the Boyle temperature. The Boyle temperature of a gas is related to its critical temperature by the equation

$$T_B = \frac{a}{bR} = \frac{27T_c}{8}$$

where a and b are van der Waals constants.

Van der Waals' equation: Perhaps the most popular of the equations of state for real gases is the van der Waals' equation:

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

For a mole of a gas we have

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

where n = Number of moles of the gas.

V = Volume in dm^3.

V_m = Molar volume of the gas.

P = Pressure.

T = Absolute temperature.

R = Universal gas constant.

a and b are the van der Waals constants of the gas, where a takes into consideration the effect of the forces of attractions; and b is the volume excluded by the atom or molecule of the gas, which is about four times the volume occupied by one mole of atoms or molecules. The van der Waals constants of a gas are related to its critical constants by the equations

$$a = 3 P_c V^2_{m,c} = \frac{27(RT_c)^2}{64P_c}$$

$$b = \frac{V_{m,c}}{3} = \frac{RT_c}{8P_c}$$

Figure 5.5 Johannes Diderik van der Waals, Dutch physicist (1837–1923). He developed one of the earliest equations of state, known as the van der Waals' equation. He won the Nobel Prize for Physics in 1910.

Some other equations of state of interest include:

Redlich-Kwong equation:

$$\left(P + \frac{a}{V_m T^{1/2}(V_m + b)}\right)(V_m - b) = RT$$

Soave modification of Redlich-Kwong:

$$\left(P + \frac{a\alpha}{(V_m + 2bV_m - b^2)}\right)(V_m - b) = RT$$

Dieterici equation:

$$P\,(V_m - b) = RTe^{-a/RTV_m}$$

Barthelot's equation:

$$\left(P + \frac{a}{TV_m^2}\right)(V_m - b) = RT$$

Clausius equation:

$$\left(P + \frac{a}{T(V_m + c)^2}\right)(V - b) = RT$$

Peng-Robinson:

$$\left(P + \frac{a\alpha}{V_m^2 + 2bV_m - b^2}\right)(V_m - b) = RT$$

Example 1 The van der Waals constants *a* and *b* of neon are 0.21 dm^6 atm mol^{-2} and 0.017 dm^3 mol^{-1} respectively. Calculate the critical constants of the gas.

(R = 0.08206 dm^6 atm K^{-1} mol^{-1})

Solution We start with critical molar volume, which is given as

$V_{m,c} = 3b$

$b = 0.017\ \text{dm}^3\ \text{mol}^{-1}$

$V_{m,c} = ?$

Substituting we have

$V_{m,c} = 3 \times 0.017\ \text{dm}^3\ \text{mol}^{-1}$

$= 0.051\ \text{dm}^3\ \text{mol}^{-1}$

$P_c = \frac{a}{3V_{m,c}^2}$

$a = 0.21\ \text{dm}^6\ \text{atm mol}^{-2}$

P_c = ?

Substituting we have

$$P_c = \frac{0.21\ \text{dm}^6\ \text{atm mol}^{-2}}{3 \times [0.051\ \text{dm}^6\ \text{mol}^{-1}]^2}$$

So $$P_c = \frac{0.21\ \cancel{\text{dm}^6}\ \text{atm}\ \cancel{\text{mol}^{-2}}}{0.0078\ \cancel{\text{dm}^6}\ \cancel{\text{mol}^{-2}}}$$

= 27 atm

Alternatively,

$$P_c = \frac{a}{27b^2}$$

P_c = ?

Substituting we have

$$P_c = \frac{0.21\ \text{dm}^2\ \text{atm mol}^{-2}}{27 \times [0.017\ \text{dm}^3\ \text{mol}^{-1}]^2}$$

$$P_c = \frac{0.21\ \cancel{\text{dm}^6}\ \text{atm}\ \cancel{\text{mol}^{-2}}}{0.0078\ \cancel{\text{dm}^6}\ \cancel{\text{mol}^{-2}}}$$

= 27 atm

$$T_c = \frac{8a}{27Rb^2}$$

a = 0.21 dm^6 atm mol^{-2}

b = 0.017 dm^3 mol^{-1}

R = 0.08206 dm^3 atm K^{-1} mol^{-1}

T_c = ?

Substituting we obtain

$$T_c = \frac{8 \times 0.21\ \text{dm}^6\ \text{atm mol}^{-2} \times 1\ \text{K}}{27 \times 0.08206\ \text{dm}^3\ \text{atm mol}^{-1} \times 0017\ \text{dm}^3\ \text{mol}^{-1}}$$

Then $T_c = \dfrac{1.7\,\cancel{\text{dm}^6}\,\cancel{\text{atm}}\,\cancel{\text{mol}^{-2}} \times 1\text{ K}}{0.0377\,\cancel{\text{dm}^6}\,\cancel{\text{atm}}\,\cancel{\text{mol}^{-2}}}$

= 45 K

Alternatively,

$T_c = \dfrac{8P_cV_{m,c}}{3R}$

T_c = ?

Substituting we have

$$T_c = \frac{8 \times 27\text{ atm} \times 0.051\text{ dm}^3\text{ atm mol}^{-1} \times 1\text{ K}}{3 \times 0.08206\text{ dm}^3\text{ atm mol}^{-1}}$$

So $T_c = \dfrac{11\,\cancel{\text{dm}^3}\,\cancel{\text{atm}}\,\cancel{\text{mol}^{-1}} \times 1\text{ K}}{0.246\,\cancel{\text{dm}^3}\,\cancel{\text{atm}}\,\cancel{\text{mol}^{-1}}}$

= 45 K

Example 2 The critical temperature and pressure of carbon dioxide are 304 K and 72.8 atm respectively. Calculate

(a) The van der Waals constant of the gas;
(b) The Boyle temperature of the gas;
(c) The critical density of the gas.

(R = 0.08206 dm^3 atm K^{-1} mol^{-1})

Solution

(a) We begin with the constant a, given by

$$a = \frac{27(RT_c)^2}{64P_c}$$

T_c = 304 K

P_c = 72.8 atm

R = 0.08206 dm^3 atm K^{-1} mol^{-1}

a = ?

Substituting we obtain

$$a = \frac{27 \times [0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{mol}^{-1} \times 304 \text{ K}]^2}{64 \times 72.8 \text{ atm}}$$

$$\text{So } a = \frac{16800 \text{ dm}^6 \text{ atm}^2 \text{ mol}^{-2} \cancel{\text{K}^2}}{1 \cancel{\text{K}^2} \times 4660 \text{ atm}}$$

$= 3.61$ dm^6 atm mol^{-2}

$$b = \frac{RT_c}{8P_c}$$

b = ?

Substituting we have

$$b = \frac{0.08206 \text{ dm}^3 \cancel{\text{atm}} \text{ mol}^{-1} \times 304 \cancel{\text{K}}}{1 \cancel{\text{K}} \times 8 \times 72.8 \cancel{\text{atm}}}$$

$= 0.043$ dm^3 mol^{-1}

(b) The Boyle temperature of a gas is given by

$$T_B = \frac{a}{bR}$$

We have already obtained a to be 3.61 dm^6 atm mol^{-2}, and b to be 0.043 dm^3 mol^{-1}.

R = 0.08206 dm^3 atm K^{-1} mol^{-1}

T_B = ?

Substituting we obtain

$$T_B = \frac{3.61 \text{ dm}^3 \text{ atm mol}^{-2} \times 1 \text{ K}}{0.043 \text{ dm}^3 \text{ mol}^{-1} \times 0.08206 \text{ dm}^3 \text{ atm mol}^{-1}}$$

$$\text{So } T_B = \frac{3.61 \cancel{\text{dm}^6} \cancel{\text{atm}} \cancel{\text{mol}^{-2}} \times 1 \text{ K}}{0.00353 \cancel{\text{dm}^6} \cancel{\text{atm}} \cancel{\text{mol}^{-2}}}$$

$= 1020$ K

Alternatively, we can apply the equation

$$T_B = \frac{27T_c}{8}$$

$T_c = 304$ K

$T_B = ?$

Substituting we have

$$T_B = \frac{27 \times 304\ \text{K}}{8}$$

$$= 1030\ \text{K}$$

The slight difference is due to rounding.

Thus at 1030 K, carbon dioxide behaves almost like a perfect gas.

(c) The density of a gas is given as

$$r = \frac{PM}{RT}$$

To obtain the critical density, we have to use the critical pressure and critical temperature, i.e

$$r_c = \frac{P_c M}{RT_c}$$

$P_c = 72.8$ atm

$M = [12 + (16 \times 2)]\ \text{g mol}^{-1} = 44\ \text{g mol}^{-1}$

$R = 0.08206\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}$

$T_c = 304$ K

$r_c = ?$

Substituting we obtain

$$r_c = \frac{72.8\ \cancel{\text{atm}} \times 44\ \text{g}\ \cancel{\text{mol}^{-1}} \times 1\ \cancel{\text{K}}}{0.082206\ \text{dm}^3\ \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}} \times 304\ \cancel{\text{K}}}$$

$$= 130\ \text{g dm}^{-3} = 1.3\ \text{kg m}^{-3}$$

Example 3 The critical pressure and van der Waals constant *a* of oxygen are

50.1 atm and 1.36 dm^6 atm mol^{-2} respectively. Estimate the radius of the oxygen atom.

(p = 3.142, $N_A = 6.02 \times 10^{23}$ mol^{-1}]

Solution We start by calculating the volume of 1 mol of the atoms of the gas. The van der Waals constant *b* is about one-fourth of this volume. The constant *b* is obtained from the relation

$$b = \frac{V_{m,c}}{3}$$

We have to obtain $V_{m,c}$ from the relation

$$V^2_{m,c} = \frac{a}{3P_c}$$

So $V_{m,c} = \sqrt{\frac{a}{3P_c}}$

$a = 1.36$ dm^6 atm mol^{-2}
$P_c = 50.1$ atm
$V_{m,c} = ?$

Substituting we have

$$V_{m,c} = \sqrt{\frac{1.36\ dm^6\ \cancel{atm}\ mol^{-2}}{3 \times 150.3\ \cancel{atm}}}$$

$= 0.095$ dm^3 mol^{-1}
$b = ?$

Substituting into the original equation yields

$$b = \frac{0.095\ dm^3\ mol^{-1}}{3}$$

$= 0.032$ dm^3 mol^{-1}

Since the volume occupied by 1 mol of the gas atoms is one-fourth the value of *b*, then

$$V = \frac{0.032\ \text{dm}^3\ \text{mol}^{-1}}{4}$$

$= 8.0 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}$

There are 6.02×10^{23} atoms in 1 mol of a substance. Thus the volume of an oxygen atom will be

$$V = \frac{8.0 \times 10^{-3}\ \text{dm}^3\ \cancel{\text{mol}^{-1}}}{6.02 \times 10^{23}\ \cancel{\text{mol}^{-1}}}$$

$= 1.3 \times 10^{-26}\ \text{dm}^3\ \text{atm}^{-1} = 1.3 \times 10^{-29}\ \text{m}^3\ \text{atm}^{-1}$

The atom is assumed to be a hard sphere of radius *r*, whose volume is given by

$$V = \frac{4}{3}\pi r^3$$

p = 3.142

r = ?

Substituting we have

$$1.3 \times 10^{-29}\ \text{m}^3 = \frac{4}{3} \times 3.142 \times r^3$$

Thus $r^3 = \frac{1.3 \times 10^{-29}\ \text{m}^3}{4.19}$

$= 3.1 \times 10^{-34}\ \text{m}^3$

Taking the cube roots of both sides yields

$$r = \sqrt[3]{3.1 \times 10^{-34}\ \text{m}^3}$$

$= 1.49 \times 10^{-10}$ m

Example 4 The second virial coefficient of argon is $1.19 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}$ at 600 K. Calculate the molar volume of the gas at this temperature if its pressure is 9.0 atm.

($R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$)

Solution We are given the second virial coefficient; thus only the first and second virial coefficients are taken into consideration under the given conditions. The virial equation of state then reduces to

$PV_m = RT + BP$

$P = 9.0$ atm $= 9.1 \times 10^5$ N m^{-2}

$R = 8.314$ N m K^{-1} mol^{-1}

$B = 1.19 \times 10^{-5}$ m^3 mol^{-1}

$T = 600$ K

$V_m = ?$

Substituting we have

$$1.19 \times 10^{-5}\,\text{N m}^{-2} \times V_m = \frac{8.314\ \text{Nm mol}^{-1} \times 600\,\cancel{\text{K}}}{1\,\cancel{\text{K}}} + \frac{1.19 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1} \times 9.1 \times 10^5\ \text{N}}{1\ \text{m}^2}$$

Thus $1.19 \times 10^{-5}\,\text{N m}^{-2} \times V_m = 5000$ N m mol^{-1}

So $$V_m = \frac{5000\,\cancel{\text{N}}\ \text{m mol}^{-1} \times 1\,\text{m}^2}{9.1 \times 10^5\,\cancel{\text{N}}}$$

$= 6 \times 10^{-3}$ m^3 mol^{-1}

Example 5 What is the pressure exerted by 5 kg of ammonia when it is compressed to a volume of 60.0 dm^3 at 30°C?

($R = 0.0821$ dm^3 atm K^{-1} mol^{-1}, $a = 4.17$ dm^6 atm mol^{-2}, $b = 0.037$ dm^3 mol^{-1})

Solution We have to apply the van der Waals' equation

$$\left(P + \frac{an^2}{V^2}\right)[V - nb] = nRT$$

$$\therefore\ P = \frac{nRT}{[V - nb]} - \frac{an^2}{V^2}$$

The amount of the gas is obtained from the relation

$$n = \frac{m}{M}$$

$M = [14 + (3 \times 1)] = 17$ g mol^{-1}

$m = 5$ kg $= 5000$ g

$n = ?$

Substituting we have

$$n = \frac{5000\,\cancel{g} \times 1\,\text{mol}}{17\,\cancel{g}}$$

$= 294$ mol

$R = 0.0821$ dm^3 atm K^{-1} mol^{-1}

$T = 30°\text{C} + 273 = 303$ K

$V = 60.0$ dm^3

$a = 4.17$ dm^6 atm mol^{-2}

$b = 0.037$ dm^3 mol^{-1}

$P = ?$

Substituting we have

$$P = \frac{294\,\cancel{\text{mol}} \times 0.0821\,\text{dm}^3\,\text{atm}\,\cancel{\text{mol}^{-1}} \times 303\,\cancel{\text{K}}}{1\,\cancel{\text{K}} \times 60.0\,\text{dm}^3 - (294\,\cancel{\text{mol}} \times 0.037\,\text{dm}^3\,\cancel{\text{mol}^{-1}})} - \frac{4.17\,\cancel{\text{dm}^6}\,\text{atm}\,\cancel{\text{mol}^{-2}} \times (294\,\cancel{\text{mol}})^2}{(60.0\,\cancel{\text{dm}^3})^2}$$

$$\text{So } P = \frac{7310\,\cancel{\text{dm}^3}\,\text{atm}}{49.1\,\cancel{\text{dm}^3}} - \frac{3.60 \times 10^5\,\text{atm}}{3600}$$

$= 49$ atm

Example 6 1 mol of helium gas exerts a pressure of 50.0 atm when compressed to a volume of 3.5 dm^3. What is the temperature of the gas if it is a van der Waals gas?

($R = 0.0821$ dm^3 atm K^{-1} mol^{-1}, $a = 0.034$ dm^6 atm mol^{-2}, $b = 0.024$ dm^3 mol^{-1})

Solution We have to apply the van der Waals' equation for 1 mol of a gas, i.e.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$\therefore\ T = \frac{\left(P + \frac{a}{V_m^2}\right)(V_m - b)}{R}$$

Since the volume is very large compared to a, then it is safe to neglect the term a/V_m^2. The above equation then reduces to

$$T = \frac{P\,(V - b)}{R}$$

P = 50.0 atm

b = 0.024 dm^3 mol^{-1}

R = 0.0821 dm^3 atm K^{-1} mol^{-1}

V_m = 3.5 dm^3 mol^{-1}

T = ?

We now substitute to obtain

$$T = \frac{50.0 \text{ atm} \times (3.5 \text{ dm}^3 \text{ mol}^{-1} - 0.024 \text{ dm}^3 \text{ mol}^{-1}) \times 1 \text{ K}}{0.0821 \text{ dm}^3 \text{ atm mol}^{-1}}$$

$$\text{So } T = \frac{170 \cancel{\text{atm}} \cancel{\text{dm}^3} \cancel{\text{mol}^{-1}} \times 1 \text{ K}}{0.0821 \cancel{\text{dm}^3} \cancel{\text{atm}^{-1}} \text{mol}^{-1}}$$

= 2100 K

Example 7 The van der Waals constant b for helium is 0.0237 dm^3 mol^{-1}. Calculate the molar volume of helium at 98 atm and –25°C; assuming the gas behaves as a van der Waals gas.

(8.314 J K^{-1} mol^{-1})

Solution The van der Waals' equation for 1 mol of a gas is

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

For the same reason stated above, the equation reduces to

$P(V_m - b) = RT$

P = 98 atm = 9.9 × 10^6 N m^{-2}

b = 0.024 dm^3 mol^{-1} = 0.0024 m^3 mol^{-1}

R = 8.314 J K^{-1} mol^{-1} = 8.314 N m K^{-1} mol^{-1}

T = 273 K – 25°C = 248 K

V_m = ?

Substituting we obtain

$$9.9 \times 10^6 \text{ N m}^{-2} \times (V_m - 0.0024 \text{ m}^3 \text{ mol}^{-1}) = \frac{8.314 \text{ Nm mol}^{-1}}{1 \cancel{\text{K}}} \times 248 \text{ K}$$

Thus $9.9 \times 10^6 \text{ N m}^{-2} \times V_m - 23760 \text{ N m mol}^{-1} = 2062 \text{ N m mol}^{-1}$

So $9.9 \times 10^6 \text{ N m}^{-2} \times V_m = 2062 \text{ N m mol}^{-1} + 23760 \text{ N m mol}^{-1} = 25822 \text{ N m mol}^{-1}$

Then $V_m = \dfrac{25822\,\cancel{\mathrm{N}}\ \mathrm{m\,mol^{-1}} \times 1\ \mathrm{m^2}}{9.9 \times 10^6\ \cancel{\mathrm{N}}}$

$= 2.6 \times 10^{-3}\ \mathrm{m^3\,mol^{-1}}$

Example 8 The Soave modification of the Redlich-Kwong equation of state for one mole of a gas is given as

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b)}$$

Express the equation in the form $PV = RT$.

Solution We begin by taking the LCM of the right-hand side of the equation, i.e.

$$P = \frac{RTV_m(V_m + b) - a\alpha(V_m - b)}{(V_m - b)(V_m + b)V_m}$$

Cross-multiplying we have

$$P(V_m - \mathrm{b})(V_m + b)V_m = RTV_m(V_m + b) - \mathrm{aa}(V_m - b)$$

Thus $P(V_m - \mathrm{b})(V_m + b)V_m + a\mathrm{a}(V_m - b) = RTV_m(V_m + b)$

We now divide the equation throughout by $V_m(V_m + b)$ to obtain

$$P(V_m - b) + \frac{a\alpha(V_m - b)}{V_m(V_m + b)} = RT$$

Also, we can divide this equation by $(V_m - b)$ to obtain

$$P + \frac{a\alpha}{(V_m + b)V_m} = \frac{RT}{(V_m + b)}$$

Finally, we now multiply this equation by $(V_m - b)$ to obtain

$$\left(P + \frac{a\alpha}{(V_m + b)V_m}\right)(V_m + b) = RT$$

Example 9 Prove that the Boyle temperature T_B of a gas which obeys the van der Waals' equation of state is given by

$$T_B = \frac{a}{bR}$$

where a and b are van der Waals constants, and R, the gas constant.

Solution We begin by writing the van der Waals' equation for n moles of a gas:

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad (5.9)$$

We now divide this equation by $(V - nb)$ to obtain

$$P + \frac{an^2}{V^2} = \frac{nRT}{V - nb}$$

Thus $P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$ (5.10)

Multiplying by V we obtain

$$PV = \frac{nRTV}{V - b} - \frac{an^2}{V} \quad (5.11)$$

We must now differentiate Equation (5.11) with respect to P. This is a partial differentiation which involves holding T constant at that particular point at which the value of T equals the Boyle temperature. In other words, we are doing our partial differentiation at the Boyle temperature, which is usually constant for a particular gas. We must also remember the fact that n, R, a and b are all constant. Now

$$\left|\frac{\partial(PV)}{\partial P}\right|_{T_B} = \frac{\partial}{\partial P}\left|\frac{nRT_BV}{V - nb}\right|_{T_B} - \frac{\partial}{\partial P}\left|\frac{an^2}{V}\right|_{T_B} \quad (5.12)$$

We now differentiate each of the two terms on the RHS by using the quotient rule, i.e.

$$\frac{\partial z}{\partial y} = \frac{v\frac{\partial u}{\partial x} - u\frac{\partial v}{\partial x}}{v^2}$$

Starting with the first term, we have

$u = nRT_BV$ $v = V - nb$

$\frac{\partial u}{\partial P} = nRT_B\frac{\partial V}{\partial P}$ (Since nRT_B is constant)

$\frac{\partial v}{\partial P} = \frac{\partial v}{\partial P} - \frac{\partial nb}{\partial P} = \frac{\partial v}{\partial P}$ (Since *nb* is constant)

Substituting into the above equation we have

$$\frac{\partial}{\partial P}\left|\frac{nRT_B V}{V - nb}\right|_{T_B} = \frac{[V - nb]nRT_B \frac{\partial V}{\partial P} - nRT_B V \frac{\partial V}{\partial P}}{(V - nb)^2} = \frac{nRT_B \partial V}{(V - nb)\partial P} - \frac{nRT_B V \partial V}{(V - nb)^2 \partial P} \quad (5.13a)$$

We now shift attention to the second term:

$u = an^2 \quad v = V$

$\frac{\partial u}{\partial P} = 0$ (Since an^2 is constant)

$\frac{\partial v}{\partial P} = \frac{\partial V}{\partial P}$

Substituting into the above equation we have

$$\frac{\partial}{\partial P}\left|\frac{an^2}{V}\right|_{T_B} = \frac{v.0 - an^2 \frac{\partial V}{\partial P}}{V^2} = -\frac{an^2 \partial V}{V^2 \partial P} \quad (5.13b)$$

Substituting Equations (5.13a) and (5.13b) into Equation (5.12), and factorizing we have

$$\left|\frac{\partial (PV)}{\partial P}\right|_{T_B} = \left[\frac{nTR_B}{V - nb} - \frac{nTR_B V}{(V - nb)^2} - \frac{an^2}{V^2}\right]_{T_B} \frac{\partial V}{\partial P}$$

Now, at the Boyle temperature, *PV* is constant, i.e., the gas obeys the ideal gas law (Boyle's law). Since the differentiation of any constant with respect to any variable is zero, it then follows that

$$\left|\frac{\partial (PV)}{\partial P}\right|_{T_B} = 0$$

Since volume is not constant, then $\partial V/\partial P$ cannot be zero. Thus the only way the equation can satisfy the above requirement, i.e. $\left|\frac{\partial (PV)}{\partial P}\right|_{T_B} = 0$ is that

$$\frac{nRT_B}{V - nb} - \frac{nRT_B V}{(V - nb)^2} + \frac{an^2}{V^2} = 0 \quad (5.14)$$

The rest of the workings involves a skilful manipulation of this equation until we get to the desired mark.

Multiplying Equation (5.14) by $(V - nb)^2V^2$, we have

$$nRT_BV^2(V - nb) - nRT_BV^3 + an^2(V - nb)^2 = 0$$

Thus $nRT_B[V^3 - V^2nb - V^3] = -an^2(V - nb)^2$

So $T_B = \dfrac{-a\cancel{n^2}(V - nb)^2}{V^2\cancel{n^2}bR}$

Then $T_B = \dfrac{a}{bR}\left[\dfrac{(V - nb)^2}{V^2}\right] = \dfrac{a}{bR}\left[\dfrac{(V - nb)}{V^2}\right]^2$

So $T_B = \dfrac{a}{bR}\left[1 - \dfrac{nb}{V^2}\right]^2$ (5.15)

Now, at very low pressure, the volume would be very large so that the term nb/V tends to zero (Since the constant b is very small). Thus, Equation (5.15) now reduces to

$$T_B = \frac{a}{bR}$$

Example 10 Show that the critical pressure, critical temperature and critical molar volume of a gas can be expressed as follows:

$$P_c = \frac{a}{3V_{m,c}^2} - \frac{a}{27b^2}$$

$$T_c = \frac{8a}{27Rb}$$

$$V_{m,c} = 3b$$

where a and b are the van der Waals constants of the gas.

Solution We begin from the van der Waals' equation for a mole of a gas:

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad (5.16)$$

From Equation (5.16), we now see that

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) - RT = 0 \quad (5.17)$$

Expanding Equation (5.17), we obtain

$$PV_m - Pb + \frac{a}{V_m} - \frac{ab}{V_m^2} - RT = 0 \quad (5.18)$$

We now multiply throughout by V^2_m to obtain

$$PV^3_m - PbV^2_m + aV_m - ab - RTV^2_m = 0 \quad (5.19)$$

Next, we divide Equation (5.19) by P to obtain the cubic equation

$$V^3_m - PbV^3_m + \frac{aV_m}{P} - \frac{ab}{P} - \frac{RTV_m^2}{P} = 0 \quad (5.20)$$

Equation (5.20) can be rearranged to obtain

$$V^3_m - \left(b + \frac{RT}{P}\right)V_m^2 + \frac{aV_m}{P} - \frac{ab}{P} = 0 \quad (5.21)$$

Now, at the critical point $T = T_c$ and $P = P_c$. Substituting these into Equation (5.20) we have

$$V^3_m - \left(b + \frac{RT_c}{P_c}\right)V_m^2 + \frac{aV_m}{P_c} - \frac{ab}{P_c} = 0 \quad (5.22)$$

We can see from Equation (5.22) that there are three values of V_m for any values of temperature and pressure. These values are all the same at the critical point, $V_m = V_{m,c}$. Thus we write

$$(V_m - V_{m,c})^3 = 0$$

Expanding this equation we have

$$V^3_m - 3V_{m,c}V^2_m + 3V^2_{m,c}V_m - V_{m,c} = 0 \quad (5.23)$$

The coefficients of the powers of V_m in Equations (5.22) and (5.23) must be the same. Thus, comparing coefficients we obtain for

V^3_m : $1 = 1$

V^2_m : $b + RT_c = 3V_{m,c}$ (5.24)

V_m : $\frac{a}{P_c} = 3V^2_{m,c}$ (5.25)

Constants : $\frac{ab}{P_c} = V^3_{m,c}$ (5.26)

From Equation (5.25) we obtain

$P_c = \frac{a}{3V^2_{m,c}}$ (5.27)

From Equation (5.27) we obtain

$$a = 3V^2_{m,c}$$

Substituting this into Equation (5.26) yields

$$\frac{3V^2_{m,c} b \cancel{P_c}}{\cancel{P_c}} = V^3_{m,c}$$

Thus $b = \frac{V^3_{m,c}}{3V^2_{m,c}} = \frac{V_{m,c}}{3}$ (5.28)

So $V_{m,c} = 3b$ (5.29)

Substituting Equation (5.29) into (5.27) we obtain

$P_c = \frac{a}{3(3b)^2} = \frac{a}{27b^2}$ (5.30)

Substituting Equations (5.22), (5.29) and (5.30) into (5.24) we obtain

$$\frac{V_{m,c}}{3} + \frac{RT_c}{a/27b^2} = 3V_{m,c}$$

Thus $\frac{27b^2 RT_c}{a} = 3V_{m,c} - \frac{V_{m,c}}{3}$

So $\frac{27b^2RT_c}{a} = \frac{8V_{m,c}}{3}$

Cross-multiplying we have

$81b^2RT_c = 8aV_{m,c}$

So $T_c = \frac{8aV_{m,c}}{81b^2R}$ (5.31)

Since $V_{m,c}/3 = b$, then Equation (5.31) finally reduces to

$T_c = \frac{8a}{27Rb^2}$ (5.32)

Example 11 What is the molar volume of a gas at 327°C and 90.0 atm if

(a) the gas is treated as an ideal gas;
(b) the gas obeys the van der Waals' equation.

($R = 0.08206$ dm^3 atm K^{-1} mol^{-1}, $a = 1.36$ dm^6 atm mol^{-2}, $b = 0.032$ dm^3 mol^{-1})

Solution

(a) We have to apply the ideal gas equation

$PV_m = RT$
$P = 90.0$ atm
$T = 273$ K + 327°C = 600 K
$R = 0.08206$ dm^3 atm K^{-1} mol^{-1}
$V_m = ?$

Substituting we have

$90.0 \text{ atm} \times V_m = \frac{0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \times 600 \cancel{\text{K}}}{1 \cancel{\text{K}}}$

So $90.0 \text{ atm} \times V_m = 49.236$ dm^3 atm mol^{-1}

Thus $V_m = \frac{49.236 \text{ dm}^3 \cancel{\text{atm}} \text{ mol}^{-1}}{90.0 \cancel{\text{atm}}}$

$= 0.547$ dm^3 mol^{-1}

(b) We have to apply the van der Waals' equation

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

We have already shown that this equation can be rearranged into

$$V_m^3 - \left(b + \frac{RT}{P}\right)V_m^2 + \frac{aV_m}{P} - \frac{ab}{P} = 0$$

a = 1.36 dm^3 atm mol^{-2}

b = 0.032 dm^3 mol^{-1}

V_m = ?

For simplicity, we omit the units, and substitute to obtain

$$V_m^3 - \left(0.032 + \frac{0.08206 \times 600}{90.0}\right)V_m^2 + \frac{1.36V_m}{90.0} - \frac{1.36 \times 0.032}{90.0}$$

Then $V_m^3 - 0.58V_m^2 + 0.015V_m - 0.000484 = 0$

This is a cubic equation, which is rather difficult to solve. The easiest way of solving a cubic equation is to use a graphing calculator. The equation can also be solved using graphical method or successive approximation beginning with a value that is as close to the answer as possible, which is the value obtained using the ideal gas equation. We will iterate until further iterations result in constant values of V_m. One of such numerical methods is the Newton-Raphson method, given by

$$x_{n+1} = x_n - \frac{f(x)}{f^{1}(x)}$$

where x_n = Initial value x.

x_{n+1} = New value of x.

$f(x_n)$ = Value of the equation $f(x)$ when $x = x_n$.

$f^{1}(x_n)$ = Value of the first derivative of $f(x)$ when $x = x_n$.

The derivative of the above equation is

$$f^{1}(V_m) = 3V_m^2 - 1.16V_m + 0.015$$

For the first iteration we have

$V_m = 0.547$

Thus $f(0.547) = -0.00215$

$f^{1}(0.547) = 0.278$

Substituting into the Newton-Raphson equation we have

$$V_m = 0.547 - \left(\frac{-0.00215}{0.278}\right)$$

$$= 0.555$$

For the second iteration we have

$V_m = 0.555$

So $f(0.555) = 0.0001404$

$f^{I}(0.555) = 0.295$

Substituting we have

$$V_m = 0.555 - \frac{0.0001404}{0.295}$$

$$= 0.555$$

V_m has now assumed a constant's value. Thus our solution is

$$V_m = 0.555 \text{ dm}^3 \text{mol}^{-1} = 555 \text{ cm}^3 \text{ mol}^{-1}$$

Example 12 1.0 mole of ammonia is at 27°C and 100.0 atm. What is the molar volume of the gas if it is a van der Waals gas? (R = 0.08206 dm^3 atm K^{-1} mol^{-1}, a = 4.17 dm^6 atm mol^{-2}, b = 0.037 dm^3 mol^{-1})

Solution As usual, we have to apply the van der Waals' equation

$$V_m^3 - \left(b + \frac{RT}{P}\right)V_m^2 + \frac{a}{P}V_m - \frac{ab}{P} = 0$$

a = 4.17 dm^6 atm mol^{-2}

b = 0.037 dm^6 mol^{-1}

R = 0.08206 dm^6 atm K^{-1} mol^{-1}

P = 100.0 atm

T = 273 K + 27°C = 300 K

For convenience, we omit the units and substitute the data into the equation to obtain

$$V_m^3 - 0.283V_m^2 + 0.0417V_m - 1.54 \times 10^{-3} = 0$$

This equation can be easily solved with a graphing calculator. Alternatively, we can resort to successive approximation by using the numerical method of Newton-Raphson:

$$x_{n+1} = x_n - \frac{f(x)}{f^1(x)}$$

The first derivative of the equation is

$$f^1(x) = 3V_m^2 - 0.566V_m + 0.0417$$

We have to obtain our initial value from the ideal gas equation:

$PV_m = RT$

Then $P = 100.0$ atm

$R = 0.08206$ dm^3 atm K^{-1} mol^{-1}

$T = 300$ K

$V_m = ?$

Substituting we have

$$100.0 \text{ atm} \times V_m = 0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \times \frac{300\,\cancel{\text{K}}}{1\,\cancel{\text{K}}}$$

Then $100.0 \text{ atm} \times V_m = 24.618 \text{ dm}^3 \text{ atm mol}^{-1}$

Thus $V_m = \dfrac{24.618 \text{ dm}^2\ \cancel{\text{atm}}\ \text{mol}^{-1}}{100.0\ \cancel{\text{atm}}}$

$= 0.246$ dm^3 mol^{-1}

For the first iteration we have

$f(0.246) = 0.00648$

$f^1(0.246) = 0.084$

Thus $V_m = 0.246 - \dfrac{0.00643}{0.084}$

$= 0.169$

For the second iteration we have

$f(0.169) = 0.00225$

$f^{1}(0.169) = 0.0317$

Thus $V_m = 0.169 - \frac{0.0025}{0.0317}$

$= 0.0980$

For the third iteration we have

$f(0.0980) = 7.70 \times 10^{-4}$

$f^{1}(0.0980) = 0.015$

Thus $V_m = 0.098 - \frac{7.70 \times 10^{-4}}{0.015}$

$= 0.047$

For the fourth iteration we have

$f(0.047) = -1.01 \times 10^{-4}$

$f^{1}(0.047) = 0.0217$

Thus $V_m = 0.047 - \left(\frac{-1.01 \times 10^{-4}}{0.0217}\right)$

$= 0.0517$

For the fifth iteration we have

$f(0.0517) = -2.35 \times 10^{-6}$

$f^{1}(0.0517) = 0.0205$

Thus $V_m = 0.0517 - \left(\frac{-2.35 \times 10^{-6}}{0.0205}\right)$

$= 0.0518$

For the sixth iteration we have

$f(0.0518) = -3.05 \times 10^{-7}$

$f^{1}(0.0518) = 0.0204$

$V_m = 0.518 - \left(\frac{-3.05 \times 10^{-7}}{0.0204}\right)$

$= 0.0518$

We have now arrived at a constant's value of 0.0518. Thus

$$V_m = 0.0518 \text{ dm}^3 \text{ mol}^{-1}$$

The disparity between this value and the ideal gas value of 0.246 $\text{dm}^3 \text{ mol}^{-1}$ shows how markedly the gas deviates from the ideal behaviour at high pressure.

Practice Problems

1. The Redlich-Kwong equation of state is given as

$$\left(p + \frac{a}{V_m T^{1/2}(V_m + b)}\right)(V_m - b) \qquad RT$$

Write the equation in the form $P = \frac{RT}{V}$

$$\left[\text{Answer}: P = \frac{RT}{V_m - b} - \frac{a}{T^{1/2} V_m (V_m + b)}\right]$$

2. The critical temperature and pressure of ammonia are 132°C and 111.5 atm respectively. What are the van der Waals constants of the gas?

($R = 0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$)

[*Answer:* $a = 4.18 \text{ dm}^6 \text{ atm mol}^{-2}$, $b = 0.0373 \text{ dm}^3 \text{ mol}^{-1}$]

3. The molar critical volume of benzene is 254.1 $\text{cm}^3 \text{ mol}^{-1}$. What is its Boyle temperature if the van der Waals constant *a* is 9.38 $\text{dm}^3 \text{ atm mol}^{-2}$?

($R = 0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$) [*Answer:* 1350 K]

4. 1.20 mol of carbon dioxide was compressed to a volume of 50.0 dm^3 at 30°C. What is the pressure exerted by the gas?

($R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$, $a = 3.59 \text{ dm}^6 \text{ atm mol}^{-2}$, $b = 0.043 \text{ dm}^3 \text{ mol}^{-1}$)

[*Answer:* 9.9 atm]

5. Estimate the radius of the helium atom if its temperature and pressure are 5.2 K and 2.26 atm respectively.

[$R = 0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)

[*Answer:* 1.33×10^{-10} m]

6. Estimate the molar volume of argon at 0°C and 15 atm, given that the second virial coefficient of the gas is 21.7 $\text{cm}^3\ \text{mol}^{-1}$.

($R = 0.08206\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}$) [*Answer:* 1.47 dm^3]

5.4 REDUCED STATE PROPERTIES AND THE PRINCIPLE OF CORRESPONDING STATES

A reduced state property is obtained by dividing the property with the corresponding critical constant. Thus

$$T_r = \frac{T}{T_c}$$

$$P_r = \frac{P}{P_c}$$

$$V_r = \frac{V_m}{V_{m,c}}$$

where T_r, P_r and V_r are reduced temperature, reduced pressure and reduced volume respectively.

The reduced form of the van der Waals' equation is obtained by substituting the reduced properties into the equation, i.e.

$$\left(P_r + \frac{3}{V_r^2}\right)[3V_r - 1] = 8T_r$$

This equation is applicable to all fluids, as it involves neither the van der Waals constant *a* nor *b*.

The principle of corresponding states that two or more substances are in corresponding states if they have the same reduced temperature, reduced pressure and reduced volume. It is evident from the above equation that two state variables are enough to fix a substance in corresponding state, as they would both have the same value for the third reduced state variable. For example, if two substances have the same reduced pressure and temperature, then they are in corresponding states, as they would both have the same reduced volume.

Example 1 12.5 mol of a gas occupies a volume of 275 cm^3 at 90.0 atm. Use the reduced van der Waals' equation to obtain the temperature of the gas, given that the critical molar volume, temperature and pressure are 59.1 $\text{cm}^3\ \text{mol}^{-1}$, 647 K and 218.3 atm respectively.

Solution We have to apply the relation

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r$$

The first step is to evaluate the reduced variables, as follows:

$$V_r = \frac{V_m}{V_{m,c}}$$

The molar volume is obtained from the relation

$V_m = \frac{V}{n}$

$V = 375\ \text{cm}^3$

$n = 2.5\ \text{mol}$

$V_m = ?$

Substituting we have

$V_m = \frac{375\ \text{cm}^3}{2.5\ \text{mol}}$

$= 150\ \text{cm}^3\ \text{mol}^{-1}$

Now $V_{m,c} = 59.1\ \text{cm}^3\ \text{mol}^{-1}$

$V_r = ?$

Substituting we have

$V_r = \frac{150\ \cancel{\text{cm}^3}\ \cancel{\text{mol}^{-1}}}{59.1\ \cancel{\text{cm}^3}\ \cancel{\text{mol}^{-1}}}$

$= 2.54$

$P_r = \frac{P}{P_c}$

$P = 90.0\ \text{atm}$

$P_c = 218.3\ \text{atm}$

$P_r = ?$

Substituting we have

$P_r = \frac{90.0 \text{ atm}}{218.3 \text{ atm}}$

$= 0.42$

$T_r = ?$

Substituting into the original equation we have

$$\left(0.41 + \frac{3}{2.54^2}\right)[(3 \times 2.54) - 1] = 8T_r$$

Thus $0.875 \times 6.62 = 8T_r$

So $8T_r = 5.79$

Then $T_r = \frac{5.79}{8}$

$= 0.72$

Now we know that the reduced pressure is defined as

$T_r = \frac{T}{T_c}$

$T_c = 647 \text{ K}$

$T = ?$

Finally, we now substitute to obtain

$$0.72 = \frac{T}{647 \text{ K}}$$

Cross-multiplying we have

$T = 0.72 \times 647 \text{ K}$

$= 470 \text{ K}$

Example 2 Derive the reduced form of the van der Waals' equation.

Solution We begin by writing the van der Waals' equation for 1 mol of a gas:

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad (5.33)$$

Now, we know from the definition of a reduced state variable that

$P = P_rP_c$ (5.34)

$T = T_rT_c$ (5.35)

$V_m = V_rV_{m,c}$ (5.36)

Substituting Equations (5.34) – (5.36) into (5.33), we have

$$\left(P_rP_c + \frac{a}{(V_rV_{m,c})^2}\right)(V_rV_{m,c} - b) = RT_rT_c \quad (5.37)$$

We also know that

$$P_c = \frac{a}{27b^2} \quad (5.38)$$

$$T_c = \frac{8a}{27Rb^2} \quad (5.39)$$

$$V_{m,c} = 3b \quad (5.40)$$

Substituting Equations (5.38) to (5.40) into (5.37) yields

$$\left(\frac{P_ra}{27b^2} + \frac{a}{9V_r^2b^2}\right)[3V_rb - b] = \frac{8\cancel{R}T_ra}{27\cancel{R}b} \quad (5.41)$$

Multiplying Equation (5.41) by 27/*a* we have

$$\left(\frac{P_r}{b^2} + \frac{3}{V_r^2b^2}\right)[3V_rb - b] = \frac{8T_r}{b} \quad (5.42)$$

Multiplying Equation (5.42) by *b* yields

$$\left(\frac{P_r}{b^2} + \frac{3}{V_r^2b}\right)[3V_rb - b] = 8T_r \quad (5.43)$$

The expansion of Equation (5.43) eliminates *b* to yield

$$3P_rV_r - P_r + \frac{9}{V_r} - \frac{3}{V_r^2} = 8T_r \quad (5.44)$$

Factorizing Equation (5.44) we have

$P_r(3V_r - 1) + \frac{3}{V_r^2}(3V_r - 1) = 8T_r$ (5.45)

From Equation (5.45) we arrive at the reduced van der Waals' equation

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r$$

Example 3 At what temperature and pressure would oxygen be in a corresponding state with 1 mol of carbon dioxide at 80.0 atm and 320 K? The critical constants of oxygen are T_c = 154.8 K and P_c = 50.1 atm. Those of carbon dioxide are T_c = 304 K and P_c = 72.8 atm.

Solution Oxygen would be in corresponding state with carbon dioxide if its reduced temperature and pressure are equal to those of carbon dioxide at the specified conditions. Thus our calculations should be aimed at working out the temperature and pressure of oxygen that will make its reduced temperature and pressure equal to those of carbon dioxide. The first step is to obtain the reduced temperature and pressure of carbon dioxide:

$P_r = \frac{P}{P_c}$

P = 80.0 atm
P_c = 72.8 atm
P_r = ?

Substituting we have

$P_r = \frac{80.0\ \cancel{\text{atm}}}{72.8\ \cancel{\text{atm}}}$

= 1.1

Similarly,

$T_r = \frac{T}{T_c}$

T = 320 K
T_c = 304 K

T_r = ?

Substituting we have

$$T_r = \frac{320\ \cancel{K}}{304\ \cancel{K}}$$

= 1.1

We now shift our attention to oxygen. For the gas to be in corresponding state with carbon dioxide its reduced pressure and temperature must be 1.1, i.e.

P_r = 1.1

T_r = 1.1

We can now obtain the required pressure from the relation

$$P_r = \frac{P}{P_c}$$

Thus $P = P_c \times P_r$

P_c = 50.1 atm

P = ?

Substituting we have

P = 50.1 atm × 1.1

= 55 atm

Similarly, the required temperature is obtained from the relation

$$T_r = \frac{T}{T_c}$$

Thus $T = \mathrm{T}_c \times T_r$

T_c = 154.8 K

T = ?

Substituting we have

T = 154.8 K × 1.1

= 170 K

Practice Problems

1. What pressure would 1 mol of methane exert at 500 K if the gas is confined in a 0.28-dm^3 vessel?

   (T_c = 190.3 K, P_c = 45.6 atm, $V_{m,c}$ = 98.7 cm^3 mol^{-1}) [*Answer:* 2.4 atm]

2. At what temperature and pressure would xenon be in corresponding state with water vapour at 100 atm and 700 K? The critical properties of xenon are T_c = 289.7 and P_c = 58 atm. Those of water vapour are T_c = 647 K and P_c = 218.3 atm.

   [*Answers:* T = 313 K, P = 26.6 atm]

5.5 GAS DENSITY

Density d is defined as mass per unit volume of a substance, i.e.

$$d = \frac{m}{V}$$

The SI unit of density is kg m^{-3}. It can also be expressed in g cm^{-3}, g dm^{-3}, etc., depending on the unit in which the volume is expressed. The densities of gases vary markedly with temperature and pressure. The relationship between gas density, temperature and pressure is derived from the ideal gas equation, as follows:

We start from the equation of state

$$PV = nRT \quad (5.46)$$

Now we know that

$$n = \frac{m}{M} \quad (5.47)$$

where m = mass of the gas.

M = molar mass of the gas.

We now substitute Equation (5.47) into (5.46) to obtain

$$PV = \frac{mRT}{M}$$

Thus $PVM = mRT$ (5.48)

We now divide Equation (5.48) by MP/m to obtain

$$\frac{V}{m} = \frac{RT}{MP} \quad (5.49)$$

Equation (5.49) is the reciprocal of gas density. We now take the reciprocal of this equation to obtain

$$d = \frac{MP}{RT} \quad (5.50)$$

Equation (5.50) is the formula for gas density. With this relation, we can work out the densities of a gas at different conditions of temperature and pressure.

Example 1 What is the density of methane at 27°C and 740 Pa?

(H = 1, C = 12, $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$)

Solution We have to apply the relation

$$d = \frac{MP}{RT}$$

The molar mass of methane, CH_4, is

$$M = [12 + (1 \times 4)]\ \text{g mol}^{-1} = 16\ \text{g mol}^{-1}$$

Other data are

$P = 740\ \text{Pa} = 0.74\ \text{kPa}$

$T = 273\ \text{K} + 27°\text{C} = 300\ \text{K}$

$R = 8.314\ \text{kPa dm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$

$d = ?$

Finally, we now substitute to obtain

$$d = \frac{16\ \text{g}\ \cancel{\text{mol}^{-1}} \times 0.74\ \cancel{\text{kPa}} \times 1\ \cancel{\text{K}}}{8.314\ \cancel{\text{kPa}}\ \text{dm}^3\ \cancel{\text{mol}^{-1}} \times 300\ \cancel{\text{K}}}$$

$= 5\ \text{mg dm}^{-3}$

Example 2 A gas has a density of 1.51 g dm^{-3} at 30°C and 1.1 atm. What is the molar mass of the gas?

($R = 0.082\ \text{atm dm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$)

Solution As usual, we have to apply the relation

$$d = \frac{MP}{RT}$$

$$\therefore\ M = \frac{dRT}{P}$$

d = 1.5 g dm^{-3}
T = 273 K + 30°C = 303 K
P = 1.1 atm
R = 0.082 atm dm^3 K^{-1} mol^{-1}
M = ?

We now substitute to obtain

$$M = \frac{1.5\ \text{g} \times 0.082\ \cancel{\text{atm}}\ \cancel{\text{dm}^3} \times 303\ \cancel{\text{K}}}{1.1\ \cancel{\text{atm}} \times 1\ \cancel{\text{K}} \times 1\ \cancel{\text{dm}^3} \times 1\ \text{mol}}$$

= 34 g mol^{-1}

Practice Problems

1. Calculate the density of acetone (propanone) vapour at 40°C and 800 T
formula of the compound is C_6H_6O.
(H = I, C = 12, O = 16, R = 62.4 dm^3
$^{-1}$) [*Ans*
2. Acrolein has a density of 2.47 g dm^{-3} at 30°C and 1.1 atm. What is the molar
(R = 0.082 dm^3 atm
$^{-1}$)
[*Answer:* 56 g mol^{-1}]

5.6 GAS STOICHIOMETRY

Gay-Lussac's law of combining volumes: Gay-Lussac's law of combining volumes describes the relationship between the volumes of gaseous reactants and products at constant temperature and pressure. It states that when gases combine to form products they do so in volumes which are in simple ratio to one another, and to the volumes of the products, if gaseous, provided the temperature and pressure remain constant.

Avogadro's law: Avogadro's law states that equal volumes of all gases at the same temperature and pressure contain the same number of molecules. Using Avogadro's law, the number of moles or stoichiometric coefficients of gaseous reactants and products are treated as volumes provided the species in the reaction are maintained at the same temperature and pressure.

Figure 5.6 Joseph Louis Gay-Lussac, French chemist (1778–1850).

Example 1 What volume of ammonia is required to react with 250 cm^3 of oxygen if they combine according to the equation $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$?

Solution The volumes of the species and their ratio are specified below:

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Volume 4 cm^3 5 cm^3 4 cm^2 6 cm^3

Volume ratio $1 : \frac{5}{4} : 1 : \frac{3}{2}$

It is very much easy to see from the volume ratio that the volume of ammonia required is

$$V = \frac{4}{5} \times 250\ cm^3$$

$$= 200\ cm^3$$

Alternatively, let the volume of NH_3 required be V. From the above equation, 5 cm^3 of O_2 reacts with 4 cm^3 of NH_3, then 250 cm^3 of O_2 would react with V of NH_3, i.e.

$4\ cm^3 = 5\ cm^3$

$V = 250\ cm^3$

We now cross-multiply to obtain

$$250\ cm^3 \times 4\ cm^3 = V \times 5\ cm^3$$

$$\therefore\ V = \frac{250\ \cancel{cm^3} \times 4\ cm^3}{4\ \cancel{cm^3}}$$

= 200 cm^3

Example 2 Dinitrogen monoxide decomposes at red heat to yield nitrogen and oxygen, as follows:

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

What volumes of oxygen and nitrogen would be obtain from the decomposition of 375.5 cm^3 of dinitrogen monoxide?

Solution We start from the equation of reaction:

$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$

Volume 2 cm^3 2 cm^3 1 cm^3

Volume ratio 2 : 2 : 1

Now, from the volume ratio we have

Volume N_2 produced $= \frac{2}{2} \times 375.5$ cm^3

= 375.5 cm^3

Volume of O_2 produced $= \frac{1}{2} \times 375.5$ cm^3

= 187.8 cm^3

Alternatively, 2 cm^3 of N_2O produces 2 cm^3 of N_2, then 375.5 cm^3 of N_2O would also produce 375.5 cm^3, i.e.

375.5 cm^3 = V

2 cm^3 = 2 cm^3

Thus 2 $cm^3 \times V$ = 375.5 $cm^3 \times$ 2 cm^3

$$\therefore\ V = \frac{375.5\ cm^2 \times 2\ \cancel{cm^3}}{2\ \cancel{cm^3}}$$

= 375.5 cm^3

Similarly, 2 cm^3 of N_2O produces 1 cm^3 of O_2, then 375.5 cm^3 of N_2O will produce 187.8 cm^3 of O_2, i.e.

2 cm^3 = 1 cm^3

375.5 cm^3 = V

So 2 $cm^3 \times V$ = 375.5 $cm^3 \times$ 1 cm^3

$\therefore\ V = \dfrac{375.5\,\cancel{\text{cm}^3} \times 1\,\text{cm}^3}{2\,\cancel{\text{cm}^3}}$

$= 187.8\ \text{cm}^3$

Example 3 Nitrogen reacts with hydrogen to yield ammonia, as follows.

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$$

What would be the total volume of the residual gases when 100 cm^3 of nitrogen is sparked with 75 cm^3 of hydrogen, assuming all volumes are measured at STP?

Solution The total volume of the residual gases is the volume of excess (unreacted) reactants and the volume of the gas produced. The excess volume of each reactant is its volume available for reaction less the amount that actually reacts.

From the equation, 3 cm^3 of H_2 reacts with 1 cm^3 of N_2, then 75 cm^3 of H_2 would react with 25.0 cm^3 of N_2, i.e.

3 cm^3 = 1 cm^3

75 cm^3 = V

Cross-multiplying we obtain

3 cm^3 × V = 1 cm^3 × 75 cm^3

Then $V = \dfrac{1\,\cancel{\text{cm}^3} \times 75\,\text{cm}^3}{3\,\cancel{\text{cm}^3}}$

= 25 cm^3

Consequently, the excess volume of N_2 = 100.0 cm^3 – 25.0 cm^3 = 75.0 cm^3

All the given volume of H_2, i.e. 75 cm^3, would react. Thus its residual volume is 0.

The volume of NH_3 produced can be obtained\from the reacting volumes of either reactants.

From the volume of H_2:

3 cm^3 of H_2 produces 2 cm^3 of NH_3, then 75 cm^3 of H_2 would produce 50 cm^3, i.e.

3 cm^3 = 2 cm^3

75 cm^3 = V

So 3 cm^3 × V = 2 cm^3 × 75 cm^3

Then $V = \dfrac{2\,\cancel{\text{cm}^3} \times 75\,\text{cm}^3}{3\,\cancel{\text{cm}^3}}$

= 50 cm^3

From the reacting volume of N_2:
1 cm^3 of N_2 produces 2 cm^3 of NH_3, then 25 cm^3 will produce 50 cm^3, i.e.

$$1\ \text{cm}^3 = 2\ \text{cm}^3$$
$$25\ \text{cm}^3 = V$$

Then $1\ \text{cm}^3 \times V = 2\ \text{cm}^3 \times 25\ \text{cm}^3$

So $V = \frac{2\cancel{\text{cm}^3} \times 25\ \text{cm}^3}{1\cancel{\text{cm}^3}}$

= 50 cm^3

The summary of the results is given below:

$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$

Volume	1 cm^3	3 cm^3	2 cm
Volume ratio	1 :	3 :	2
Initial volume	100 cm^3	75 cm^3	0
Final volume	25 cm^3	75 cm^3	50 cm^3
Residual volume	75.0 cm^3	0	50 cm^3

So Volume of residual gases = Volume unreacted gases + Volume of ammonia

= 75 cm^3 + 50 cm^3 = 125 cm^3

Example 4 35 cm^3 of carbon monoxide was sparked with 350.0 cm^3 of air containing 21% of oxygen, to produce carbon dioxide. The mixture of gases was then passed through lime water. Calculate the final volume of the residual gases, assuming that all the volumes are measured at STP

Solution The very first step is to obtain the volume of oxygen (21% of 350 cm^3) available for reaction:

$$V = \frac{21}{100} \times 350.0\ \text{cm}^3$$

= 73.5 cm^3

The volume of air remaining = 350.0 cm^3 – 75.5 cm^3 = 276.5 cm^3

We can now calculate the reacting volumes of the reactants, as well as the volume of the CO_2 produced. The equation of reaction is

$2CO(g) + O_2(g) \rightarrow 2CO(g)$

Volume 2 cm^3 1 cm^3 2 cm^3
Volume ratio 2 : 1 : 2

From the equation, 2 cm^3 of CO requires 1 cm^3 of O_2, then 35 cm^3 of N_2 would equally require 17.5 cm^3, i.e.

2 cm^3 = 1 cm^3
35 cm^3 = V
Thus 2 cm^3 × V = 35 cm^3 × 1 cm^3

$$\text{So } V = \frac{35\,\cancel{\text{cm}^3} \times 1\,\text{cm}^3}{2\,\cancel{\text{cm}^3}}$$

$$= 17.5\ \text{cm}^3$$

Thus the residual volume of O_2 = 73.5 cm^3 − 17.5 cm^3 = 56.0 cm^3

The volume of CO_2 produced is obtained as follows:

2 cm^3 of CO produces 2 cm^3 of CO_2, then 35 cm^3 of CO would produce 35 cm^3 of CO_2, i.e.

2 cm^3 = 2 cm^3
35 cm^3 = V
So 2 cm^3 × V = 2 cm^3 × 35 cm^3

$$\text{Thus } V = \frac{2\,\cancel{\text{cm}^3} \times 35\,\text{cm}^3}{2\,\cancel{\text{cm}^3}}$$

$$= 35\ \text{cm}^3$$

Using the volume of O_2, we have

1 cm^3 of O_2 produces 2 cm^3 of CO_2, then 17.5 cm^3 of O_2 would also produce 35 cm^3, i.e.

1 cm^3 = 2 cm^3
17.5 cm^3 = V
So 1 cm^3 × V = 17.5 cm^3 × 2 cm^3

$$\text{Thus } V = \frac{17.5\,\cancel{\text{cm}^3} \times 2\,\text{cm}^3}{1\,\cancel{\text{cm}^3}}$$

$$= 35\ \text{cm}^3$$

The summary of these results is given as follows:

$2CO(g) + O_2(g) \rightarrow 2CO(g)$

Volume 2 cm^3 1 cm^3 2 cm^3

Volume ratio 2 : 1 : 2

Initial volume 35 cm^3 73.5 cm^3 0

Final volume 35 cm^3 17.5 cm^3 35 cm^3

Residual volume 0 56.0 cm^3 35 cm^3

The CO_2 produced would be absorbed by lime water; thus

Volume of residual gases = volume of air remaining + volume of unreacted oxygen

= 56.0 cm^3 + 274.5 cm^3 = 330.5 cm^3

Example 5 50 cm^3 of methane was sparked with 150 cm^3 of air containing 21% of oxygen. Calculate the volume of the residual gases if methane combines with oxygen as follows:

$$CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g)$$

Solution We begin by calculating the volume of oxygen by obtaining the value of 21% of 150 cm^3 of air, i.e.

$V = \frac{21}{100} \times 150 \text{ cm}^3$

= 31.5 cm^3

Then volume of air remaining = 150.0 cm^3 − 31.5 cm^3 = 118.5 cm^3

We can now proceed to the equation of reaction to specify the volume ratio, the volume of each specie reacting or being produced, and the residual volume of each specie:

$CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g)$

Volume 1 cm^3 2 cm^3 2 cm^3 1 cm^3

Volume ratio 1 : 2 : 2 : 1

Volume available 50 cm^3 31.5 cm^3 0 0

Reacting volume 15 cm^3 30 cm^3 30 cm^3 15 cm^3

Residual volume 35 cm^3 1.5 cm^3 30 cm^3 15 cm^3

Finally, we now calculate the total volume of residual gases as follows.

V = remaining volume of air + excess reactants + volume of products

= 118.5 cm^3 + 35 cm^3 + 1.5 cm^3 + 30 cm^3 + 15 cm^3 = 200 cm^3

Practice Problems

1. You are required to produce 500 cm^3 of ammonia through the Haber process. What volumes of nitrogen and hydrogen would you require to obtain this result? The equation of reaction is $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$. [*Answer:* N_2 = 250 cm^3, H_2 = 750 cm^3]

(C = 12, O = 16, Na =23) [*Answer:* 8.3 g]

2. 250 cm^3 of carbon monoxide was sparked with 1050 cm^3 of air containing 21% of oxygen. Calculate the total volume of the residual gases after the resulting mixture is passed through alkaline pyrogallol? The equation of reaction is $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$.

[*Answer:* 830 cm^3]

3. Calculate the volumes of nitrogen and hydrogen required to produce 750 cm^3 of ammonia if the two gases react according to the equation $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$.

[*Answers:* N_2 = 375 cm^3, H_2 = 1130 cm^3]

4. 50 cm^3 of methane was mixed with 75 cm^3 of steam. What would be the volume of the residual gases? The equation of reaction is $CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g)$.

[*Answer*: 225 cm^3]

5. 55 cm^3 of methane was sparked with oxygen at 40°C and 720 Torr. What volume of steam would be produced at STP? The equation of reaction is $CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g)$.

(H = 1, C = 12) [*Answer:* 91 cm^3]

5.7 MOLAR VOLUME OF GASES

The molar volume V_m of a gas is the volume occupied by 1 mole of that gas at given conditions of temperature and pressure. One mole of every gas occupies a volume of approximately 22.4 dm^3 at STP. Thus the volume V of a gas at STP is given as

$$V = n \times 22.4\ dm^3 mol^{-1}$$

Example 1 Calculate the volume of 13.7 g of methane at STP

(H = 1, C = 12)

Solution We must first work out the amount of methane from the relation

$$n = \frac{m}{M}$$

The molecular formula of methane is CH_4. Thus

M = [12 + (4 ×1)] g mol^{-1} = 16 g mol^{-1}
m = 13.7 g
n = ?

Then $n = \frac{13.7\,\cancel{g} \times 1\text{ mol}}{16\,\cancel{g}}$

= 0.87 mol at STP

Finally, we now convert this amount to the volume at STP using the relation

$$V = n \times 22.4\text{ dm}^3\text{ mol}^{-1}$$

Substituting we have

$V = 0.87\,\cancel{\text{mol}} \times \frac{22.4\text{ dm}^3}{1\,\cancel{\text{mol}}}$

= 20 dm^3

Example 2 20.0 g of zinc carbonate was heated vigorously to a constant mass at STP What volume of carbon dioxide is produced at 800 mmHg and 30°C?

(Molar volume of gases = 22.4 $dm^3 mol^{-1}$, C = 12, O = 16, Zn = 65)

Solution The equation of reaction is

$ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

Mole ratio 1 : 1 : 1

We have to work out the amount of $ZnCO_3$ heated from the relation

$n = \frac{m}{M}$

Now M = [65 + 12 + (16 × 3)] g mol^{-1} = 126 g mol^{-1}
m = 20.0 g
n = ?

We should now substitute to obtain

$$n = \frac{22.0\,\cancel{g} \times 1\,\text{mol}}{126\,\cancel{g}}$$

$= 0.160$ mol

Now, from the equation, 1 mol of $ZnCO_3$ produces 1 mol of CO_2, then 0.160 mol of $ZnCO_3$ would also produce 0.160 mol of CO_2 at STP, i.e.

$$n = 0.16 \text{ mol at STP}$$

We now need to convert this amount to volume:

$$V = n \times 22.4 \text{ dm}^3 \text{mol}^{-1}$$

Substituting we obtain

$$V = 0.160\,\cancel{\text{mol}} \times \frac{22.4\ \text{dm}^3}{1\,\cancel{\text{mol}}}$$

$= 3.58 \text{ dm}^3$

This is the volume at STP, i.e. 273 K and 760 mmHg. We must now finish it off by calculating the new volume of the gas at the new pressure and temperature, i.e. 800 mmHg and 30°C; using the equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore\ V_2 = \frac{P_1V_1T_2}{P_2T_1}$$

$P_1 = 760$ mmHg

$V_1 = 3.58 \text{ dm}^3$

$T_1 = 273$ K

$T_2 = 273$ K + 30°C = 303 K

$P_2 = 800$ mmHg

$V_2 = ?$

Finally, we now substitute to obtain

$$V_2 = \frac{760\,\cancel{\text{mmHg}} \times 3.50\ \text{dm}^3 \times 303\,\cancel{\text{K}}}{800\,\cancel{\text{mmHg}} \times 273\,\cancel{\text{K}}}$$

$= 4 \text{ dm}^3$

Practice Problem

Calculate the amount of 2.15 dm^3 of chlorine at STP. (Molar volume = 22.4 $dm^3\ mol^{-1}$) [*Answer:* 0.010 mol]

5.8 RELATIVE VAPOUR DENSITY

The vapour density of a gas is the number of times a given volume of that gas is as heavy as the same volume of hydrogen at a given temperature and pressure, i.e.

$$\text{V.D.} = \frac{\text{Mass of a volume of a gas or vapour}}{\text{Mass of an equal volume of hyrogen}}$$

Vapour density is related to relative molecular mass M_r by the relation

$$\text{V.D.} = \frac{1}{2} \times M_r$$

Vapour density has no units since it is only a ratio.

Example 1 Show that the vapour density of a gas or vapour is related to its relative molecular mass M_r by the relation

$$\text{V.D.} = \frac{1}{2} \times M_r$$

Solution We must start by defining vapour density:

$$\text{V.D.} = \frac{\text{Mass of a volume of a gas or vapour}}{\text{Mass of an equal volume of hydrogen}}$$

Considering 1 cm^3 of the gas, we have

$$\text{V.D.} = \frac{\text{Mass of 1 cm}^3\text{ of a gas or vapour}}{\text{Mass of 1 cm}^3\text{ of hydrogen}}$$

Since equal volumes of gases contain the same number of molecules at the same temperature and pressure, then

$$\text{V.D.} = \frac{\text{Mass of 1 molecule of a gas or vapour}}{\text{Mass of 1 molecule of hydrogen}}$$

The mass of 1 molecule of a substance is its relative molecular mass M_r. Since the relative molecular mass of hydrogen is 2, then

$$\text{V.D.} = \frac{1}{2} \times M_r$$

Example 2 Calculate the vapour density of oxygen.

(O = 16)

Solution This a direct application the relation

$$\text{V.D.} = \frac{1}{2} \times M_r$$

We must, however, be careful not to substitute the relative atomic mass of oxygen for its relative molecular mass. Since the molecular formula of oxygen is O_2, then

$M_r = 16 \times 2 = 32$

V.D. = ?

We can now substitute to obtain

$\text{V.D.} = \frac{1}{2} \times 32$

$= 16$

Practice Problems

1. What is the vapour density of benzene vapour?
   (H = 1, C = 12) [*Answer:* 39]
2. The vapour pressure of cyclohexane vapour is 49. What is its molar mass?
   [*Answer:* 98 g mol^{-1}]

5.9 DIFFUSION OF GASES

Diffusion is the movement of the particles of a substance through a medium, from the region of higher concentration to a region of lower concentration. Diffusion is fastest in gases, and slowest in liquids.

Rate of diffusion: The rate of diffusion of a gas is the volume of the gas diffusing per second or the rate of change of its volume as a result of diffusion. Mathematically,

$$R = \frac{V}{t}$$

where R = rate of diffusion

V = volume of the gas

t = time

The rate of diffusion of a gas is governed by Graham's law, which states that the rate of diffusion of a gas is inversely proportional to the square root of its density provided the temperature and pressure remain constant. Since the relative molecular mass of a gas is proportional to its density, Graham's law can also be stated thus: the rate of diffusion of a gas is inversely proportional to the square root of its relative molecular mass provided the temperature and pressure remain constant. Mathematically,

$$R \propto \frac{1}{\sqrt{\rho}} \propto \frac{1}{\sqrt{M_r}}$$

Thus the relative rate of diffusion of two gases is given as

$$\frac{R_1}{R_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_{r2}}{M_{r1}}}$$

where R_1 = The rate of diffusion of the gas with density r_1 and relative molecular mass M_{r1}.

R_2 = The rate of diffusion of the gas with density r_2 and relative molecular mass M_{r2}.

Since the rate of diffusion of a gas is inversely proportional to time, then we can state, from Graham's law, that the time required for a gas to diffuse is directly proportional to its density or relative molecular mass, i.e.

$$\frac{t_2}{t_1} = \frac{R_1}{R_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_{r2}}{M_{r1}}}$$

where t_1 and t_2 are the time required for equal volumes of gases 1 and 2 to diffuse under the same conditions.

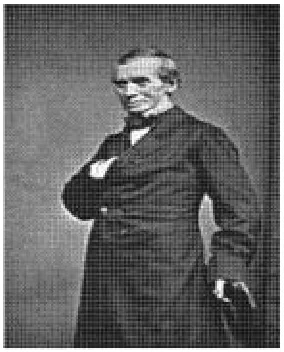


Figure 5.7 Thomas Graham, Scottish chemist (1805–1869). He formulated the Graham's law in 1833.

Example 1 550 cm^3 of a gas diffuses through air in 30 min. What is the rate of diffusion of the gas in $cm^3 s^{-1}$?

Solution We have to apply the relation

$$R = \frac{V}{t}$$

$V = 550\ cm^3$

$t = 30 \times 60\ s = 1800\ s$

$R = ?$

Substituting we have

$$R = \frac{550\ cm^2}{1800\ s}$$

$= 0.31\ cm^3 s^{-1}$

Example 2 How long will it take 100 cm^3 of a gas to diffuse through a porous pot if its rate of diffusion is 3.5 $cm^3 s^{-1}$?

Solution We have to apply the relation

$$R = \frac{V}{t}$$

$$\therefore\ t = \frac{V}{R}$$

$R = 3.5\ \text{cm}^3\,\text{s}^{-1}$

$V = 100\ \text{cm}^3$

$t = ?$

Substituting we have

$$t = \frac{100\,\cancel{\text{cm}^3} \times 1\ \text{s}}{3.5\,\cancel{\text{cm}^3}}$$

$= 30\ \text{s}$

Example 3 Which of the following gases will have the highest rate of diffusion under the same conditions?

(i) CH_4 (ii) O_2 and (iii) NH_3

(H = 1, C = 12, N = 14, O = 16)

Solution We have to recall that the rate of diffusion of a gas is inversely proportional to density or relative molecular mass, i.e., the rates of diffusion of the gases will decrease as densities or relative molecular masses increase. Thus we need to work out the relative molecular masses of the gases. The gas with the lowest molar mass will have the highest rate of diffusion.

$M_r\,(CH_4) = 12 + (1 \times 4) = 16$

$M_r\,(O_2) = 16 \times 2 = 32$

$M_r\,(NH_3) = 14 + (1 \times 4) = 17$

Thus methane will have the highest rate of diffusion, followed by ammonia. Oxygen has the slowest rate of diffusion.

Example 4 450 cm^3 of oxygen can diffuse through a porous pot in 40.0 s. What volume of ammonia will diffuse through the porous pot in 30.0 s under the same conditions?

(H = 1, N = 14, O = 16)

Solution We must first work out the rate of diffusion of ammonia:

$$\frac{R_1}{R_2} = \sqrt{\frac{M_2}{M_1}}$$

Let the rates of diffusion of oxygen and ammonia with R_1 and R_2 respectively. We can easily work out R_1 from the data given in the question by using the relation

$R = \frac{V}{t}$

$V = 450\ \text{cm}^3$
$t = 40.0\ \text{s}$
$R_1 = ?$

Substituting we obtain

$R_1 = \frac{450\ \text{cm}^2}{40.0\ s}$

$= 11.3\ \text{cm}^3\,\text{s}^{-1}$
$M_{r1} = 16 \times 2 = 32$
$M_{r2} = 14 + (1 \times 3) = 17$
$R_2 = ?$

We can now substitute into the original equation to obtain

$$\frac{11.3\ \text{cm}^2}{1\ s \times R_2} = \sqrt{\frac{17}{32}}$$

Squaring both sides of the equation we have

$$\frac{127.7\ \text{cm}^6}{1\ s^2 \times R_2^2} = \frac{17}{32}$$

Cross-multiplying we have

$127.7\ \text{cm}^6 \times 32 = 17 \times 1\ \text{s} \times R^2_2$

Thus $R_2 = \sqrt{\frac{127.7\ \text{cm}^6}{1\ \text{s}^2 \times 17}}$

$= 15.5\ \text{cm}^3\,\text{s}^{-1}$

We can now use this rate of diffusion to work out the volume of the gas that would diffuse in 30.0 s:

$R = \frac{V}{t}$

$\therefore\ V_2 = R_2 \times t$

$V_2 = ?$

Substituting we have

$V_2 = \frac{15.5\ \text{cm}^3}{1\cancel{\text{s}}} \times 30.0\cancel{\text{s}}$

$= 465\ \text{cm}^3$

Example 5 Two gases *x* and *y* are put in a porous pot. The rate of diffusion of *y* was found to be one-third that of *x* under the same conditions. What is the vapour density of *x* if *y* has a vapour density of 25?

Solution We have to apply the relation

$$\frac{R_x}{R_y} = \sqrt{\frac{\rho_y}{\rho_x}}$$

Let the rate of diffusion of *x* be *R*. Then

$R_Y = R/3$

$r_y = 25$

$r_x = ?$

Substituting we have

$\frac{R}{R/3} = \sqrt{\frac{25}{\rho_x}}$

Thus $\frac{3\cancel{R}}{\cancel{R}} = \sqrt{\frac{25}{\rho_x}}$

We now square both sides to obtain

$$\frac{25}{r_x} = 9$$

Cross-multiplying we have

$r_x \times 9 = 25$

So $r_x = \frac{25}{9}$

$= 2.8$

Example 6 250 cm^3 of nitrogen diffuses in 35.5 s. How long would it take 500 cm^2 of hydrogen to diffuse under the same conditions?

(H = 1, N = 14)

Solution We have to apply the relation

$$\frac{t_2}{t_1} = \sqrt{\frac{M_{r2}}{M_{r1}}}$$

We know that 250 cm^3 of nitrogen diffuses in 35.5 s, then 500 cm^3 of the gas will diffuse in

$t_1 = \frac{500\,\cancel{cm^3}}{250\,\cancel{cm^3}} \times 35.5$ s

$= 70$ s

$M_{r1} = 14 \times 2 = 28$

$M_{r2} = 2 \times 1 = 2$

$t_2 = ?$

Substituting we have

$$\frac{t}{70\ s} = \sqrt{\frac{2}{28}}$$

Cross-multplying we obtain

$$t_2 = 70\ s \times 0.27 = 20\ s$$

Alternatively, we can apply the relation

$$\frac{R_1}{R_2} = \sqrt{\frac{M_{r2}}{M_{r1}}}$$

Now, we know that

$R = \frac{V}{t}$

V_1 = 250 cm^3

t = 35.5 s

R_1 = ?

Substituting we have

$R_1 = \frac{250 \text{ cm}}{35.5\, s}$

= 7.04 cm^3 s^{-1}

M_{r1} = 14 × 2 = 28

M_{r2} = 2 × 1= 2

R_2 = ?

We now substitute to obtain

$$\frac{7.04 \text{ cm}^3 s^{-1}}{R_2} = \sqrt{\frac{2}{28}}$$

Cross-multiplying we obtain

R_2 × 0.27 = 7.04 cm^3 s^{-1}

Then $R_2 = \frac{7.04 \text{ cm}^3 s^{-1}}{0.27}$

= 26 cm^3 s^{-1}

The time required for 500 cm^3 of the gas to diffuse is obtained from the relation

$R = \frac{V}{t}$

$$\therefore\ t = \frac{V}{R}$$

$$\text{So } t = \frac{500\ \cancel{\text{cm}^3} \times 1\ \text{s}}{26\ \cancel{\text{cm}^3}}$$

$$= 20\ \text{s}$$

Practice Problems

1. 350 cm^3 of a gas diffuses through a porous pot in 10 min. What is its rate of diffusion?

   [*Answer:* 0.6 $\text{cm}^3\,\text{s}^{-1}$]
2. In an experiment to determine the rate of diffusion of a gas, a student discovered that 650 cm^3 of the gas diffused in 136.3 s. What was the error in his result if the actual rate of diffusion of the gas is 4.71 $\text{cm}^3\,\text{s}^{-1}$?

   [*Answer:* 0.10 s]
3. 180 cm^3 of a gas diffuses in 20 seconds. How long will it take 400 cm^3 of oxygen to diffuse under the same conditions if the gas has a vapour density of 15?

   (O = 16) [*Answer:* 46 s]
4. The rate of diffusion of methane is 3 times as fast as that of a gas x. What is the molar mass of x?

   (C = 12, H = 1) [*Answer:* 144 g mol^{-1}]

5.10 MOLE FRACTION

The mole fraction x of gas in a mixture of gases is the number of moles of the gas divided by the total number of moles of the gases in the mixture, i.e.

$$x_i = \frac{n_i}{n_t} \quad (5.51)$$

where x_i = The mole fraction of a gas i.

n_i = The number of moles of a gas i.

n_t = The total number of moles of the gases present in the mixture.

The relationship between mole fraction and partial pressure is obtained as follows:

Consider a mixture of four gases i, j, k, and l. Applying Dalton's law of partial pressure, we have

$P_t = P_i + P_j + \mathrm{P}_k + P_l$ (5.52)

Also, $n_t = n_i + n_j + n_k + n_j$ (5.53)

Now, we know from the ideal gas law that

$P_i = \frac{n_i RT}{V}$ (5.54)

$P_j = \frac{n_j RT}{V}$ (5.55)

$P_k = \frac{n_k RT}{V}$ (5.56)

$P_l = \frac{n_l RT}{V}$ (5.57)

Substituting Equations (5.54)-(5.57) into (5.52) we obtain

$P_t = \frac{n_i RT}{V} + \frac{n_j RT}{V} + \frac{n_k RT}{V} + \frac{n_j RT}{V}$ (5.58)

We now factorise Equation (5.58) to obtain

$P_t = (n_i + n_j + n_k + n_j) \frac{RT}{V}$ (5.59)

Substituting Equation (5.52) into (5.59) we have

$P_t = \frac{n_t RT}{V}$

Thus $V = \frac{n_t RT}{P_t}$ (5.60)

We now substitute Equation (5.60) into (5.54)-(5.57) to obtain

$P_i = \frac{n_i}{n_t} P_t$ (5.61)

$P_j = \frac{n_j}{n_t} P_t$ (5.62)

$P_k = \frac{n_k}{n_t} P_t$ (5.63)

$P_l = \frac{n_l}{n_t} P_t$ (5.64)

Finally, we now substitute Equation (5.51) into (5.61)-(5.64) to obtain

$P_i = x_i P_t$ or $x_i = \frac{P_i}{P_t}$

$P_j = x_j P_t$ or $x_j = \frac{P_j}{P_t}$

$P_k = x_k P_t$ or $x_k = \frac{P_k}{P_t}$

$P_l = x_l P_t$ or $x_l = \frac{P_l}{P_t}$

Thus the mole fraction of a gas can also be obtained by dividing its partial pressure by the total pressure of the mixture.

Example 1 A mixture of gases contains 20.0 g of nitrogen and 3.0 g of helium. Calculate the total pressure of the mixture if the partial pressure of helium is 1.0×10^5 Pa.

(He = 4.0, N = 14)

Solution The total pressure of the mixture is obtained from the relation

$P_i = x_i P_t$

$\therefore P_t = \frac{P_i}{x_i}$

We proceed by working out the amount of each gas from the relation

$$n = \frac{m}{M}$$

For nitrogen we have

$m = 20.0$ g

$M = 14 \times 2 = 28$ g mol^{-1}

$n = ?$

Substituting we obtain

$$n = \frac{20.0\,\cancel{g} \times 1\,\text{mol}}{28\,\cancel{g}}$$

= 0.71 mol

For helium we have

m = 3.0 g

M = 4.0 g mol^{-1}

n = ?

Substituting we obtain

$$n = \frac{3.0\,\cancel{g} \times 1\,\text{mol}}{4.0\,\cancel{g}}$$

= 0.75 mol

Then n_t = 0.71 mol + 0.75 mol = 1.46 mol

We can now determine the mole fraction of helium from the relation

$$x = \frac{n}{n_t}$$

n = 0.75 mol

n_t = 1.46 mol

x = ?

Thus $x = \frac{0.75\,\cancel{\text{mol}}}{1.46\,\cancel{\text{mol}}}$

= 0.51

P = 1.0 × 10^5 Pa

P_t = ?

Finally, we now substitute into the original equation to obtain

$$P_t = \frac{1.0 \times 10^6\ \text{Pa}}{0.51}$$

= 2.0 × 10^5 Pa

Example 2 A mixture of gases containing 12 g of hydrogen, 10 g of neon, and 8 g of nitrogen is confined in a 1.5-dm^3 cylinder at 1.5 atm and 25°C. Calculate the partial pressure of each gas.

(H = 1, N = 14, Ne = 20, $R = 0.082 \text{ atm dm}^3 \text{ K}^{-1} \text{mol}^{-1}$)

Solution The partial pressure of each gas is determined from the relation

$$P_i = x_i P_t$$

We proceed by calculating the amount of each gas, using the relation

$$n = \frac{m}{M}$$

For hydrogen we have

m = 12 g

$M = 1 \times 2 = 2 \text{ g mol}^{-1}$

n = ?

Thus $n = \dfrac{12\cancel{g} \times 1 \text{ mol}}{2\cancel{g}}$

= 6 mol

For nitrogen we have

m = 8 g

$M = 14 \times 2 = 28 \text{ gmol}^{-1}$

n = ?

Thus $n = \dfrac{8\cancel{g} \times 1 \text{ mol}}{28\cancel{g}}$

= 0.3 mol

For neon we have

m = 10 g

$M = 20 \text{ g mol}^{-1}$

n = ?

$n = \dfrac{10\cancel{g} \times 1 \text{ mol}}{20\cancel{g}}$

= 0.5 mol

Thus n_t = 6 mol + 0.3 mol + 0.5 mol = 7 mol

We can now determine the mole fraction of each gas from the relation

$$x = \frac{n}{n_t}$$

For hydrogen we have

$$x = \frac{6\ \cancel{\text{mol}}}{7\ \cancel{\text{mol}}}$$

= 0.9

For nitrogen we have

$$x = \frac{0.3\ \cancel{\text{mol}}}{7\ \cancel{\text{mol}}}$$

= 0.04

For neon we have

$$x = \frac{0.5\ \cancel{\text{mol}}}{7\ \cancel{\text{mol}}}$$

= 0.07

We must now work out the total pressure of the mixture from the relation

$$P_t = \frac{n_t RT}{V}$$

V = 1.5 dm^3

n_t = 7 mol

R = 0.082 atm $\text{dm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$

T = 273 + 25°C = 298 K

P_t = ?

Substituting we have

$$P_t = \frac{7\ \cancel{\text{mol}} \times 0.082\ \text{atm}\ \cancel{\text{dm}^3} \times 298\ \cancel{\text{K}}}{1\ \cancel{\text{mol}} \times 1\ \cancel{\text{K}} \times 1.5\ \cancel{\text{dm}^3}}$$

= 114 atm

Finally, we now substitute into the original equation to obtain

P_H = 0.9 × 114 atm = 100 atm
P_N = 0.04 × 114 atm = 5 atm
P_{Ne} = 0.07 × 114 atm = 8 atm

Example 3 A cylinder contains a mixture of four gases A, B, C and D. Calculate the mole fraction of each gas if the partial pressures of the gases are 0.5 atm, 1.8 atm, 0.2 atm and 0.7 atm respectively.

Solution The mole fraction of each gas is determined from the relation

$$x_i = \frac{P_i}{P_t}$$

However, we must first obtain the total pressure of the mixture from the relation

$P_t = P_A + P_B + P_C + P_D$
P_A = 0.5 atm
P_B = 1.8 atm
P_C = 0.2 atm
P_D = 0.7 atm
P_t = ?

We now substitute to obtain

$$P_t = 0.5 \text{ atm} + 1.8 \text{ atm} + 0.2 \text{ atm} + 0.7 \text{ atm} = 3.2 \text{ atm}$$

We can now substitute into the original relation to obtain

$x_A = \frac{0.5\ \cancel{\text{atm}}}{3.2\ \cancel{\text{atm}}}$

= 0.2

$x_B = \frac{1.8\ \cancel{\text{atm}}}{3.2\ \cancel{\text{atm}}}$

= 0.56

$x_C = \frac{0.2\ \cancel{\text{atm}}}{3.2\ \cancel{\text{atm}}}$

$= 0.06$

$x_D = \frac{0.7\ \cancel{\text{atm}}}{3.2\ \cancel{\text{atm}}}$

$= 0.2$

Practice Problems

1. A cylinder contains three gases, A, B and C whose amounts are 0.2 mol, 0.8 mol and 1.2 mol respectively. Calculate the partial pressure of each gas if the gases occupy a volume of 2.5 dm^3 at 1.1 atm and −10°C.

   (R = 0.082 atm dm^3 K^{-1} mol^{-1}) [*Answer:* P_A = 2 atm, P_B = 6.8 atm, P_C = 11 atm]
2. A mixture of gases contains four gases, A, B, C and D. The partial pressures of the gases are 2.5 atm, 0.8 atm, 1.9 atm and 2.7 atm respectively. Calculate the mole fraction of each gas. [*Answers:* P_A = 0.32, P_B = 0.1, P_C = 0.24, P_D = 0.34]

5.11 THE KINETIC THEORY OF GASES

The kinetic theory of gases can be summarized by the following postulates or assumptions:

1. The molecules of a gas are in a state of constant, random motion colliding with one another and with the walls of the container.
2. The collisions of gas molecules are perfectly elastic, i.e., momentum is conserved.
3. The force of attraction between gas molecules is negligible.
4. The actual volume occupied by the molecules of the gas is negligible compared with the total volume of the container.

5.11.1 Molecular Velocity of Gases

Three types of molecular velocities have been obtained from the kinetic theory of gases. These are:

Most probable velocity c_P: This is the velocity of the maximum number of molecules of a gas at a particular temperature. This is given as

$$c_P = \sqrt{\frac{2kT}{m}} - \sqrt{\frac{2RT}{M}}$$

where R = Universal gas constant.

m = Mass of the gas.

T = Absolute temperature of the gas.

M = Molar mass of the gas.

k = Boltzmann constant.

Average velocity c: This is the average of the velocities of the molecules of the gas. Suppose we have *n* molecules with velocities c_1, c_2 … c_n, then *c* is given as

$$c = \frac{c_1 + c_2 + c_3 + \ldots + c_n}{n}$$

Since it is not possible to measure the velocities of all the individual molecules, a convenient formula from which the average velocity is calculated is given as

$$c = \sqrt{\frac{8kT}{\pi m}} - \sqrt{\frac{8RT}{\pi M}}$$

where p = 3.142.

All other parameters are as defined above.

The root-mean-square (rms) velocity c: This is the square root of the mean or average of the squares of the velocities of the molecules of a gas at a certain temperature. Suppose we have *n* molecules with velocities c_1, c_2 … c_n, then *c* is given as

$$c = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \ldots + c_n^2}{n}}$$

Since it is impossible to measure the individual velocities of the molecules, a convenient formula for rms velocity as obtained from the kinetic theory of gases is given as

$$c = \sqrt{\frac{3P}{\rho}} - \sqrt{\frac{3RT}{M}}$$

where P = The pressure of a gas in pascals.

r = The density of a gas.

All other parameters are as defined above.

The expression on the right-hand side shows that rms speed is independent of pressure.

Example 1 Obtain the most probable velocity of air at 28°C assuming air behaves as an ideal gas.

(R = 8.314 J K^{-1} mol^{-1}, M = 29 g mol^{-1})

Solution The most probable velocity is given by the relation

$$c_P = \sqrt{\frac{2RT}{M}}$$

R = 8.314 J K^{-1} mol^{-1} = 8.314 kg m^2 s^{-2} K^{-1} mol^{-1}

T = 273 K + 28°C = 301 K

M = 29 g mol^{-1} = 0.029 kg mol^{-1}

c_P = ?

Substituting we obtain

$$c_P = \sqrt{\frac{2 \times 8.314\,\cancel{\text{kg}}\ \text{m}^{-2}\,\text{s}^{-2}\ \cancel{\text{mol}^{-1}} \times 301\,\cancel{\text{K}}}{1\,\cancel{\text{K}} \times 0.029\,\cancel{\text{kg}}\ \cancel{\text{mol}^{-1}}}}$$

= 410 m s^{-1}

Example 2 Obtain the average velocity of air at 28°C assuming air behaves as an ideal gas.

(R = 8.314 J K^{-1} mol^{-1}, M = 29 g mol^{-1}, p = 3.142)

Solution The average velocity is given by the relation

$$c = \sqrt{\frac{8RT}{\pi M}}$$

R = 8.314 J K^{-1} mol^{-1} = 8.314 kg m^2 s^{-2} K^{-1} mol^{-1}

T = 273 K + 28°C = 301 K

M = 29 g mol^{-1} = 0.029 kg mol^{-1}

p = 3.142

c = ?

Substituting we have

$$c = \sqrt{\frac{2 \times 8.314\ \cancel{\text{kg}}\ \text{m}^{-2}\ \text{s}^{-2}\ \cancel{\text{mol}^{-1}} \times 301\ \cancel{\text{K}}}{1\ \cancel{\text{K}} \times 3.142 \times 0.029\ \cancel{\text{kg}}\ \cancel{\text{mol}^{-1}}}}$$

= 470 m s^{-2}

Example 3 Calculate the temperature at which the average velocity of oxygen would be three times its average velocity at 27°C.

(R = 8.314 J K^{-1} mol^{-1}, O = 16)

Solution The unknown temperature is obtained from the relation

$$c_2 = 3c_1$$

c_1 and c_2 are the average velocities at 27°C and the unknown temperature respectively.

So $\sqrt{\frac{8RT_2}{\pi M}} = 3 \times \sqrt{\frac{8RT_1}{\pi M}}$

Thus $\sqrt{T_2} = 3 \times \sqrt{T_1}$

T_1 = 273 K + 27°C = 300 K

T_2 = ?

Substituting we obtain

$$\sqrt{T_2} = 3 \times \sqrt{300\ \text{K}}$$

We now square both sides of the equation to obtain

T_2 = 9 × 300 K

= 2700 K

Example 4 What fraction of the average velocity of a gas at 35°C is that at 25°C? Hence calculate the average velocity of the gas at 25°C if the rms velocity is 1810 m s^{-1} at 35°C.

Solution

(a) Since average velocity is directly proportional to the square root of temperature, we expect that the ratio of the average velocities will be equal to the ratio of the square roots of the two temperatures. In other words,

$$\frac{c_1}{c_2} = \sqrt{\frac{T_1}{T_2}}$$

T_1 = 273 K + 25°C = 298 K

T_2 = 273 K + 35°C = 308 K

Substituting we have

$$\frac{c_1}{c_2} = \sqrt{\frac{298\,\cancel{K}}{308\,\cancel{K}}}$$

So $\frac{c_1}{c_2} = \sqrt{0.968}$

= 0.984

(b) We know that

$$\frac{c_1}{c_2} = 0.984$$

c_2 = 1810 m s^{-1}

c_1 = ?

Substituting we have

$$\frac{c_1}{1810\ \text{ms}^{-1}} = 0.984$$

Cross-multiplying we obtain

c_1 = 0.984 × 1810 m s^{-1}

= 1780 m s^{-1}

Example 5 Prove that the rms velocity of the molecules of a gas is given by the relation

$$c = \sqrt{\frac{3P}{\rho}}$$

where P = The pressure of the gas.
  r = The density of the gas.

Solution We start by considering a cube of sides *l* (Fig. 5.8) enclosing a volume of a gas of *N* molecules, of which the mass of each is *m*. The sides or walls of the cube are oriented along the Cartesian coordinates x, y, z.

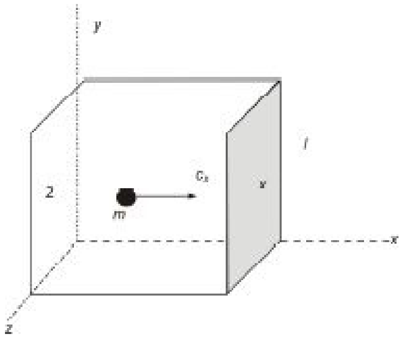


Figure 5.8 A cube enclosing a volume of a gas. One molecule is shown travelling in the *x* direction towards face *x*.

We consider a molecule of mass *m* moving in the positive *x*-direction towards the face *x* of the container with velocity u_1. The momentum *p* before collision with the wall is $mu_{1.}$ The molecule bounces back after the collision, and moves away in the opposite direction. Since momentum is conserved, the molecule moves back with the same velocity u_1, such that the momentum after collision is $–mu_1$. The minus sign indicates that the direction of the molecule is now opposite to the direction before collision.

The change in momentum Dp is defined as

Dp = momentum before collision – momentum after collision

Thus Dp_x $= mu_1 - (-mu_1) = mu_1 + mu_1$

$= 2mu_1$ (5.65)

After the collision, the molecule travels across to the opposite wall of the cube before returning to strike the face *x* again. If the distance between the walls of the cube is *l*, then the total distance covererd by the molecule is 2*l*. Now we know that velocity is the rate of change of displacement, i.e.

$$u = \frac{l}{t}$$

$$\therefore\ t = \frac{l}{u}$$

Thus the time taken to complete the process described above is given as

$$t = \frac{2l}{u_1} \quad (5.66)$$

We also know that the rate of change of momentum is defined as

$$\frac{\Delta p}{t} = \frac{mc}{t} \quad (5.67)$$

Substituting Equations (5.65) and (5.66) into (5.67) we have

$$\frac{\Delta P_x}{t} = \frac{2mc_1}{2l} \times u_1 = \frac{mc_1^2}{l} \quad (5.68)$$

We know that pressure is defined as

$$P = \frac{F}{A} \quad (5.69)$$

Force can be defined as the rate of change of momentum. Thus the force exerted on the wall *x* of the cube is given by Equation (5.68). The area *A* of the cube is l^2. Substituting this and Equation (5.68) into (5.69) we obtain

$$P = \frac{mc_1^2}{l} \times \frac{l}{l^2} = \frac{mc_1^2}{l^3} \quad (5.70)$$

From this we can now express the total pressure exerted on the face *x* by the molecules travelling in that direction as

$$P = \frac{mc_1^2 + mc_2^2 + \ldots + mc_N^2}{l^3}$$

Since all the molecules are identical, then we can factorise the above equation to obtain

$$P = \frac{m(c_1^2 + c_2^2 + \ldots + c_N^2)}{l^3} \quad (5.71)$$

Now the mean square velocity of the molecules is defined as

$$c^2 = \frac{c_1^2 + c_2^2 + \ldots + c_N^2}{N}$$

Cross-multiplying we have

$Nc^2 = u^2_1 + u^2_2 + \ldots + u^2_n$ (5.72)

Substituting Equation (5.72) into (5.71) we obtain

$$P = \frac{Nmc^2}{l^3}$$

Only an average of one-third of the molecules travel in the x-direction. Thus the actual pressure exerted by the molecules of the gas on the face x is given as

$$P = \frac{Nmc^2}{3l^3}$$

Since the volume V of the cube is l^3, then the above equation becomes

$P = \frac{Nmc^2}{3V}$ (5.73)

We now cross-multiply to obtain

$$3PV = Nmc^2$$

The term Nm represents the molar mass M, or mass of 1 mole of the gas, molecules. Thus the above equation becomes

$3PV = Mc^2$ (5.74)

Equation (5.74) is called the kinetic theory equation. For n moles of the gas we have

$$3PV = nMc^2$$

Dividing Equation (5.74) by V we obtain

$3P = \frac{Mc^2}{V}$ (5.75)

The term M/V represents the density ρ of the gas. Substituting this into Equation (5.75) yields

$$3P = rc^2$$

Finally, we can now finish it off by making c^2 the subject of the formula, and taking the square roots of both sides to obtain

$$c = \sqrt{\frac{3P}{\rho}} \quad (5.76)$$

We can as well proceed further to show that the rms velocity is independent of pressure. The density of a gas is given by

$$r = \frac{PM}{RT}$$

Substituting into Equation (5.76) we have

$$c = \sqrt{\frac{3P}{PM} \times RT} = \sqrt{\frac{3RT}{M}} \quad (5.77)$$

Example 6 The density of helium is 178.6 g dm^{-3} at STP Calculate the rms velocity of the gas at STP

Solution We have to apply the relation

$$c = \sqrt{\frac{3P}{\rho}}$$

P = 760 mmHg = 101325 kg m^{-1} s^{-2}
r = 178.6 g dm^{-3} = 178.8 kg m^{-3}
c = ?

We can now substitute to obtain

$$c = \sqrt{\frac{3 \times 101325 \cancel{kg} \times 1 m^3}{1 s^2 \times 1 m \times 178.6 \cancel{kg}}}$$

= 41.26 m s^{-1}

Example 7 What is the rms velocity of molecules of carbon dioxide at 33°C?

(C = 12, O = 16, R = 8.314 J mol^{-1} K^{-1})

Solution We have to apply the relation

$c = \sqrt{\frac{3RT}{M}}$

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 8.314 \text{ kg m}^{2} \text{ s}^{-2} \text{ K}^{-1} \text{mol}^{-1}$

$T = 33°\text{C} + 273 \text{ K} = 306 \text{ K}$

$M = 12 + (2 \times 16) = 44 \text{ g mol}^{-1} = 0.044 \text{ kg mol}^{-1}$

$c = ?$

Substituting we obtain

$$c = \sqrt{\frac{3 \times 8.314 \cancel{\text{kg}} \text{ m}^{2} \cancel{\text{mol}^{-1}} \times 306 \cancel{\text{K}}}{1\text{s}^{2} \times 1 \cancel{\text{K}} \times 0.044 \cancel{\text{kg}} \cancel{\text{mol}^{-1}}}}$$

$= 420 \text{ m s}^{-1}$

Example 8 At what temperature would the rms velocity of oxygen be three times its value at 40°C?

Solution We have to apply the relation

$$c_2 = 3c_1$$

c_1 and c_2 are the rms velocities at 40°C and the unknown temperature respectively.

So $\sqrt{\frac{3RT_2}{M}} = \sqrt{\frac{3RT_1}{M}}$

Terms appearing on both sides of the equation cancel out, so that we now obtain

$\sqrt{T_2} = 3 \times \sqrt{T_1}$

$T_1 = 40°\text{C} + 273 \text{ K} = 313 \text{ K}$

$T_2 = ?$

We now substitute to obtain

$$\sqrt{T_2} = 3 \times \sqrt{313 \text{ K}}$$

Squaring both sides we have

$T_2 = 9 \times 303 \text{ K}$

= 2820 K

Practice Problems

1. Calculate the most probable velocity of carbon dioxide at 28°C.

   (R = 8.314

   16) [*An*

2. The most probable velocity of a gas is 424.2 m s^{-1} at 30°C. What is its averag

   3.142)

   [*Answer:* 494.4 m s^{-1})

3. Calculate the rms velocity of hydrogen chloride at 27°C.

   (H = 1, Cl =

   $^{-1}$) [*Answ*

4. Calculate the temperature at which the rms velocity of carbon dioxide will b

   (C = 12, O =

   $^{-1}$) [*Ans*

5.11.2 Collision Frequency and Mean Free Path

The frequency of collisions Z of a gas is the number of collisions per cubic metre of the gas per second. The frequency of collision per molecule or collision number of the gas is given by

$$Z_1 = \sqrt{2}\pi\sigma^2 c\, \mathcal{N}$$

The total number of collisions of all molecules is given by

$$Z_{11} = \frac{1}{\sqrt{2}}\, ps^2 c\, \mathcal{N}^2$$

where p = 3.142

s = Collisions diameter or molecular diameter.

c = Average speed of molecules.

$\mathcal{N}$ = Number of molecules per cubic metre of the gas = N/V

$\mathcal{N}$ can be obtained by multiplying the number of moles of the gas by Avogadro’s number, i.e.

$$\mathcal{N} = N_A n$$

The number of moles of the gas can be obtained from the ideal gas equation, i.e.

$PV = nRT$

$\therefore\ n = \frac{PV}{RT}$

For a unit volume we have

$n = \frac{P}{RT}$

Thus $\mathcal{N} = \frac{N_A P}{RT} = \frac{P}{KT}$

where K = Boltzmann’s constant = $R/N_A = 1.38 \times 10^{-23}$ J K^{-1}

The mean free path l is the average distance travelled by the molecules of a gas between collisions. This is given as:

$$l = \frac{1}{\sqrt{2}\pi\sigma^2\mathcal{N}} = \frac{KT}{\sqrt{2}\pi\sigma^2 P}$$

The average time taken to complete two successive collisions is given by

$$t = \frac{\lambda}{c}$$

Example 1 The collision diameter of hydrogen is 2.76 Å. Calculate the frequency of collision per molecule (Collision number) and total number of collisions at 760 mm Hg and 20°C.

($R = 8.314$ J K^{-1} mol^{-1}, $K = 1.38 \times 10^{-23}$ J K^{-1}, p = 3.142, $N_A = 6.02 \times 10^{-23}$ mol^{-1}, H = 1.0)

Solution The collision number of the gas is given by the equation

$Z_1 = \sqrt{2}\pi s^2 c\mathcal{N}$

$c = \sqrt{\frac{8RT}{\pi M}}$

$R = 8.314$ kg m^2 s^{-2} K^{-1} mol^{-1}

T = 273 K + 20°C = 293 K

p = 3.142

M = (1.0 × 2) g mol^{-1} = 2.0 g mol^{-1} = 0.0020 kg mol^{-1}

c = ?

Substituting we obtain

$$c = \sqrt{\frac{8 \times 8.314\ \cancel{\text{kg}}\ \text{m}^2\ \text{s}^{-2}\ \cancel{\text{mol}^{-1}} \times 293\ \cancel{\text{K}}}{1\ \cancel{\text{K}} \times 3.142 \times 0.0020\ \cancel{\text{kg}}\ \cancel{\text{mol}^{-1}}}}$$

= 1761 m s^{-1}

$$N = \frac{N_A P}{RT}$$

N_A = 6.02 × 10^{23} mol^{-1}

P = 760 mm Hg = 1.01 × 10^{5} N m^{-2}

R = 8.314 J K^{-1} mol^{-1} = 8.314 N m K^{-1} mol^{-1}

T = 293 K

N = ?

Substituting we obtain

$$N = \frac{6.02 \times 10^{23} \times 1.01 \times 10^{5}\ \cancel{\text{N}} \times 1\ \cancel{\text{mol}} \times 1\ \cancel{\text{K}}}{1\ \cancel{\text{mol}} \times 1\ \text{m}^2 \times 8.314\ \cancel{\text{N}\ \text{m}} \times 293\ \cancel{\text{K}}}$$

= 2.50 × 10^{25} m^{-3}

Alternatively,

$$N = \frac{P}{KT}$$

K = 1.38 × 10^{-23} J K^{-1} = 1.38 × 10^{-23} N m K^{-1}

N = ?

Substituting we have

$$N = \frac{1.01 \times 10^{5}\ \cancel{\text{N}} \times 1\ \cancel{\text{K}}}{1\ \text{m}^2 \times 1.38 \times 10^{-23}\ \cancel{\text{N}\ \text{m}} \times 293\ \cancel{\text{K}}}$$

= 2.50 × 10^{25} m^{-3}

s = 2.76 Å = 2.76 × 10^{-10} m

Z_1 = ?

Finally, we now substitute into the original equation to obtain

$$Z_1 = \frac{\sqrt{2} \times 3.142 \times (2.76 \times 10^{-10}\ \mathrm{m})^2 \times 1761\ \mathrm{m\ s^{-1}} \times 2.50 \times 10^{26}}{1\ \mathrm{m^3}}$$

$$\text{Thus } Z_1 = \frac{1.49 \times 10^{10}\ \cancel{\mathrm{m^3}}\ \mathrm{s^{-1}}}{1\ \cancel{\mathrm{m^3}}}$$

$= 1.49 \times 10^{10}\ \mathrm{s^{-1}}$

The total collision frequency is obtained from the relation

$$Z_{11} = \frac{\pi\sigma^2 \bar{c} N^2}{\sqrt{2}}$$

Z_{11} = ?

All the required data have been obtained above. Substituting we obtain

$$Z_{11} = \frac{3.142 \times (2.76 \times 10^{-10}\ \mathrm{m})^2 \times 1761\ \mathrm{m\ s^{-1}} \times (2.50 \times 10^{25})^2}{1x \times (1\ \mathrm{m^3})^2 \times \sqrt{2}}$$

$$\text{Thus } Z_{11} = \frac{2.63 \times 10^{36}\ \mathrm{m^3\ s^{-1}}}{1.414\ \mathrm{m^6}}$$

$= 1.86 \times 10^{35}\ \mathrm{m^{-6}\ s^{-1}}$

Example 2 The total frequency of collision of a gas at 27°C and 1.0 atm is 1.06 × 10^{35} $\mathrm{m^{-3}\ s^{-1}}$. Calculate the effective volume of the molecule of the gas.

(R = 8.314 J $\mathrm{K^{-1}\ mol^{-1}}$, K = 1.38 × 10^{-23} J $\mathrm{K^{-1}}$, N_A = 6.02 × 0^{-23} $\mathrm{mol^{-1}}$, M = 44 g $\mathrm{mol^{-1}}$)

Solution We can conceive the molecule of a gas as a sphere having a volume

$$V = \frac{4}{3}\pi\sigma^3$$

The collision diameter can be obtained from the total collisions frequency, using the equation

$Z_{11} = \frac{\pi\sigma^2 c(N^1)^2}{\sqrt{2}}$

$c = \sqrt{\frac{8RT}{\pi M}}$

R = 8.314 kg m^2 s^{-2} K^{-1} mol^{-1}
T = 273 K + 27°C = 300 K
p = 3.142
M = 0.044 kg mol^{-1}
c = ?

Substituting we have

$$c = \sqrt{\frac{8 \times 8.314\ \cancel{kg}\ m^2 s^{-2}\ \cancel{mol^{-1}} \times 300\ \cancel{K}}{1\cancel{K} \times 3.142 \times 0.044\ \cancel{kg}\ \cancel{mol^{-1}}}}$$

= 379.9 m s^{-1}

$N = \frac{P}{KT} = \frac{N_A P}{RT}$

P = 1 atm = 1.01 × 10^5 N m^{-2}
K = 1.38 ×10^{-23} N m K^{-1}
T = 300 K
N = ?

Substituting we have

$$N = \frac{1.01 \times 10^5\ \cancel{N} \times 1\cancel{K}}{1\ m^2 \times 1.38 10^{-23}\ \cancel{N} m \times 300\ \cancel{K}}$$

= 2.44 × 10^{25} m^{-3}
Z_{11} = 1.06 × 10^{35} m^{-3} s^{-1}
p = 3.142
s = ?

Substituting we obtain

$$1.06 \times 10^{35}\ m^{-3}\ s^{-1} = \frac{3.142 \times \sigma^2 \times 379.9\ ms^{-1} \times (2.44 \times 10^{25}\ m^{-3})^2}{\sqrt{2}}$$

Cross multiplying we have

$1.50 \times 10^{35}\ \mathrm{m^{-3}\,s^{-1}} = 7.11 \times 10^{53} \times \sigma^{2}\ \mathrm{m^{-5}\ s^{-1}}$

Thus s^2 = $\dfrac{1.50 \times 10^{35}\ \mathrm{m^{-3}}\ \cancel{\mathrm{s^{-1}}}}{7.11 \times 10^{53}\ \mathrm{m^{-5}}\ \cancel{\mathrm{s^{-1}}}}$

$= 2.11 \times 10^{-19}\,\mathrm{m^2}$

We now take the square roots of both sides to obtain

s = $\sqrt{2.11 \times 10^{-19}\,\mathrm{m^2}}$

$= 4.59 \times 10^{-10}$ m

V = ?

Finally, we can now substitute into the original equation to obtain

$V = \dfrac{4}{3} \times 3.142 \times (4.59 \times 10^{-10}\ \mathrm{m})^3$

$= 4.05 \times 10^{-28}\,\mathrm{m^3}$

Example 3 The molecular diameter of nitrogen is 375 pm. Calculate the mean free path for the gas at 37°C and 0.30 atm. Hence determine the average time between successive collisions.

(R = 8.314 J K^{-1} mol^{-1}, K = 1.38 × 10^{-23} J K^{-1}, p = 3.142, N = 14)

Solution We have to apply equation

l = $\dfrac{KT}{\sqrt{2}\pi\sigma^2 P}$

K = 1.38 × 10^{-23} N m K^{-1}

T = 273 K + 37°C = 310 K

p = 3.142

s = 375 pm = 3.75 × 10^{-10} m

P = 0.30 atm = 3.0 × 10^{4} N m^{-2}

l = ?

We now substitute to obtain

l = $\dfrac{1.38 \times 10^{-23}\ \cancel{\mathrm{N}}\ \mathrm{m} \times 310\ \cancel{\mathrm{K}} \times 1\ \mathrm{m^2}}{\sqrt{2} \times 3.142 \times (3.75 \times 10^{-10}\ \mathrm{m})^2 \times 3.0 \times 10^4\ \cancel{\mathrm{N}} \times 1\ \cancel{\mathrm{K}}}$

Then l = $\frac{4.28 \times 10^{-21}\ \mathrm{m}^3}{1.9 \times 10^{-14}\ \mathrm{m}^2}$

= 2.3×10^{-7} m = 230 nm

The average time between collisions is given by

$$t = \frac{\lambda}{c}$$

We have to obtain the average velocity from the relation

$c = \sqrt{\frac{8RT}{\pi M}}$

M = (2 × 14) g mol^{-1} = 28 g mol^{-1} = 0.028 kg mol^{-1}

R = 8.314 kg $\mathrm{m}^2\mathrm{s}^{-2}$ K^{-1} mol^{-1}

T = 310 K

p = 3.142

c = ?

Substituting we obtain

$c = \sqrt{\frac{8 \times 8.314\ \cancel{\mathrm{kg}}\ \mathrm{m}^2\ s^{-2}\ \cancel{\mathrm{mol}^{-1}} \times 310\ \cancel{\mathrm{K}}}{1\ \mathrm{mol} \times 1\ \cancel{\mathrm{K}} \times 3.142 \times 0.028\ \cancel{\mathrm{kg}}\ \cancel{\mathrm{mol}^{-1}}}}$

= 484.1 m s^{-1}

l = 2.30 $\times 10^{-7}$ m

t = ?

Finally, we now substitute to obtain

$t = \frac{2.3 \times 10^{-7}\ \cancel{\mathrm{m}} \times 1\ s}{484.1\ \cancel{\mathrm{m}}}$

= 4.8×10^{-10} s = 480 ps

Example 4 The mean free path of oxygen at 47°C is 605 nm. What is the pressure of the gas, given that its molecular diameter is 3.61 Å?

(K = 1.38×10^{-23} J K^{-1}, p = 3.142)

Solution We have to determine the pressure from the relation l $= \frac{KT}{\sqrt{2}\pi\sigma^2 P}$

l $= 605$ nm $= 6.05 \times 10^{-7}$ m

$T = 273$ K + 47°C = 320 K

$K = 1.38 \times 10^{-23}$ N m K^{-1}

s $= 3.61$ Å $= 3.61 \times 10^{-10}$ m

p $= 3.142$

$P = ?$

Substituting we obtain

$$6.05 \times 10^{-7}\text{ m} = \frac{1.38 \times 10^{-23}\text{ N m} \times 320\,\cancel{\text{K}}}{\sqrt{2} \times 3.142 \times (3.61 \times 10^{-10}\text{ m})^2 \times P \times 1\,\cancel{\text{K}}}$$

Thus $6.05 \times 10^{-7}\text{ m} = \frac{4.4 \times 10^{-21}\text{ N m}}{5.79 \times 10^{-19}\text{ m}^2}$

Cross-multiplying we have

4.4×10^{-21} N m $= 3.50 \times 10^{-25}$ m^3

So $P = \frac{4.4 \times 10^{-21}\text{ N m}}{3.50 \times 10^{-25}\text{ m}^3}$

$= 1.3 \times 10^{4}$ N m^{-2}

Practice Problems

1. The collision diameter of oxygen is 361 pm. Calculate its collision number and total frequency of collisions at 0°C and 1 atm.

   ($R = 8.314$ J K^{-1} mol^{-1}, $K = 1.38 \times 10^{-23}$ J K^{-1}, p = 3.142, O = 16)

   [*Answers:* 6.6×10^{9} s^{-1}, 8.8×10^{34} m^{-3} s^{-1}]

2. Calculate the mean free path of hydrogen at 30°C and 760 Torr, given that the collision diameter of the gas is 276 pm; hence determine the average time between collisions.

   ($R = 8.314$ J K^{-1} mol^{-1}, $K = 1.38 \times 10^{-23}$ J K^{-1}, p = 3.142, O = 16)

   [*Answers:* 122 nm, 270 ps]

SUMMARY

- Gas pressure is the force exerted by the molecules of a gas per unit area of a vessel in which it is confined.
- Dalton’s law of partial pressure states that, in a mixture of gases that do not react chemically together, the total pressure of the mixture of gases is the sum of the individual pressures or partial pressures of its constituent gases, i.e.

$$P_t = P_1 + P_2 + P_3 + \ldots + P_n$$

- Boyle’s law states that the volume of a gas is inversely proportional to its pressure provided the temperature remains constant. It is given by

$$P_1V_1 = P_2V_2, \text{ etc.}$$

- Charles’s law states that the volume of a gas is directly proportional to its absolute temperature provided the pressure remains constant. It is given by

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}, \text{ etc.}$$

- The general gas equation is obtained by combining Boyle’s and Charles’s laws. It is given by

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

- The ideal gas equation or equation of state for perfect (ideal) gases shows the relationship between the volume, amount, temperature and pressure of an ideal gas. It is given by

$$PV = nRT$$

- Gases deviate from the ideal behaviour at high pressure and low pressure due to the effect of intermolecular forces. Several equations of state have been proposed for real gases.
- The critical temperature of a gas is the temperature above which it cannot be liquefied by mere compression.
- The Boyle temperature of a gas is the temperature at which it behaves almost like an ideal gas. It is given as

$$T_B = \frac{a}{bR} = \frac{27T_c}{8}$$

- A reduced state property is obtained by dividing the property by the corresponding critical property of the gas.

- The principle of corresponding states that two or more substances are in corresponding states if they have the same reduced pressure, temperature and volume.
- Gay-Lussac’s law of combining volumes states that when gases react, they do so in volumes which are simple ratios to one another and to the volume of the products, if gaseous, provided the temperature and pressure remain constant.
- The molar volume of a gas is the volume occupied by 1 mol of a gas at STP It is numerically equal to 22.4 $dm^3 mol^{-1}$.
- The vapour density of a gas is the number of times a volume of that gas is as heavy as the same volume of hydrogen at a particular temperature and pressure. It is given as

$$\text{V.D.} = \frac{1}{2} \times M_r$$

- Diffusion is the movement of the particles of a substance from the region of higher concentration to that of a lower concentration.
- The rate of diffusion of a gas is the volume of a gas diffusing per second. It is given as

$$R = \frac{V}{t}$$

- Graham’s law of diffusion of gases states that the rate of diffusion of a gas is inversely proportional to the square root of its density or molar mass, provided the temperature and pressure remain constant. The relative time required for the same volume of two different gases to diffuse under the same conditions is given by

$$\frac{t_2}{t_1} = \frac{R_1}{R_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_{r2}}{M_{r1}}}$$

- The mole fraction of a gas in a mixture of gases is its partial pressure divided by the total pressure of the mixture. It’s given as

$$x_i = \frac{n_i}{n_t} = \frac{P_i}{P_t}$$

- The most probable velocity of a gas is the velocity of the maximum number of molecules of a gas at a particular temperature. It is given as

$$c_P = \sqrt{\frac{2RT}{M}}$$

- The average velocity of a gas is the average velocity of the molecules of the gas. It is given as

$$c = \sqrt{\frac{8RT}{\pi M}}$$

- The root-mean-square (rms) velocity of a gas is the square root of the mean or average of the squares of the velocities of its molecules at a particular temperature. It is given as

$$c = \sqrt{\frac{3RT}{M}}$$

- The frequency of collisions of a gas is the number of collisions per cubic metre of a gas per second. It is given as

$$Z_l = \sqrt{2} ps^2 N$$

- The total number of collisions of all molecules of a gas is given by

$$Z_{11} = \frac{1}{\sqrt{2}} ps^2 c N^2$$

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. Which of these is true of ideal gases?
   A. They exert pressure.
   B. Their rates of diffusion are slower than those of liquids.
   C. The cohesive forces between the molecules is very high.

D. They do not confirm to Boyle’s law.

E. Their molecules cannot translate.

2. Which of these is **NOT** true of ideal gases?

A. They exert pressure.

B. Their volumes reduce with pressure.

C. Their volumes increase with temperature at constant pressure.

D. They have a volume of 22.4 dm^3 at STP

E. None of the above.

3. What is 850 mmHg in atm?

A. 0.99 atm B. 1.1 atm

C. 1.2 atm D. 1.3 atm

E. 1.5 atm

4. What is the value of 1.35×10^3 N m^{-2} in Torr?

A. 10.1 Torr B. 10.5 Torr

C. 11.2 Torr D. 15.7 Torr

E. 18.2 Torr

5. What is the actual pressure of oxygen if it’s collected over water at 790.0 mmHg and 10°C?

(SVP of water at 10°C = 9.2 mmHg)

A. 760.0 mmHg B. 780.8 mmHg

C. 790.0 mmHg D. 799.2 mmHg

E. 800.0 mmHg

6. Hydrogen was collected over water at 15°C. What is the saturated vapour pressure of water at 15°C if the pressures of the wet and dry hydrogen are 772.7 mmHg and 760.0 mmHg respectively?

A. 12.7 mmHg B. 15.5 mmHg

C. 30 mmHg D. 1123.2 mmHg

E. 1532.7 mmHg

7. A gas has a volume of 200.0 cm^3 at 770 mmHg by what factor would its volume decrease if the pressure is tripled at constant temperature?

A. 3 B. 4

C. 5 D. 7

E. 8

8. What is the pressure of a gas when its volume is 50.0 cm^3, given that its volume is 27.7 cm^3 at 615 mmHg and constant temperature?

A. 315 mmHg B. 320 mmHg

C. 341 mmHg D. 400 mmHg

E. 420 mmHg

9. What would be the volume of 250.0 cm^3 of a gas if its temperature is increased from 20°C to 27°C at constant pressure?

A. 250 cm^3 B. 256 cm^3

C. 275 cm^3 D. 280 cm^3

E. 300 cm^3

10. Which of these is the SI unit of temperature?

A. F B. K

C. °C D. °K

E. °R

11. What is the temperature of gas at STP?

A. −274°C B. 273 K

C. 273 °C D. 280°C

E. 280 K

12. The ideal gas equation is given as $PV = nRT$. What does R represent?

A. Rate of diffusion B. Volume

C. Molar gas constant D. Pressure

E. Molar volume

13. What is the amount of 7.47 dm^3 of oxygen at STP?

A. 0.12 mol B. 0.33 mol

C. 0.35 mol D. 0.40 mol

E. 0.50 mol

(Molar volume of gases at STP = 22.4 dm^3 mol^{-1})

14. Which of the following gases would have the slowest rate of diffusion under the same conditions?

(i) SO_2 (ii) N_2O (iii) NH_4 (iv) CH_4 (v) CO_2

A. CO_2 B. NH_4

C. SO_2 D. N_2O

E. CH_4

15. Which of these would diffuse the fastest?

(i) gold (ii) mercury (iii) turpentine (iv) hydrogen chloride (v) ethanol

A. Gold B. Mercury

C. Turpentine D. Hydrogen chloride

E. Ethanol

16. How long will it take 300.0 cm^3 of a gas to diffuse if its rate of diffusion is 0.920 $cm^3 s^{-1}$?

A. 300 s B. 320 s

C. 325 s D. 326 s

E. 350 s

17. Equal volume of all gases contains the same number of molecules at the same temperature and pressure. This is a statement of

A. Avogadro’s law B. Gay-Lussac’s law

C. Charles’s law D. Gauss’ law

E. Boyle’s law

18. Which scientist discovered the relationship between the rate of diffusion of a gas and its density?

A. Boyle B. Graham

C. Gay-Lussac D. Avogadro

E. Newton

19. Which of the following is the van der Waals’ equation for *n* moles of a real gas?

A. $\left(P + \frac{an^2}{V^2}\right)[V - nb] = nRT$

B. $\left(P + \frac{a^2n^2}{V^2}\right)(V - nb) = nRT$

C. $\left(P + \frac{a^2}{V^2}\right)(V - nb) = nRT$

D. $\left(P + \frac{n^2}{V^2}\right)(nV - b) = nRT$

E. $\left(P + \frac{n^2}{V^2}\right)(V - n^2 b) = nRT$

20. What is the rms velocity of oxygen STP?

(R = 8.314 J K^{-1} mol^{-1}, O = 16)

A. 131 m s^{-1} B. 133 m s^{-1}

C. 206 m s^{-1} D. 450 m s^{-1}

E. 461 m s^{-1}

21. Which of these does **NOT** affect the rms velocity of a gas?

A. Pressure B. Temperature

C. Molecular mass D. Density

E. None of the above

22. Which of these statements is correct?

A. The rms velocity of a gas molecule is directly proportional to its relative molecular mass.

B. The rms velocity of a gas is independent of pressure.

C. The rms velocity of a gas is directly proportional to the square root of pressure.

D. The rms velocity of a gas is inversely proportional to the square root of its molar mass.

E. The temperature of a gas increases by a factor of 2 when its rms velocity is increased by a factor of 4.

23. The critical temperature of ethane is 282.4 K. At which of the following temperatures would it not be possible to liquefy the gas by compression?

A. 190.0 K B. 250.5 K

C. 280.0 K D. 282.1 K

E. 285.1 K

24. Which of the following is/are **TRUE** of an ideal gas?

i. Momentum is conserved during the collision of its molecules.

ii. Cohesive forces between the molecules are very high.

iii. The volume of the molecules is negligible.

iv. An increase in temperature increases the average kinetic energy of the molecules.

A. i and ii B. i and iv

C. iii and iv D. iv only

E. ii and iii

25. At what temperature would the most probable speed of oxygen be 500.0 m s^{-1}?

(R = 8.314 J K^{-1} mol^{-1}, O = 16.0)

A. 400 K B. 402.5 K

C. 479 K D. 481 K

E. 485 K

26. At what temperature would the average speed of chlorine double its most probable speed at 27°C?

(R = R = 8.314 J K^{-1} mol^{-1}, Cl = 35.5)

A. 273 K B. 236 K

C. 300 K D. 800 K

E. 943 K

27. What is the average velocity of a gas whose mean free path is 4.62×10^{-7} m if the average time between collisions is 4.35×10^{-10} s?

A. 100 m s^{-1} B. 1050 m s^{-1}

C. 1060 m s^{-1} D. 1200 m s^{-1}

E. 3200 m s^{-1}

28. The correct unit of the frequency of collisions per molecule is

A. $m^3 s^{-1}$ B. s^{-1} cm^3

C. m s^{-1} D. m s^{-1}

E. None of the above

29. A molecule of a gas occupies a volume of 3.97×10^{-28} m^3. What is the molecular diameter of the gas?

A. 2.08×10^{-19} m B. 8.25×10^{-11}

C. 2.51×10^{-10} m D. 4.56×10^{-10} m

E. 7.35×10^{-10} m

30. Which of these is **NOT** a unit of pressure?

A. cP B. kg m s^{-1}

C. Pa s D. N s m^{-2}

E. None of the above

31. Which of the following are **TRUE** of atmospheric pressure?

i. It increases with altitude.

ii. It decreases with altitude.

iii. The relative atmosphe pressure between two altitudes increases with temperature.

iv. The atmospheric pressure at the sea level is 760 Torr.

A. i and ii B. ii and iii

C. i and iv D. ii and iv

E. iii and iv

32. Which of the following is/are **TRUE** of a real gas?

i. Its second virial coefficient is negligible.

ii. Its compressibility factor is almost unity.

iii. It behaves almost like an ideal gas.

iv. It deviates markedly from the ideal behaviour when its temperature is far from the Boyle temperature.

A. i and ii B. iv only

C. ii and iii D. iii and iv

E. All of the above

33. The critical temperature of ammonia is 405 K. At what temperature would its volume obtained using the ideal gas equation be closest to that obtained using the van der Waals' equation?

A. 405 K B. 812 K

C. 1000 K D. 1320 K

E. 1370 K

34. The van der Waals constants of air are 1.4 dm^6 atm mol^{-2} and 0.039 dm^3 mol^{-1}. At which of the following temperatures would it not be possible to liquefy air by compression?

A. 1050 K B. 2500 K

C. 3300 K D. 3320 K

E. 3325 K

35. The critical molar volume of hydrogen is 65.6 cm^3 mol^{-1}. Which of these is an estimate of its van der Waals constant?

A. 0.0201 $dm^3 mol^{-1}$ B. 0.0218 $dm^3 mol^{-1}$

C. 0.0219 $dm^3 mol^{-1}$ D. 0.0263 $dm^3 mol^{-1}$

E. 0.0403 $dm^3 mol^{-1}$

36. The reduced pressure of methane is 1.10 at 50.0 atm. What is the critical pressure of the gas?

A. 40.0 atm B. 40.0

C. 42.5 atm D. 45.5 atm

E. 45.5

37. The reduced volume of neon was obtained to be 0.475. What is the molar volume of the gas if its van der Waals constant is 0.0170 $dm^3 mol^{-1}$?

A. 19.7 $cm^3 mol^{-1}$ B. 20.0 $cm^3 mol^{-1}$

C. 21.9 $cm^3 mol^{-1}$ D. 24.2 $cm^3 mol^{-1}$

E. 25.5 $cm^3 mol^{-1}$

ESSAY TYPE QUESTIONS

Gas pressure

38. (a) State Dalton’s law of partial pressure.

(b) A mixture of three gases has a total pressure of 1015 mmHg. Calculate the pressure of the third gas if the partial pressures of two of the gases are 330 mmHg and 550 mmHg.

39. What is atmospheric pressure? Explain how it varies with altitude.

40. Derive the barometric formula

$$\ln\left(\frac{P_h}{P_0}\right) = -\frac{Mgh}{RT}$$

41. Calculate the atmospheric pressure on a mountain that is 5.0×10^3 m above the sea level at 27°C. The atmospheric pressure at the sea level is 1.0 atm. The effect of other factors may be neglected.

($R = 8.314$ J K^{-1} mol^{-1}, $g = 9.8$ m s^{-2}, molar mass of air = 29 g mol^{-1})

42. At what altitude above the sea level would the atmospheric pressure be as low as 0.38 atm at 25°C if the pressure at the sea level is 1.0 atm? The effect of other factors may be neglected.

($R = 8.314$ J K^{-1} mol^{-1}, $g = 9.8$ m s^{-2}, molar mass of air = 29 g mol^{-1})

Gas laws

43. (a) The following table shows the result obtained during an experiment on the relationship between the volume and pressure of a gas at constant temperature.

Pressure (mmHg)	760	750	740	730	720	710	700
Volume (cm^3)	300.0	304.0	308.1	312.3	316.6	321.1	325.7

(i) Plot the graph of pressure against the reciprocal of the volume.

(ii) What is the slope of the graph?

(iii) From the graph, determine the volume of the gas at 692 mmHg.

(iv) From the graph, determine the pressure of the gas when its volume is 310 cm^3.

(v) Which gas law does the graph verify?

44. A gas has a volume of 450 cm^3 at 740 mmHg and −3°C. What would be the volume of the gas if the pressure is halved at constant temperature?

45. How many moles of methane are there in 553 cm^3 of the gas at 2.7 atm and –50°C if it behaves as an ideal gas?

(R = 0.082 atm dm^3 K^{-1} mol^{-1})

Critical constants of gases and equations of state for real gases

46. What do you understand by critical temperature? Hence explain the critical constants of a gas.

47. Starting from the van der Waals' equation, derive an equation for:

(a) Critical pressure;

(b) Critical molar volume;

(c) Critical temperature.

48. (a) What is Boyle temperature?

(b) What is compressibility factor?

(c) Calculate the Boyle temperature of a gas whose van der Waals constant is 0.027 dm^3 mol^{-1} if its critical pressure is 12.8 atm.

(R = 0.08206 dm^3 atm K^{-1} mol^{-1})

49. (a) Why do you think it was necessary to modify the ideal gas equation in order to be applicable to real gases? Hence suggest a reason why many equations of state have been developed for real gases.

(b) Express the Redlich-Kwong equation in the form of a cubic equation.

50. Calculate the critical constants of a gas whose van der Waals constants are 4.47 dm^3 atm mol^{-2} and 0.057 dm^3 mol^{-1}.

(R = 0.08206 dm^3 atm K^{-1} mol^{-1})

51. What are the van der Waals constants of a gas whose critical molar volume and pressure are 127.4 cm^3 mol^{-1} and 50.5 atm respectively.

(R = 0.08206 dm^3 atm K^{-1} mol^{-1})

52. Calculate the volume occupied by 2.5 moles of hydrogen at 0°C and 100.0 atm by treating it as a van der Waals gas. The van der Waals constant b is 0.027 dm^3 mol^{-1}. You may neglect the term an^2/V^2.

(R = 8.314 J K^{-1} mol^{-1})

53. Starting from the van der Waals' equation, show that the Boyle temperature of a gas is given by

$$T_B = \frac{a}{bR}$$

54. Express the van der Waals' equation in the form of a cubic equation.

55. Calculate the molar volume of carbon dioxide at 0°C and 100.0 atm. The van der Waals constants of the gas are 3.59 dm^6 atm mol^{-2} and 0.043 dm^3 mol^{-1}.

(R = 8.314 J K^{-1} mol^{-1})

56. Calculate the molar volume of oxygen at 100.0°C and 0.500 atm by treating it as a van der Waals gas. The van der Waals constant of the gas is 1.36 dm^6 atm mol^{-1}. At low pressure, the volume would be very large such that b may be ignored.

(R = 8.314 J K^{-1} mol^{-1})

57. The molar volume of hydrogen is 2.49 × 10^{-3} m mol^{-1} at a pressure of 10.0 atm and 27°C. Estimate the radius of the hydrogen atom by treating it as a van der Waals gas. The term a/V^2 may be neglected.

(H = 1, R = 8.314 J K^{-1} mol^{-1}, p = 3.14, N_A = 6.02 × 10^{23} mol^{-1})

58. Show that the critical compressibility factor of a van der Waals gas is 0.375.

59. Calculate the temperature at which 100.0 moles of air will exert a pressure of 100.0 atm when confined in a 55.00-dm^3 cylinder, given that air is a van der Waals gas.

(R = 0.0821 dm^3 atm mol^{-1} K^{-1}, a = 1.4 dm^6 atm mol^{-2}, b = 0.039 dm^3 mol^{-1})

Reduced state properties and the principle of corresponding states

60. (a) What is a reduced state variable?

(b) Derive the reduced form of the van der Waals' equation.

61. At what temperature and pressure would methane be in corresponding state with water vapour at 100.0 atm and 500.0 K? The critical constants of methane are P_c = 45.6 atm and T_c = 190.6 K. Those of water vapour are P_c = 218.3 atm, T_c = 647 K.

62. Use the reduced form of the van der Waals' equation to estimate the molar volume of ethane at 100.0 atm and 250°C. The critical constants of the gas are P_c = 50.5 atm, $V_{m,c}$ = 127.4 cm^3 mol^{-1} and T_c = 282.1 K.

Molar volume of gases at STP

63. 27.7 g of calcium carbonate was heated until it decomposes completely at STP What is the volume of the gas produced at 3°C and 840 mmHg?

(Molar volume of gases at STP = 22.4 $dm^3 mol^{-1}$, C = 12, O = 16, Ca = 40)

Diffusion of gases

64. 500.0 cm^3 of a gas having a vapour density of 16 diffuses through a porous partition in 30 min. What volume of hydrogen would diffuse through the same porous partition within this time frame, if the conditions are constant?

(H = 1)

65. 300.0 cm^3 of a gas x diffuses twice as fast as another gas y. What is the relative molecular mass of y if that of x is 4?

66. 400.0 cm^3 of carbon dioxide diffuses through a porous partition in 1.0 hour. How long would it take 400 cm^3 of another gas with the relative molecular mass of 36.5 to diffuse through the same porous partition?

(C = 12, O = 16)

Mole fraction

67. Show that the partial pressure of a gas can be expressed as

$$P_i = x_i P_t$$

where x_i = Mole fraction.

P_t = Total pressure.

68. (a) In a mixture of three gases, two gases have mole fractions of 0.15 and 0.55. What is the mole fraction of the third gas?

(b) Air contains 21 g of oxygen and 78 g of nitrogen per 100 g of air. Calculate the partial pressure of each gas when the atmospheric pressure is 760 Torr, assuming the masses of other constituents are negligible.

(N = 14, O = 16)

69. A vessel contains 5.0 g of methane, 10.0 g of ethane and 3.7 g of propane. If the total pressure of the mixture is 1.1 atm, calculate

(a) the mole fraction of each gas;

(b) the partial pressure of each gas.

(H = 1, C = 12)

70. A mixture of three gases has a pressure of 800.0 mmHg. The partial pressures of two of the gases are 350 mmHg and 150 mmHg. Calculate the mole fraction of each gas.

71. A mixture of gases containing 1.5 g of benzene vapour, 2.00 g of ethene and 0.30 g of neon was confined in a 2.00-dm^3 vessel at 15°C. Calculate

(a) the partial pressure of each gas;

(b) the mole fraction of each gas.

(H = 1, C = 12, Ne = 20, $R = 62.4\ dm^3\ Torr\ K^{-1}\ mol^{-1}$)

72. A vessel contains five gases whose partial pressures are 100.0 kPa, 50.0 kPa, 72.5 kPa, 95.0 kPa and 80.5 kPa. What is the mole fraction of each gas?

The kinetic theory of gases

73. (a) State the basic postulates of the kinetic theory of gases.

(b) Why do you think gases do not actually behave like the ideal gases?

74. Water vapour is at a temperature of 2050 K. Calculate

(a) its most probable velocity;

(b) its rms velocity;

(c) its average velocity.

(H = 1, O = 16, $\pi = 3.14$)

75. The most probable speed of a gas is 326.5 m s^{-1} at 500.0 K. Calculate its most probable speed at 730 K.

(H = 1, O = 16, $R = 8.314\ J\ K^{-1}\ mol^{-1}$)

76. At what temperature would the average speed of oxygen be equal to that of hydrogen at –50°C?

(H = 1.0, O = 16.0, $R = 8.314\ J\ K^{-1}\ mol^{-1}$)

77. (a) Calculate the rms velocity of carbon tetrachloride (CCl_4) at 20°C.

(C = 12, Cl = 35.5, R = 8.314 J K^{-1} mol^{-1})

(b) Calculate the temperature at which the rms velocity of carbon dioxide is 171.8 ms^{-1}.

(C = 12, O = 16, R = 8.314 J K^{-1} mol^{-1})

78. (a) At what temperature would the rms velocity of helium be half its rms velocity at STP?

(He = 4.00, R = 8.314 J K^{-1} mol^{-1})

(b) Prove that the rms velocity of a gas molecule is given by

$$c = \sqrt{\frac{3RT}{M}}$$

where T = The absolute temperature of a gas.

R = Universal gas constant.

M = The molecular mass of a gas.

79. Briefly explain the following:

(a) Collisions frequency.

(b) Mean free path.

80. The collision diameter of carbon dioxide is 4.59 Å at 890 Torr and 37°C. Calculate

(a) the frequency of collisions per molecule;

(b) the total frequency of collision.

(C = 12, O = 16, p = 3.14, R = 8.314 J K^{-1} mol^{-1}, $K = 1.38 \times 10^{-23}$ J K^{-1})

81. The total collisions frequency of methane is 4.39×10^{35} m^{-3} s^{-1} at 27°C. What is the pressure exerted by the gas if the collisions diameter is 4.14 Å?

(R = 8.314 J K^{-1} mol^{-1}, p = 3.14, $K = 1.38 \times 10^{-23}$ J K^{-1}, H = 1, C = 12)

82. The collisions frequency of per molecules of oxygen was measured to be 3.42×10^{9} s^{-1} at 1.7 atm and 27°C. What volume would be occupied by 1.5 mol of the gas under this conditon?

(R = 8.314 J K^{-1} mol^{-1}, p = 3.14, $K = 1.38 \times 10^{-23}$ J K^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1}, O = 16)

83. What is the mean free path of argon at 10.0 atm and 0°C, given that its molecular diameter is 396 pm; hence determine the average time between collisions.

(R = 8.314 J K^{-1} mol^{-1}, p = 3.14, $K = 1.38 \times 10^{-23}$ J K^{-1}, Ar = 40)

84. The free mean path of a gas is 1.93×10^{-7} m at 27°C and an unknown pressure. What is the mean free path of the gas at 57°C if the gas is maintained at the same pressure?

85. The mean free path of nitrogen is 2.97×10^{-8} m at 47°C. What is the pressure exerted by the gas, given that its collisions diameter is 375 pm?

$(K = 1.38 \times 10^{-23}\text{ J K}^{-1}, p = 3.142,)$

86. The mean free path of carbon dioxide is 7.37×10^{-10} m at 100.0 atm. What is the temperature of the gas?

$(K = 1.38 \times 10^{-23}\text{ J K}^{-1}, s = 456\text{ pm}, p = 3.14)$

Answers

1. A 2. B 3. B 4. A 5. B 6. A
7. A 8. C 9. B 10. B 11. B 12. C
13. B 14. C 15. D 16. D 17. A 18. B
19. A 20. E 21. A 22. D 23. E 24. B
25. D 26. E 27. C 28. E 29. D 30. A
31. D 32. B 33. E 34. E 35. C 36. D 37. D 41. 0.27 atm 42. 8400 m
43. (e) Boyle's law 44. 900 cm^3 45. 0.082 mol
48. (c) 114 K
50. $V_{m,c}$: 0.17 dm^3 , P_c: 51 atm, T_c: 5000 K,
51. a: 2.46 dm^6 atm mol^{-2}, b: 0.0425 dm^3 mol^{-1}
52. 0.62 dm^3 55. 0.0697 dm^3 56. 61.2 dm^3
57. 141 pm 59. 650 K 61. 147.3 K and 20.9 atm
62. 288 cm^3 mol^{-1} 63. 5.68 dm^3 64. 2000 cm^3
65. 16 66. 66 s
68. (a) 0.30
(b) O_2: 140 Torr, N_2: 620 Torr
69. (a) Methane: 0.43, ethane: 0.46, propane: 0.12
(b) methane: 0.47 atm, ethane: 0.51 atm, propane: 0.13 atm
70. 0.44, 0.19, 0.38
71. (a) Benzene: 170 Torr, ethane, 640 Torr, neon: 130 Torr
(b) Benzene: 0.18, ethane: 0.68, neon: 0.14

72. 0.215, 0.126, 0.182, 0.239, 0.202 respectively

74. (a) 1380 ms^{-1} (b) 1690 ms^{-1}
(c) 1550 ms^{-1}

75. 390 ms^{-1} 76. 3570 ms^{-1}

77. (a) 218 ms^{-1} (b) 52 K

78. (a) 68.3 K

80. (a) 1.0×10^{11} s^{-1} (b) 1.4×10^{35} m^{-3} s^{-1}

81. 1.8×10^{5} Pa 82. 3.2×10^{-5} m^{3}

83. 5.36 nm, 141 ns 84. 2.1×10^{-7} m

85. 2.4×10^{5} Pa 86. 498 K

6

Chapter The Solid and Liquid States

The molecules of solids are held together by very strong intermolecular forces that permit no translational movements. Thus the molecules of solids can only vibrate about a fixed position. When the temperature of a solid is raised, the intermolecular forces are weakened and the molecules become more agitated. At a particular temperature, the intermolecular forces are so weakened that the rigid structure of the solid collapses, such that the molecules can now undergo translational movement characteristic of fluids. This process is called melting, and the temperature at which this occurs is called melting point.

The melting points of ice and sodium chloride, for example, are 0°C and 801°C respectively. The reverse of this process is called freezing or solidification, and the temperature at which this occurs is called freezing point. The freezing and melting points of a substance are equal. The freezing points of water and sodium chloride, for example, are 0°C and 801°C respectively.

One way of classifying solids is to consider the ways in which their particles (molecules, ions or atoms) are arranged. A crystalline solid is one in which the constituent particles are arranged in a regular pattern. Such a solid is called a crystal. Examples of crystalline solids include metals, sodium chloride, diamond, graphite, potassium chloride, etc. On the other hand, an amorphous solid is one whose constituent particles are not arranged in any regular pattern. Examples include butter, rubber, plastic, etc.

Another way of classifying solids is based on the nature of bonding between their particles. On this basis a solid can be metallic, ionic, molecular or covalent network. Metals consist of cations that are held together by a sea of electrons, e.g., aluminium, sodium, copper, etc. All metals are good conductors of heat and electricity. Ionic solids consist of cations and anions that are held together by electrostatic force of attraction, e.g., sodium chloride, sodium nitrate, calcium chloride, etc. Ionic solids are strong electrolytes. A network solid consists of atoms that are covalently linked throughout its extent, e.g., carbon, boron, silicon dioxide, etc. Network solids have high melting and boiling points, and can neither conduct electricity nor heat. Molecular solids consist of molecules, e.g., naphthalene, ice, sulphur, etc. Molecular solids have low melting and boiling points, and can neither conduct electricity nor heat.

The molecules of liquids are closely held together by intermolecular forces which are not as strong as those found in solids. Thus the molecules of liquids can undergo translational motion in addition to vibrational movement. Because of their nature, liquids usually assume the shape of the container into which they are poured. When a liquid is heated, its intermolecular forces become weakened. The attractive forces may become so low that molecules escape from the surface of the liquid, i.e., translate to the gaseous state. This process is called vaporisation or evaporation.

Vaporisation occurs at all temperatures, but increases with temperature. Vaporisation also depends on the nature of a liquid. A volatile substance, such as methylated spirit, vaporises easily. On the other hand, water does not, as it contains hydrogen bonding. Hydrogen bonding are strong intermolecular forces arising from the covalent linking of hydrogen with highly electronegative elements like nitrogen or fluorine. This gives rise to the formation of a dipole in which the hydrogen atom is partially positive, and the other element partially negative.

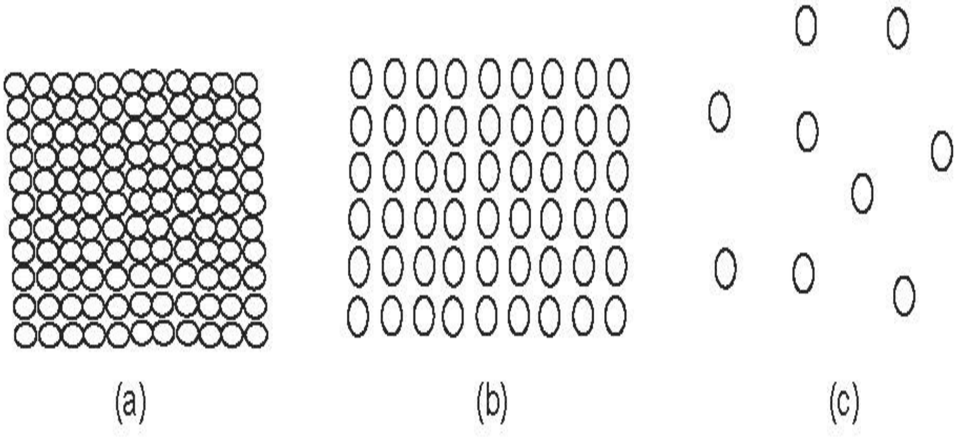

(a) (b) (c)

Figure 6.1 The states of matter showing how the molecules are separated.

6.1 VAPOUR PRESSURE AND CHANGE OF STATE

The pressure exerted by the vapour of a liquid is called its vapour pressure. The vapour pressure when the liquid and its vapour are in dynamic equilibrium is called saturated vapour pressure. A situation whereby two phases (or states) of a substances are in dynamic equilibrium is called phase equilibrium. Dynamic equilibrium refers to a situation in which two opposite process are occurring at the same rate. For example, if the rate at which the vapour of a liquid is being formed is equal to the rate at which the vapour condenses back into the liquid, then the system is said to be in dynamic equilibrium.

A phase diagram is a graphical representation of the behaviour or states (solid, liquid and gas) of a substance under different conditions of temperature and pressure. A point on this graph at which the three phases or states are in dynamic equilibrium is called the triple point of the substance. This corresponds to the point at which the lines representing the three states coincide.

The boiling point T_b of a liquid is the temperature at which its vapour pressure equals the prevailing atmospheric pressure. Thus the higher the atmospheric pressure, the higher the temperature at which a liquid boils. The normal boiling point of a liquid is the boiling point when the atmospheric pressure is exactly 1 atm. The normal boiling points of water and ethanol, for example, are 100°C and 78°C respectively. The high boiling point of water, in spite of its low molecular mass, can be attributed to hydrogen bonding.

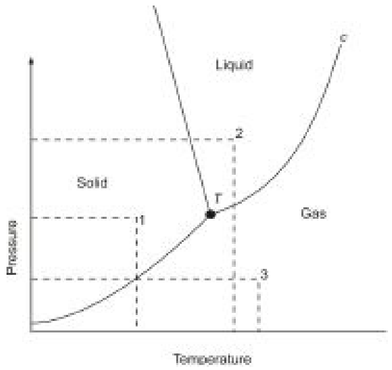


Figure 6.2 A typical phase diagram. The state of a substance at any temperature and pressure can be obtained by tracing them on the diagram, as indicated by points 1, 2 and 3. Two states are in equilibrium along each of the three lines. The three states are in equilibrium at the triple point, marked *T* on the diagram.

An approximate value for the standard heat of vaporisation of a liquid that does not involve hydrogen bonding can be obtained from its normal boiling point, using Trouston’s rule; which states that the molar entropy of vaporisation of a liquid is approximately equal to 85 J K^{-1} mol^{-1}, i.e.

$$\frac{\Delta H_v^\circ}{T_b} = 85 \text{ J K}^{-1} \text{ mol}^{-1}$$

In other words, Trouston's rule states that the ratio of the standard molar heat of vaporisation of a liquid to its normal boiling point is approximately equal to 85 J K^{-1} mol^{-1}, provided the liquid does not involve hydrogen bonding. Such liquids include benzene, bromine, methane, helium, etc.

The Clausius-Clapeyron equation shows the variation of vapour pressure with temperature. The Clausius-Clapeyron equation for liquid-vapour equilibria is given as

$$dp/dT = \frac{\Delta H_v^\circ}{T(V_g - V_l)} \quad (6.1)$$

where $\frac{dP}{dT}$ = The variation of vapour with temperature.

Figure 6.3 Frederick Thomas Trouston, Irish physicist (1863–1922).

ΔH°_V = Molar heat of vaporisation.

T = Absolute temperature.

V_g = Molar volume of the substance in the gaseous state.

V_l = Molar volume of the substance in the liquid state.

For solid-gas equilibria Equation (6.1) is given as

$$\frac{dP}{dT} = \frac{\Delta H_s^\circ}{T(V_g - V_s)} \quad (6.2)$$

where ΔH°_s = Molar heat of sublimation of the substance.

V_s = Molar volume of the substance in the solid state.

For solid-liquid equilibria we have

$$\frac{dP}{dT} = \frac{\Delta H^{\circ}_{f}}{T(V_{l} - V_{s})} \quad (6.3)$$

where ΔH^{o}_{V} = Molar heat of fusion of the substance.

Figure 6.4 Rudolf Clausius, German physicist (1822–1888).

Example 1 Derive the Clausius-Clapeyron equation and show that its integrated form for liquid-vapour equilibria can be given as

$$\ln P = \frac{-\Delta H^{\circ}_{V}}{R}\left(\frac{1}{T}\right) + \mathrm{C}$$

where P = Vapour pressure at absolute temperature T.

$\mathrm{D}H^{o}_{V}$ = Molar heat of vaporisation.

R = Gas constant.

Solution The free energy change of all equilibrium processes is zero. Thus at equilibrium, the free energies of a pure substance in two different phases 1 and 2 are equal, i.e.

$$G_{1} = G_{2} \quad (6.4)$$

Free energy is a function of temperature and pressure. If the temperature and pressure are increased by dT and dP respectively, the free energy is increased by dG. The new condition for equilibrium then becomes

$$G_{1} + \mathrm{d}G_{1} = G_{2} + \mathrm{d}G_{2} \quad (6.5)$$

Subtracting Equation (6.4) from (6.5) we have

$$\mathrm{d}G_{1} = \mathrm{d}G_{2} \quad (6.6)$$

But $\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T$ (See Chapter 11)

Substituting into Equation (6.6) we have

$V_1 \mathrm{d}P - S_1 \mathrm{d}T = V_2 \mathrm{d}P - S_2 \mathrm{d}T$ (6.7)

Collecting the like terms we have

$V_2 \mathrm{d}P - V_1 \mathrm{d}P = S_2 \mathrm{d}T - S_1 \mathrm{d}T$

So $(V_2 - V_1)\mathrm{d}P = (S_2 - S_1)\mathrm{d}T$ (6.8)

Thus $\Delta V \mathrm{d}P = \Delta S \mathrm{d}T$ (6.9)

where $\Delta V = V_2 - V_1$ = Change in molar volume of the substance between phases 1 and 2.

$\Delta S = S_2 - S_1$ = Change in molar entropy of the substance between phases 1 and 2.

We now divide Equation (6.9) by $\Delta V \mathrm{d}T$ to obtain

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta S}{\Delta V} \quad (6.10)$$

Equation (6.10) is called the Clapeyron equation.

But $\Delta S = \frac{\Delta H}{T}$

Substituting into Equation (6.10) we have

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta H}{T\Delta V} \quad (6.11)$$

Equation (6.11) is the Clausius-Clapeyron's equation. It can be expressed for different types of equilibria as given in Equations (6.4)-(6.6). In Equation (6.4), V_l is negligibly small when compared to V_g at a temperature far off from the critical temperature. Thus Equation (6.4) reduces to

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta H_v^\circ}{TV_g} \quad (6.12)$$

We know from the ideal gas equation that

$$V = RT/P$$

Substituting into Equation (6.12) we obtain

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{P\Delta H_v^\circ}{RT^2} \quad (6.13)$$

We can rearrange Equation (6.13) by dividing through by P and multiplying through by dT to obtain

$\frac{dP}{P}$ = $\frac{\Delta H_v^\circ}{RT^2}$ dT (6.14)

Now using the term dP/P = d ln P and taking the integrals of both sides we have

Úd In P = $\int\frac{\Delta H_v^\circ}{RT^2}$ dT (6.15)

We can bring out the term DH_v^o/R from the integral since it is only a constant. Thus Equation (6.15) becomes

ln P = $\frac{\Delta H_v^\circ}{R}$ Ú T^{-2} dT

Thus ln P = $\frac{-\Delta H_v^\circ}{R}\left(\frac{1}{T}\right)$ + C (6.16)

Equation (6.16) can be written in terms of common logarithm as

$$\log P = \frac{-\Delta H_v^\circ}{2.303R}\left(\frac{1}{T}\right) + C$$

where C is the constant of integration that corresponds to the intercept of the graph of log P against 1/T. The slope of the graph corresponds to – DH_v^o /2.303 R.

A plot of log P against 1/T gives a straight-line graph, where $\frac{-\Delta H_v^\circ}{2.303R}$ is the slope (gradient), and C the constant of integration that corresponds to the intercept of the graph. Thus the molar heat of vaporisation can easily be determined by equating $\frac{-\Delta H_v^\circ}{2.303R}$ to the slope of the graph.

Example 2 Show that the integrated form of the Clausius-Clapeyron equation can be given as

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_v^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where ΔH_V^o = Molar heat of vaporisation.

P_1 = Vapour pressure at absolute temperature T_1.

P_2 = Vapour pressure at corresponding temperature T_2.

R = Gas constant.

Solution All we have to do is to integrate Equation (6.12) in Example 1 above within the limits $P = P_1$ at T_1 and $P = P_2$ at T_2, i.e.

$$\int_{P_1}^{P_2} \text{d In } P = \int_{T_1}^{T_2} \frac{\Delta H_V^o}{RT^2}\,\text{d}T$$

So $$\int_{P_1}^{P_2} \text{d In } P = \frac{\Delta H_V^o}{R}\int_{T_1}^{T_2} T^{-2}\,\text{d}T$$

Integrating we have

$$[\ln P]_{P_1}^{P_2} = -\frac{\Delta H_V^o}{R}\left[\frac{1}{T}\right]_{T_1}^{T_2}$$

Inserting the limits, we have

$$\ln P_2 - \ln P_1 = \frac{-\Delta H_V^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Applying the law[1] of logarithms we obtain

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

In terms of common logarithm we have

$$\log\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V^o}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

We can as well repeat the procedure for a solid-gas equilibria since V_s is negligibly small compared to V_g. Thus we can replace DH_V^o with DH_s^o to obtain the integrated Clausius-Clapeyron equation for solid-gas equilibria as

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_v^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\text{or}\quad \log\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_v^\circ}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Example 3 Estimate the boiling point of benzene given that its standard molar heat of vaporisation is 30.8 kJ mol^{-1}.

Solution Benzene does not contain hydrogen bonding. Thus we can obtain an approximate boiling point of the liquid from Trouston's rule:

$$\frac{\Delta H_V^\circ}{T_b} = 85 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\therefore\ T_b = \frac{\Delta H_V^\circ}{85 \text{ J K}^{-1} \text{ mol}^{-1}}$$

ΔH_V^o = 30.8 kJ mol^{-1} = 30800 J mol^{-1}

T_b = ?

Substituting we have

$$T_b = \frac{30800\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}} \times 1 \text{ K}}{85\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}}$$

= 360 K = 87°C

The experimental value is 80°C.

Example 4 Estimate the standard molar heat of vaporisation of liquid argon which boils at –186°C.

Solution We have to apply Trouston's rule, i.e.

$$\frac{\Delta H_V^\circ}{T_b} = 85 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\therefore\ \Delta H_V^o = T_b \times 85 \text{ J K}^{-1} \text{ mol}^{-1}$$

---

[1] According to one of the laws of logarithms, ln *a* – ln *b* = *a*/*b*

T_b = 273 K – 186°C = 87 K

ΔH_V^o = ?

Substituting we have

$$\mathrm{D}H_V^o = 87\ \cancel{\mathrm{K}} \times \frac{85\ \mathrm{J\ mol^{-1}}}{1\ \cancel{\mathrm{K}}}$$

= 7.4 kJ mol^{-1}

The experimental value is about 6.5 kJ mol^{-1}.

Example 5 A plot of log *P* against 1/*T* for various values of vapour pressure of ethanol and corresponding absolute temperatures gives a graph whose slope is –2271.9 K. What is the heat of vaporisation of the liquid?

(R = 8.314 J K^{-1} mol^{-1})

Solution We have to apply the Clausius-Clapeyron's equation

$$\log P = \frac{-\Delta H_V^o}{2.303\,R}\left(\frac{1}{T}\right) + \mathrm{C}$$

We are given the slope of the graph to be –2271.9 K. Since the slope of the graph corresponds to $-\Delta H_V^o/2.303\ R$, then we can equate $-\Delta H_V^o\ /2.303\ R$ to –2271.9 K to obtain

$$\frac{-\Delta H_V^o}{2.303\,R} = -2271.9\ \mathrm{K}$$

R = 8.314 J K^{-1} mol^{-1}

ΔH_V^o = ?

Substituting we have

$$\frac{-\Delta H_V^o}{2.303 \times 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}} = -2271.9\ \mathrm{K}$$

Cross-multiplying we have

$$-\Delta H_V^o = \frac{19.15\ \text{J mol}^{-1}}{1\ \cancel{\text{K}}} \times (-2271.9\ \cancel{\text{K}}) = -43.51\ \text{kJ mol}^{-1}$$

Thus $\Delta H_V^o = 43.51\ \text{kJ mol}^{-1}$

Example 6 The following data show the vapour pressures of water at different temperatures. Plot a graph of log *P* against 1/*T*, and determine the heat of vaporisation of water.

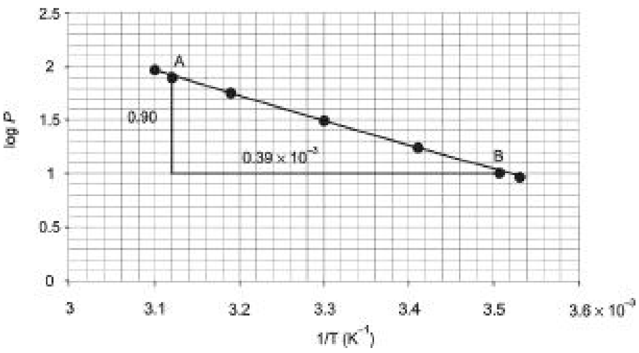
P/mmHg	9.21	17.54	31.82	55.32	92.51
T/°C	10	20	30	40	50

($R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$)

Solution The first step is to draw up the table of log *P* and 1/*T*, as follows:

P/mmHg	9.21	17.54	31.82	55.32	92.51
T/°C	10	20	30	40	50
T/*K*	283	293	303	313	323
$1/T \times 10^{-3}/\text{K}^{-1}$	3.53	3.41	3.30	3.19	3.10
log *P*	0.96	1.24	1.50	1.74	1.97

The plot of log *P* against 1/*T* is shown below:



The slope of the graph is

$$m = \frac{(\log P)_B - (\log P)_A}{(1/T)_B - (1/T)_A}$$

So $m = \frac{-0.90 \times 1\ \text{K}}{0.39 \times 10^{-3}} = -2307.7\ \text{K}$

Now we know that

$$\frac{-\Delta H_V^\circ}{2.303R} = m$$

So $\frac{-\Delta H_V^\circ}{2.303R} = -2307.7\ \text{K}$

$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$

$\Delta H_V^o = ?$

Substituting we have

$$\frac{-\Delta H_V^\circ}{2.303 \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}} = -2307.7\ \text{K}$$

Cross-multiplying we have

$$-\Delta H_V^o = \frac{19.15\ \text{J mol}^{-1}}{1\ \cancel{\text{K}}} \times (-2307.7\ \cancel{\text{K}}) = -44.2\ \text{kJ mol}^{-1}$$

Thus $\Delta H_V^o = 44.2\ \text{kJ mol}^{-1}$

Example 7 The vapour pressure of benzene is 94.6 Torr at 25°C. What is the vapour pressure of the liquid at 50°C, given that its molar heat of vaporisation is 30.8 kJ mol^{-1}?

($R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$)

Solution We have to apply the relation

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H^\circ_V}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

P_1 = 94.6 Torr

T_1 = 273 K + 25°C = 298 K

T_2 = 273 K + 50°C = 323 K

R = 8.314 J K^{-1} mol^{-1}

ΔH^o_V = 30.8 kJ mol^{-1} = 30800 J K^{-1} mol^{-1}

P_2 = ?

Substituting we have

$$\ln\left(\frac{P_2}{94.6\text{ Torr}}\right) = \frac{30800\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}} \times 1\text{ K}}{8.314\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}}\left(\frac{1}{298\text{ K}}-\frac{1}{323\text{ K}}\right)$$

Then $\ln\left(\frac{P_2}{94.6\text{ Torr}}\right) = 3704.6\ \cancel{\text{K}} \times \frac{2.60\times10^{-4}}{1\ \cancel{\text{K}}} = 0.96$

Taking the antilogarithms of both sides we obtain

$$\frac{P_2}{94.6\text{ Torr}} = e^{0.96} = 2.61$$

Cross-multiplying we have

P_2 = 2.61 × 94.6 Torr

= 247 Torr

Alternatively, we can apply the relation

$$\ln P = \frac{-\Delta H^\circ_V}{R}\left(\frac{1}{T}\right) + C$$

We must first obtain the value of the constant C from the initial vapour pressure and corresponding absolute temperature, i.e. 94.6 Torr and 298 K. Substituting we have

$$\ln 94.6 = \frac{-30800\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}} \times 1\ \cancel{\text{K}}}{8.314\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}}\left(\frac{1}{298\ \cancel{\text{K}}}\right) + C$$

So 4.55 = −12.45 + C

Thus C = 4.55 + 12.45 = 17.00

Finally, we can now substitute the new temperature, i.e. 323 K, constant C and other relevant data into the equation to obtain the new pressure, i.e.

$$\ln P = \frac{-30800\ \cancel{J}\ \cancel{mol^{-1}} \times 1\ \cancel{K}}{8.314\ \cancel{J}\ \cancel{mol^{-1}}}\left(\frac{1}{323\ \cancel{K}}\right) + 17.00$$

So $\ln P = -11.48 + 17.00 = 5.52$

Taking the natural antilogarithms of both sides yields

$P = e^{5.52}$

$= 250$ Torr

Note that the slight difference is due to rounding.

Example 8 The normal boiling point of carbon tetrachloride is 77°C. Estimate the boiling point of the liquid under a reviewed pressure of 800 mm Hg.

($R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$)

Solution It is very convenient to apply the Clausius-Clapeyron equation of the form

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

We have no idea of the heat of vaporisation of carbon tetrachloride. However, we can obtain an approximate using Trouston's rule, i.e.

$$T_b = \frac{\Delta H_V^o}{85\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

$\therefore\ \Delta H_V^o = T_b \times 85\ \text{J K}^{-1}\ \text{mol}^{-1}$

$T_b = 273\ \text{K} + 77°\text{C} = 350\ \text{K}$

$\Delta H_V^o = ?$

Substituting we have

$$\Delta H_V^o = 350\ \cancel{K} \times \frac{85\ \text{J mol}^{-1}}{1\ \cancel{K}}$$

$= 29750\ \text{J mol}^{-1}$

The temperature corresponding to the new vapour pressure will be the new boiling point of the liquid. We must also note that the normal boiling point corresponds to a vapour pressure of 760 mm Hg. Thus

P_1 = 760 mmHg
P_2 = 800 mm Hg
T_1 = 350 K
R = 8.314 J K^{-1} mol^{-1}
T_2 = ?

Substituting we have

$$\ln\left(\frac{800}{760}\right) = \frac{29750\ \cancel{\text{J mol}^{-1}} \times 1\ \text{K}}{8.314\ \cancel{\text{J mol}^{-1}}}\left(\frac{1}{350\ \text{K}} - \frac{1}{T_2}\right)$$

So $0.051 = \frac{3578.30\ \cancel{\text{K}}}{350\ \cancel{\text{K}}} - \frac{3578.30\ \text{K}}{T_2}$

Then $0.051 = 10.22 - \frac{3578.30\ \text{K}}{T_2}$

Thus $\frac{3578.30\ \text{K}}{T_2} = 10.22 - 0.051 = 10.17$

Cross-multiplying we have

$10.17\ T_2 = 3578.30$ K

So $T_2 = \frac{3578.30\ \text{K}}{10.17}$

= 352 K

Example 9 The vapour pressure of methanol is 122.7 mmHg at 25°C. What is the heat of vaporisation of the liquid if the vapour pressure is 368.1 mmHg at 50°C?

(R = 8.314 J K^{-1} mol^{-1})

Solution We are applying the relation

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

P_1 = 122.7 mmHg

P_2 = 368.1 mmHg

T_1 = 273 K + 25°C = 298 K

T_2 = 273 K + 50°C = 323 K

R = 8.314 J K^{-1} mol^{-1}

ΔH_V^o = ?

Substituting we have

$$\ln\left(\frac{368.1}{122.7}\right) = \frac{\Delta H_V^\circ}{8.314\ \mathrm{J\ K^{-1}mol^{-1}}}\left(\frac{1}{298\ \mathrm{K}}-\frac{1}{323\ \mathrm{K}}\right)$$

So $1.1 = \frac{2.60\times10^{-4}\ \cancel{\mathrm{K}^{-1}}\ \Delta H_V^\circ}{8.314\ \mathrm{J}\ \cancel{\mathrm{K}^{-1}}\ \mathrm{mol^{-1}}}$

Cross-multiplying we obtain

$$2.60 \times 10^{-4}\,\Delta H_V^o = 9.145\ \mathrm{J\ mol^{-1}}$$

Thus $\Delta H_V^o = \frac{9.145\ \mathrm{J\ mol^{-1}}}{2.60\times10^{-4}}$

= 35.2 kJ mol^{-1}

Example 10 The density of ice and water at 0°C are 0.916 g cm^{-3} and 0.9998 g cm^{-3} respectively. At what temperature would ice melt if the pressure increases by 1.5 atm, given that the heat of fusion of ice is 6.01 kJ mol^{-1}?

(H = 1, O = 16)

Solution We have to apply the Clausius-Clapeyron equation for solid-liquid equilibria, i.e.

$$\frac{dP}{dT} = \frac{\Delta H_f^\circ}{T(V_1 - V_s)}$$

Molar volume can be obtained by multiplying the volume per unit mass (specific volume) v by the molar mass of water, i.e.

$V = M \times v$

$M = [16 + (2 \times 1)]\ \text{g mol}^{-1} = 18\ \text{g mol}^{-1}$

Specific volume is the reciprocal of density, i.e.

$$v = \frac{V}{M} = \frac{1}{\rho}$$

The density of ice is 0.916 g cm^{-3}. Thus

$$v_s = \frac{1}{0.916\ \text{g cm}^{-3}} = 1.0917\ \text{cm}^3\ \text{g}^{-1}$$

$$\text{Then } V\text{s} = 18\ \cancel{\text{g}}\ \text{mol}^{-1} \times \frac{1.0917\ \text{cm}^3}{1\ \cancel{\text{g}}}$$

$= 19.6506\ \text{cm}^3\ \text{mol}^{-1} = 1.96506 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}$

The density of water is 0.998 g cm^{-3}. Thus

$$v_l = \frac{1}{0.998\ \text{g cm}^{-3}} = 1.002\ \text{cm}^3\ \text{g}^{-1}$$

$$\text{Then } V_l = 18\ \cancel{\text{g}}\ \text{mol}^{-1} \times \frac{1.0002\ \text{cm}^3}{1\ \cancel{\text{g}}}$$

$= 18.0036\ \text{cm}^3\ \text{mol}^{-1} = 1.80036 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}$

Other data are

$T = 273\ \text{K} + 25°\text{C} = 298\ \text{K}$

$\Delta H_f^o = 6.01\ \text{kJ mol}^{-1} = 6010\ \text{N m mol}^{-1}$

$dP = 1.5\ \text{atm} = 151987.5\ \text{N m}^{-2}$

$dT = ?$

Substituting into the original equation we obtain

$$\frac{151987.5\ \text{N m}^{-2}}{dT} = \frac{6010\ \text{N m}\ \cancel{\text{mol}^{-1}}}{298\ \text{K} \times (1.80036 \times 10^{-5} - 1.96506 \times 10^{-5})\ \text{m}^3\ \cancel{\text{mol}^{-1}}}$$

Cross-multiplying we have

$6010\ \text{N m} \times \mathrm{d}T = -74.5964\ \text{N m K}$

Thus $\mathrm{d}T = \frac{-74.5964\ \cancel{\text{N}}\cancel{\text{m}}\ \text{K}}{6010\ \cancel{\text{N}}\cancel{\text{m}}}$

$= -0.0124\ \text{K}$

Thus the melting point of ice would decrease by 0.0124 K. Since the normal melting point of ice is 273 K (0°C), then its new melting point would be

$$T_m = 273\ \text{K} - 0.0124\ \text{K} = 272.988\ \text{K}$$

Practice Problems

1. Estimate the molar heat of vaporisation c
−269°C. [

2. The normal boiling point of water is 100°C. At what temperature would it b
of vaporisation of water is 44 kJ mol^{-1}. The atmospheric temperature may be
(R = 8.314 J K^{-1} mol^{-1},
$^{-2}$)

3. The vapour pressure of ethanol is 58.9 mmHg at 25°C. What is the heat of va
(R
$^{-1}$)
[Answer: 43.5 kJ mol^{-1}]

6.2 DENSITY OF SOLIDS

The density of a substance is defined as the volume occupied by a unit mass of that substance, i.e.

$$\rho = \frac{m}{V}$$

Being an intensive property, density can be determined from any size of a substance provided we can determine the mass and volume of the sample.

The density of metals and ionic compounds with cubic structures can be determined from the unit cells of their crystals lattice. A unit cell is the repeating unit of the crystal structure of a solid. Since all the edges of a cube are equal, then the volume of a unit cell is the cube of the length of one of its edges, i.e.

$$V = a^3$$

where a is the length of an edge of the cube.

The edge length of a cubic unit cell is calculated from the radius of its constituent atoms, as follows:

- Simple cubic: Each unit cell consists of an atom, and two atoms are in contact at the cell edge. Thus the edge length is given as

$$a = 2r$$

where r is the atomic radius.

- Body-centred cubic (bcc): Each unit cell consists of two atoms, and four atoms are in contact along the body diagonal of the unit cell. Using Pythagoras' theorem, it can be deduced that the edge length is related to the atomic radius by the equation

$$a = 4r(3)^{-1/2}$$

The length of the body diagonal is $4r$.

- Face-centred cubic (fcc) or cubic closed-packing: Each unit cell consists of four atoms, and four atoms are in contact along the face diagonal. Using Pythagoras' theorem, the edge length of the unit cell can be deduced to be

$$a = 4r(2)^{-1/2}$$

The mass of a unit cell is the total mass of its constituent atoms. Since the atomic mass A of an element is the mass of 1 mole of its atoms, then the mass of an atom is given by

$$m = \frac{A}{N_A}$$

Substituting into the original equation yields

$$\rho = \frac{nA}{N_A a^3}$$

where n is the number of atoms in the unit cell.

For an ionic compound we have

$$\rho = \frac{\sum nA_i}{N_A a^3}$$

where n is the number of an ion in a unit cell. For an ionic compound with a formula of the form AB, the unit cell contains the same number of anions and cations. Thus the above relation can be written as

$$\rho = \frac{n\sum A_i}{N_A a^3}$$

Example 1 What is the density of aluminium if the volume of a 50.0 g sample of the metal was found to be 18.6 cm^3?

Solution This is a direct application of the relation

$$\rho = \frac{m}{V}$$

m = 50.0 g

V = 18.6 cm^3

ρ = ?

Substituting we have

$$\rho = \frac{50.0\ \text{g}}{18.6\ \text{cm}^3}$$

$$= 2.70\ \text{g cm}^{-3}$$

Example 2 In a laboratory experiment to determine the density of cobalt, a piece of the metal was dropped into a measuring cylinder containing water to the 10.0 cm^3 mark. What is the mass of the metal if its density and the final volume of water in the cylinder are 8.80 g cm^{-3} and 20.0 cm^3 respectively?

Solution As usual, we have to apply the relation

$$\rho = \frac{m}{V}$$

$\therefore\ m = \text{r} \times V$

The volume of the sample is the volume of water displaced, i.e.

$V = 20.0\ \text{cm}^3 - 10.0\ \text{cm}^3 = 10.0\ \text{cm}^3$

$\rho = 8.80\ \text{g cm}^{-3}$
$m = ?$

Substituting we have

$$m = \frac{8.80\ \text{g}}{1\ \cancel{\text{cm}^3}} \times 10.0\ \cancel{\text{cm}^3}$$

$$= 88.0\ \text{g}$$

Example 3 A piece of iron was carefully grinded into a cube of side 2.08 cm. What is the density of iron if the mass of the cube is 70.8 g?

Solution This example illustrates how the density of a regular solid can be obtained from the knowledge of mathematics. As usual, we apply the relation

$$\rho = \frac{m}{V}$$

The volume of a cube is the cube of its side, i.e.

$V = l \times l \times l = l^3$
$l = 2.08\ \text{cm}$
$V = ?$
Thus $V = (2.08\ \text{cm})^3 = 9.0\ \text{cm}^3$
$m = 70.8\ \text{g}$
$\rho = ?$

Substituting we obtain

$$\rho = \frac{70.8\ \text{g}}{9.0\ \text{cm}^3}$$

$$= 7.9\ \text{g cm}^{-3}$$

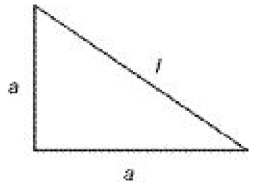
Example 4 Calculate the density of silver given that it crystallises in the fcc structure and that its atomic radius is 144 pm.

(Ag = 107.87)

Solution As usual, we have to apply the relation

$$\rho = \frac{m}{V}$$

The unit cell of a fcc structure is a cube consisting of four atoms. The diagonal of a face of the cube should be four times the radius of one atom. From this we can obtained the length of the side of the unit cell as follows:



where *l* is the diagonal of a face of the cube.

From Pythagoras' theorem,

Hypotenuse (diagonal)^2 = side^2 + side^2

$l = 4 \times r = 4 \times 144$ pm = 576 pm.

Then $(576\text{ pm})^2 = a^2 + a^2$

Thus $331776\text{ pm}^2 = 2a^2$

So $a^2 = \frac{331776\text{ pm}^2}{2} = 165888\text{ pm}^2$

Taking the square roots of both sides we obtain

$$a = \sqrt{165888\text{ pm}^2} = 407.3\text{ pm} = 4.073 \times 10^{-8}\text{ cm}$$

The volume of a cube is the cube of its side. Thus

$$V = (4.073 \times 10^{-8}\text{ cm})^3 = 6.76 \times 10^{-23}\text{ cm}^3$$

Now, we shift attention to the mass of the unit cell. The atomic mass given is the mass of one mole of atoms of the metal. Thus the mass of an atom should be obtained from the relation.

$m = \frac{A}{N_A}$

$A = 107.9\text{ g mol}^{-1}$

$N_A = 6.02 \times 10^{23}\text{ mol}^{-1}$

$m = ?$

Substituting we have

$m = \frac{107.87\text{ g }\cancel{\text{mol}^{-1}}}{6.02 \times 10^{23}\ \cancel{\text{mol}^{-1}}}$

$= 1.79 \times 10^{-22}$ g

Since a unit contains 4 atoms, then the total mass of the unit cell is

$$m = 4 \times 1.79 \times 10^{-22}\,\text{g} = 1.17 \times 10^{-22}\,\text{g}$$

Finally, we can now substitute into the original equation to obtain

$$\rho = \frac{1.79 \times 10^{-22}\,\text{g}}{6.02 \times 10^{23}\,\text{cm}^3}$$

$= 10.6$ g cm^{-3}

This is very close to the experiment value of 10.5 g cm^{-3}.
But we don't have to show all these details. We can always apply the relation

$$\rho = \frac{nA}{N_A a^3}$$

$A = 107.87$ g mol^{-1}
$n = 4$
$N_A = 6.02 \times 10^{23}$ mol^{-1}
$a = 4.07 \times 10^{-8}$ cm
$\rho = ?$

Substituting we have

$$\rho = \frac{4 \times 107.87\,\text{g}\,\cancel{\text{mol}^{-1}}}{6.02 \times 10^{23}\,\cancel{\text{mol}^{-1}} \times (4.07 \times 10^{-8}\,\text{cm})^3}$$

So $\rho = \dfrac{431.48\,\text{g}}{40.6\,\text{cm}^3}$

$= 10.6$ g cm^{-3}

Example 5 The atomic radius of sodium is 190 pm. What is the density of the metal if it has the bcc structure?

(Na = 22.99)

Solution We have to apply the relation

$$\rho = \frac{nA}{N_A a^3}$$

For a bcc structure we know that

$a = 4r(3)^{-½}$

$r = 190 \text{ pm} = 1.90 \times 10^{-8} \text{ cm}$

$a = ?$

Then $a = \dfrac{4 \times 1.90 \times 10^{-8} \text{ cm}}{3^{1/2}}$

$= 4.39 \times 10^{-8} \text{ cm}$

$n = 2$

$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$

$A = 22.99 \text{ g mol}^{-1}$

$\rho = ?$

Substituting we obtain

$$\rho = \frac{2 \times 22.99 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1} \times (4.39 \times 10^{-8} \text{ cm})^3}$$

Then $\rho = \dfrac{45.98 \text{ g } \cancel{\text{mol}^{-1}}}{50.93 \text{ cm}^3 \cancel{\text{mol}^{-1}}}$

$= 0.90 \text{ g cm}^{-3}$

The experimental value is 0.95 g cm^{-3}.

Example 6 Calculate the density of sodium chloride if it has the fcc structure. The edge of the unit cell is 564 pm.

(Na = 22.99, Cl = 35.45)

Solution We have to apply the relation

$$\rho = \frac{\sum n_i A_i}{N_A a^3}$$

$n_1 = 4$

$n_2 = 4$

$A_1 = 22.99 \text{ g mol}^{-1}$

$A_2 = 35.45 \text{ g mol}^{-1}$

$a = 564 \text{ pm} = 5.64 \times 10^{-8} \text{ cm}$

$N_A = 6.02 \times 10^{-23} \text{ mol}^{-1}$

ρ = ?

Substituting we have

$$\rho = \frac{4[22.99\ \text{g mol}^{-1} + 35.45\ \text{g mol}^{-1}]}{6.02 \times 10^{23}\ \text{mol}^{-1} \times (5.64 \times 10^{-8}\ \text{cm})^3}$$

$$\text{Thus } r = \frac{233.76\ \text{g}\ \cancel{\text{mol}^{-1}}}{108\ \text{cm}^3\ \cancel{\text{mol}^{-1}}}$$

$= 2.16$ g mol^{-1}

Example 7 The density of nickel is 8.91 g cm^{-3}. Estimate the atomic radius of the metal if its crystal structure is ccp.

(Ni = 58.71)

Solution We must first obtain the edge length from the relation

$$\rho = \frac{nA}{N_A a^3}$$

$n = 4$

$N_A = 6.02 \times 10^{23}$ mol^{-1}

$A = 58.71$ g mol^{-1}

$\rho = 8.91$ g cm^{-3}

a = ?

Substituting into the equation yields

$$\frac{8.91\ \text{g}}{1\ \text{cm}^3} = \frac{4 \times 58.71\ \text{g}\ \cancel{\text{mol}^{-1}}}{6.02 \times 10^{23}\ \cancel{\text{mol}^{-1}} \times a^3}$$

Cross-multiplying we obtain

$5.36 \times 10^{24}\ \text{g} \times a^3 = 234.84\ \text{g cm}^3$

$$\text{Thus } a^3 = \frac{234.84\ \cancel{\text{g}}\ \text{cm}^3}{5.36 \times 10^{24}\ \cancel{\text{g}}}$$

$= 4.38 \times 10^{-23}$ cm^3

Taking the cube roots of both side yields

$$a = \sqrt[3]{4.38 \times 10^{-23}\ \text{cm}^3} = 3.52 \times 10^{-8}\,\text{cm}$$

Now, for a bcc structure we know that

$a = 4r(2)^{-1/2}$

$r = ?$

Substituting we have

$$3.52 \times 10^{-8}\ \text{cm} = \frac{4r}{2^{1/2}}$$

Cross-multiplying we have

$4r = 4.98 \times 10^{-8}\,\text{cm}$

So $r = \frac{4.98 \times 10^{-8}\ \text{cm}}{4}$

$= 1.25 \times 10^{-8}\,\text{cm} = 12.5\ \text{pm}$

Example 8 What is the structure of caesium bromide if its density is 4.43 g cm^3, and the edge length of its unit cell 4.31Å?

(Br = 79.91, Cs = 132.91)

Solution The number of ions in a unit cell determines the structure of an ionic crystal. Thus we have to work out the number of atoms in the unit cell from the relation

$\rho = \frac{n\sum A}{N_A a^3}$

$\rho = 4.43\ \text{g cm}^{-3}$

$A_l = 79.91\ \text{g mol}^{-1}$

$A_2 = 132.91\ \text{g mol}^{-1}$

$N_A = 6.02 \times 10^{-23}\ \text{mol}^{-1}$

$a = 4.31\ \text{Å} = 4.31 \times 10^{-8}\,\text{cm}$

$n = ?$

Substituting we have

$$\frac{4.43}{1\ \text{cm}^3} = \frac{n \times (79.91\ \text{g mol}^{-1} + 132.91\ \text{g mol}^{-1})}{6.02 \times 10^{23}\ \text{mol}^{-1} \times (4.31 \times 10^{-8}\ \text{cm})^3}$$

Cross-multiplying we have

$212.82\ \text{g cm}^3\ \text{mol}^{-1} \times n = 213.52\ \text{g cm}^3\ \text{mol}^{-1}$

Then $n = \frac{213.52\ \cancel{\text{g}}\ \cancel{\text{cm}^3}\ \cancel{\text{mol}^{-1}}}{212.82\ \cancel{\text{g}}\ \cancel{\text{cm}^3}\ \cancel{\text{mol}^{-1}}}$

= 1

Since the unit cell contains one Cs^+ and Br^-, then the compound has a simple cubic structure.

Practice Problems

1. Aluminium crystallises in the ccp structure. What is the density of the metal if its atomic radius is 143 pm?
   (Al = 26.98) [Answer: 2.70 g cm^{-3}]
2. Caesium chloride has the simple cubic structure. What is the cell length if its density of the compound is 3.99 g cm^{-3}?
   (Cl = 35.45, Cs = 132.91) [Answer: 412 pm]
3. Titanium has the bcc structure. Calculate the atomic radius of the metal if its density is 4.51 g cm^{-3}?
   (Ti = 47.90) [Answer: 142 pm]
4. What is the structure of lithium chloride if its density is 2.07 g cm^{-3}, and the cell length 4.04 Å?
   (Li = 6.94, Cl = 35.45) [Answer: fcc (ccp)]

6.3 X-RAY CRYSTALLOGRAPHY

X-ray crystallography is the use of x-rays in the study of crystals. The structures of crystals are determined by means of x-ray diffraction–the interference between waves of x-rays caused by layers of atoms in their path. When a crystal is examined with a beam of x-rays, diffraction causes a series of spots, called diffraction pattern, when detected photographically. An intense spot or strong reflection is caused by constructive interference–the combination of two waves to produce a resultant wave of a higher amplitude than each of the original waves.

Constructive interference occurs if the trough and crest of two waves match exactly. The second type of interference, called destructive interference, is the combination of two waves to produce a wave of lower amplitude than each of the original waves, or no wave at all, i.e., the two waves cancel out.

The spacing of atoms can be calculated from the angle of incidence or scattering of the x-rays for which constructive interference occurs (causing an intense spot in the diffraction pattern) and their wavelength by the equation

$$2d\sin\theta = n\lambda$$

where d = Spacing of atoms.

θ = Angle of incidence or scattering of x-rays for which constructive interference occurs.

n = An integer representing the order of scattering.

λ = The wavelength of x-rays.

The above equation is called Bragg law or equation, named for the English physicist Sir William Lawrence Bragg, who first derived it in 1912. We often need to consider first-order scattering, i.e. n = 1. Thus the above equation now reduces to

$$2d\sin\theta = \lambda$$

It should also be noted that the spacing of the atoms is twice the metallic radius.

Figure 6.6 Sir William Lawrence Bragg, British physicist (1890–1971). He won the Nobel Prize for Physics with his son, Sir William Henry Bragg, in 1915.

Example 1 A crystal of pure silver was examined with a beam of x-rays of wavelength 122 pm. Calculate the metallic radius of the metal if an intense spot was obtained at an angle of 12.3° from the layers of the crystal.

Solution We have to apply the Bragg equation:

$2d\sin\theta = \lambda$

$\therefore\ d = \frac{\lambda}{2\sin\theta}$

Substituting we have

$d = \frac{122\ \text{pm}}{2\sin 12.5°}$

So $d = \frac{122\ \text{pm}}{2 \times 0.213}$

$= 286$ pm

Since the separation of atoms is twice the metallic radius, it then follows that the metallic radius of silver is

$r = \frac{286\ \text{pm}}{2}$

$= 143$ pm

Example 2 A crystal of aluminium was examined with 88.2-pm x-rays. What is the angle of the relection for which constructive interference occurred if the metallic radius of the metal was obtained to be 125 pm?

Solution As usual, we have to apply the relation

$2d\sin\theta = \lambda$

$\therefore\ \sin\theta = \frac{\lambda}{2d}$

$\lambda = 88.2$ pm

$d = 2 \times 125$ pm $= 250$ pm

$\theta = ?$

Substituting we have

$\sin\theta = \frac{88.2\ \cancel{\text{pm}}}{2 \times 250\ \cancel{\text{pm}}}$

$= 0.18$

Thus $\theta = \sin^{-1} 0.18$

$= 10.4°$

Example 3 The metallic radius of copper was obtained to be 128 pm when the crystal of the metal was examined with a beam of x-rays. Calculate the wavelength of the x-rays if an intense spot was obtained at an angle of 15.5°.

Solution We have to apply the relation

$l = 2d\text{sin}q$

$d = 2 \times 128 \text{ pm} = 256 \text{ pm}$

$q = 15.5°$

$l = ?$

Substituting we have

$l = 2 \times 256 \text{ pm} \times \text{sin}15.5°$

So $l = 512 \text{ pm} \times 0.267$

$= 137 \text{ pm}$

Practice Problems

1. A crystal of caesium was examined with a beam of 175 pm x-rays. Calculate the metallic radius of the metal if an intense spot was obtained at angle of 9.44° from the layers of the crystal. [*Answer:* 267 pm]
2. The metallic radius of magnesium was obtained to be 150 pm during an experiment on x-ray diffraction. What is the wavelength of the x-rays used if an intense spot was formed at 8.20° from the layers of the crystal? [*Answer:* 43 pm]

6.4 DETERMINATION OF VISCOSITY OF LIQUIDS FROM STOKES' LAW

The determination of the viscosity of a liquid from Stokes' law involves dropping a spherical object of known radius and density into a liquid of known density, and noting the time required for the sphere to transverse a specified length of the liquid. The viscosity of the liquid is determined by applying the relation derived below. Unlike the viscosity of gases, the viscosity of liquids reduces with temperature.

Stokes' law describes the drag force on a spherical body moving through a liquid medium at a specific velocity. It is given as

$$F_d = 6phvd \quad (6.17)$$

where F_d = Drag force on the sphere.

h = Viscosity of the liquid.
v = Velocity of the sphere.
d = Diameter of the sphere.

Three forces act on a body falling through a liquid medium, as shown below:

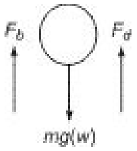


Figure 6.7 Forces acting on a body in a liquid medium.

The only force acting downwards is the weight w of the body. The other two forces act upwards, i.e., in opposition to the weight of the body. These are the drag force F_d caused by the resistance of the liquid, and the buoyant force or upthrust F_b. If a viscous medium is selected such that the sphere falls slowly, then the sphere will attain a constant velocity called terminal velocity. At this velocity, the two upward forces just balance the weight of the sphere, such that the net force on the sphere now becomes

$F_b + F_d = mg$ (6.18)

Now, the weight of the sphere is given as

$mg = V\mathrm{r}_s g = \frac{4}{3}\pi r^3 \rho_s g$ (6.19)

The upthrust on the body is the weight of the liquid displaced. This is given as

$F_b = m_L g = V\mathrm{r}_L g$ (6.20)

The volume of the sphere is equal to the volume of the liquid displaced, i.e.

$$V = \frac{4}{3}\pi r^3$$

Thus, Equation (6.20) becomes

$F_b = \frac{4}{3}\pi r^3 \rho_L g$ (6.21)

Substituting Equations (6.17) and (6.21) into Equation (6.18) we have

$\frac{4}{3}\pi r^3 \rho_L g + 6\mathrm{ph}vd = \frac{4}{3}\pi r^3 \rho_s g$ (6.22)

Now we know that the diameter of a sphere is twice its radius. Thus

$12ph vr = \frac{4}{3}\pi r^3 \rho_s g - \frac{4}{3}\pi r^3 \rho_L g$

So $12ph vr = \frac{4\pi r^3 g(\rho_s - \rho_L)}{3}$ (6.23)

Then $h = \frac{2r^2 g(\rho_s - \rho_L)}{9v}$ (6.24)

where r = Radius of the sphere.
v = Terminal velocity = v/t.
g = Acceleration due to gravity.
r_s = Density of sphere.
r_L = Density of liquid medium.

Figure 6.8 Sir George Stokes, British mathematician and physicist (1819–1903).

Example 1 In a laboratory experiment to determine the viscosity of a liquid, a Teflon sphere of diameter 2.4 mm was carefully dropped into the liquid in a very long cylinder. Calculate the viscosity of the liquid at the prevailing temperature if the ball attained a terminal velocity of 3.1 m s^{-1}. The densities of teflon and the liquid are 2200 kg m^{-3} and 105 kg m^{-3} respectively.

(g = 9.8 m s^{-2})

Solution We have to apply the relation

$h = \frac{2r^2 g(\rho_s - \rho_L)}{9v}$

r = 2.4/2 = 1.2 mm = 0.0012 m
g = 9.8 m s^{-2}
r_s = 2200 kg m^{-3}
r_L = 1050 kg m^{-3}

v = 3.1 m s^{-1}

h = ?

Substituting we have

$$h = \frac{2 \times (0.0012\,\text{m})^2 \times 9.8\,\text{m}s^{-2} \times (2200 - 1050)\,\text{kg}}{9 \times 3.1\,\text{m}s^{-1} \times 1\,\text{m}^3}$$

$$\text{So } h = \frac{0.03246\,\text{kg}\,\cancel{\text{m}^3}\,s^{-2}}{27.9\,\text{m}s^{-1} \times 1\,\cancel{\text{m}^3}}$$

= 1.16 × 10^{-3} kg $m^{-1}s^{-1}$ = 1.16 cP

Example 2 In a laboratory experiment to determine the viscosity of glycerol, a brass ball of radius 1.2 mm was dropped into the liquid and the time taken to transverse two marks of the cylinder was noted. What is the terminal velocity attained by the ball if the viscosity was obtained to be 0.095 Pa s? The densities of brass and glycerol are 8400 kg m^{-3} and 1259.37 kg m^{-3} respectively; hence determine the length between the two marks of the cylinder if it took 12 s for the sphere to transverse the marks.

(g = 9.8 m s^{-2})

Solution We have to apply the relation

$$h = \frac{2r^2 g(\rho_s - \rho_L)}{9v}$$

$$\therefore\ v = \frac{2r^2 g(\rho_s - \rho_L)}{9\eta}$$

h = 0.95 Pa s = 0.95 kg $m^{-1}s^{-1}$

r = 1.2 mm = 0.0012 m

r_s = 8400 kg m^{-3}

r_L = 1259.37 kg m^{-3}

g = 9.8 m s^{-2}

h = ?

Substituting we have

$$v = \frac{2 \times (0.0012\,\text{m})^2 \times 9.8\,\text{m}s^{-2} \times (8400 - 1259.37)\,\text{kg} \times 1\,\text{m}}{9 \times 0.95\,\text{kg}\,s^{-1} \times 1\,\text{m}^3}$$

Thus $v = \frac{0.2015\ \cancel{\text{kg}}\ \cancel{\text{m}^2}\ \text{s}^{-1} \times 1\ \text{m}}{8.55\ \cancel{\text{kg}}\ \text{s}^{-2} \times 1\ \cancel{\text{m}^2}}$

= 0.024 m s^{-1} = 2.4 cm s^{-1}

The terminal velocity is defined as

$v = \frac{l}{t}$

So $l = v \times t$

t = 15 s

l = ?

Substituting we have

$l = \frac{0.024\ \text{m}}{1\ \cancel{\text{s}}} \times 15\ \cancel{\text{s}}$

= 0.36 m = 36 cm

Example 3 Calculate the density of a liquid at a temperature at which its viscosity is 0.593 cP, given that a teflon ball of radius 1.2 mm attained a terminal velocity of 7.45 m s^{-1} in the liquid. The density of teflon is 2200 kg m^{-3}.

(g = 9.8 m s^{-2})

Solution We have to apply the relation

h $= \frac{2r^2 g(\rho_s - \rho_L)}{9v}$

h = 0.593 cP = 0.593 × 10^{-3} kg $\text{m}^{-1}\,\text{s}^{-1}$

r = 1.2 mm = 0.0012 m

r_s = 2200 kg m^{-3}

g = 9.8 m s^{-2}

v = 7.46 m s^{-1}

r_L = ?

Substituting we have

$$0.593 \times 10^{-3}\ \text{kg m}^{-1}\text{s}^{-1} = \frac{2 \times (0.0012\text{m})^2 \times 9.8\ \text{ms}^{-1} \times (2200\ \text{kgm}^{-3} - \rho_L)}{9 \times 7.46\ \text{ms}^{-1}}$$

Cross-multiplying we obtain

$0.0621\ \text{kg s}^{-2} - 2.82 \times 10^{-5}\,\text{m}^3\text{s}^{-2}\text{r}_L = 0.0398\ \text{kg s}^{-2}$

So $2.82 \times 10^{-5}\,\text{m}^3\text{s}^{-2}\text{r}_L = 0.0621\ \text{kg s}^{-2} - 0.0398\ \text{kg s}^{-2} = 0.0223\ \text{kg s}^{-2}$

Thus $\text{r}_L = \dfrac{0.0223\ \text{kg}\ \cancel{\text{s}^{-2}}}{2.82 \times 10^{-5}\,\text{m}^3\ \cancel{\text{s}^{-2}}}$

$= 791\ \text{kg m}^{-3}$

Practice Problems

1. In a laboratory experiment to determine the viscosity of castor oil, a cylinder was filled with the liquid and marked 21.8 cm apart. Calculate the viscosity of the liquid if it took 10 s for a steel ball of radius 0.12 mm to cross the marks. The densities of the liquid and steel are 956.14 kg m^{-3} and 7800 k g m^{-3} respectively.

   ($g = 9.8\ \text{m s}^{-2}$) [*Answer:* 0.985 Pa s]

2. The above experiment was repeated with another liquid whose viscosity was found to be 1490 cP. What is the terminal velocity attained by the ball if the density of the liquid is 1230 kg m^{-3}?

   ($g = 9.8\ \text{m s}^{-2}$) [*Answer:* 0.0138 m s^{-1} or 1.38 cm s^{-1}]

6.5 SURFACE TENSION

The surface of a liquid tends to minimise its surface area when disturbed, behaving like a stretched elastic skin or membrane. This phenomenon is called surface tension g. Surface tension arises due to an internal, unbalanced cohesive forces exerted on the molecules at the surface of a liquid by other molecules. The SI unit of surface tension is N m^{-1}.

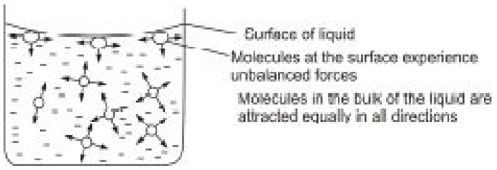


Figure 6.9 Forces on the molecules of a liquid. Surface tension arises from unbalanced forces acting on the molecules at the surface.

The surfaced tension of a liquid is determined by means of capillary action, which is the rise of a liquid through a very narrow tube, using the relation

$$g = \tfrac{1}{2} r h r g \cos q$$

where r = The radius of the tube.

h = The height of the liquid in the tube.

g = Acceleration due to gravity.

r = The density of the liquid.

q = The angle of contact of the liquid with the tube.

The angle of contact is 0 for most liquids. Since cos 0 = 1, then the above equation reduces to

$$g = \tfrac{1}{2} r h r g$$

Example 1 In an experiment to determine the surface tension of glycerol, the liquid rises to a height of 2.05 cm in a capillary tube of radius 0.50 mm. What is the surface tension of the liquid, given that its density at the prevailing temperature is 1259.4 kg $\mathrm{m^{-3}}$?

$$(g = 9.8\ \mathrm{m\ s^{-2}})$$

Solution We have to apply the equation

$g = \tfrac{1}{2} r h r g$

$r = 0.50\ \mathrm{mm} = 0.0005\ \mathrm{m}$

$h = 2.05\ \mathrm{cm} = 0.0205\ \mathrm{m}$

$\mathrm{r} = 1259.4\ \mathrm{kg\ m^{-3}}$

$g = 9.8\ \mathrm{m\ s^{-2}}$

$g = ?$

Substituting we have

$$g = \frac{1}{2} \times 0.0005\ \mathrm{m} \times 0.0205\ \mathrm{m} \times \frac{1259.4\ \mathrm{kg}}{1\ \mathrm{m^3}} \times 9.8\ \mathrm{m\ s^{-2}}$$

$$\text{So}\ \ g = \frac{0.0223\ \mathrm{kg}\ \cancel{\mathrm{m^3}}\ \mathrm{s^{-2}}}{1\ \cancel{\mathrm{m^3}}}$$

$$= 0.0633\ \mathrm{kg\ s^{-2}} = 0.0633\ \mathrm{N\ m^{-1}}$$

Note: 1 N = 1 kg m $\mathrm{s^{-2}}$.

Example 2 The surface tension of mercury is 0.436 N m^{-1}. What is the height of the liquid in a capillary tube of radius 0.25 mm if the density of the liquid is 15.55 g cm^{-3}?

(g = 9.8 m s^{-2})

Solution As usual, we have to apply the relation

g = ½rhrg

$\therefore\ h = \frac{2\gamma}{\rho g r}$

g = 0.436 N m^{-1} = 0.436 kg s^{-2}

r = 13.60 g cm^{-3} = 13600 kg m^{-3}

g = 9.8 m s^{-2}

r = 0.25 mm = 0.00025 m

h = ?

Substituting we obtain

$$h = \frac{2 \times 0.436\,\mathrm{kg\,s^{-2}} \times 1\,\mathrm{m^3}}{13600\,\mathrm{kg} \times 9.8\,\mathrm{m s^{-2}} \times 0.00025\,\mathrm{m}}$$

Then $h = \frac{0.872\,\cancel{\mathrm{kg}}\,\cancel{s^{-2}}\,\mathrm{m^3}}{38.10\,\cancel{\mathrm{kg}}\,\mathrm{m^2}\,\cancel{s^{-2}}}$

= 0.026 m = 2.60 cm

Example 3 In a laboratory experiment to determine the surface tension of a liquid, it was found to rise through a height of 3.50 cm in a capillary tube of radius 2.5 mm. What is the density of the liquid if its surface tension is 0.072 N m^{-1}?

(g = 9.8 m s^{-2})

Solution We have to apply the relation

g = ½rhrg

$\therefore$ r $= \frac{2\gamma}{rhg}$

g = 0.072 N m^{-1} = 0.072 kg s^{-2}

r = 2.5 mm = 0.00025 m

h = 3.50 cm = 0.035 m

g = 9.8 m s^{-2}

r = ?

Substituting we have

$$r = \frac{2 \times 0.072\,\mathrm{kg\,s^{-2}}}{0.0025\,\mathrm{m} \times 0.035\,\mathrm{m} \times 9.8\,\mathrm{ms^{-2}}}$$

$$\text{Then } r = \frac{0.144\,\mathrm{kg}\,\cancel{s^{-2}}}{8.6 \times 10^{-4}\,\mathrm{m^3}\,\cancel{s^{-2}}}$$

= 170 kg m^{-3}

Practice Problems

1. What is the surface tension of benzene if it rises to a height of 2.70 cm in a capillary tube of radius 0.250 mm?
The density of benzene is 873.8 kg m^{-3}.
(g = 9.8 m s^{-2}) [*Answer:* 0.0289 N m^{-1}]
2. A liquid rises through a height of 3.50 cm in a capillary tube of radius 0.25 mm. What is the density of the liquid if its surface tension is 0.0728 N m^{-1}?
(g = 9.8 m s^{-2}) [*Answer:* 1700 kg m^{-3}]

SUMMARY

- A solid is a rigid substance characterised by very strong intermolecular forces.
- A crystalline solid is a solid whose particles are orderly arranged.
- An amorphous solid is a solid whose particles are not arranged in any regular pattern.
- Metallic solids consist of cations that are held together by a sea of electrons.
- Ionic solids consist of cations and anions held together by electrostatic force of attraction.
- A network solid consists of atoms that are covalently linked throughout its extent.

- Molecular solids consist of molecules.
- The melting or freezing point of substance is the temperature at which it melts or solidifies.
- A liquid is a substance which takes the shape of the container in which it is poured.
- The normal boiling point of a liquid is the temperature at which its vapour pressure equal 1 atm.
- The vapour pressure of a liquid is the pressure exerted by its vapour. The pressure exerted when the vapour and the liquid are in equilibrium is called saturated vapour pressure.
- Phase equilibrant describes the process in which two phases of a substance are in dynamic equilibrium.
- Dynamic equilibrium refers to the situation in which two opposite process are occurring at equal rate.
- A phase diagram is a graphical representation of the behaviour of a substance in its three phases under different conditions of pressure and temperature.
- Triple point is the point on a phase diagram at which the three phases of a substance are in dynamic equilibrium.
- The relationship between vapour pressure and temperature is given by the Clausius-Clapeyron’s equation

$$\ln P = \frac{-\Delta H_{\mathrm{v}}^{\circ}}{R}\left(\frac{1}{T}\right) + C \text{ or } \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\mathrm{v}}^{\circ}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

- A unit cell is the repeating unit of a crystal.
- A simple cubic structure consists of one atom per unit cell. The side length of the unit cell is related to atomic radius by the relation

$$a = 2r$$

- A body-centred cubic structure consists of two atoms per unit cell. The side length of the unit cell is related to atomic radius by the relation

$$a = 4r(3)^{-1/2}$$

- A face-centred cubic (cubic closed-packed) structure consists of four atoms per unit cell. The side length of the unit cell is related to the atomic radius by the relation

$$a = 4r(2)^{-1/2}$$

- The density of a crystalline solid is obtained from the relation

$$r = \frac{\sum n_i A_i}{N_A a^3}$$

- The structures of crystals can be determined by means of x-ray diffraction. The wavelength of the x-rays is related to the angle of scattering of the x-rays by the Bragg equation:

$$2d\text{sinq} = \text{l}$$

- The viscosity of a liquid reduces with temperature. It can be obtained from Stokes' law, using the relation

$$h = \frac{2r^2 g(\rho_s - \rho_L)}{9v}$$

- Surface tension is a phenomenon in which the surface of a liquid behaves likes a stretched elastic membrane. It can be obtained by means of capillary action, using the relation

$$\text{g} = \tfrac{1}{2} rh\text{r}g$$

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. Which of the following is/are **TRUE** of solids?
   i. Their molecules are held together by very strong intermolecular forces.
   ii. Their molecules can neither vibrate nor translate.
   iii. Their melting point increases with pressure.
   iv. They cannot translate to the gaseous phase without first passing through the liquid phase.
   A. i and ii B. i only
   C. ii and iv D. iv only
   E. None of the above.
2. Which of these is a crystalline solid?
   A. Polystyrene B. Sulphur
   C. Polyvinylacetate D. Lead
   E. Rubber
3. The normal boiling point of benzene is 80°C. Which of the following

temperatures is likely to be the boiling point of the liquid if it is heated in a region that is above the sea level?

A. 25°C B. 50°C
C. 72°C D. 80°C
E. 85°C

4. Which of the following is responsible for the high boiling point of water in comparison to its small molecular mass?

A. Hydrogen bonding B. London forces
C. Low molecular mass D. Metallic bonding
E. Covalent bonding

Use the information given below to answer questions 5-6.

Liquid	Boiling point/°C
Water	100
Argon	−186
Ethanol	78
Mercury	84
Rubidium	705

5. Which of the liquids is the most volatile?

A. Water B. Argon
C. Ethanol D. Mercury
E. Rubidium

6. Which of the liquids would have the slowest rate of evaporation under same conditions?

A. Water B. Argon
C. Ethanol D. Mercury
E. Rubidium

7. Which of the following is/are **NOT** true of evaporation?

i. It occurs at all temperatures.
ii. It occurs within the bulk of a liquid.
iii. Its rate decreases with temperature.
iv. It only occurs at the surface of a liquid.

A. i and ii B. ii and iii
C. ii and iv D. i and iv
E. iii only

8. The atomic radius of polonium is 190 pm. What is the side length of its unit cell if the metal has a simple cubic structure?

A. 95 pm B. 100 pm
C. 380 pm D. 439 pm
E. 537 pm

9. Water has a density of 1000 kg m^{-3}. What should be the mass of 250 cm^3 of water?

A. 100 g B. 150 g
C. 200 g D. 220 g
E. 250 g

10. Which of the following is/are **TRUE** of the viscosity and vapour pressure of liquids?

i. They increase with temperature.
ii. They are both dependent on temperature.
iii. They increase as humidity reduces.
iv. They reduce with density.

A. i and ii B. ii only
C. i and iv D. iii only
E. iv only

11. The normal boiling point of chlorine is −34°C. Estimate the heat of vaporisation of the element.

A. 19 kJ mol^{-1} B. 20 kJ mol^{-1}
C. 21 kJ mol^{-1} D. 22 kJ mol^{-1}
E. 28 kJ mol^{-1}

12. The plot of the logarithm of the vapour pressures of methanol against the reciprocals of the corresponding absolute temperatures produces a graph whose slope is −1843.6 K^{-1}. What is the heat of vaporisation of the liquid?

A. 30.2 kJ mol^{-1} B. 32.5 kJ mol^{-1}
C. 35.3 kJ mol^{-1} D. 35.5 kJ mol^{-1}
E. 40.3 kJ mol^{-1}

13. What is the specific volume of castor oil if its density is 956 kg m^{-3}?

A. 1.05×10^{-3} kg m^{-3} B. 1.05×10^{-3} m^3 kg^{-1}
C. 1.25×10^{-3} kg^{-1} D. 9.56×10^{-3} kg m^{-3}
E. 9.56×10^{2} m^3 kg^{-1}

ESSAY TYPE QUESTIONS

Vapour pressure and states of matter

14. State the properties of solids.
15. Explain crystalline and amorphous solid with examples.
16. Using water as an example, explain the process of phase transition from the particulate theory of matter.
17. The Clausius-Clapeyron's equation for liquid-gas equilibria is given as

$$\frac{dP}{dT} = \frac{\Delta H_V^o}{T(V_g - V_l)}$$

Starting from this equation, show that the integrated form of the Clausius-Clapeyron's equation can be given as

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where P_2 = Vapour pressure at absolute temperature T_2.

P_1 = Vapour pressure at absolute temperature T_1.

ΔH^o_V = Molar heat of vaporisation.

R = Universal gas constant.

18. (a) State Trouston's rule and its limitation.

(b) The boiling point of fluorine is −188°C. Estimate its heat of vaporisation.

19. The following data of vapour pressure were obtained for ethanol:

P/Torr	58.9	78.7	104.2	136.6	177.7
T/°C	25	30	35	40	45

Plot the graph of log P against $1/T$, and obtain the heat of vaporisation of the liquid from the graph.

($R = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$)

20. The following data was obtained for the vapour pressure of benzene at various temperatures:

P/mm Hg	30.3	48.9	76.5	116.1	171.6	181.2
T/°C	0	10	20	30	40	50

(a) Plot a graph of log P against $1/T$, and determine the heat of vaporisation of benzene from the graph.

(b) From the graph, determine the vapour pressure of benzene at 35°C.

($R = 8.314$ J K^{-1} mol^{-1})

21. The vapour pressure of water is 17.54 mm Hg at 20°C. What is its vapour pressure at 55°C, given that its heat of vaporisation is 44 kJ mol^{-1}.

($R = 8.314$ J K^{-1} mol^{-1})

22. The vapour pressure of methanol is 155.2 Torr at 30°C. What is the heat of vaporisation of the liquid if its vapour pressure is 369.6 Torr at 50°C?

($R = 8.314$ J K^{-1} mol^{-1})

23. The vapour pressure of a liquid whose normal boiling point is 85°C is 40.5 mm Hg at 25°C. What is the vapour pressure of the liquid at 75°C, assuming Trouston's law applies?

($R = 8.314$ J K^{-1} mol^{-1})

Density of solids

24. The atomic radius of gold is 146 pm. What is the density of the metal if it crystallises in the fcc structure?

(Au = 196.97)

25. Calculate the density of lead if it has the fcc structure, and its atomic radius, 175 pm.

(Pb = 207.19)

26. Calculate the density of iron, given that it has the bcc structure. The atomic radius of the metal is 126 pm.

(Fe = 55.85)

27. The length of the unit cell of calcium fluoride is 4.98 Å. What is the density of the compound if it has the fcc structure?

(F = 19.00, Ca = 40.08)

28. What is the structure of zinc blende (zinc sulphide) if its density and side length of unit cell are 4.09 g cm^{-3} and 5.41 Å respectively?

(S = 32.06, Zn = 56.37)

29. What is the structure of potassium if its density is 0.86 g cm^{-3}? The edge length of its unit cell is 5.08 Å.

(K = 39.10)

30. Copper has the ccp structure and a density of 8.92 g cm^{-3}. What is the atomic radius of the metal?

(Cu = 63.45)

31. Calculate the side length of the unit cell of lithium chloride; given that its density is 2.068 g cm^{-3}, and that it has the fcc structure.

(Li = 6.94, Cl = 35.45)

32. What is the atomic radius of platinum, given that it has the ccp structure, and that its density is 21.45 g cm^{-3}?

(Pt = 195.09)

X-ray crystallography

33. A crystal of magnesium was examined with a beam of 90.7 pm x-rays. What is the metallic radius of the metal if an intense spot was obtained for an angle of scattering of 8.68°?

34. A crystal of barium was examined with 102 pm x-rays. What is the metallic radius of the metal if constructive interference was obtained for an angle of incidence of 6.83°?

35. The metallic radius of calcium was obtained to be 180 pm during an experiment on x-ray diffraction. What is the wavelength of the x-rays if an intense spot was obtained for an angle of scattering of 20.1° from the layers of the crystal?

36. The metallic radius of rubidium was obtained to be 235 pm when it was examined with 78.5-pm x-rays. Calculate the angle of intense reflection of the x-rays from the layers of the crystal.

Viscosity of liquids

37. Beginning from Stokes' law, show that the viscosity of a liquid is related to its density and that of a sphere moving in it by the equation

$$h = \frac{2r^2 g(\rho_s - \rho_L)}{9v}$$

where r_s = The density of the sphere.
r_L = The density of the liquid.
r = The radius of the sphere.
g = Acceleration due to gravity.
v = The terminal velosity of the sphere.

38. Explain how the viscosity of a liquid differ from that of a gas.

39. Calculate the viscosity of acetone at a temperature at which the density of the liquid is 784.6 kg m^{-3} if a teflon sphere of radius 1.2 mm attained a terminal velocity of 14 m s^{-2} in the liquid. The density of teflon is 2200 kg m^{-3}.

(g = 9.8 m s^{-2})

40. The terminal velocity of a teflon sphere of radius 1.2 mm in water is 4.2 m s^{-1} at a particular temperature. What is the viscosity of water at this temperature, given that the densities of teflon and water are 2200 kg m^{-3} and 1000 kg m^{-3} respectively?

(g = 9.8 m s^{-2})

41. The viscosity of a liquid is 0.925 Pa s. What is the density of the liquid if the terminal velocity of a brass sphere of radius is 1.2 mm in the liquid is 2.56 cm s^{-1}? The density of brass is 8400 kg m^{-3}.

(g = 9.8 m s^{-2})

42. The viscosity of a liquid at a particular temperature is 1500 cP. What is the density of the liquid if the terminal velocity of a brass sphere of radius 1.5 mm moving in it is 2.4 cm s^{-1}? The density of brass is 8400 kg m^{-3}.

(g = 9.8 m s^{-2})

43. The viscosity of a liquid is 0.527 kg m^{-1} s^{-1} when its density is 950 kg m^{-3}. Calculate the terminal velocity of a steel sphere of radius 1.5 mm in the liquid, given that the density of steel is 7800 kg m^{-3}.

(g = 9.8 m s^{-2})

44. What would be the terminal velocity of a copper sphere of radius 1.2 mm in a liquid whose density and viscosity are 500.0 kg m^{-3} and 1.2 cP respectively? The density of copper is 8900 kg m^{-3}.

(g = 9.8 m s^{-2})

Surface tension

45. What do you understand by capillarity, and how does it vary with the density of a liquid?

46. Ethanol rises to a height of 2.33 cm in a capillary tube of radius 0.25 mm.What is the surface tension of the liquid if its density is 789 kg m^{-3}?

(g = 9.8 m s^{-2})

47. A liquid rises to a height of 2.12 cm in a tube of radius 0.25 mm. What is the surface tension of the liquid if its density is 850 kg m^{-3}?

(g = 9.8 m s^{-2})

48. The surface tension of a liquid is 0.070 N m^{-1}. To what height of a capillary tube of radius 0.10 mm would it rise if its density is 950 kg m^{-3}?

(g = 9.8 m s^{-2})

49. A liquid rises to a height of 1.7 cm in a capillary tube of radius 0.25 mm. What is the density of the liquid if its surface tension is 0.0625 N m^{-1}?

(g = 9.8 m s^{-2})

50. A liquid rises to a height of 1.50 cm in a capillary tube. What is the radius of the tube if the density and surface tension of the liquid are 1.80 × 10^{3} kg m^{-3} and 0.135 N m^{-1} respectively?

(g = 9.8 m s^{-2})

Answers

1. B 2. D 3. E 4. A 5. B 6. E
7. B 8. C 9. E 10. B 11. B 12. C
13. B
18. (b) 7.2 kJ mol^{-1}
21. 120 mmHg
22. 35.3 kJ mol^{-1}
23. 237 Torr
24. 18.6 g cm^{-3}
25. 11.4 g cm^{-3}
26. 7.53 g cm^{-3}
27. 20 g cm^{-3}
28. fcc
29. bcc
30. 128 pm
31. 515 pm

32. 139 pm
33. 150 pm
34. 214 pm
35. 250 pm
36. 4.79°
39. 3.2×10^{-4} Pas
40. 9.0×10^{-4} Pas
41. 850 kgm^{-3}
42. 1.1×10^{3} kgm^{-3}
43. 6.4 cms^{-1}
44. 22 ms^{-1}
46. 0.023 Nm^{-1}
47. 0.022 Nm^{-1}
48. 15 cm
49. 3000 kgm^{-3}
50. 1.02 mm

7

Chapter

Properties of Solutions

A solution is a homogeneous mixture formed when a solute dissolves in a solvent, i.e.

Solution = Solvent + Solute

A solvent is a substance which dissolves another substance called the solute. A sugar solution, for example, is obtained by dissolving sugar (the solute) in water (the solvent). A solute or solvent may be gas, liquid or solid. Water is called a universal solvent because it is the most abundant solvent available.

7.1 CONCENTRATION

Concentration C is the amount of a solute present in a given solvent. A concentrated solution is a solution that contains a large amount of the solute in a small amount of the solvent. The concentration of a substance is indicated by inserting its symbol in square brackets, [ ]. For example, [X] means concentration of X.

Concentration is measured in mol dm^{-3}*, which is the number of moles of the solute contained in 1 dm^{3} of the solvent. This is called molar concentration or molarity, and is given by the relation

$$C = \frac{n}{V}$$

where C = Molar concentration.

n = Number of moles of the solute.

V = Volume of the solvent in dm^{3}.

The unit mol dm^{-3} is often shortened to M (pronounced molar).

Concentration can also be measured in g dm^{-3}, which is the mass of the solute present in a 1 dm^{3} of the solvent. This is called mass concentration, and is given by the relation

$$\rho = \frac{m}{V}$$

where r = Mass concentration.

m = Mass of solute in g.

V = Volume of solvent in dm^3.

[*] This unit is also the same as mole per litre (mol L^{-1})

The relationship between molar and mass concentrations is derived as follows: The mass of a given amount of a substance is given by the relation

$$m = M \times n$$

Substituting this into the formula for mass concentration we obtain

$$\rho = \frac{Mn}{V} = MC$$

Thus mass concentration is the product of molarity and molar mass.

Dilution: Dilution is the reduction of the concentration of a solution by adding more of the solvent. A dilute solution is one which contains a small amount of the solute in a large amount of the solvent.

The principle of dilution is based on the fact that the amount of a solute in a solvent will always remain constant, regardless of the amount of the solvent added, provided no more solute is introduced into the solution. For example, a solution prepared by dissolving a cube of sugar in a cup of water would still contain the same amount of sugar even if the solution is made up to a barrel, or any other volume for that matter. What has changed is the concentration, but the number of moles of the substance remains the same. Since the number of moles of a substance in solution is given by $n = CV$, then we have

$C_1V_1 = C_2V_2$, etc.

where C_1 = Initial concentration of the solution.

V_1 = Initial volume of the solution.

C_2 = Final concentration of the solution.

V_2 = Final volume of the solution.

This equation is known as dilution law.

Standard solution: A standard solution is a solution of known concentration. A molar solution is the solution that contains exactly 1 mol of the solute. Standard solutions are important in volumetric analysis[1] where the amount of a substance in a solution is determined by titrating it against the standard solution of another substance.

Standard solutions are prepared with a volumetric flask, which comes in different sizes. The first step is to calculate the quantity of the solute needed to be dissolved in a specific amount of the solvent, usually distilled water, to produce a solution of the required concentration. The amount of a solid solute, such as a base, required to make a standard solution is easilly obtained by weighing it out using an accurate balance. For example, if a 20 g dm^{-3} solution of potassium hydroxide is required, all we need to do is to weigh 20 g of the base, dissolve it in a 1-dm^3 volumetric flask and make up the volume to the 1 dm^3 mark.

On the other hand, it is not possible to prepare standard solutions of liquids, such as acids, by weighing. The volume of the liquid which contains the required amount of the substance must first be obtained from careful calculations. The required volume is then measured with an appropriate apparatus, such as a measuring cylinder or burrete, before the required standard solution can be prepared.

[1] Volumetric analysis is treated in Chapter 8.

Example 1 5.5 g of sodium chloride was made up to 25 cm^3 of solution. Calculate:

(a) the molar concentration of the resulting solution;

(b) the mass concentrations of the resulting solution.

(Na = 23.0, Cl = 35.5)

Solution

(a) The molar concentration of the solution is calculated from the relation

$$C = \frac{n}{V}$$

The number of moles of the salt is obtained from the relation

$$n = \frac{m}{M}$$

$M = (23.0 + 35.5)\ \text{g mol}^{-1}$
$= 58.5\ \text{g mol}^{-1}$
$m = 5.5$ g
$n = ?$

Substituting we obtain

$$n = \frac{5.5\,\cancel{g} \times 1\text{ mol}}{58.5\,\cancel{g}}$$

$= 0.094$ mol

$V = 25\text{ cm}^3 = 0.025\text{ dm}^3$

$C = ?$

Finally, substituting into the original equation yields

$$C = \frac{0.094\text{ mol}}{0.025\text{ dm}^3}$$

$= 3.8$ M (mol dm^{-3})

Alternatively, we can work from the first principle:
0.025 dm^3 contains of 0.094 mol of NaCl, therefore, 1.0 dm^3 will contain x, i.e.,

$0.025\text{ dm}^3 = 0.094$ mol

$1.0\text{ dm}^3 = x$

Thus $0.025 \times x = 1.0\text{ dm}^3 \times 0.094$ mol

$$\text{So } x = \frac{1.0\,\cancel{\text{dm}^3} \times 0.094\text{ mol}}{0.025\,\cancel{\text{dm}^3}}$$

$= 3.8$ mol

Since 1.0 dm^3 of the solvent contains 3.8 mol of the solute, then, the molarity of the solution is 3.8 M.

(b) We have to apply the relation

$$\rho = \frac{m}{V}$$

$m = 5.5$ g

$V = 0.025\text{ dm}^3$

$\rho = ?$

Substituting we obtain

$$\rho = \frac{5.5\text{ g}}{0.025\text{ dm}^3}$$

$= 220\text{ g dm}^{-3}$

We can as well work from the first principle:

0.025 dm^3 of solvent contains 5.5 g of the solute, then 1.0 dm^3 will contain x, i.e.

0.025 dm^3 = 5.5 g

1.0 dm^3 = x

Thus $0.025 \times x = 1.0\ dm^3 \times 5.5\ g$

$$x = \frac{1.0\ \cancel{dm^3} \times 5.5\ g}{0.025\ \cancel{dm^3}}$$

$$= 220\ g$$

Since 1.0 dm^3 of the solvent contains 220 g of the solute, then the mass concentration of the solution will be 220 g dm^{-3}.

Alternatively, we can also apply the relation

$\rho = MC$

$M = 58.5\ g\ mol^{-1}$

$C = 3.8\ mol\ dm^{-3}$

$\rho = ?$

Substituting we obtain

$$\rho = \frac{5.5\ g}{1\ \cancel{mol}} \times 3.8\ \cancel{mol}\ dm^{-3}$$

$$= 220\ g\ dm^{-3}$$

Example 2 Calculate the amount of a solute in 250 cm^3 of a 1.5-M solution of the solute.

Solution We have to apply the relation

$$C = \frac{n}{V}$$

$\therefore\ n = C \times V$

$C = 1.5\ mol\ dm^{-3}$

$V = 250\ cm^3 = 0.025\ dm^3$

$n = ?$

Substituting we obtain

$$n = \frac{1.5\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 0.025\ \cancel{\text{dm}^3}$$

$= 60$ mol

Alternatively, we can work from the first principle:

1.0 dm^3 of solvent contains 1.5 mol of the solute, then 0.025 dm^3 would contain x, i.e.

1.0 $\text{dm}^3 = 1.5$ mol

0.025 $\text{dm}^3 = x$

Thus $1.0 \times x = 0.025\ \text{dm}^3 \times 1.5$ mol

$$\text{Then } x = \frac{0.025\ \cancel{\text{dm}^3} \times 1.5\ \text{mol}}{1.0\ \cancel{\text{dm}^3}}$$

$= 60$ mol

Example 3 What volume of a 0.50 M solution of sodium chloride must be evaporated to dryness in order to obtain 10.2 g of the salt as residue?

(Na = 23.0, Cl = 35.5)

Solution The applicable relation is

$$C = \frac{n}{V}$$

$$\therefore\ V = \frac{n}{C}$$

The number of moles of the salt has to be calculated from the relation

$$n = \frac{m}{M}$$

$M = (23.0 + 35.5)\ \text{g mol}^{-1} = 58.5\ \text{g mol}^{-1}$

$m = 10.2$ g

$n = ?$

$$\text{So } n = \frac{10.2\ \cancel{\text{g}} \times 1\ \text{mol}}{58.5\ \cancel{\text{g}}}$$

$= 0.174$ mol

$C = 0.50 \text{ mol dm}^{-3}$

$V = ?$

Finally, we now substitute to obtain

$$V = \frac{0.174 \cancel{\text{mol}} \times 1 \text{ dm}^3}{0.50 \cancel{\text{mol}}}$$

$= 0.35 \text{ dm}^3 = 350 \text{ cm}^3$

Alternatively, we can work from the first principle, as follows:

1.0 dm^3 of solution contains 0.50 mol of the solute, then x will contain 0.174 mol, i.e.

$1.0 \text{ dm}^3 = 0.50 \text{ mol}$

$x = 0.174 \text{ mol}$

Then $x \times 0.50 \text{ mol} = 1.0 \text{ dm}^3 \times 0.174 \text{ mol}$

$$\text{Thus } x = \frac{1.0 \text{ dm}^3 \times 0.174 \cancel{\text{mol}}}{0.50 \cancel{\text{mol}}}$$

$= 0.35 \text{ dm}^3 = 350 \text{ cm}^3$

Example 4 What volume of water must be added to 20.0 cm^3 of a 0.70-M sulphuric acid solution to reduce its concentration to 0.010 M?

Solution The volume of the solvent required to be added is obtained by subtracting the initial volume of the solution from the volume after dilution. The final volume is calculated from the dilution law:

$C_1V_1 = C_2V_2$

$C_1 = 0.70 \text{ M}$

$V_1 = 20.0 \text{ cm}^3$

$C_2 = 0.010 \text{ M}$

$V_2 = ?$

Substituting we have

$0.70 \text{ M} \times 20 \text{ cm}^3 = 0.010 \text{ M} \times V_2$

$$\text{Thus } V_2 = \frac{0.70 \cancel{\text{M}} \times 20.0 \text{ dm}^3}{0.010 \cancel{\text{M}}}$$

$= 1400 \text{ cm}^3$

Thus the required volume of the solvent is

$V = 1400\ \text{cm}^3 - 20.0\ \text{cm}^3$

$= 1380\ \text{cm}^3$

Example 5 Calculate the concentration of the solution from which 500.0 cm^3 of a 0.21-M solution was prepared if the original volume of the solution was 50.0 cm^3.

Solution We have to apply the relation

$C_1V_1 = C_2V_2$

$V_1 = 50.0\ \text{cm}^3$

$C_2 = 0.21\ \text{M}$

$V_2 = 500.0\ \text{cm}^3$

$C_1 = ?$

Substituting we have

$C_1 \times 50.0\ \text{cm}^3 = 0.21\ \text{M} \times 500.0\ \text{cm}^3$

So $C_1 = \dfrac{0.21\,\text{M} \times 500.0\,\cancel{\text{cm}^3}}{50.0\,\cancel{\text{cm}^3}}$

$= 2.1\ \text{M}$

Example 6 What volume of a 20.8-M concentrated hydrochloric acid solution is required to prepare 2.5 dm^3 of a 0.15-M solution of the acid ?

Solution We have to apply the relation

$C_1V_1 = C_2V_2$

$C_1 = 20.8\ \text{M}$

$V_2 = 2.5\ \text{dm}^3$

$C_2 = 0.15\ \text{M}$

$V_1 = ?$

Substituting we have

$20.8\ \text{M} \times V_1 = 0.150\ \text{M} \times 2.5\ \text{dm}^3$

Then $V_1 = \dfrac{0.21\,\cancel{\text{M}} \times 2.5\ \text{dm}^3}{20.8\,\cancel{\text{M}}}$

$= 0.018\ \text{dm}^3$

This volume of the concentrated solution must be made up to 2.5 dm^3 to obtain a 0.150-M solution of the acid.

Example 7 What mass of sodium hydroxide, NaOH, is required to prepare a 0.010-M solution of the base.

(Na = 23.0, O = 16.0, H = 1.0)

Solution To prepare a 0.010-M solution of NaOH, we have to make up 0.010 mol of the base to 1 dm^3 of the solvent. The mass equivalent of this amount of the base is obtained from the relation

$$n = \frac{m}{M}$$

$$\therefore \ m = n \times M$$

M = (23.0 + 16.0 + 1.0) g mol^{-1} = 40.0 g mol^{-1}

n = 0.010 mol

m = ?

Substituting we have

$$m = 0.010 \cancel{\text{mol}} \times \frac{40.0 \text{ g}}{1 \cancel{\text{mol}}}$$

= 0.40 g

This means 0.40 g of the base must be weighed and make up to 1 dm^3 of solution. If a larger volume of the solution is required, then we have to multiply this amount of the base by the volume of the solution required. For example, if 10 dm^3 of solution is required, then the mass to be weighed will be

10 × 0.40 g = 4.0 g

Example 8 What mass of sodium carbonate is required to make 20.5 dm^3 of a 6.3-g dm^3 solution of the salt?

(C = 12, O = 16, Na = 23)

Solution We have to make up 6.3 g of the solute to 1 dm^3 of solution to obtain 1 dm^3 of a 6.3-g dm^{-3} solution.

The mass required to make 20.5 dm^3 of the same solution is

20.5 × 6.3 g = 130 g

Example 9 What volume of a concentrated sulphuric acid solution is required to prepare a 0.050-M solution of the acid, given that the density and percentage composition of the acid are 1.84 g cm^{-3} and 98% respectively?

(H = 1, O = 16, S = 32)

Solution The concentration of 0.050-M means 0.050 mol of the pure acid is present in 1.0 dm^3 of solution. The mass of this amount of the acid is obtained from the relation

$$n = \frac{m}{M}$$

$$\therefore\ m = n \times M$$

$M = [(2 \times 1) + 32 + (4 \times 16)]\ \text{g mol}^{-1} = 98\ \text{g mol}^{-1}$

$n = 0.050$ mol

$m = ?$

Substituting we have

$$m = 0.050\ \cancel{\text{mol}} \times \frac{98\ \text{g}}{1\ \cancel{\text{mol}}}$$

$= 4.9$ g

We must now calculate the volume of this mass of the pure acid from its density, using the relation

$$\rho = \frac{m}{V}$$

$$\therefore\ V = \frac{m}{\rho}$$

$m = 4.9$ g

$\rho = 1.84\ \text{g cm}^{-3}$

Substituting we have

$$V = \frac{4.9\ \cancel{\text{g}} \times 1\ \text{cm}^3}{1.84\ \cancel{\text{g}}}$$

$= 2.7\ \text{cm}^3$

This is the required volume of the pure acid. Finally, we have to determine the volume of the concentrated acid solution containing this volume of the pure acid. The percentage composition of 98% means 1.0 cm^3 of the concentrated acid solution contains 0.98 cm^3 of the pure acid. Thus x would contain 2.7 cm^3 of the pure acid, i.e.

$1.0\ \text{cm}^3 = 0.98\ \text{cm}^3$

$x = 2.7\ \text{cm}^3$

$x \times 0.98\ \text{cm}^3 = 1.0\ \text{cm}^3 \times 2.7\ \text{cm}^3$

$$\therefore\ x = \frac{1.0\ \cancel{\text{cm}^3} \times 2.7\ \text{cm}^3}{0.98\ \cancel{\text{cm}^3}}$$

$= 2.8\ \text{cm}^3$

This is the volume of the concentrated acid solution that should be made up to 1.0 dm^3 of solution to obtain a 0.050-M acid solution.

Alternatively, we can first obtain the molar concentration of the concentrated acid solution. We can then calculate the volume required to make 0.050-M acid solution from dilution law. We begin by calculating the mass of the pure acid in 1.0 dm^3 of the acid solution:

$$\rho = \frac{m}{V}$$

$\therefore\ m = r \times V$

$\rho = 1.84\ \text{g cm}^{-3}$

$V = 1.0\ \text{dm}^3 = 1000.0\ \text{cm}^3$

$m = ?$

Substituting we obtain

$$m = \frac{1.84\ \text{g}}{1\ \cancel{\text{cm}^3}} \times 1000.0\ \cancel{\text{cm}^3}$$

$= 1840\ \text{g}$

But the composition of the pure acid in the concentrated acid solution is 98%. Thus the mass of the pure acid in 1.0 dm^3 of the concentrated acid solution is

$m = 0.98 \times 1840\ \text{g}$

$= 1800 \text{ g}$

This means that the mass concentration of the pure acid is 1800 g dm^{-3}. We have to convert this to molarity using the relation

$\rho = CM$

$\therefore C = \frac{\rho}{M}$

$M = 98 \text{ g mol}^{-1}$

$C = ?$

Substituting we obtain

$C = \frac{1800 \cancel{\text{g}} \times 1 \text{ mol}}{98 \cancel{\text{g}} \times 1 \text{ dm}^3}$

$= 18 \text{ M}$

We can now calculate the volume of the concentrated acid required from the dilution law:

$C_1V_1 = C_2V_2$

$C_1 = 18 \text{ M}$

$C_2 = 0.050 \text{ M}$

$V_2 = 1.0 \text{ dm}^3$

$V_1 = ?$

Substituting we have

$18 \text{ M} \times V_1 = 0.050 \text{ M} \times 1.0 \text{ dm}^3$

So $V_1 = \frac{0.50 \cancel{\text{M}} \times 1.0 \text{ dm}^3}{18 \cancel{\text{M}}}$

$= 0.0028 \text{ dm}^3 = 2.72 \text{ cm}^3$

Example 10 What is the concentration of nitric acid, HNO_3, solution prepared by making up 6.0 cm^3 of the concentrated acid to 1.0 dm^3 of solution, given that the acid has a density and percentage composition of 1.52 g cm^{-3} and 68% respectively?

(H = 1, N = 14, O = 16)

Solution We have to begin by calculating the volume of the pure acid in 6.0 cm^3 of the concentrated acid solution. Since the percentage composition of the acid in the concentrated acid solution is 68%, then the volume of the pure acid in 6.0 cm^3 of the concentrated acid solution will be

$V = 0.68 \times 6.0\ \text{cm}^3$

$= 4.1\ \text{cm}^3$

The mass equivalence of this volume of the pure acid is calculated from the relation

$\rho = \frac{m}{V}$

$\therefore\ m = r \times V$

$\rho = 1.52\ \text{g cm}^{-3}$

$V = 4.1\ \text{cm}^3$

$m = ?$

Substituting we have

$m = \frac{1.52\ \text{g}}{1\ \cancel{\text{cm}^3}} \times 4.1\ \cancel{\text{cm}^3}$

$= 6.2\ \text{g}$

This is the mass of the pure acid present in 1.0 dm^3 of the solution, i.e. the mass concentration of the resulting acid solution is 6.2 g dm^{-3}. The molarity is obtained from the relation

$C = \frac{\rho}{M}$

$M = [1 + 14 + (3 \times 16)]\ \text{g mol}^{-1} = 63\ \text{g mol}^{-1}$

$C = ?$

Substituting we have

$C = \frac{6.2\ \cancel{\text{g}} \times 1\ \text{mol}}{63\ \cancel{\text{g}} \times 1\ \text{dm}^3}$

$= 0.098\ \text{M}$

Alternatively, we can calculate the concentration of the resulting solution from dilution law. To do this we must first calculate the mass of 1.0 dm^3 of the concentrated acid solution:

$\rho = \frac{m}{V}$

$\therefore\ m = r \times V$

$\rho = 1.52\ \text{g cm}^{-3}$

$V = 1.0 = 1000.0\ \text{cm}^3$

$m = ?$

Substituting we obtain

$m = \frac{1.52\ \cancel{g}}{1\ \cancel{\text{cm}^3}} \times 1000.0\ \cancel{\text{cm}^3}$

$= 1520\ \text{g}$

Since the mass composition of the acid in the concentrated acid solution is 68%, then, the mass of the pure acid in the same volume of the concentrated acid solution will be

$$m = 0.68 \times 1520\ \text{g} = 1.0 \times 10^3\ \text{g}$$

This is the mass of the pure acid in 1.0 dm^3 of the solution, i.e., the mass concentration of the pure acid is $1.0 \times 10^3\ \text{g dm}^{-3}$. The molarity of the acid is obtained from the relation

$C = \frac{\rho}{M}$

$M = 63\ \text{g}$

$C = ?$

Substituting we have

$C = \frac{1.0 \times 10^3\ \cancel{g} \times 1\ \text{mol}}{63\ \cancel{g} \times 1\ \text{dm}^3}$

$= 16\ \text{M}$

The concentration of the resulting solution can now be calculated from the dilution law:

$C_1V_1 = C_2V_2$

$C_1 = 16\ M$

V_1 = 6.0 cm^3 = 0.0060 dm^3

V_2 = 1.0 dm^3

C_2 = ?

Substituting we obtain

16 M × 0.0060 dm^3 = C_2 × 1.0 dm^3

So $C_2 = \dfrac{16\ \text{M} \times 0.0060\ \cancel{\text{dm}^3}}{1.0\ \cancel{\text{dm}^3}}$

= 0.096 M

Note that the slight difference is due to rounding.

Practice Problems

1. 2.20 g of a solute is present in 55.0 cm^3 of a solution. What is the mass concentration and molarity of the resulting solution, given that the molar mass of the solute is 160 g mol^{-1}. [*Answer:* 40 g dm^{-3}, 0.30 M]
2. A 0.15-M solution of sulphuric acid was prepared by making up 6.7 cm^3 of the concentrated acid to 16.5 cm^3. What is the concentration of the acid solution?

   [*Answer:* 0.37 M]
3. What amount of water must be added to 500.0 cm^3 of 0.500-M solution of nitric acid solution to make a 0.200-M solution of the acid?

   [*Answer:* 750.0 cm^3]
4. What mass of potassium hydroxide is required to make 9.0 dm^3 of a 0.15-M solution of the base?

   (H = 1, O = 16, K = 39) [*Answer:* 75.6 g]
5. What volume of concentrated hydrochloric acid solution of density 1.25 g cm^{-3} and percentage composition of 20.24% is required to make 15.5 dm^3 of a 0.100-M solution?

   (H = 1.0, Cl = 35.5) [*Answer:* 223 cm^3]
6. You are asked to dissolve 6.8 cm^3 of a concentrated sulphuric acid solution in distilled 250 cm^3 of distilled water and make up the solution to 1000 cm^3 by adding more water. What is the molarity of the resulting solution, given

that the density and percentage composition of the acid are 1.84 g cm^{-3} and 98% respectively.

(H = 1, O = 16, S = 32) [*Answer:* 0.12 M]

7.2 MOLALITY

Molality is the number of moles of a solute dissolved in one kilogram (kg) of a solvent, i.e.

Molality $= \frac{n}{m}$

where n = Number of moles of the solute.

m = Mass of solvent in kg.

The unit of molality is mol kg^{-1}, called molal (m).

Example 1 Calculate the molality of 50.0 g of sodium chloride dissolved in 200.0 g of water.

(Na = 23.0, Cl = 35.5)

Solution We have to apply the relation

$$\text{Molality} = \frac{n}{m}$$

We now convert 50.0 g of NaCl to moles using the relation

$n = \frac{m}{M}$

M = (23.0 + 35.5) g mol^{-1} = 58.5 g mol^{-1}

$n = \frac{50.0\,\cancel{g} \times 1\,\text{mol}}{58.5\,\cancel{g}}$

= 0.855 mol

m = 220 g = 0.22 kg

Molality = ?

Substituting we have

Molality $= \frac{0.855\,\text{mol}}{0.22\,\text{kg}}$

$= 3.9\ m$

Example 2 Calculate the amount of ethanol, C_2H_5OH, that must be added to 11.0 g of water to produce a solution whose molality is 1.8 *m*.

Solution We have to apply the relation

$$\text{Molality} = \frac{n}{m}$$

$$\therefore\ n = \text{Molality} \times m$$

$\text{Molality} = 1.8 \text{ mol kg}^{-1}$

$m = 11.0 \text{ g} = 0.011 \text{ kg}$

$n = ?$

Substituting we have

$$n = \frac{1.8 \text{ mol}}{1\ \cancel{\text{kg}}} \times 0.011\ \cancel{\text{kg}}$$

$$= 0.020 \text{ mol}$$

Example 3 To what mass of a solvent must 0.0125 mol of a substance be added to produce a solution whose molality is 2.80 *m*?

Solution We have to apply the relation

$$\text{Molality} = \frac{n}{m}$$

$$\therefore\ m = \frac{n}{\text{Molality}}$$

$n = 0.0125 \text{ mol}$

$\text{Molality} = 2.80 \text{ mol kg}^{-1}$

$m = ?$

Substituting we have

$$m = \frac{0.0125\ \cancel{\text{mol}} \times 1 \text{ kg}}{2.80\ \cancel{\text{mol}}}$$

$$= 4.46 \times 10 - 3 \text{ kg} = 4.46 \text{ g}$$

Practice Problems

1. Calculate the molality of the solution prepared by dissolving 2.5 g of sodium hydroxide, NaOH, in 150 g of water.

   (H = 1, O = 16, Na = 23) [*Answer:* 0.42 *m*]

2. What mass of sodium chloride, NaCl, must be added to 100 g of water to make a solution whose molality is 0.85 *m*?

   (Na = 23.0, Cl = 35.5) [*Answer:* 50 g]

7.3 SOLUBILITY AND SOLUBILITY PRODUCT

A saturated solution is a solution that contains the maximum amount of the solute that it can dissolve at a particular temperature. In a saturated solution, the dissolved and undissolved solute are in a state of dynamic equilibrium, i.e., the solute dissolves at the same rate at which the crystals of the solute are being formed from the solution.

A saturated solution is prepared by dissolving the solute in the solvent at a particular temperature until the crystals of the solute start forming. The solution is then filtered to remove the undissolved solute particles. The solubility of the solute at that temperature is obtained by evaporating the solution to dryness, and weighing the residue.

The solubility S of a solute, measured in g dm^{-3} or M, is the maximum amount of a solute that can be dissolved by 1 dm^3 of a solvent at a particular temperature. In other words, the solubility of a solute at a particular temperature is the concentration of the solute in a saturated solution at that temperature.

The factors affecting solubility include temperature, pressure and polarity. Increasing the temperature of a solution could either increase or decrease the solubility of a solid solute, depending on its nature. For solutes which dissolve endothermically, an increase in temperature means more energy would be available for bond breaking, apart from that available from the solvent. Hence, solubility would be increased. Examples of such solutes are sodium chloride, sodium fluoride, silver chloride, potassium nitrate, etc. On the other hand, solid substances which dissolve exothermically need to dissipate energy to dissolve. It then follows that an increase in the temperature of their solutions reduces the extent to which heat can be dissipated, hence the solubility decreases. Examples of such solutes include silver fluoride, magnesium chloride, lithium chloride, calcium hydroxide, aluminium nitrate, etc.

Pressure has no effect on the solubility of solids, but the solubility of most gases increases with pressure. The effect of pressure on gas solubility is observed when a bottle of soft drink is opened. Carbon dioxide, a gas used as a preservative, escapes due to reduced pressure.

Polar substances like ionic compounds and ethanol are readily soluble in a polar solvent like water. The solubility of some organic solutes, such as ethanol, in water is due to the presence of the hydroxyl group (−OH) which forms the hydrogen bond with water. Non-polar substances like covalent compounds will dissolve in non-polar solvents like toluene, benzene, turpentine, etc.

Just like chemical reactions, we can calculate the reaction quotient, called ion product Q_{sp}, for substances in solution. Consider a solute M_xA_y dissolved in solution:

$$M_xA_y(s) \text{ Æ } yM^{y+}(aq) + xA^{x-}(aq)$$

where M^{y+} and A^{x-} are the ions of the solute. y and x are the stoichiometric coefficients or number of moles of the ions. The ion product Q_{sp} is given as

$$Q_{sp} = \frac{[M^{y+}]^m[A^{x-}]^a}{[MA]}$$

Since the concentration of a pure solid is constant, then the denominator can be taken to be unity, such that the equation now becomes

$$Q_{sp} = [M^{y+}]^m\ [A^{x-}]^a$$

This is the general expression for the ion product of a substance in solution.

At equilibrium or when the solution is saturated, the ion product is called solubility product K_{sp}, i.e.

$$Q_{sp} \text{ at equilibrium} = K_{sp}$$

Thus K_{sp} is the equilibrium constant of a solution. It is defined as a temperature-dependent constant referring to a stage of dynamic equilibrium or saturated solution. The following practical information can be obtained from ion product:

If $Q_{sp} = K_{sp}$ Solution is at equilibrium, i.e., solution is saturated and no more solute dissolves.

If $Q_{sp} < K_{sp}$ Solution is unsaturated and no precipitate forms. More solute dissolves until equilibrium is attained.

If $Q_{sp} > K_{sp}$ The solute precipitates.

The above information provides us with an invaluable tool in qualitative analysis, as the knowledge of solubility equilibria helps to predict whether a salt will precipitate from solution, or not.

Example 1 200.0 cm^3 of a saturated solution of sodium chloride, NaCl, was found to contain 25.0 g of the dissolved in it at 20°C. What is the solubility of the salt at this temperature?

(Na = 23.0, Cl = 35.5)

Solution The solubility of the solute at the specified temperature is its concentration in the saturated solution. Thus the solubility in g dm^{-3} is given by the relation

$$S = \frac{m}{V}$$

m = 25.0 g

V = 200.0 cm^3 = 0.20 dm^3

S = ?

Substituting we obtain

$$S = \frac{25.0\ g}{0.20\ dm^3}$$

= 130 g dm^{-3}

Alternatively, we can work from the first principle:

0.20 dm^3 of saturated solution contains 25.0 g of the solute, then 1.0 dm^3 of the solution would contain x , i.e.

25.0 g = 0.20 dm^3

x = 1.0 dm^3

So $x \times 0.20\ dm^3 = 25.0\ g \times 1.0\ dm^3$

$$\text{Thus, } x = \frac{25.0\ g \times 1.0\ \cancel{dm^3}}{0.20\ \cancel{dm^3}}$$

= 130 g

Since 1.0 dm^3 of the saturated solution contains 130 g of the solute, then the solubility of the solute is 130 g dm^{-3}.

The solubility in M is calculated from the relation

$$S = \frac{\rho}{M}$$

M = (23 + 35.5) = 58.5 g mol^{-1}

S = ?

Substituting we obtain

$S = \frac{130\,\cancel{g} \times 1\text{ mol}}{58.5\,\cancel{g} \times 1\text{ dm}^3}$

= 2.2 M

We can as well apply the relation

$$S = \frac{n}{V}$$

The number of moles of the solute in the saturated solution is obtained from the relation

$n = \frac{m}{M}$

m = 25.0 g
M = 58.5 g
n = ?

Thus $n = \frac{25.0\,\cancel{g} \times 1\text{ mol}}{58.5\,\cancel{g}}$

= 0.43 mol
V = 0.20 dm^3
S = ?

Substituting we obtain

$S = \frac{0.43\text{ mol}}{0.20\text{ dm}^3}$

= 2.2 M

Alternatively, we can work from the first principle:
0.20 dm^3 of saturated solution contains 0.43 mol of the solute, then 1.0 dm^3 of saturated solution would contain x, i.e.

0.20 dm^3 = 0.43 mol
1.0 dm^3 = x

So $x \times 0.20\ \text{dm}^3 = 0.43\ \text{mol} \times 1.0\ \text{dm}^3$

Thus $x = \dfrac{0.43\ \text{mol} \times 1.0\ \cancel{\text{dm}^3}}{0.20\ \cancel{\text{dm}^3}}$

$= 2.2\ \text{mol}$

Since 1.0 dm^3 of saturated solution contains 2.2 mol of the solute, then the solubility of the solute at the prevailing temperature is 2.2 M.

Example 2 2500.0 g of a solution was cooled from 100 to 75°C, causing crystallization of some of the solute. Find the mass of the solution that would deposit 320.0 g of the solute if the solution weighs 2000.0 g after filtration.

Solution The mass of the solute which crystallized on cooling the solution is the difference in the masses of the solution before and after filtration. Thus the mass of the solute deposited by 2500.0 g of the solvent is

$$m = 2500.0\ \text{g} - 2000.0\ \text{g} = 500.0\ \text{g}$$

The amount of solution that will deposit 320.0 g of the solute is calculated as follows:

2500.0 g of the solution deposits 500.0 g of the solute, then x would deposit 320.0 g, i.e.

$2500.0\ \text{g} = 500.0\ \text{g}$

$x = 320.0\ \text{g}$

So $x \times 500.0\ \text{g} = 2500.0\ \text{g} \times 320.0\ \text{g}$

Then $x = \dfrac{2500.0\ \text{g} \times 320.0\ \cancel{\text{g}}}{500.0\ \cancel{\text{g}}}$

$= 1600\ \text{g}$

Example 3 1750.0 g of a solution containing sodium chloride and potassium chlorate in ratio 5:2 was cooled from 80 to 35°C. The solution was then filtered and reweighed. Calculate the percentage impurity in the sodium chloride crystals obtained, given that the mass of the solution is 800.0 g after filtration.

Solution The crystals contain both sodium chloride and potassium chlorate. The percentage impurity in the sodium chloride is the percentage by mass of potassium chlorate in the crystallized solutes.

The mass of the solutes that crystallized on cooling the solution is

$$m = 1750.0 - 800.0 = 950.0 \text{ g}$$

The mass of potassium chlorate in the crystallized solute is

$m = \frac{2}{7} \times 950.5 g$

$= 271.4$ g

Thus the percentage P of impurity in the sodium chloride crystal is

$m = \frac{271.4 \cancel{g}}{950.5 \cancel{g}} \times 100\%$

$= 28.6\%$

Example 4 Calculate the ion product of a calcium hydroxide, $Ca(OH)_2$, solution containing 8.0 g of the solute dissolved in 2.5 dm^3 of the solution at 25°C.

(H = 1, O = 16, Ca = 40)

Solution The first step is to write the balanced equation for the dissolution:

$$Ca(OH)_2(s) \Leftrightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

Thus $Q_{sp} = [Ca^{2+}][OH^-]^2$

The molar concentration of the dissolved solute is calculated from the relation

$$C = \frac{n}{V}$$

The amount of the dissolved solute is obtained from the relation

$n = \frac{m}{M}$

$M = [40 + (2 \times 16) + (2 \times 1)] \text{ g mol}^{-1} = 74 \text{ g mol}^{-1}$

$m = 8.0$ g

$n = ?$

Substituting we have

$n = \frac{8.0 \cancel{g} \times 1 \text{ mol}}{74 \cancel{g}}$

$= 0.11$ mol

$V = 2.5 \text{ dm}^3$

C = ?

Substituting we obtain

$$C = \frac{0.11\ \text{mol}}{2.5\ \text{dm}^3}$$

= 0.044 M

Alternatively, we can first obtain the molarity concentration from the relation

$$\rho = \frac{m}{V}$$

m = 8.0 g

V = 2.5 dm^3

ρ = ?

Substituting we have

$$\rho = \frac{8.0\ \text{g}}{2.5\ \text{dm}^3}$$

= 3.2 g dm^3

We can now calculate the molarity from the relation

$$C = \frac{\rho}{M}$$

M = 74 g mol^{-1}

C = ?

Substituting we have

$$C = \frac{3.2\ \cancel{\text{g}} \times 1\ \text{mol}}{74\ \cancel{\text{g}} \times 1\ \text{dm}^3}$$

= 0.043 mol

Note that the slight difference is due to rounding.

Since the dissolution of 1 mol of the solute produces 1 mol of Ca^{2+}, then the molarity of the two substances must be equal, i.e.

$$[Ca(OH)_2] = [Ca^{2+}] = 0.044\ \text{mol}$$

Since the dissolution of 1 mol of the solute produces 2 mol of OH^-, then the molarity of the ion must be twice that of the solute, i.e.

$[OH^-] = 2 \times [Ca(OH)_2] = 2 \times 0.044$ mol $= 0.088$ mol

$Q_{sp} = ?$

Finally, we can now substitute to obtain

$Q_{sp} = 0.044\ M \times (0.088\ M)^2$

Thus $Q_{sp} = 0.044\ M \times 7.7 \times 10^{-3}\ M^2$

$= 3.4 \times 10^{-4}\ M^3$

Example 5 250 cm^3 of a saturated solution of silver chloride contains 2.5×10^{-7} mol of the salt at a particular temperature. Calculate the solubility product of the salt at the prevailing temperature.

Solution The equation of dissolution is

$$AgCl(s) \Leftrightarrow Ag^+(aq) + Cl^-(aq)$$

The fact that the solution is saturated means equilibrium has been established between the solute and its ions. Thus the ion product to be calculated here must be termed the solubility product. K_{sp}, i.e.

$$K_{sp} = [Ag^+][Cl^-]$$

The molar concentration of the solute is obtained from the relation

$C = \frac{n}{V}$

$n = 2.5 \times 10^{-7}$ mol

$V = 250\ cm^3 = 0.25\ dm^3$

$C = ?$

Substituting we obtain

$C = \frac{2.5 \times 10^{-7}\ mol}{0.25\ dm^3}$

$= 1.0 \times 10^{-6}\ M$

Alternatively, we can obtain the molarity as follows:

If 250 cm^3 of water dissolves 2.5×0^{-7} mol of the solute at room temperature, then 1000 cm^3 (1 dm^3) would dissolve x at the same temperature, i.e.

$250\ cm^3 = 2.5 \times 10^{-7}$ mol

$1000\ \text{cm}^3 = x$

Thus $x \times 250\ \text{cm}^3 = 2.5 \times 10^{-7}\ \text{mol} \times 1000\ \text{cm}^3$

So $x = \dfrac{2.5 \times 10^{-7}\ \text{mol} \times 1000\ \cancel{\text{cm}^3}}{250\ \cancel{\text{cm}^3}}$

$= 1.0 \times 10^{-6}\ \text{mol}$

Since 1.0 dm^3 of water contains 1.0×10^{-6} mol of the solute, then the molarity of the solute is 1.0×10^{-6} M.

The above equation shows that 1 mol of AgCl produces 1 mol each of Ag^+ and Cl^-. Thus the concentrations of the two ions must be equal to that of the solute, i.e.

$[\text{AgCl}] = [\text{Ag}^+] = [\text{Cl}^-] = 1.0 \times 10^{-6}\ \text{M}$

$K_{sp} = ?$

We now substitute to obtain

$K_{sp} = 1.0 \times 10^{-6}\ \text{M} \times 1.0 \times 10^{-6}\ \text{M}$

$= 1.0 \times 10^{-12}\ \text{M}^2$

Example 6 The solubility product of barium sulphate is $2.5 \times 10^{-11}\ \text{M}^2$ at a certain temperature. Calculate the solubility in mol dm^{-3} and g dm^{-3} at this temperature.

(O = 16.0, S = 32.1, Ba = 137.3)

Solution The solubility in mol dm^{-3} of the solute is the mass concentration of its ions in a saturated solution. The equation for the dissolution is:

$$\text{BaSO}_4(s) \Leftrightarrow \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)$$

So $K_{sp} = [\text{Ba}^{2+}][\text{So}_4^{2-}]$

$K_{sp} = 2.5 \times 10^{-11}\ \text{M}^2$

$S = [\text{Ba}^{2+}] = [\text{So}_4^{2-}] = ?$

Substituting we have

$2.5 \times 10^{-11}\ \text{M}^2 = S \times S$

So $S^2 = 2.5 \times 10^{-11}\ \text{M}^2$

Taking the square roots of both sides, we obtain

$S = \pm\sqrt{2.5 \times 10^{-11}\ M^2}$

$= -5.0 \times 10^{-6}\ \text{M}$ or $5.0 \times 10^{-6}\ \text{M}$

Since concentration cannot be negative, we have to disregard the negative term to obtain

$$S = 5.0 \times 10^{-6}\ \text{M}$$

The solubility in g dm^{-3} is the mass concentration of the ion in the saturated solution. Thus

$S = MC$

$M = [137.3 + 32.1 + (16 \times 4)]\ \text{g mol}^{-1} = 233.4\ \text{g mol}^{-1}$

$C = 5.0 \times 10^{-6}\ \text{mol dm}^{-3}$

$S = ?$

Substituting we obtain

$$S = \frac{233.4\ \text{g}}{1\ \cancel{\text{mol}}} \times 5.0 \times 10^{-6}\ \cancel{\text{mol}}\ \text{dm}^{-3}$$

$$= 1.2 \times 10^{-3}\ \text{g dm}^{-3}$$

Example 7 Predict whether silver chloride would precipitate when 10.0 cm^3 of 1.0-mM copper(I) chloride solution is added to 100.0 cm^3 of a 0.8-mM solution of silver sulphate.

$$(K_{sp} = 1.6 \times 10^{-10}\ \text{M}^2)$$

Solution If the concentrations of Ag$^+$ and Cl$^-$ in the final solution are such that Q_{sp} for AgCl exceeds its solubility product, then the salt will precipitate. The equation for the dissolution of the salt is

$$\text{AgCl}(s) \Leftrightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq)$$

$Q_{sp} = [\text{Ag}^+][\text{Cl}^-]$

The molar concentration of the ions in solution is obtained from the relation

$$C = \frac{n}{V}$$

Since the volume is additive, then the total volume of the mixture would be

$$V = 100.0\ \text{cm}^3 + 10.0\ \text{cm}^3 = 110.0\ \text{cm}^3 = 0.11\ \text{dm}^3$$

The amount of each ion is obtained from the volume of the original solution, as follows:

$$n = C \times V$$

The equation for the dissolution of copper(I) chloride is

$$\text{CuCl}(s) \Leftrightarrow \text{Cu}^+(aq) + \text{Cl}^-(aq)$$

Since 1.0 mM of the solute produces 1 mol of Cl^-, then the concentration of Cl^- must be 1.0 mM or 1.0×10^{-3} mol dm^{-3}.

V = 10.0 cm^3 = 0.010 dm^3

n = ?

Substituting we obtain

$$n = \frac{1.0 \times 10^{-3}\,\mathrm{mol}}{1\,\cancel{\mathrm{dm}^3}} \times 0.010\,\cancel{\mathrm{dm}^3}$$

$= 1.0 \times 10^{-5}$ mol

$[\mathrm{CI}^-]$ = ?

We now substitute to obtain

$$[\mathrm{CI}^-] = \frac{1.0 \times 10^{-5}\,\mathrm{mol}}{0.11\,\mathrm{dm}^3}$$

$= 9.1 \times 10^{-5}$ M

We now repeat the same procedure for Ag^+:

$$\mathrm{Ag_2SO_4}(s) \Leftrightarrow 2\mathrm{Ag}^+(aq) + \mathrm{SO_4}^{2-}(aq)$$

Since 2 mol of Ag^+ is produced for every mol of $\mathrm{Ag_2SO_4}$ dissolved, then the molar concentration of the ion is

C = $2 \times 0.80 \times 10^{-3}$ mol dm^{-3} = 1.6×10^{-3} mol dm^{-3}

V = 100.0 cm^3 = 0.10 dm^3

n = ?

Substituting we have

$$n = \frac{1.6 \times 10^{-3}\,\mathrm{mol}}{1\,\cancel{\mathrm{dm}^3}} \times 0.10\,\cancel{\mathrm{dm}^3}$$

$= 1.6 \times 10^{-4}$ mol

$[\mathrm{Ag}^+]$ = ?

Substituting we have

$$[\mathrm{Ag}^+] = \frac{1.6 \times 10^{-4}\,\mathrm{mol}}{0.11\,\mathrm{dm}^3}$$

$= 1.5 \times 10^{-3}$ M

$Q_{sp} = ?$

Finally, we now substitute to obtain

$Q_{sp} = 9.1 \times 10^{-5}\ \text{M} \times 1.5 \times 10^{-3}\ \text{M}$

$= 1.4 \times 10^{-7}\ \text{M}^2$

Comparing this value to the solubility product, we see that $Q_{sp} > K_{sp}$. Thus the salt would precipitate.

Example 8 What volume of 0.20-mM solution of silver carbonate must be added to 100.0 cm^3 of 0.40-mM solution of barium sulphate to effect the precipitation of barium carbonate.

$$(K_{sp} = 8.1 \times 10^{-9}\ \text{M}^2)$$

Solution The solution would be saturated with ions of barium carbonate, i.e., Ba^{2+} and CO_3^{2-}, at equilibrium. Thus if we know the volume of 0.20-mM solution of silver carbonate that will make the resulting solution saturated with Ba^{2+} and CO^{2-}_3 then we can anticipate that any additional volume will make $Q_{sp} > K_{sp}$, resulting in the precipitation of the salt. Thus our primary goal is to obtain the volume at which $Q_{sp} = K_{sp}$.

The equation for the dissolution of $BaSO_4$ is

$$BaCO_3(s) \Leftrightarrow Ba^{2+}(aq) + CO_3^{2-}(aq)$$

So $K_{sp} = [Ba^{2+}][CO_3^{2-}]$

The concentration of each ion after mixing the two solutions is obtained from the relation

$C = \frac{n}{V}$

$V = 0.10\ \text{dm}^3 + x$

where V is the total volume of the mixture, and x the volume of Ag_2CO_3 added to the other solution. The amount of each ion is obtained from its original solution, as follows:

$$n = C \times V$$

Starting from $BaSO_4$, we have

$$BaSO_4(aq) \Leftrightarrow Ba^{2+}(aq) + SO_4^{2-}(aq)$$

The equation shows that 1 mol of Ba^{2+} is produced for every mol of $BaSO_4$

dissolved. Thus 0.40 mM of $BaSO_4$ must produce 0.40 mM of Ba^{2+}, i.e.

$C = 0.40 \times 10^{-3}\,\text{mol dm}^{-3}$
$V = 100.0\,\text{cm}^3 = 0.10\,\text{dm}^3$
$n = ?$

Substituting we have

$$n = \frac{0.40 \times 10^{-3}\,\text{mol}}{1\,\cancel{\text{dm}^3}} \times 0.10\,\cancel{\text{dm}^3}$$

$$= 4.0 \times 10^{-5}\,\text{mol}$$

$[Ba^{2+}] = ?$

Substituting we have

$$[Ba^{2+}] = \frac{0.4 \times 10^{-5}\,\text{mol}}{0.10\,\text{dm}^3 + x}$$

For Ag_2CO_3, we have

$$Ag_2CO_3(s) \Leftrightarrow 2Ag^+(aq) + CO_3^{2-}(aq)$$

The equation shows that 1 mol of Ag_2CO_3 produces 1 mol of CO_3^{2-}. Thus 0.20 mM of Ag_2CO_3 will equally produce 0.20 mM of CO_3^{2-}, i.e.

$C = 0.20 \times 10^{-3}\,\text{mol dm}^{-3}$
$V = x$
$n = ?$

Substituting we have

$n = 0.20 \times 10^{-3}\,\text{mol dm}^{-3} \times x = 0.20 \times 10^{-3}x\,\text{mol dm}^{-3}$

$[CO_3^{2-}] = ?$

Substituting we obtain

$$[CO_3^{2-}] = \frac{0.20 \times 10^{-3}x\,\text{mol dm}^{-3}}{0.10\,\text{dm}^3 + x}$$

$K_{sp} = 8.1 \times 10^{-9}\,\text{mol}^2\,\text{dm}^{-6}$

Substituting into the expression for the solubility product we have

$$8.1 \times 10^{-9}\ \text{mol}^2\,\text{dm}^{-6} = \left(\frac{4.0 \times 10^{-6}\ \text{mol}}{0.10\ \text{dm}^3 + x}\right) \times \left(\frac{0.20 \times 10^{-3}\,x\ \text{mol dm}^{-3}}{0.10\ \text{dm}^3 + x}\right)$$

We now simplify and omit the units to obtain

$$8.1 \times 10^{-9} = \frac{8.0 \times 10^{-8}x}{x^2 + 0.20x + 0.010}$$

Cross-multiplying and rearranging the result leads to the quadratic equation

$$8.1 \times 10^{-9}x^2 - 7.8 \times 10^{-8}\ x + 8.1 \times 10^{-11} = 0$$

We now solve this equation using the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$a = 8.1 \times 10^{-9}$, $b = -7.8 \times 10^{-6}$, $c = 8.1 \times 10^{-11}$

Substituting we have

$$x = \frac{-(-7.8 \times 10^{-8}) \pm \sqrt{(-7.8 \times 10^{-8})^2 - 4(8.1 \times 10^{-9})(8.1 \times 10^{11})}}{2(8.1 \times 10^{-9})}$$

So $x = \frac{7.8 \times 10^{-8} \pm 7.8 \times 10^{-8}}{1.6 \times 10^{-8}}$

Thus $x = 0$ or $x = 9.8$

0 is obviously not admissible. Thus $x = 9.8\ \text{dm}^3$. Consequently, we have to add a volume just above 9.8 dm^3 to effect the precipitation of $BaCO_3$.

Practice Problems

1. Sodium sulphate, Na_2SO_4, is dissolved in distilled water at 30°C until its c solution.

16)

380 g dm^{-3}, 2.7 M]

2. Copper(II) sulphate is to be obtained from 1950.0 g of a saturated solution c
weighs 900.0 g

66.7%]

3. The molarity of a saturated solution of sodium carbonate is 1.3×10^{-2} M at a

4. The solubility product of barium sulphate is 4.5×10^{-13} M^2 at 25°C. What is t
5. Predict whether the addition of 50.0 cm^3 of a 0.50-mM solution of barium su

M^2)

No, because $Q_{sp} < K_{sp}$]

6. You intend to precipitate copper(I) bromide by adding 20.0 cm^3 of a copper(I

M^2)

[*Answer:* > 1.5 mM]

7.3.1 Effect of the Formation of Complex Ions on Solubility

The formation of a complex ion increases the solubility of a substance by removing its cations from solution through chemical reaction, such that more of the solute dissolves. If a precipitate has already been formed, then the precipitate disappears as the ion product now falls below the solubility product, requiring more of the solute to attain equilibrium or saturation.

The added reagent usually occupies the central position in the complex, with atoms from the cation arranged around these central atoms. For example, if enough aqueous ammonia is introduced into a solution of copper(II) sulphate, it reacts with the copper(II) ions to form a complex, as follows:

$$Cu^{2+}(aq) + 4NH_3(aq) \Leftrightarrow [Cu(NH_3)_4]^{2+}(aq)$$

The equilibrium constant for the formation of a complex ion is called formation constant K_f. It is expressed just like any other type of equilibrium constant. For example, the formation constant of the above reaction is expressed as

$$K_f = \frac{\left[[Cu(NH_3)_4]^{2+}\right]}{[Cu^{2+}][NH_3]^4}$$

Note that we have indicated the complex ion with curly brackets,{ }, in order to avoid mixing it up with concentration.

The formation of a complex ion could occur in a series of steps. In this case, the formation constant of each stage is called the stepwise formation constants K_{fn}. For example, there are four stages in the formation of the above complex:

1. $Cu^{2+}(aq) + NH_3(aq) \Leftrightarrow [Cu(NH_3)]^{2+}(aq)$ $K_{f1} = \frac{[\{Cu(NH_3)_4\}^{2+}]}{[Cu^{2+}][NH_3]}$

2. $[Cu(NH_3)]^{2+}(aq) + NH_3(aq) \Leftrightarrow [Cu(NH_3)_2]^{2+}(aq)$ $K_{f2} = \frac{[\{Cu(NH_3)_2\}^{2+}]}{[Cu(NH_3]^{2+}][NH_3]}$

3. $[Cu(NH_3)_2]^{2+}(aq) + NH_3(aq) \Leftrightarrow [Cu(NH_3)_3]^{2+}(aq)$ $K_{f3} = \frac{[\{Cu(NH_3]_3\}^{2+}]}{[\{Cu(NH_3)_2\}^{2+}][NH_3]}$

4. $[Cu(NH_3)_3]^{2+}(aq) + NH_3(aq) \Leftrightarrow [Cu(NH_3)_4]^{2+}(aq)$ $K_{f4} = \frac{[\{Cu(NH_3]_4\}^{2+}]}{[\{Cu(NH_3)_2\}^{2+}][NH_3]}$

The overall formation constant K_f is the product of the stepwise formation constants, i.e.

$$K_f = K_{f1} \times K_{f2} \times K_{f3} \times K_{f4}$$

The overall equilibrium constant K_o when a complex forms is the product of the formation constant and solubility product, i.e.

$$K_o = \mathrm{K_f} \times K_{sp}$$

Example 1 Aqueous ammonia was introduced into a saturated solution of silver chloride, leading to the formation of the complex $[Ag(NH_3)_2]^+$. What is the new equilibrium constant of the mixture if the solubility product of the salt and the formation constant of the complex are 1.6×10^{-10} M^2 and 1.6×10^7 M^{-2} respectively?

Solution The overall equilibrium constant is given as

$K_o = K_{sp} \times K_f$

$K_{sp} = 1.6 \times 10^{-10}\ \text{M}^2$

$K_f = 1.6 \times 10^{-7}\ \text{M}^{-2}$

$K_o = ?$

Substituting we have

$K_o = 1.6 \times 10^{-10}\ \cancel{\text{M}^2} \times \dfrac{1.6 \times 10^{-7}}{1\cancel{\text{M}^2}}$

$= 2.6 \times 10^{-3}$

Example 2 What is the solubility of copper(II) sulphide in a 0.25-M ammonia solution?

$(K_{sp} = 8.5 \times 10^{-45}\ \text{M}^2,\ K_f = 1.2 \times 10^{13}\ \text{M}^{-4})$

Solution When copper(II) sulphide is dissolved in the solution, there will be formation of a complex as follows:

$$\text{Cu}^{2+}(aq) + 4\text{NH}_3(aq) \Leftrightarrow [\text{Cu(NH}_3)_4]^{2+}(aq)$$

So $K_f = \dfrac{\left[\{\text{Cu(NH}_3)_4\}^{2+}\right]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$

The equation for the dissolution of copper(II) sulphide is

$$\text{CuS}(aq) \Leftrightarrow \text{Cu}^{2+}(aq) + \text{S}^{2-}(aq)$$

$K\text{sp} = [\text{Cu}^{2+}][\text{S}^{2-}]$

As we have noted earlier, the solubility of a substance is the equilibrium concentrations of its ions in solution, which can be obtained from the solubility product and the stoichiometry of dissolution. In this example, there is the formation of a complex, leading to a rise in the solubility of the salt. Thus we must obtain the solubility of the salt from the overall equilibrium constant of the solution, which is given by

$K_o = K_f \times K_{sp}$

$K_f = 1.2 \times 10^{13}\ \text{M}^{-4}$

$K_{sp} = 8.5 \times 10^{-45}\ \text{M}^2$

Substituting these values and the corresponding equilibrium expressions we have

$$\frac{[\{Cu(NH_3)_4\}^{2+}]}{[\cancel{Cu^{2+}}][NH_5]^4} \times [\cancel{Cu^{2+}}][S^{2-}] = \frac{1.2 \times 10^{13}}{1 M^2} \times 8.5 \times 10^{-45}\ M^2$$

Thus $[\{Cu(NH_3)_4\}^{2+}][S^{2-}] = 1.0 \times 10^{-31}\ M^2 \times [NH_3]^4$

Let the equilibrium concentration of CuS be *S*. From the second equation, 1 mol of CuS produces 1 mol each of Cu^{2+} and S^{2-}, then the equilibrium concentrations of the ion would also be *S*. We also know that 1 mol of Cu^{2+} will produce 1 mol of the complex $[Cu(NH_3)_4]^{2+}$. Then, the concentration of the complex in the saturated solution will also be *S*. Thus,

$[\{Cu(NH_3)_4\}^{2+}] = [S^{2-}] = S$

$[NH_3]^4 = 0.25\ M$

$S = ?$

Substituting we obtain

$$S \times S = \frac{1.0 \times 10^{-31}}{M^2} \times (0.25\ M)^4$$

So $S^2 = \frac{1.0 \times 10^{-31}}{M^2} \times 3.9 \times 10^{-3}\ M^4$

Then $S^2 = 4.0 \times 10^{-34}\ M^2$

Taking the square roots of both sides we obtain

$S = \pm\sqrt{4.0 \times 10^{-34} M^2}$

$= -2.0 \times 10^{-17}\ M$ or $2.0 \times 10^{-17}\ M$

Since solubility cannot be negative, we disregard the negative term such that $S = 2.0 \times 10^{-17}\ M$.

A comparison of this value with the solubility of the solute in water shows that the formation of the complex increases the solubility of the salt by a factor of 2.4×10^4.

Example 3 What is the solubility of silver chloride in a solution containing 0.10 M of bromide ion?

$$(K_f = 1.3 \times 10^7\ M^{-2},\ K_{sp} = 1.6 \times 10^{-10}\ M^2)$$

Solution Ag^+ from the salt will form a complex with the Br^- as follows:

$$Ag^+(aq) + 2Br^-(aq) \Leftrightarrow [AgBr_2]^-(aq)$$

$K_f = \frac{[\{AgBr_2\}^-]}{[Ag^+][Br^-]^2}$

The dissolution of the salt is given as

$$AgCl(s) \Leftrightarrow Ag^+(aq) + Cl^-(aq)$$

$K_{sp} = [Ag^+][CI^-]$

As usual, the overall equilibrium constant is obtained from the relation

$K_o = K_f \times K_{sp}$

$K_f = 1.3 \times 10^7\ M^{-2}$

$K_{sp} = 1.6 \times 10^{-10}\ M^2$

Substituting we have

$$\frac{[\{AgBr_2\}^-]}{[\cancel{Ag^+}][Br^-]^2} \times [\cancel{Ag^+}][CI^-] = \frac{1.3 \times 10^7}{1\cancel{M^2}} \times 1.6 \times 10^{-10}\ \cancel{M^2}$$

Thus $[\{AgBr_2\}^-][CI^-] = 2.1 \times 10^{-3} \times [Br^-]^2$

From the above equation, the dissolution of 1 mol of the salt produces 1 mol each of Ag^+ and Cl^-. Thus if the concentration of the salt in the saturated solution is S, then the concentration of the ions must also be S. Similarly, the equation for the formation of the complex shows that 1 mol of Ag^+ produces 1 mol of $[AgBr_2]^-$; then the concentration of the complex would also be S, i.e.

$[\{AgBr_2\}^-] = [CI^-] = S$

$[Br^-] = 0.10\ M$

$S = ?$

Substituting we have

$S \times S = 2.1 \times 10^{-3} \times 0.10\ M$

Thus $S^2 = 2.1 \times 10^{-4}\ M$

Taking the square roots of both sides we have

$S = \sqrt{2.1 \times 10^{-4} M}$

$= 1.4 \times 10^{-2}\ M$

Example 4 The solubility product of mercury(II) sulphide is $1.4 \times 10^{-53}\ M^2$. What concentration of chloride ions must be present in the solution to increase its solubility by a factor of 1000?

$$(K_f = 1.2 \times 10^5\, \text{M}^{-4})$$

Solution Hg^{2+} forms a complex with the Cl^- as follows:

$$\text{Hg}^{2+}(aq) + 4\text{Cl}^-(aq) \Leftrightarrow [\text{HgCl}_4]^{2-}(aq)$$

So $K_f = \dfrac{\left[\{\text{HgCI}_4\}^{2-}\right]}{[\text{Hg}^{2+}][\text{CI}^-]}$

The salt dissolves as follows:

$$\text{HgS}(s) \Leftrightarrow \text{Hg}^{2+}(aq) + \text{S}^{2-}(aq)$$

$K_{sp} = [\text{Hg}^{2+}][\text{S}^{2-}]$

The overall equilibrium constant is given as

$K_o = K_f \times K_{sp}$

$K_f = 1.2 \times 10^7\ \text{M}^{-4}$

$K_{sp} = 1.4 \times 10^{-53}\ \text{M}^2$

$K_o = ?$

Substituting we have

$$\frac{\left[\{\text{HgCI}_4\}^{2-}\right]}{[\cancel{\text{Hg}^{2+}}][\text{CI}^-]} \times [\cancel{\text{Hg}^{2+}}][\text{S}^{2-}] = \frac{1.2 \times 10^7}{1\,\text{M}^4} \times 1.4 \times 10^{-53}\ \text{M}^2$$

Then $[\{\text{HgCI}_4\}^{2-}]\,[\text{S}^{2-}] = 1.7 \times 10^{-49}\ \text{M}^2 \times [\text{CI}^-]^4$

Thus $[\text{CI}^-]^4 = \dfrac{\left[\{\text{HgCI}_4\}^{2-}\right][\text{S}^{2-}] \times 1\,\text{M}}{1.7 \times 10^{-49}}$

The dissolution of the salt produces 1 mol each of Hg^{2+} and S^{2-}. Thus the equilibrium concentration of each of the ions in pure water is equal to the solubility S of the salt, i.e.

$[\text{Hg}^{2+}] = [\text{S}^{2-}] = S$

$S = ?$

Substituting into the expression for the K_{sp} of the salt we have

$1.4 \times 10^{-53}\ \mathrm{M}^2 = S \times S$

Thus $S^2 = 1.4 \times 10^{-53}\ \mathrm{M}^2$

Taking the square roots of both sides we have

$S = \sqrt{1.4 \times 10^{-53}\,\mathrm{M}^2}$

$= 3.7 \times 10^{-27}\,\mathrm{M}$

This is an extremely low solubility. If the solubility is increased by a factor of 1000 by the formation of the complex ion, then the new equilibrium concentration or solubility of the salt becomes

$$S = 1000 \times 3.7 \times 10^{-27}\,\mathrm{M} = 3.7 \times 10^{-24}\,\mathrm{M}$$

Since 1 mol of Hg^{2+} produces 1 mol of the complex, then the equilibrium concentration of the complex must be equal to that of the ion, i.e.

$[Hg^{2+}] = [\{HgCl_4\}^{2-}] = [S^{2-}] = 3.7 \times 10^{-24}\,\mathrm{M}$

$[CI^-] = ?$

Substituting into the above equation we have

$$[CI^-]^4 = \frac{(3.7 \times 10^{-24}\,\mathrm{M})^2 \times 1\,\mathrm{M}^2}{1.7 \times 10^{-49}} = 81\ \mathrm{M}^4$$

Finally, we take the fourth roots of both sides to obtain

$[CI^-] = \sqrt[4]{81\,\mathrm{M}^4}$

$= 3.0\ \mathrm{M}$

Example 5 Calculate the concentration of silver ions in a solution containing 0.20 M of silver chloride and 2.5 M of ammonia if the formation constant of the complex $[Ag(NH_3)_2]^+$ is $1.6 \times 10^7\,\mathrm{M}^{-2}$.

Solution We expect the concentration of Ag^+ to be relatively low due to the formation of the complex ion. The equation for the formation of the complex is

$$Ag^+(aq) + 2NH_3(aq) \Leftrightarrow [Ag(NH_3)_2]^+(aq)$$

So $K_f = \dfrac{[\{Ag(NH_3)_2\}^+]}{[Ag^+][NH_3]^2}$

$K_f = 1.6 \times 10^7\,\mathrm{M}^{-2}$

Substituting we have

$$1.6 \times 10^{7}\,\mathrm{M}^{-2} = \frac{[\{\mathrm{Ag(NH_3)_2}\}^+]}{[\mathrm{Ag}^+][\mathrm{NH_3}]^2}$$

Cross-multiplying we obtain

$$1.6 \times 10^{7}\ \mathrm{M}^{-2} \times [\mathrm{Ag}^+]\ [\mathrm{NH_3}]^2 = [\{\mathrm{Ag(NH_3)_2}\}^+]$$

$$\therefore\ [\mathrm{Ag}^+] = \frac{[\{\mathrm{Ag(NH_3)_2}\}^+] \times 1\,\mathrm{M}^2}{1.6 \times 10^7 \times [\mathrm{NH_3}]^2}$$

This is the concentration of Ag^+ after the formation of the complex.
The equation for the dissolution of the salt is

$$\mathrm{AgCl}(s) \Leftrightarrow \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

We can see from this equation that 0.20-M solution of AgCl would produce 0.20 M of Ag^+. It is equally obvious from the equation for the formation of the complex that 0.20 M of Ag^+ would produce 0.20 M of the complex, i.e.

$[\{\mathrm{Ag(NH_3)_2}\}^+] = 0.20$ M

$[\mathrm{NH_3}] = 2.5$ M

$[\mathrm{Ag}^+] = ?$

Substituting we obtain

$$[\mathrm{Ag}^+] = \frac{0.20\,\mathrm{M} \times 1\,\mathrm{M}^2}{1.60 \times 10^7 \times [2.5\,\mathrm{M}]^2}$$

$$\text{So } [\mathrm{Ag}^+] = \frac{0.20\,\mathrm{M}}{1.0 \times 10^8\,\mathrm{M}^2}$$

$$= 2.0 \times 10^{-9}\,\mathrm{M}$$

Practice Problems

1. Calculate the solubility of silver chromate in a 2.0-M solution of ammonia? ($K_f = 1.6 \times 10^7\ \mathrm{M}^3$)

[*Answer:* 5.2×10^{-2} M]

2. What concentration of cyanide ions, CN^-, would increase the solubility of water?

$(K_f = 7.7 \times 10^{36}$ $M^2)$

[*Answer:* 7.1×10^{-7} M]

7.3.2 The Solubility of Gases

As stated earlier, the solubilities of most gases increase with pressure. This is quantitatively given by Henry's law:

$$S = K_H \times P$$

where S = Solubility of the gas.

P = Partial pressure of the gas.

K_H = Henry's constant.

Example 1 1000.0 cm^3 of air contains 0.78 g of carbon dioxide at 20°C. Determine the solubility of the gas in water at this temperature.
(C =12, O = 16, $K_H = 2.3 \times 10^{-3}$ M atm^{-1}, $R = 0.082$ atm dm^3 mol^{-1} K^{-1})

Solution We have to apply Henry's law, i.e.

$$S = K_H \times P$$

The ideal gas law is given as

$$PV = nRT$$

$$\therefore\ P = \frac{nRT}{V}$$

The number of moles of the gas is obtained from the relation

$$n = \frac{m}{M}$$

$M = [12 + (16 \times 2)]$ g mol^{-1}

$= 44$ g mol^{-1}

$m = 0.78$ g

$n = ?$

Substituting we obtain

$$n = \frac{0.78\ \cancel{g} \times 1\ \text{mol}}{44\ \cancel{g}}$$

$= 0.018$ mol

$R = 0.082\ \text{dm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1}$

$T = 20°\text{C} + 273\ \text{K} = 293\ \text{K}$

$V = 1000.0\ \text{cm}^3 = 1.0\ \text{dm}^3$

$P = ?$

Substituting we have

$$P = \frac{0.018\ \cancel{\text{mol}} \times 0.082\ \cancel{\text{dm}^3}\ \text{atm} \times 293\ \cancel{\text{K}}}{1.0\ \cancel{\text{dm}^3} \times 1\ \cancel{\text{K}} \times 1\ \cancel{\text{mol}}}$$

$= 0.43$ atm

$K_H = 2.3 \times 10^{-3}\ \text{M atm}^{-1}$

$S = ?$

Substituting into the original equation we have

$$S = \frac{2.3 \times 10^{-3}\ \text{M}}{1\ \cancel{\text{atm}}} \times 0.43\ \cancel{\text{atm}}$$

$= 9.9 \times 10^{-4}$ M or 0.99 mM

Figure 7.1 William Henry, English chemist (1775–1856). He formulated Henry's law in 1803.

Example 2 Calculate the maximum concentration of oxygen in river water on a day in which the temperature does not exceed 20°C, given that the mass concentration of oxygen in air is 150 mg dm^{-3}.

(O = 16, $K_H = 1.3 \times 10^{-3}$ M atm^{-1}, $R = 0.082$ atm dm^3 mol^{-1} K^{-1})

Solution We have to apply the equation

$S = K_H \times P$

$P = \frac{nRT}{V}$

The number of moles of oxygen per dm^3 of air is calculated from the relation

$n = \frac{m}{M}$

$M = (16 \times 2)$ g mol^{-1}
= 32 g mol^{-1}
m = 150 mg = 0.15 g
n = ?

Substituting we have

$$n = \frac{0.15\,\cancel{g} \times 1\text{ mol}}{32\,\cancel{g}}$$

= 0.0047 mol
R = 0.082 atm dm^3 mol^{-1} K^{-1}
T = 20°C + 273 = 293 K
V = l.0 dm^3
P = ?

Substituting we obtain

$$P = \frac{0.0047\,\cancel{\text{mol}} \times 0.082\text{ atm}\,\cancel{\text{dm}^3} \times 293\,\cancel{\text{K}}}{1.0\,\cancel{\text{dm}^3} \times 1\,\cancel{\text{K}} \times 1\,\cancel{\text{mol}}}$$

= 0.11 atm
$K_H = 1.3 \times 10^{-3}$ M atm^{-1}
S = ?

Finally, we now substitute into the original relation to obtain

$$S = \frac{1.3 \times 10^{-3}\text{ M}}{1\,\cancel{\text{atm}}} \times 0.11\,\cancel{\text{atm}}$$

= 1.4 × 10^{-4} M

Example 3 10.7 g of oxygen dissolves in 700.0 cm^3 of a solvent at 30°C when the partial pressure of the gas is 0.33 atm. Calculate the mass solubility of the gas in the solvent when its partial pressure is increased to 1.0 atm.

Solution We have to apply the relation

$$S = K_H \times P$$

The solubility when the partial pressure is 0.33 atm is

$$S_1 = K_H \times 0.33 \text{ atm}$$

The solubility when the partial pressure is 1.0 atm is

$$S_2 = K_H \times 1.0 \text{ atm}$$

Dividing S_2 by S_1 we have

$$\frac{S_2}{S_1} = \frac{\cancel{K_H} \times 1.0 \cancel{\text{atm}}}{\cancel{K_H} \times 0.33 \cancel{\text{atm}}} = 3.0$$

We now cross-multiply to obtain

$$S_2 = S_1 \times 3.0$$

The initial solubility S_1 can be determined from the relation

$S_1 = \frac{m}{V}$

m = 10.7 g

V = 700.0 cm^3 = 0.70 dm^3

S_1 = ?

Substituting we have

$S_1 = \frac{10.7 \text{ g}}{0.70 \text{ dm}^3}$

= 15 g dm^3

S_2 = ?

Finally, we can now substitute into the above equation to obtain

S_2 = 15 g dm^3 × 3.0

= 45 g dm^3

Practice Problems

1. Nitrogen readily dissolves in water to form an acidic solution. Compute the

concentration of the gas in water at 20°C, given that the mass concentration of nitrogen is 0.78 g dm^{-3}.

(N = 14, $R = 0.082$ atm dm^{3} mol^{-1} K^{-1}, $K_H = 0.70 \times 10^{-3}$ M atm^{-1})

[*Answer:* 0.47 mM]

2. By what factor will the solubility of a gas in acetone increase if its pressure is increased from 0.12 atm to 0.44 atm at a constant temperature? [*Answer:* 3.7]

7.4 COLLIGATIVE PROPERTIES OF SOLUTIONS

Colligative properties are properties which depend on the relative amount of solute and solvent molecules, but are independent of their nature. In other words, all solutes, regardless of their physical or chemical identity, would have the same effect when equal amounts are dissolved in the same amount of the same or different solvents. Colligative properties include vapour pressure lowering, boiling-point elevation, freezing-point depression and osmotic pressure.

7.4.1 Vapour Pressure Lowering

The vapour pressure of a solvent is lowered by the presence of a solute. Consider a non-volatile solute dissolved in a solvent. The new vapour pressure of the solvent is given by Raoult's law:

$$P = x_1 \times P°$$

where P = The new vapour pressure of the solvent after the dissolution of the solute.

x_1 = The mole fraction of the solvent.

$P°$ = The vapour pressure of the pure solvent.

The vapour pressure lowering, ΔP, of the solvent is given by

$$\mathrm{D}P = P^o - P$$

From the above equation we have

$$\mathrm{D}P = P^o - x_1 \times P^o$$

So $\mathrm{D}P = P^o(1 - x_1)$

Since the solution is a binary mixture, then $x_1 + x_2 = 1$.

Thus $\mathrm{D}P = x_2 \times P^o$

where x_2 is the mole fraction of the solute.

This equation is an alternative way of stating Raoult's law. We can as well divide the equation by P^o to obtain

$$\therefore \frac{\Delta P}{P^\circ} = \frac{P^\circ - P}{P^\circ} = x_2$$

The term $\frac{\Delta P}{P^\circ}$ is called relative lowering of vapour pressure.

The molar mass of a solute can be determined from the vapour pressure lowering of a solvent by using the relation

$$M_2 = \frac{P^\circ m_2}{\Delta n_1} - \frac{P^\circ m_2}{(P^\circ - P)n_1}$$

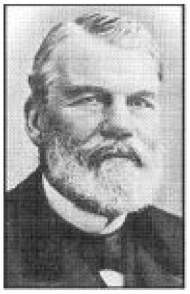


Figure 7.2 François-Marie Raoult, French chemist (1830–1901).

where M_2 = Molar mass of the solute.

n_1 = Number of moles of the solvent.

m_2 = Mass of the solute dissolved in the solvent.

A solution that obeys Raoult's law is called an ideal solution. All the molecular interactions in such a solution are identical.

Example 1 Calculate the reduction in pressure of 40% aqueous glucose solution if the vapour pressure of pure water at the prevailing temperature is 760.0 Torr.

(H = 1.0, C = 12.0, O = 16.0)

Solution Using Raoult's law we have

$$\Delta P = x_2 \times P^o$$

Since the solution is 40% glucose

$$m_2 = \frac{40}{100} \times 100.0 \text{ g}$$

$= 40.0$ g

Thus the mass of the solvent (i.e., water) is

$$m_1 = 100.0\ \text{g} - 40.0\ \text{g} = 60.0\ \text{g}$$

The number of moles of each substance is calculated from the relation

$$n = \frac{m}{M}$$

For the solute ($C_6H_{12}O_6$)

$M_2 = [(12.0 \times 6) + (1.0 \times 12) + (16.0 \times 6)] = 180.0\ \text{g mol}^{-1}$

$n_2 = ?$

Substituting we have

$$n_2 = \frac{40.0\ \cancel{\text{g}} \times 1\ \text{mol}}{180.0\ \cancel{\text{g}}}$$

$= 0.222\ \text{mol}$

For the solvent (H_2O):

$M_1 = [(1.0 \times 2) + 16.0] = 18.0\ \text{g mol}^{-1}$

$n_1 = ?$

Substituting we obtain

$$n_2 = \frac{60.0\ \text{g} \times 1\ \cancel{\text{mol}}}{18.0\ \cancel{\text{mol}}}$$

$= 3.33\ \text{mol}$

The mole fraction of each component is obtained from the relation

$$x_2 = \frac{n_2}{n_t}$$

$n_t = n_1 + n_2$

Then $n_t = 3.33\ \text{mol} + 0.222\ \text{mol} = 3.552\ \text{mol}$

$x_2 = ?$

Substituting we have

$$x_2 = \frac{0.222\ \cancel{\text{mol}}}{3.552\ \cancel{\text{mol}}}$$

$= 0.0625$

P^o = 760.0 Torr

ΔP = ?

Finally, we now substitute into the original equation to obtain

ΔP = 0.0625 × 760.0 Torr

= 47.5 Torr

Alternatively, we can apply the relation

$$P = x_1 \times P^o$$

Since the total mole fraction must be 1, then

x_1 = 1.000 – 0.0625 = 0.9375

P^o = 760.0 Torr

P = ?

Substituting we have

P = 0.9375 × 760.0 Torr = 712.5 Torr

But $\Delta P = P^o - P$

ΔP = ?

Thus ΔP = 760.0 Torr – 712.5 Torr

= 47.5 Torr

Example 2 Water has a vapour pressure of 19.0 mmHg at 22°C. What pressure will be exerted by 100.0 g of water when it dissolves 25.0 g of common salt at the same temperature?

(H = 1.0, O = 16.0, Na = 23.0, Cl = 35.5)

Solution We have to apply Raoult's law:

$$P = x \times P^o$$

The number of mole of each substance is obtained from the relation

$$n = \frac{m}{M}$$

For the solvent:

M_1 = [(2 × 1.0) + 16.0] g mol^{-1} = 18.0 g mol^{-1}

m_1 = 100.0 g

n_1 = ?

Substituting we obtain

$n_1 = \frac{100.0\,\cancel{g} \times 1\,\text{mol}}{18.0\,\cancel{g}}$

$= 5.56$ mol

For the solute (NaCl):

$M_2 = (23.0 + 35.5)\ \text{g mol}^{-1} = 58.5\ \text{g mol}^{-1}$

$m_2 = 25.0$ g

$n_2 = ?$

Substituting we have

$n_2 = \frac{25.0\,\cancel{g} \times 1\,\text{mol}}{58.5\,\cancel{g}}$

$= 0.427$ mol

However, we must take note that NaCl is an ionic compound which dissociates into two moles of ions (particles) in solution, as follows:

$$\text{NaCl}(s)\ \text{Æ}\ \text{Na}^+(aq) + \text{Cl}^-(aq)$$

Thus 0.427 mol of NaCl would be present in solution as 0.427 mol of Na^+ and 0.427 mol of Cl^-. This brings the total number of moles of particles of the solute in solution to

$$n_2 = 2 \times 0.427\ \text{mol} = 0.854\ \text{mol}$$

The mole fraction of the solvent is obtained from the relation

$x_2 = \frac{n_1}{n_t}$

$n_t = n_1 + n_2$

Thus $n_t = 5.56\ \text{mol} + 0.854\ \text{mol} = 6.414\ \text{mol}$

$x_1 = ?$

Substituting we have

$x_1 = \frac{5.56\,\cancel{\text{mol}}}{6.414\,\cancel{\text{mol}}}$

$= 0.867$

$P_1 = 19.0$ mmHg

$P_2 = ?$

Finally, we now substitute

$P_2 = 0.867 \times 19.0$ mmHg

$= 16.5$ mmHg

Alternatively, we can apply the relation

$$DP = x_2 \times P^o$$

Since the mole fraction of water is 0.867, then for the solute we have

$$x_2 = 1.000 - 0.867 = 0.133$$

We can as well substitute into the above relation to obtain

$x_2 = \frac{0.854 \text{ mol}}{6.414 \text{ mol}}$

$= 0.133$

Note that the slight difference is due to rounding.

$P^o = 19.0$ mmHg

$\Delta P = ?$

Substituting we have

$\Delta P = 0.133 \times 19.0$ Hg $= 2.527$ mmHg

But $\Delta P = P^o - P$

So $P = P^o - \Delta P$

$P = ?$

Finally, we now substitute to obtain

$$P = 19.0 \text{ mmHg} - 2.527 \text{ mmHg} = 16.5 \text{ mmHg}$$

Example 3 Show that the molar mass of a solute dissolved in a solvent is given by the relation

$M_2 = \frac{P^o m_2}{\Delta P n_1}$

where M_2 = Molar mass.

P^o = Vapour pressure of the pure solvent.

n_1 = Number of moles of the solvent.

m_2 = Mass of the solute dissolved in the solvent.

ΔP = Decrease in vapour pressure of the solvent on dissolving the solute.

Solution We start from the relation

$\Delta P = x_2 \times P^o$ (7.1)

Dividing Equation (7.1) by P^o we have

$\frac{\Delta P}{P^o} = x_2$ (7.2)

The mole fraction of the solute is given by the relation

$x_2 = \frac{n_2}{n_1 + n_2}$ (7.3)

Substituting into Equation (7.2) we have

$\frac{\Delta P}{P^o} = \frac{n_2}{n_1 + n_2}$ (7.4)

Since the solution is dilute, then we can assume that $n_1 + n_2$ ª n_1. It then follows that

$\frac{\Delta P}{P^o} = \frac{n_2}{n_1}$ (7.5)

Cross-multiplying we obtain

$P^o n_2 = \Delta P n_1$

So, $n_2 = \frac{\Delta P n_1}{P^o}$ (7.6)

Now, we know that the number of moles of the solute is given by the relation

$n_2 = \frac{m_2}{M_2}$

Substituting this into Equation (7.6) we have

$\frac{m_2}{M_2} = \frac{\Delta P n_1}{P^o}$ (7.7)

Cross-multiplying we obtain

$m_2 P^o = M_2 \Delta P n_1$

So $M_2 = \frac{P^o m_2}{\Delta P n_1}$ (7.8)

Example 4 The vapour pressure of pure water was reduced from 22.50 to 22.05 mmHg when 20.0 g of a solute was dissolved in 100.0 g of the solvent. Determine the molar mass of the solute.

(H = 1, O = 16)

Solution We have to apply the relation

$$M_2 = \frac{P^{\circ} m_2}{\Delta P n_2}$$

The number of moles of the solvent is obtained from the relation

$n_1 = \frac{m_1}{M_1}$

$M_1 = [(1 \times 2) + 16]$ g mol^{-1} = 18 g mol^{-1}

$m_1 = 100.0$ g

$n_1 = ?$

Substituting we have

$$n_1 = \frac{100.0 \cancel{g} \times 1 \text{ mol}}{18 \cancel{g}}$$

= 5.6 mol

The decrease in vapour pressure is obtained from the relation

D$P = P^o - P$

$P^o = 22.50$ mmHg

$P = 22.05$ mmHg

$\Delta P = ?$

Substituting we have

$\Delta P = 22.50$ mmHg – 22.05 mmHg = 0.45 mmHg

$M_2 = 20.0$ g

$M_2 = ?$

Substituting into the original equation yields

$$M_2 = \frac{22.50\ \cancel{\text{mmHg}} \times 20.0\ \text{g}}{0.45\ \cancel{\text{mmHg}} \times 5.6\ \text{mol}}$$

So, $M_2 = \frac{450\ \text{g}}{2.52\ \text{mol}} = 180\ \text{g mol}^{-1}$

Practice Problems

1. Calculate the vapour pressure of the solution prepared by dissolving 1.5 g of sodium chloride in 100.0 g of water at a temperature at which the vapour pressure of pure water is 55.5 Torr.

   (H = 1.0, O = 16.0, Na = 23.0, Cl = 35.5) [*Answer:* 55.2 Torr]

2. The dissolution of 3.5 g of a compound in 50.4 cm^3 of water reduces its vapour pressure by 0.29 Torr at a certain temperature. Determine the molar mass of the compound if the vapour pressure of the pure solvent at the same temperature is 80.5 Torr.

   (H = 1, O = 16, r = 1.0 g cm^{-3}) [*Answer:* 340 g mol^{-1}]

7.4.2 Boiling-point Elevation

An implication of the reduction in the vapour pressure of a liquid on the dissolution of a solute is an increase in its boiling point. The elevation of boiling point, which is usually very small, is given by the relation

$$\Delta T_b = k_b \times m = \frac{k_b m_2}{m_1 M_2}$$

where k_b = Boiling-point or ebullioscopic constant of the solvent.

m_2 = Mass of the solute in g.

m_1 = Mass of the solvent in kg.

M_2 = Molar mass of the solute.

m = Molality of the solution.

The molar mass of a solute can be determined by measuring the elevation in the boiling point of a solvent when a specific amount of the solute is dissolved in a known mass of the solvent. The determination of molar mass from boiling-point elevation is called ebullioscopy. The ebullioscopic constants of some solvents are given in Table 7.1.

Table 7.1: Ebullioscopic constants

Substance	k_b */ K kg mol*$^{-1}$
Benzene (C_6H_6)	2.53
Camphor ($C_{10}H_{16}O$)	5.95
Chloroform ($CHCl_3$)	3.63
Diethyl ether ($C_4H_{10}O$)	2.02
Ethanol (C_2H_6O)	1.22
Water (H_2O)	0.51

Example 1 Show that the boiling point elevation of a liquid is given by the relation

$$DT_b = k_b \times m$$

where all parameters are as defined above.

Solution When a solute is dissolved in a solvent at its normal boiling point T_0, the vapour pressure reduces. As we have explained earlier, the solution would no longer boil at T_0. The solution must then be heated to another temperature T for it to boil. We can relate this change in boiling point to vapour pressure by using the Clausius-Clapeyron's equation

$$\ln \frac{P^\circ}{P} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \quad (7.9)$$

where P^o = The vapour pressure of the solution at temperature T.

P = The vapour pressure of the solution at temperature T_0.

From Equation (7.9) we have

$$\ln \frac{P^\circ}{P} = \frac{\Delta H_{vap}}{R}\left(\frac{T - T_0}{TT_0}\right) \quad (7.10)$$

Since ΔT is very small for dilute solutions, then T ª T_0. We can then make the reasonable assumption that TT_0 ª T_0^2. Consequently, Equation (7.10) now becomes

$$\ln \frac{P^\circ}{P} = \frac{\Delta H_{vap}}{R}\left(\frac{\Delta T_b}{T_0^2}\right) \quad (7.11)$$

where $\Delta T_b = T - T_0$.

We can as well write Equation (7.11) as

$$\ln \frac{P}{P_0} = -\frac{\Delta H_{vap}}{R}\left(\frac{\Delta T_b}{T_0^2}\right) \quad (7.12)$$

Equation (7.12) could be written in terms of the mole fraction of the solute, using Raoult’s law as follows:

$$\ln(1 - x_2) = -\frac{\Delta H_{vap}}{R}\left(\frac{\Delta T_b}{T_0^2}\right) \quad (7.13)$$

Note: $\frac{P}{P^\circ} = x_1 = (1 - x_2)$

Since x_2 is very small for dilute solutions, it then follows that $\ln(1 - x_2) \approx -x_2$. Then

$$-x_2 = -\frac{\Delta H_{vap}}{R}\left(\frac{\Delta T_b}{T_0^2}\right)$$

Thus $x_2 = \frac{\Delta H_{vap}}{R}\left(\frac{\Delta T_b}{T_0^2}\right) \quad (7.14)$

$\therefore \Delta T_b = \frac{RT_0^2 x_2}{\Delta H_{vap}} \quad (7.15)$

But $x_2 = \frac{n_2}{n_1 + n_2} \propto \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1} = \frac{w_2/M_1}{w_1/M_2}$

Substituting into Equation (7.15) we have

$$DT_b = \frac{RT_0^2}{\Delta H_{vap}}\left(\frac{w_2 M_1}{w_1 M_2}\right) \quad (7.16)$$

where

m_2 = Mass of the solute in g.

m_1 = Mass of the solvent in kg.

M_1 = Molar mass of the solvent in kg mol^{-1}.

M_2 = Molar mass of the solute.

But molality $m = \frac{w_2}{w_1 M_2}$

So $$\Delta T_b = \left(\frac{RT_0^2}{\Delta H_{vap}}\right)(mM_1) \quad (7.17)$$

$$\therefore \Delta T_b = k_b m \quad (7.18)$$

where $k_b = \frac{RT_0^2 M_1}{\Delta H_{vap}}$

Example 2 Calculate the boiling-point elevation of 250.00 cm^3 of a 0.10-M aqueous solution of glucose, $C_6H_{12}O_6$, given that the density of the solution is 1.0058 g cm^{-3}.

(k_b = 0.51 K kg mol^{-1}, H = 1, C = 12, O = 16)

Solution We should apply the relation

$$\Delta T_b = \frac{k_b m_2}{m_1 M_2}$$

The number of moles of the solute is obtained from the relation

$n_2 = C \times V$

$C = 0.10 \text{ mol dm}^{-3}$

$V = 250.00 \text{ cm}^3 = 0.25 \text{ dm}^3$

$n_2 = ?$

Substituting we have

$$n_2 = \frac{0.10 \text{ mol}}{1 \cancel{\text{dm}^3}} \times 0.25 \cancel{\text{dm}^3}$$

$= 0.025 \text{ mol}$

The mass of the solute is obtained from the relation

$m_2 = n_2 \times M_2$

$M_2 = [(12 \times 6) + (1 \times 12) + (16 \times 6)] \text{ g mol}^{-1} = 180 \text{ g mol}^{-1}$

$m_2 = ?$

Substituting we have

$$m_2 = 0.025 \cancel{\text{mol}} \times \frac{180 \text{ g}}{1 \cancel{\text{mol}}}$$

$= 4.5 \text{ g}$

The mass of the solution is calculated from the relation

$$\rho = \frac{m}{V}$$

$\therefore\ m = r \times V$

$\rho = 1.0058 \text{ g cm}^{-3}$

$V = 250.00 \text{ cm}^3$

$m = ?$

Substituting we have

$$m = \frac{1.0058 \text{ g}}{1 \cancel{\text{cm}^3}} \times 250.00 \cancel{\text{cm}^3}$$

$= 251.45 \text{ g}$

The mass of the solvent is obtained by subtracting the mass of the solute from that of the solution, i.e.

m_1 = 251.45 g − 4.5 g = 247.0 g = 0.247 kg

k_b = 0.51 K kg mol^{-1}

ΔT_b = ?

Finally, we substitute into the original equation to obtain

$$\Delta T_b = \frac{0.51\,\text{K}\,\cancel{\text{kg}}\,\cancel{\text{mol}^{-1}} \times 4.5\,\cancel{\text{g}}}{0.247\,\cancel{\text{kg}} \times 180\,\cancel{\text{g}}\,\cancel{\text{mol}^{-1}}}$$

= 0.052 K

Example 3 Calculate the mass of polyethylene required to raise the boiling point of 10.5 kg of benzene by 0.12 K, given that the molar mass of the compound is 48 kg mol^{-1}.

(k_b = 2.53 K kg mol^{-1})

Solution We have to apply the relation

$$\Delta T_b = \frac{k_b m_2}{m_1 M_2}$$

$$\therefore\ m_2 = \frac{DT_b m_1 M_2}{k_b}$$

ΔT_b = 0.12 K

m_1 = 10.5 kg

M_2 = 48 kg mol^{-1}

k_b = 2.53 K kg mol^{-1}

m_B = ?

Substituting we have

$$m_2 = \frac{0.12\,\cancel{\text{K}} \times 10.5\,\text{kg} \times 48\,\cancel{\text{kg}}\,\cancel{\text{mol}^{-1}}}{2.53\,\cancel{\text{K}}\,\cancel{\text{kg}}\,\cancel{\text{mol}^{-1}}}$$

= 23.9 kg

Example 4 The addition of 1.5 g of an organic compound to 150.00 g of carbon tetrachloride increases its boiling point by 0.0354 K. Calculate the molecular mass of the compound.

(k_b = 4.95 K kg mol^{-1})

Solution We have to apply the relation

$$\Delta T_b = \frac{k_b m_2}{m_1 M_2}$$

$$\therefore M_2 = \frac{k_b m_2}{\Delta T_b M_1}$$

k_b = 4.95 K kg mol^{-1}

m_2 = 1.5 g

m_1 = 150.00 g = 0.15 kg

ΔT_B = 0.0354 K

M_2 = ?

Substituting we have

$$M_2 = \frac{4.95\ \cancel{\text{K}}\ \cancel{\text{kg}}\,\text{mol}^{-1} \times 1.5\ \text{g}}{0.0354\ \cancel{\text{K}} \times 0.15\ \cancel{\text{kg}}}$$

$= 1.40 \times 10^3$ g mol^{-1}

Practice Problems

1. 50.0 g of ethanoic acid, CH_3COOH, was dissolved in 100.0 g of water. At what temperature would the resulting solution boil if the boiling point of pure water is 100.00°C?

   (H = 1, C = 12, O = 16, 0.51°C kg mol^{-1}) [*Answer:*105.31°C]
2. A solution was prepared by dissolving 25.0 g of a molecular solute in 395.5 g of carbon disulphide. Determine the molecular mass of the solute if the boiling point of the solvent is increased by 0.12 K.

   (K_b= 2.40 K kg mol^{-1}) [*Answer:* 1300 g mol^{-1}]

7.4.3 Depression of Freezing Point

The presence of a solute reduces the freezing point of a solvent by a value given by the equation

$$\Delta T_f = k_f \times m = \frac{k_f m_2}{m_1 M_2}$$

ΔT_f = Freezing-point depression.

k_f = Freezing-point or cryoscopic constant of the solvent.

All other parameters are as defined above. The cryoscopic constants of some solvents are given in Table 7.2.

Table 7.2: Cyoscopic constants

Substance	kb / K kg mol^{-1}
Benzene (C_6H_6)	5.12
Camphor ($C_{10}H_{16}O$)	37.7
Chloroform ($CHCl_3$)	4.70
Diethyl ether ($C_4H_{10}O$)	1.79
Ethanol (C_2H_6O)	1.99
Water (H_2O)	1.86

The molar mass of a substance can be determined by measuring the freezing-point depression of a solvent when a known amount of the solute is dissolved in it. This process is called cryoscopy. Cryoscopy is a more accurate method than ebullioscopy because solutes cause higher reduction in freezing point than boiling point. Similar calculations are encountered in boiling-point elevation and freezing-point depression. Nevertheless, we would solve a couple of more examples to illustrate situations that are specific to freezing-point depression.

Example 1 50.0 g of an organic compound was dissolved 1.0 kg of liquid camphor. Calculate the freezing-point depression of the solvent.

$$(k_f = 40.0 \text{ K kg mol}^{-1},\ M_2 = 14 \text{ kg mol}^{-1})$$

Solution The solute is a molecular compound, hence

$$\Delta T_f = \frac{k_f m_2}{m_1 M_2}$$

k_f = 40.0 K kg mol^{-1}

m_2 = 50.0 g

m_1 = 1.0 kg

M_2 = 14 kg mol^{-1} = 1400 g mol^{-1}

ΔT_f = ?

Substituting we obtain

$$\Delta T_f = \frac{40\ \text{K}\ \cancel{\text{kg}}\ \cancel{\text{mol}^{-1}} \times 50.0\ \cancel{\text{g}}}{1.0\ \cancel{\text{kg}} \times 1400\ \cancel{\text{g}}\ \cancel{\text{mol}^{-1}}}$$

= 1.4 K

Example 2 The addition of 0.50 g of a molecular solute to 100.0 g of cyclohexane lowers its boiling point by 0.39°C. Calculate the molar mass of the solute.

(K_f = 20.1°C kg mol^{-1})

Solution We have to apply the relation

$$\Delta T_f = \frac{k_f m_2}{m_1 M_2}$$

$$\therefore\ M_2 = \frac{k_f M_2}{\Delta T_f m_1}$$

K_f = 20.1°C kg mol^{-1}

m_2 = 0.50 g

ΔT_f = 0.39°C

m_1 = 100.0 g = 0.10 kg

M_2 = ?

Substituting we have

$$M_2 = \frac{20.1^\circ\cancel{\text{C}}\ \cancel{\text{kg}}\,\text{mol}^{-1} \times 0.50\ \text{g}}{0.39^\circ\cancel{\text{C}} \times 0.10\ \cancel{\text{kg}}}$$

= 260 g mol^{-1}

Example 3 Calculate the mass of glucose required to reduce the freezing point of a 550.0-g solution of ethanoic acid by 0.11 K.

(ΔT_f = 3.59 K kg mol^{-1})

Solution We have to apply the relation

$$\Delta T_f = \frac{k_f m_2}{m_1 M_2}$$

$$\therefore\ m_2 = \frac{\Delta T_f m_1 M_2}{k_f}$$

ΔT_f = 0.11 K

m_1 = 550.0 g = 0.55 kg

M_2 = [(12 × 6) + (1 × 12) + (16 × 6)] g mol^{-1} = 180 g mol^{-1}

k_f = 3.59 K kg mol^{-1}

m_2 = ?

Substituting we obtain

$$m_2 = \frac{0.11\ \cancel{\text{K}} \times 0.55\ \cancel{\text{kg}} \times 180\ \text{g}\ \cancel{\text{mol}^{-1}}}{3.59\ \cancel{\text{K}}\ \cancel{\text{kg}}\ \cancel{\text{mol}^{-1}}}$$

= 3.0 g

Practice Problem

The addition of 1.5 g of an organic compound to 100.0 g of benzene reduces its freezing point of water by 0.22 K. Calculate the molecular mass of the compound.

(k_f = 5.12 K kg mol^{-1}) [*Answer:* 350 g mol^{-1}]

7.4.4 Osmotic Pressure

Osmosis is the movement of solvent molecules from the region of higher concentration to a region of lower concentration through a semipermeable membrane. The pressure required to prevent osmosis taking place is called osmotic pressure Π.

Osmotic pressure is given by the van’t Hoff equation

$$\prod = CRT = \frac{mRT}{MV}$$

where $\prod$ = Osmotic pressure.
m = Mass of the solute.
M = Molar mass of the solute
V = Volume of the solvent in dm^3.
R = Universal gas constant.
T = Absolute temperature.
C = Molar concentration of the solute.

Osmotic pressure, like other colligative properties, can be used to determine the molar masses of compounds, expecially large molecules. This process is called osmometry.

Example 1 Calculate the osmotic pressure of a 0.011-M glucose solution at 40°C.

(R = 0.0821 dm^3 atm K^{-1} mol^{-1})

Solution We have to apply the relation

$\prod = CRT$

C = 0.011 mol dm^{-3}

R = 0.0821dm^3 atm K^{-1} mol^{-1}

T = 273 K + 40°C = 313 K

$\prod$ = ?

Substituting we have

$$\prod = \frac{0.011\,\cancel{mol}}{\cancel{dm^3}} \times \frac{0.0821\,\cancel{dm^3}\,atm}{1\,\cancel{mol} \times 1\,\cancel{K}} \times 313\,\cancel{K}$$

= 0.28 atm

Since osmotic pressure is a colligative property, it then implies that the osmotic pressure of any 0.011-M solution of a molecular solute would be 0.28 atm.

Example 2 What mass of glucose must be dissolved in 150.0 cm^3 of water to produce a solution having an osmotic pressure of 2.4 atm at 25°C?

(M = 180 g mol^{-1}, R = 0.0821 dm^3 atm $K^{-1}$$mol^{-1}$)

Solution The applicable relation is

$$\Pi = \frac{mRT}{MV}$$

$$\therefore\ m = \frac{\Pi MV}{RT}$$

$R = 0.0821\ \text{dm}^3\ \text{atm K}^{-1}\text{mol}^{-1}$

$T = 25°\text{C} + 273\ \text{K} = 298\ \text{K}$

$\Pi = 2.4\ \text{atm}$

$M = 180\ \text{g mol}^{-1}$

$V = 150.0\ \text{cm}^3 = 0.15\ \text{dm}^3$

$m = ?$

Substituting we have

$$m = \frac{2.4\,\cancel{\text{atm}} \times 180\ \text{g}\,\cancel{\text{mol}^{-1}} \times 0.15\,\cancel{\text{dm}^3} \times 1\,\cancel{\text{K}}}{0.0821\,\cancel{\text{dm}^3}\ \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}} \times 298\,\cancel{\text{K}}}$$

$= 2.6\ \text{g}$

Example 3 1.8 g of polyethylene $\left[C_2H_4\right]_n$ was dissolved in 150.0 cm^3 of benzene at 25°C to produce a solution whose osmotic pressure is 0.71 kPa. Calculate the molar mass of the compound, hence determine the number of ethylene units in the polymer.

($H = 1$, C = 12, $R = 8.314\ \text{J K}^{-1}\text{mol}^{-1}$)

Solution We have to apply the relation

$$\Pi = \frac{mRT}{MV}$$

$$\therefore\ M = \frac{mRT}{\Pi V}$$

$m = 1.8\ \text{g}$

$R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} = 8.314\ \text{kPa dm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$

$T = 25°\text{C} + 273\ \text{K} = 298\ \text{K}$

$\Pi = 0.71\ \text{kPa}$

$V = 150.0\ \text{cm}^3 = 0.15\ \text{dm}^3$

M = ?

Substituting we have

$$M = \frac{1.8\ \text{g} \times 8.314\ \cancel{\text{kPa}}\ \cancel{\text{dm}^3}\ \text{mol}^{-1} \times 298\ \cancel{\text{K}}}{0.71\ \cancel{\text{kPa}} \times 0.15\ \cancel{\text{dm}^3} \times 1\ \cancel{\text{K}}}$$

$= 42000\ \text{g mol}^{-1} = 42\ \text{kg mol}^{-1}$

The number of monomer (repeating) units of the polymer is obtained by dividing the molar mass of the polymer by that of the monomer. The molar mass of ethylene (ethene), C_2H_4, is

$M = [(12 \times 2) + (4 \times 1)]\ \text{g mol}^{-1} = 28\ \text{g mol}^{-1}$

$$\text{So } n = \frac{42000\ \cancel{\text{g}}\ \cancel{\text{mol}^{-1}}}{28\ \cancel{\text{g}}\ \cancel{\text{mol}^{-1}}}$$

$= 1500$

Practice Problems

1. What is the osmotic pressure of 0.050-M of a non-electrolyte solution at STP?

   (R = 0.0821 $\text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}$) [*Answer:* 1.2 atm]

2. 250.0 mg of polystyrene $\left[C_8H_8\right]_n$ was dissolved in 100.0 cm^3 of toluene to produce a solution whose osmotic pressure is 3.45×10^{-4} atm at 28°C. Calculate the molar mass of polystyrene, hence determine the number of styrene units in the polymer.

   (H = 1, C =12, R = 0.082 $\text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}$) [*Answer:* 180 kg mol, 1700]

3. A solution was prepared by dissolving 0.20 g of sucrose, $C_{12}H_{22}O_{11}$, in 50.0 cm^3 of pure water. At what temperature would the osmotic pressure of the resulting solution be 0.22 atm?

   (H = 1, C =12, O = 16, R = 0.082 $\text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}$) [*Answer:* 230 K]

7.4.5 Abnormal Molar Masses

Great care should be taken when using colligative properties to calculate molar masses. First, it should be noted that we have assumed ideal-dilute solutions in our treatment of colligative properties; hence the equations we have specified would not work for concentrated solutions unless adequate corrections are made to them.

Abnormal molar masses are also obtained for solutes that dissociate in solution, as in the case of electrolytes or ionic substances. When sodium chloride, for example, is dissolved in solution, it dissociates into sodium ions, Na^+, and chloride ions, Cl^-. The solvent has no capability to 'match up' the two ions, and would subsequently 'interpret' this to mean two molecules or solutes. Consequently, the colligative property measured would be twice the expected value. Since molar mass is inversely proportional to colligative property, it then follows that the molar mass obtained would be half the normal value. To account for this dissociation, we introduce the van't Hoff factor i into the relations for colligative properties of electrolyte solutions.

Theoretically, we expect the van't Hoff factor to be equal to the total number of moles of ions that could be produced by the dissociation of the solute, but this is not always the case because of ion pairing. In other words, ionic solutes are not totally dissociated in solution; thus the van't Hoff factors of substances are usually less than the theoretical values, depending on concentration of the solution. The van't Hoff factors of 0.05-m solutions of some electrolytes are given in Table 7.3.

Table 7.3: Van't Hoff factors of 0.05-m electrolyte solutions

Electrolyte	i (expected)	i (observed)
NaCl	2.0	1.9
$MgCl_2$	3.0	2.7
$MgSO_4$	2.0	1.3
$FeCl_3$	4.0	3.4
HCl	2.0	1.9

(Adapted from Steven S. Zumdahl, Chemical Principles (3rd Edition), Houghton Mifflin Company, Boston)

The molar masses obtained without taking the dissociation of ionic solutes into consideration are the normal, expected or actual values. Those obtained from experiments are called observed, measured or experimental values. The van’t Hoff factor is obtained using the relation

$$i = \frac{\text{Normal or actual molar mass}}{\text{Observed or experimental molar mass}} = \frac{\text{Observed or experimental value of colligative property}}{\text{Normal or actual value of colligatve property}}$$

$$= \frac{\text{Number of moles of solute after dissociation}}{\text{Number of moles of solute dissolved}}$$

Another cause of abnormal molar mass is the association of molecules. For example, when ethanoic acid, an organic solute, is dissolved in benzene, it exists as the dimer $(CH_3COOH)_2$, i.e.

$$2CH_3COOH \Leftrightarrow (CH_3COOH)_2$$

The colligative property obtained in this case would be half the actual value, and the experimental or measured molar mass would be twice as big.

Apart from the measurements of molar mass, we can also determine the degree of dissociation or association of molecules from colligative properties.

Example 1 The observed osmotic pressure of 0.16-M solution of $MgCl_2$ is 10.5 atm at 25°C. What is the actual van’t Hoff factor of the electrolyte?

$$(R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})$$

Solution $MgCl_3$ dissociates in solution to produce 3 mol of ions as follows:

$$MgCI_3(s) \text{ Æ } Mg^{2+}(aq) + 2CI^-(aq)$$

Thus the expected value for *i* is 3. However, the actual or experimental value should be lower than this due to ion pairing. To calculate this we have to apply the relation

$\prod = iCRT$

Thus $i = \frac{\Pi}{CRT}$

$\prod = 10.5$ atm

$C = 0.16 \text{ mol dm}^{-3}$

R = 0.0821 dm^3 atm K^{-1} mol^{-1}
T = 25°C + 273 = 298 K
i = ?

Substituting we have

$$i = \frac{10.5\ \text{atm} \times 1\ \cancel{\text{dm}^3} \times 1\ \cancel{\text{mol}} \times 1\ \cancel{\text{K}}}{0.16\ \cancel{\text{mol}} \times 0.0821\ \cancel{\text{dm}^3}\ \cancel{\text{atm}} \times 298\ \cancel{\text{K}}}$$

= 2.7 atm

Thus the experimental value of *i* is lower than the expected value by 0.3.

Example 2 Calculate the boiling point of a dilute aqueous solution produced by dissolving 100.0 g of sodium chloride in 1.2 kg of water if the boiling point of pure water is 373.15 K. Assume complete dissociation of the solute.

(Na = 23.0, Cl = 35.5, k_b = 0.51 K kg mol^{-1})

Solution We first calculate the boiling-point elevation the relation

$$\Delta T_b = \frac{ik_b m_2}{m_1 M_2}$$

i = 2 (Since the solute is assumed to dissociate completely)
k_b = 0.51 K kg mol^{-1}
m_2 = 100.0 g
m_1 = 1.2 kg
M_2 = (23.0 + 35.5) g mol^{-1} = 58.5 g mol^{-1}
ΔT_b = ?

Substituting we have

$$\Delta T_b = \frac{2 \times 0.51\ \text{K}\ \cancel{\text{kg}}\ \cancel{\text{mol}^{-1}} \times 100.0\ \cancel{\text{g}}}{1.2\ \cancel{\text{kg}} \times 58.5\ \cancel{\text{g}}\ \cancel{\text{mol}^{-1}}}$$

= 1.45 K

The boiling point of the solution is obtained by adding this temperature to the boiling point of water, i.e.

T_b = 373.15 K + 1.48 K

= 374.63 K

Example 3 The dissolution of 6 g of sodium chloride in 1 kg of water lowers its freezing point by 0.363°C. Calculate the apparent degree of dissociation and the van’t Hoff factor of the electrolyte.

(k_f = 1.86 °C kg mol^{-1}, Na = 23, Cl = 35.5)

Solution The very first step is to determine the van’t Hoff factor of the electrolyte. Since we are given the actual or experimental freezing-point lowering of the solution, then we have to determine the van’t Hoff factor from the relation

$$i = \frac{[\Delta T_f]_{\text{observed}}}{[\Delta T_f]_{\text{expected}}}$$

The expected freezing-point lowering is calculated by disregarding the dissociation of the solute, i.e.

$$(\Delta T_f)_{\text{expected}} = \frac{k_f m_2}{m_1 M_2}$$

k_f = 1.86 °C kg mol^{-1}

m_2 = 6 g

m_1 = 1 kg

M_2 = (23 + 35.5) g mol^{-1} = 58.5 g mol^{-1}

$(\Delta T_f)_{\text{expected}}$ = ?

Substituting we have

$$(\Delta T_f)_{\text{expected}} = \frac{1.86\text{°C}\,\cancel{\text{kg}}\,\cancel{\text{mol}^{-1}} \times 6\,\cancel{\text{g}}}{1\,\cancel{\text{kg}} \times 58.5\,\cancel{\text{g}}\,\cancel{\text{mol}^{-1}}}$$

= 0.191°C

$(\Delta T_f)_{\text{observed}}$ = 0.363°C

i = ?

Substituting we have

$$i = \frac{0.363\cancel{^\circ C}}{0.191\cancel{^\circ C}}$$

= 1.90

The apparent degree of dissociation of the solute is obtained from the relation

$$i = \frac{\text{Number of moles of solute present in solution}}{\text{Number of moles of solute dissolved}}$$

NaCl dissociates in solution as follows:

$$\mathrm{NaCl}(s) \Leftrightarrow \mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq)$$

If we assume that 1 mol of the solute is dissolved in solution, and that a is the amount dissociated, then the amounts of each species or particle present in the solution would be:

NaCl(s) 1− a
Na^+(aq) a
Cl^-(aq) a

Thus the total number of moles particles in solution is 1− a + a + a = 1 + a

Finally, we substitute to obtain

$$\frac{1+\alpha}{1} = 1.90$$

Cross-multiplying we have

1 + a = 1.90

∴ a = 1.90 – 1 = 0.90

Thus the apparent degree of dissociation of the salt is 0.90 or 90%.

Example 4 The observed osmotic pressure of a solution containing 1.5 g of hydrochloric acid in 250 cm^3 of solution is 7.62 atm at 25°C. What is the apparent degree of dissociation of the acid? Hence determine the apparent or observed molar mass of the acid.

(R = 0.0821 dm^3 atm K^{-1} mol^{-1}, H = 1, Cl = 35.5)

Solution The first step is to calculate the van’t Hoff factor of the solution, from the relation

$$i = \frac{\Pi_{\text{observed}}}{\Pi_{\text{expected}}}$$

The expected osmotic pressure of the solution is obtained by disregarding the dissociation of the acid, i.e.

$\Pi_{\text{expected}} = CRT$

where $C = \frac{n}{V}$

V = 250 cm^3 0.25 dm^3

The number of moles of the solute is obtained from the relation

$n = \frac{m}{M}$

m = 1.5 g

M = (1 + 35.5) g mol^{-1}

n = ?

Substituting we have

$n = \frac{1.5\,\cancel{g} \times 1\text{ mol}}{36.5\,\cancel{g}}$

= 0.0411 mol

C = ?

Substituting we have

$C = \frac{0.0411\text{ mol}}{0.25\text{ dm}^3}$

= 0.164 mol dm^{-3}

R = 0.0821 dm^3 atm K^{-1} mol^{-1}

T = 25°C + 273 = 298 K

$\prod_{\text{expected}} = ?$

We now substitute to obtain

$$\prod_{\text{expected}} = \frac{0.164\,\cancel{\text{mol}}}{\cancel{\text{dm}^3}} \times \frac{0.0821\,\cancel{\text{dm}^3}\,\text{atm}}{1\,\cancel{\text{K}} \times 1\,\cancel{\text{mol}}} \times 298\,\cancel{\text{K}}$$

$= 4.01$ atm

$\prod_{\text{experimental}} = 7.62$

$i = ?$

We can now substitute into the original relation to obtain

$$i = \frac{7.62\,\cancel{\text{atm}}}{4.01\,\cancel{\text{atm}}}$$

$= 1.90$

As usual, the apparent degree of dissociation of the solute is obtained from the relation

$$i = \frac{\text{Number of moles of solute present in solution}}{\text{Number of moles of solute dissolved}}$$

HCl(*aq*) is an electrolyte which dissociates as follows:

$\text{HCl}(s) \Leftrightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$

Initial number of moles 1 0 0

Equilibrium number of moles 1 – a a a

Total equilibrium number of moles = 1 – a + a + a = 1 + a

where a is the degree of dissociation of the solute.

We now substitute to obtain

$$\frac{1 + \alpha}{1} = 1.90$$

Cross-multiplying we have

$1 + a = 1.90$

$\therefore\ a = 1.90 - 1 = 0.90$

The apparent degree of dissociation of HCl, therefore, is 90%. The apparent (experimental or observed) molar mass of the solute is obtained from the relation

$$\underline{i} = \frac{M_{\text{expected}}}{M_{\text{apparent}}}$$

$M_{expected} = 36.5 \text{ g mol}^{-1}$

$M_{apparent} = ?$

Finally, we now substitute to obtain

$$1.90 = \frac{36.5 \text{ g mol}^{-1}}{M_{\text{apparent}}}$$

Cross-multiplying we have

$1.90 \times M_{apparent} = 36.5 \text{ g mol}^{-1}$

So $M_{apparent} = \frac{36.5 \text{ g mol}^{-1}}{1.90}$

$= 19.2 \text{ g mol}^{-1}$

Example 5 The dissolution of 0.5046 g of potassium sulphate in 100 g of water raises its boiling point by 0.0385°C. Calculate the apparent degree of dissociation of the solute. Hence obtain the apparent molar mass of the acid.

$(k_b = 0.51 \text{ °C kg mol}^{-1}, M_2 = 174 \text{ g mol}^{-1})$

Solution The first step is to determine the van’t Hoff factor from the relation

$$i = \frac{(\Delta T_b)_{\text{observed}}}{(\Delta T_b)_{\text{expected}}}$$

The expected increase in boiling point is obtained from the relation

$$(\Delta T_b)_{\text{expected}} = \frac{k_b m_2}{m_1 M_2}$$

$k_b = 0.51 \text{ °C kg mol}^{-1}$

$m_2 = 0.5046 \text{ g}$

M_2 = 174 g mol^{-1}
m_1 = 100 g = 0.1 kg
$(\Delta T_b)_{\text{expected}}$ = ?

Substituting we have

$$(\Delta T_b)_{\text{expected}} = \frac{0.51^\circ\mathrm{C}\,\cancel{\mathrm{kg}}\,\cancel{\mathrm{mol}^{-1}} \times 0.5046\,\cancel{\mathrm{g}}}{174\,\cancel{\mathrm{g}}\,\cancel{\mathrm{mol}^{-1}} \times 0.1\,\cancel{\mathrm{kg}}}$$

= 0.0148°C
$(\Delta T_b)_{\text{observed}}$ = 0.0385°C
i = ?

Substituting we have

$$i = \frac{0.0385\,\cancel{^\circ\mathrm{C}}}{0.0148\,\cancel{^\circ\mathrm{C}}}$$

= 2.60

The apparent degree of dissociation is obtained from the relation

$$i = \frac{\text{Number of moles of solute present in solution}}{\text{Number of moles of solute dissolved}}$$

Assuming 1 mol of the solute was dissolved and that a mol of this dissociated, then the total number of moles of particle present in the solution is obtained as follows:

$K_2SO_4(s) \Leftrightarrow 2K^+(aq) + SO_4^{2-}(aq)$
Initial number of moles 1 0 0
Equilibrium number of moles 1− a 2a a
Total equilibrium number of moles = 1 − a + 2a + a = 1 + 2a

Finally, we now substitute to obtain

$$\frac{1+2\alpha}{1} = 2.90$$

Thus 1 + 2a = 2.90
So 2a = 2.90 – 1 = 1.90

$$\therefore\ a = \frac{1.90}{2}$$

= 0.95

Thus the apparent degree of dissociation of the solute is 95%.

Example 6 5.00 g of ethanoic acid lowers the freezing point of 100 g of benzene by 2.16°C. Calculate the van’t Hoff factor of the acid and its apparent degree of association, given that the acid dimerizes in benzene.

(k_f = 5.10 °C kg mol^{-1}, M_2 = 60 g mol^{-1})

Solution The van’t Hoff factor of the acid is obtained from the relation

$$i = \frac{[\Delta T_f]_{\text{observed}}}{[\Delta T_f]_{\text{expected}}}$$

$$(\Delta T_f)_{\text{expected}} = \frac{k_f m_2}{m_1 M_2}$$

k_f = 5.10 °C kg mol^{-1}

m_2 = 5.00 g

m_1 = 100 g = 0.1 kg

M_2 = 60 g mol^{-1}

$(\Delta T_f)_{\text{expected}}$ = ?

Substituting we have

$$(\Delta T_f)_{\text{expected}} = \frac{5.10\,°\text{C}\,\cancel{\text{kg}}\,\cancel{\text{mol}^{-1}} \times 5.00\,\cancel{\text{g}}}{0.1\,\cancel{\text{kg}} \times 60\,\cancel{\text{g}}\,\cancel{\text{mol}^{-1}}}$$

= 4.25°C

$(\Delta T_f)_{\text{observed}}$ = 2.16°C

i = ?

Substituting we have

$$i = \frac{2.16\,°\text{C}}{4.25\,°\cancel{\text{C}}}$$

= 0.508

The degree of association of the solute is obtained from the relation

$$i = \frac{\text{Number of moles of solute present in solution}}{\text{Number of moles of solute dissolved}}$$

Suppose we dissolved 1 mol of the acid and a mol of it associated, then the total number of moles of it present in solution is obtained as follows:

$2CH_3COOH(aq) \Leftrightarrow [CH_3COOH(aq)]_2$

Initial number of moles 1 0

Equilibrium number of moles 1−a $\frac{\alpha}{2}$

Total equilibrium number of moles = $1-\alpha+\frac{\alpha}{2}=\frac{2-\alpha}{2}$

We can now substitute to obtain

$$\frac{2-\alpha/2}{1} = 0.508$$

So 2 − a = 1.016

Then a = 2 – 1.016 = 0.984

Thus the acid is 98.4% associated. As usual, the apparent molar mass of the acid is obtained from the relation

$$i = \frac{M_{expected}}{M_{apparent}}$$

$M_{expected}$ = 60 g mol^{-1}

$M_{apparent}$ = ?

Substituting we have

$$\frac{60\ \text{g mol}^{-1}}{M_{apparent}} = 0.508$$

Cross-multiplying we have

$M_{apparent} \times 0.508 = 60$ g mol^{-1}

So $M_{apparent} = \frac{60\ \text{g mol}^{-1}}{0.508}$

= 118 g mol^{-1}

Practice Problem

A solution containing 0.60 g of magnesium sulphate, $MgSO_4$, in 100 g of water freezes at −0.121°C. Calculate

(a) the van’t Hoff factor of the solute;
(b) the apparent degree of dissociation of the solute;
(c) the apparent molar mass of the solute.

(k_f = 1.86 °C kg mol^{-1}, O = 16, Mg = 24, S = 32)

[*Answers:* (a) 1.34 (b) 34% (c) 89.6 g mol^{-1}]

7.5 CONDUCTANCE OF SOLUTIONS

The conductance *C*, of a substance is its ability to conduct electricity. It is the exact opposite of resistance, which is the opposition to the flow of electric current. Since ions are the carriers of electric charge in a solution, then a solution must contain mobile ions for it to conduct electricity.

Solutions of ionic compounds conduct electricity to a very large extent because they undergo complete dissociation in solution. These compounds are called strong electrolytes. On the other hand, solutions of certain compounds, such as weak acids, only conduct electricity to a low extent because they are partially dissociated in solution. Such solutes are termed weak electrolytes. Solutions of most covalent compounds do not conduct electricity at all because the compounds are not made up of ions. These compounds are termed non-electrolytes.

The conductance of a solution is given as

$$C = \frac{1}{R} = \frac{A}{\rho l} = \frac{\kappa A}{l}$$

where R = Resistance of solution in ohms (Ω).

A = Area of solution compartment in cm^2.
l = Length of solution compartment in cm.

The term 1/r is the inverse of resistivity called conductivity or specific conductance k (Greek small letter kappa). It measured in siemens S, which is defined as

$$1 \text{ S} = 1\ \Omega^{-1}\ \text{cm}^{-1}$$

The term l/A, measured in cm^{-1}, is called cell constant. It is constant for a given electrolyte compartment regardless of the nature of the electrolyte.

The molar conductivity or molar conductance L (Greek capital letter lambda) of a substance is the conductivity of the solution containing 1 mol of the substance. This is given as

$$L = kV_m = \frac{\kappa}{C}$$

where V_m = Molar volume or volume of the solution containing 1 mole of the substance.

C = Concentration of the solution.

Friedrich Kohrausch (Fig. 7.3) discovered that the conductivity of an infinitely dilute solution is the sum of the conductivities of the ions of the solute. This statement, called the law of independent mobilities of ions, is given by the relation

$$L^{\cdot} = n_a l_a + n_c l_c$$

where $L^{\cdot}$ = The molar conductivity at infinite dilution.

n_a = The number of moles of anions.

n_a = The number of moles of cations.

l_a = The molar conductivity of anions.

l_c = The molar conductivity of cations.

A solution is said to be infinitely dilute if the solute is dissolved in so much of the solvent that the anions and cations are too widely separated to interact.

The ratio of molar conductivity to the molar conductivity at infinite dilution is a measure of the degree of ionisation of weak acids. This is given by Ostwald's dilution law:

Figure 7.3 Friedrich Wilhem Kohlrausch, German physicist (1840–1910).

$$\frac{1}{\Lambda} = \frac{1}{\Lambda^{\infty}} + \frac{\Lambda C}{k_a \Lambda^2}$$

where C = Concentration of the electrolyte.

K_c = Equilibrium constant of electrolyte or dissociation constant of a monoprotic acid.

We can make K_a the subject of the above relation to obtain

$$K_c = \frac{\alpha^2}{V(1-\alpha)}$$

For *n* moles of the electrolyte we have

$$K_c = \frac{n\alpha^2}{V(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

where V = Volume measure of the solution.

$a = \frac{\Lambda}{\Lambda^{\infty}}$ = Degree of dissociation or fraction of the electrolyte converted to ions at equilibrium.

Example 1 The resistance of a cell containing 0.0493 M of an electrolyte solution was found to be 30.5 W. Calculate the molar conductivity of the solution if the cell constant is 0.333 cm^{-1}, hence determine the molar volume of the solution.

Solution We have to apply the relation

$$L = \frac{\kappa}{C}$$

The conductivity is determined from the relation

$$\frac{1}{R} = k \times \frac{A}{l}$$

$$\therefore\ k = \frac{1}{R} \times \frac{l}{A}$$

$$R = 30.5\ \Omega$$

$\frac{l}{A} = 0.333\ \text{cm}^{-1}$

$k = ?$

Substituting we obtain

$$k = \frac{1}{30.5\,\Omega} \times 0.333\ \text{cm}^{-1}$$

$= 0.0109\ \text{S}$

$C = 0.0493\ \text{mol dm}^{-3} = 0.0493 \times 10^{-3}\ \text{mol cm}^{-3}$

$L = ?$

Finally, we substitute to obtain

$$L = \frac{0.0109\ \text{S} \times 1\ \text{cm}^3}{0.0493 \times 10^{-3}\ \text{mol}}$$

$= 221\ \text{S cm}^3\ \text{mol}^{-1}$

To obtain the molar volume, we have to apply the relation

$L = kV_m$

$\therefore\ V_m = \frac{\kappa}{\Lambda}$

$V_m = ?$

Substituting we have

$$V_m = \frac{221\ \text{S}\ \cancel{\text{cm}^3}\ \text{mol}^{-1}}{0.0109\ \cancel{\text{S}}}$$

$= 20300\ \text{cm}^3\ \text{mol}^{-1} = 20.3\ \text{dm}^3\ \text{mol}^{-1}$

Example 2 Calculate the molar conductivity of magnesium chloride at infinite dilution, given that the ionic molar conductivities of Mg^{2+} and Cl^- are 106.2 S cm^3 mol^{-1} and 76.3 S cm^3 mol^{-1} respectively.

Solution We have to apply the relation

$$L^{\cdot} = n_a l_a + n_c l_c$$

The equation of dissociation is

$$MgCl_2(s) \Leftrightarrow Mg^{2+}(aq) + 2Cl^{-}(aq)$$

$n_a = 2$

$n_c = 1$

$l_a = 76.3$ S cm^3 mol^{-1}

$l_c = 106.\ 2$ S cm^3 mol^{-1}

$L^{\cdot} = ?$

Substituting we have

$L^{\cdot} = (2 \times 76.3$ S cm^3 mol^{-1}) + 106. 2 S cm^3 mol^{-1}

So $L^{\cdot} = 152.6$ S cm^3 mol^{-1} + 106. 2 S cm^3 mol^{-1}

$= 258.8$ S cm^3 mol^{-1}

Example 3 1 mol of carbonic acid was dissolved in 2.5 dm^3 of water at a certain temperature, and the molar conductance was measured to be 0.827 S cm^3 mol^{-1}. Calculate the ionization constant of the acid. The molar conductivities of CO_3^{2-} and H^+ are 138.6 S cm^3 mol^{-1} and 349.8 S cm^3 mol^{-1} respectively.

Solution We have to apply the relation

$$K_a = \frac{n\alpha^2}{V(1-\alpha)}$$

We have to determine *a* from the relation

$$a = \frac{\Lambda}{\Lambda^{\infty}}$$

$L^{\cdot} = n_a l_a + n_c l_c$

The dissociation constant of the acid is determined from the dissociation

$$H_2CO_3(aq) \Leftrightarrow 2H^+(aq) + CO_3^{2-}(aq)$$

$l_a = 138.6$ S cm^3 mol^{-1}

$n_a = 2$

$l_c = 349.8$ S cm^3 mol^{-1}

$n_c = 1$

$L^{\cdot}$ = ?

Substituting we obtain

$L^{\cdot}$ = (2 × 349.8 S cm^{3} mol^{-1}) + 138.6 S cm^{3} mol^{-1}

Then $L^{\cdot}$ = 699.6 S cm^{3} mol^{-1} + 138.6 S cm^{3} mol^{-1} = 838.2 S cm^{3} mol^{-1}

L = 0.827 S cm^{3} mol^{-1}

a = ?

Substituting we obtain

a = $\frac{0.827\,\cancel{\text{S}}\,\cancel{\text{cm}^3}\,\cancel{\text{mol}^{-1}}}{838.2\,\cancel{\text{S}}\,\cancel{\text{cm}^3}\,\cancel{\text{mol}^{-1}}}$

= 9.87 × 10^{-4}

V = 2.5 dm^{3}

K_a = ?

Substituting we obtain

K_a = $\frac{1\ \text{mol} \times (9.87 \times 10^{-4})^2}{2.5\ \text{dm}^3 \times (1 - 9.87 \times 10^{-4})}$

So K_a = $\frac{9.75 \times 10^{-7}\ \text{mol}}{2.5\ \text{dm}^3}$

= 3.9 × 10^{-7} M

Example 4 The dissociation constant of 1.5-M solution of ethanoic acid was measured to be 1.8 × 10^{-5} M^{2} at 25°C. If the molar ionic conductivities of H^+ and $CH_3CO_2^-$ are 349.8 S cm^{3} mol^{-1} and 40.9 S cm^{3} mol^{-1} respectively, calculate the molar conductivity and specific conductance of the acid at the given temperature.

Solution The molar conductivity is obtained from the relation

a = $\frac{\Lambda}{\Lambda^{\infty}}$

∴ L = a$L^{\cdot}$

$L^{\cdot}$ is obtained from the relation

$$L^{\cdot} = n_a \mathrm{l}_\mathrm{a} + n_c \mathrm{l}_\mathrm{c}$$

The equation of dissociation is

$$CH_3COOH(aq) \Leftrightarrow H^+(aq) + CH_3CO_2^-(aq)$$

l_a = 40.9 S cm^3 mol^{-1}

n_a = 1

l_c = 349.8 S cm^3 mol^{-1}

n_c = 1

$L^{\cdot}$ = ?

Substituting we have

$$L^{\cdot} = 349.8 \text{ S cm}^3 \text{ mol}^{-1} + 40.9 \text{ S cm}^3 \text{ mol}^{-1} = 390.7 \text{ S cm}^3 \text{ mol}^{-1}$$

a is obtained from the relation

$K_a = \frac{C\alpha^2}{1-\alpha}$

$K_a = 1.8 \times 10^{-2}$ M^2

C = 1.5 M

a = ?

Dropping the units and substituting, we obtain

$$1.8 \times 10^{-5} = \frac{1.5\alpha^2}{1-\alpha}$$

Cross-multiplying we have

$$1.5a^2 = 1.8 \times 10^{-5} - 1.8 \times 10^{-5}a$$

From which we obtain

$$1.5a^2 + 1.8 \times 10^{-5}a - 1.8 \times 10^{-5} = 0$$

We now solve this quadratic equation using the quadratic formula

a $= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

a = 1.5, b = 1.8×10^{-5}, $c = -1.8 \times 10^{-5}$

Substituting we have

$$a = \frac{-1.8\times10^{-5} \pm \sqrt{(1.8\times10^{-5})^2 - 4(1.5)(-1.8\times10^{-5})}}{2(1.5)}$$

$$\text{Thus } a = \frac{-1.8\times10^{-5} \pm 1.1\times10^{-4}}{3.0}$$

So $a = -1.3 \times 10^{-4}$ or $a = 9.2 \times 10^{-5}$

Since the negative value is inadmissible, then $a = 9.2 \times 10^{-5}$

$L = ?$

Substituting we have

$L = 9.2 \times 10^{-5} \times 390.7$ S cm^3 mol^{-1}

$= 0.036$ S cm^3 mol^{-1}

The conductivity of the solution is calculated from the relation

$$L = \frac{\kappa}{C}$$

$\therefore\ k = LC$

$C = 1.5\, M = 1.5 \times 10^{-3}$ mol cm^{-3}

$k = ?$

Substituting we have

$$k = \frac{0.036 \text{ S } \cancel{\text{cm}^3}}{1 \cancel{\text{mol}}} \times \frac{1.5\times10^{-3} \cancel{\text{mol}}}{1 \cancel{\text{cm}^3}}$$

$= 5.4 \times 10^{-5}$ S

Practice Problems

1. The resistance of a cell containing 0.055 M of an electrolyte is 40.5 Ω. Calculate the molar conductivity of the electrolyte, given that the cell constant is 0.221 cm^{-1}.

[*Answer:*100 S cm^3 mol^{-1}]

2. Calculate the molar conductivity of hydrochloric acid, HCl, at infinite dilution, given that the ionic molar conductivities of H^+ and Cl^- are 349.8 S cm^3 mol^{-1} and 76.3 S cm^3 mol^{-1} respectively. [*Answer:* 426.1 S cm^3 mol^{-1}]
3. The molar conductance of a 0.042 M of ethanoic acid, CH_3COOH, is 0.133 S cm^3 mol^{-1} at a certain temperature. Calculate the ionization constant of the acid at this temperature given that ionic conductivities of H^+ and $CH_3CO_2^-$ are 349.8 S cm^3 mol^{-1} and 40.9 S cm^3 mol^{-1} respectively. [*Answer:* 4.9 × 10^{-9} M]

SUMMARY

- A solution is a homogeneous mixture consisting of a solute dissolved in a solvent.
- The concentration of a solution is the amount of the solute present in a given amount of the solvent.
- Molar concentration or molarity is given by the relation

$$C = \frac{n}{V}$$

- Mass concentration is given by the relation

$$r = \frac{m}{V}$$

- The dilution law is given by the relation

$$C_1V_1 = C_2V_2$$

- A standard solution is a solution of known concentration. A molar solution is a solution containing exactly 1 mol of the solute.
- A saturated solution is a solution that contains the maximum amount of the solute that it can dissolve at a particular temperature.
- The molality of a solution is the number of moles of a solute present in 1 kg of the solvent. It is given by

$$\text{Molality} = \frac{n}{m(kg)}$$

- The solubility of a solute at a particular temperature is its concentration in a saturated solution at a particular temperature. Solubility depends on temperature, pressure, and polarity.

- The ionic product Q_{sp} of a solution is the product of the concentrations of the ions of a solute in solution, with each concentration raised to its stoichiometric coefficient.
- The solubility product K_{sp} of a solute is a temperature-dependent constant referring to a stage of dynamic equilibrium or saturated solution. It is equal to the ion product at equilibrium or at saturation.
- The formation of a complex increases the solubility of a solute by increasing the equilibrium constant of the solution.
- The solubility of a gas increases with pressure.This is given by Henry's law:

$$S = K_H \times P$$

- Colligative properties of solutions are those properties which are functions of the relative amount of solute and solvent molecules, but are independent of the nature of the solute.
- The presence of a solute reduces the vapour pressure of a solvent. The vapour pressure lowering of a solvent is given by Raoult's law:

$$P = x_A \times P^o \text{ or } \Delta P = x_B \times P^o$$

- Vapour pressure lowering is related to the molar mass of a solute by the equation

$$M_B = \frac{P^\circ m_B}{\Delta P n_A}$$

- The presence of a solute increases the boiling point of a solvent. The use of boiling-point elevation to determine the molar mass of a substance is called ebullioscopy.
- The boiling-point elevation of a solvent is related to the molar mass of the solute by the equation

$$\Delta T_b = \frac{i k_b m_2}{m_1 M_2} = i \times k_b \times m$$

- The presence of a solute reduces the freezing point of a solvent. The use of freezing-point depression to determine the molar mass of a substance is called cryoscopy.
- The freezing-point depression of a solvent is related to its molar mass by the equation

$$\Delta T_f = \frac{ik_f m_2}{m_1 M_2} = i \times k_f \times m$$

- Osmosis is the movement of solvent molecules from the region of higher concentration to a region of lower concentration through a semipermeable membrane. The use of osmosis to determine molar mass is called osmometry.
- The pressure required to prevent osmosis from taken place is called osmotic pressure. Osmotic pressure and the molar mass of a solute are related by the equation

$$\Pi = \frac{imRT}{MV} = iCRT$$

- The conductance of a solution is its ability to conduct electricity. Conductivity is given by

$$C = \frac{1}{R} = \frac{A}{\rho l} = \frac{\kappa A}{l}$$

- The molar conductivity or molar conductance L of a substance is the conductivity of the solution containing 1 mol of the substance. This is given as

$$L = kV_m = \frac{\kappa}{C}$$

- The law of independent motilities of ions states that the molar conductivity of a substance at infinite dilution is the sum of the conductivities of the ions of the solute, i.e.

$$L^{\cdot} = n_a l_a + n_c l_c$$

- The ionization constant of a weak monoprotic acid is given by the Ostwald's dilution law:

$$K_a = \frac{n\alpha^2}{V(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. 100.0 cm^3 of a saturated solution of sodium chloride, NaCl, contains 20.0 g of the compound at a certain temperature. What is the molar solubility of sodium chloride at this temperature?

   (Na = 23.0, Cl = 35.5)

   A. 0.0034 M B. 0.011 M
   C. 2.10 M D. 2.50 M
   E. 3.42 M

2. 100.0 cm^3 of a saturated solution of sodium hydroxide, NaOH, contains 0.25 mol of the base at 25°C. What is the mass solubility of the base at this temperature?

   (H = 1, O = 16, Na = 23)

   A. 10 g dm^{-3} B. 80 g dm^{-3}
   C. 90 g dm^{-3} D. 100 g dm^{-3}
   E. 200 g dm^{-3}

3. Which of the following is **NOT** likely to dissolve in water?

   A. Sodium chloride B. Magnesium chloride
   C. Toluene D. Ethanol
   E. Hydrogen chloride

4. Which of the following affects the solubility of gases?

   A. Temperature B. Reactivity
   C. Molarity D. pH
   E. Pressure

5. Which of these is **NOT** a colligative property?

   A. Vapour pressure lowering
   B. Freezing-point depression
   C. Boiling-point elevation
   D. Polarity
   E. Osmotic pressure

6. The technique of determining the molar mass of a substance through the measurement of boiling-point elevation is called

   A. Molarity B. Cryoscopy
   C. Osmometry D. Ebullioscopy
   E. Molecularity

7. The use of osmotic pressure to determine the molecular mass of a solute is called

A. Osmosis B. Osmometry

C. Thermometry D. Crystallography

E. Diffraction

8. Which of these combinations have the **SAME** units?

A. Osmotic pressure and boiling-point elevation

B. Boiling point and osmotic pressure

C. Freezing point and osmotic pressure

D. Freezing point and Henry's constants

E. Cryoscopic and ebullioscopic constants

9. What is the osmotic pressure of 0.0010-M solution of glucose at 25°C?

(R = 0.0821 dm^3 atm K^{-1} mol^{-1})

A. 0.022 atm B. 0.024 atm

C. 0.025 atm D. 0.12 atm

E. 0.24 atm

ESSAY TYPE QUESTIONS

Concentration

10. Define the following terms:

(a) Solution (b) Solute (c) Saturated solution (d) Molar solution (e) Solvent

11. (a) What is solubility?

(b) Explain how each of the following affects the solubility of a substance:

(i) Temperature (ii) Polarity (iii) Pressure

12. Explain each of the following terms:

(i) Dilution (ii) Dilute solution (iii) Concentrated solution (iv) Molarity (v) Mass concentration

13. Explain how would you prepare the saturated solution of a compound at a certain temperature.

14. 10.3 g of sodium carbonate was dissolved in 200.0 cm^3 of water. Calculate the mass and molar concentrations of the resulting solution.

(C = 12, O = 16, Na = 23)

15. Calculate the mass of sodium hydroxide in 250.0 cm^3 of a 0.050-M solution of the compound.

(H = 1, O = 16, Na = 23)

16. What is the molarity of a solution whose mass concentration is 20.8 g dm^{-3}, given that the molar mass of the solute is 180 g mol^{-1}?

17. What volume of water must be added to 50.0 cm^3 of a 0.25-M solution to produce a 0.052-M solution?

18. 25.0 cm^3 of water was added to 50.5 cm^3 of a solution to produce a 0.21-M solution. Calculate the initial concentration of the solution.

19. What mass of potassium hydroxide must be added to 500.0 cm^3 of water to produce a 0.25-M solution?

(H = 1, O = 16, K = 39)

20. What volume of 20.8-M concentrated hydrochloric acid solution is required to prepare 2.5 dm^3 of a 0.150-M solution of the acid?

21. Determine the molarity of a solution prepared by adding 6.5 cm^3 of concentrated sulphuric acid to 1.0 dm^3 of water, given that the composition and density of the acid are 98% and 1.84 g cm^{-3} respectively.

(H = 1, O = 16, S = 32)

22. What volume of concentrated nitric acid solution is required to prepare a 0.0500-M solution, given that the density and percentage composition of the acid are 1.52 g cm^{-3} and 68% respectively.

(H = 1, N = 14, O = 16)

Molality

23. (a) What is molality?

(b) Calculate the molality of the solution prepared by dissolving 6.2 g of sodium chloride in 50 g of water.

(Na = 23.0, Cl = 35.5)

24. (a) Calculate the molality of 25% by mass aqueous solution of ethanol, C_2H_5OH.

(H = 1, C = 12, O = 16)

Solubility and solubility product

25. (a) Distinguish between ion and solubility products.

(b) Briefly explain the significance of ion product in qualitative analysis.

26. Predict if calcium sulphate would precipitate when 200.0 cm^3 of 0.50-M

solution of calcium chloride is added to 100.0 cm^3 of 0.5-mM solution of silver sulphate. The solubility product of calcium sulphate is 2.4×10^{-5} M^2.

27. What volume of 0.250-M solution of lead(II) iodide must be added to 250.0 cm^3 of 0.750-mM solution of calcium sulphate to effect the precipitation of lead(II) sulphate?

$$(K_{sp} = 1.60 \times 10^{-8}\,\mathrm{M}^2)$$

28. You are required to precipitate silver iodide from a 25.00 cm^3 of a 0.015-mM solution of silver sulphate by adding 10.00 cm^3 of lead(II) iodide solution? What should be the minimum molarity of the solution?

$$(K_{sp} = 1.5 \times 10^{-16}\,\mathrm{M}^2)$$

29. 1.5×10^{-4} g of silver chloride, is contained in 1.0 dm^3 of water at a certain temperature. Calculate the ion product of the compound.

(Cl = 35.5, Ag = 63.5)

30. A saturated solution of calcium carbonate, $CaCO_3$, contains 0.0093 g of the compound per dm^3 of solution at 25°C. Calculate the solubility product of the compound at this temperature.

(C = 12, O = 16, Ca = 40)

31. The solubility product of copper(II) bromide, CuBr, is 4.2×10^{-8} M^3 at 25°C. What is the molar and mass solubilities of the compound at this temperature?

(Cu = 63.5, Br = 79.9)

32. Calculate the molar solubility of silver phosphate, Ag_3PO_4, at the temperature at which its solubility product is 1.3×10^{-20} M^4.

33. Explain how the formation of a complex ion increases the solubility of a substance.

34. Silver iodide was dissolved in a solution containing chloride ions leading to the formation of the complex $[AgCl_2]^-$. What is the overall equilibrium constant of the solution?

$$(K_f = 2.5 \times 10\,\mathrm{M}^{-5},\ K_{sp} = 1.5 \times 10^{-16}\,\mathrm{M}^2)$$

35. Calculate the solubility of nickel hydroxide, $Ni(OH)_2$, in 2.0-M solution of ammonia.

$$(K_f = 5.6 \times 10^{8}\,\mathrm{M}^{-6},\ K_{sp} = 6.5 \times 10^{-18}\,\mathrm{M}^3)$$

36. The solubility product of iron(II) hydroxide, $Fe(OH)_2$, is 2.0×10^{-39} M^3 at a certain temperature. What concentration of cyanide ions must be present in

solution to increase the solubility of the compound by a factor of 10000?

($K_f = 7.7 \times 10^{36}\ \mathrm{M}^{-6}$)

37. The solubility product of silver carbonate is $6.2 \times 10^{-12}\ \mathrm{M}^3$. What concentration of chloride ions must be present in solution to increase the solubility of the salt by 100 times its solubility in pure water?

($K_f = 2.5 \times 10^{5}\ \mathrm{M}^{-2}$)

38. Calculate the concentration of copper(II) ions in a solution containing 0.25-M copper(II) sulphide and 2.0 M of ammonia.

($K_f = 1.2 \times 10^{13}\ \mathrm{M}^{-4}$, $K_{sp} = 8.5 \times 10^{-45}\ \mathrm{M}^2$).

39. Calculate the concentration of mercury(II) ions in a solution containing 0.15-M mercury (II) sulphide and 2.5 M of chloride ions.

($K_f = 1.2 \times 10^{5}\ \mathrm{M}^{-4}$, $K_{sp} = 1.6 \times 10^{-52}\ \mathrm{M}^2$)

40. Calculate the solubility of oxygen in water when the partial pressure of the gas is 0.48 atm.

($K_H = 1.3\ \mathrm{mM\ atm}^{-1}$)

41. 250.0 cm^3 of air contains 0.20 g of carbon dioxide at 20°C. Determine the concentration of the gas in water at this temperature.

(C =12, O = 16, $K_H = 23\ \mathrm{mM\ atm}^{-1}$, $R = 0.082\ \mathrm{atm\ dm}^3\ \mathrm{mol}^{-1}\ \mathrm{K}^{-1}$)

42. The concentration of helium in water is 5 mM at a particular temperature. What is the partial pressure of the gas under this condition?

($K_H = 0.5\ \mathrm{mM\ atm}^{-1}$)

43. The solubility of a gas in acetone is 0.25 M when its partial pressure is 0.11 atm. Calculate the solubility of the gas in the same solvent at the same temperature if the partial pressure of the gas is raised to 0.45 atm.

Colligative properties of solutions

44. (a) What do you understand by colligative properties? Give two examples.

(b) Explain briefly the effect of the presence of solutes on the boiling and freezing points of liquids.

45. The vapour pressure of 200.0 g of phenol, C_6H_5OH, is 68.9 kPa at a certain temperature. Calculate the vapour pressure of the compound when 2.5 g of rubber is completely dissolved in it.

(H = 1, C = 12, O = 16, molar mass of rubber = 150 kg mol^{-1})

46. Calculate the vapour pressure lowering of 5.0% by mass aqueous sodium chloride solution, given that the vapour pressure of pure water at the prevailing temperature is 700.00 Torr. Assume the solute is 100% dissociated.

(H = 1.0, O = 16, Na = 23, Cl = 35.5)

47. What is the vapour pressure of 0.086-M solution of sodium chloride at a temperature at which the vapour pressure of pure water is 760.0 mmHg? Take the density of the solution to be 1.002 g cm^{-3} and assume it is 100% dissociated.

(H = 1, O = 16)

48. The vapour pressure of pure water was reduced from 22.50 to 22.39 mmHg when 1.5 g of a molecular solute was dissolved in 24.5 g of the solvent. Determine the molar mass of the solute.

(H = 1, O = 16)

49. The addition of 830.0 mg of an amine to 500.0 g of water reduces its freezing point by 0.10 K. What is the molar mass of the amine?

(k_f = 1.86 K kg mol^{-1})

50. To what extent would the addition of 500.0 mg of ethanol, C_2H_6O, lower the freezing point of 50.0 g of water?

(k_f = 1.86 K kg mol^{-1})

51. 20.0 g of natural rubber, $[C_5H_8]_n$, was dissolved in 100.0 g of benzene to produce a sticky solution that freezes at 5.52°C. Given that the normal freezing point of benzene is 5.50°C, determine

(a) the molecular mass of the rubber;

(b) the number of repeating units of the rubber.

(H = 1, C = 12, k_f = 5.12 K kg mol^{-1})

52. 0.50 g of polyethylene was dissolved in 750.0 g of carbon tetrachloride at room temperature. What is the molecular mass of the polyethylene if it reduces the freezing point of the solvent by 0.51 K? Hence determine the number of ethylene units in the polymer. The molecular mass of the monomer is 28 g mol^{-1}.

(k_f= 29.8 K kg mol^{-1})

53. 2.5 g of sucrose, $C_{12}H_{22}O_{11}$ was dissolved in 100.0 g of water. At what temperature would the solution boil if pure water boils at 100°C?

(k_b = 0.51 K kg mol^{-1}, H = 1 C = 12, O = 16)

54. The density of 0.030-M solution of barium chloride is 1.05 g cm^{-3}. Calculate the boiling-point elevation of the solution.

(k_b = 0.51 K kg mol^{-1}, i = 2.7, Cl = 35.5, Ba = 137.3)

55. Calculate the boiling-point elevation of 7.5% by mass aqueous solution of sucrose.

(k_b = 0.51 K kg mol^{-1}, H = 1, C = 12, O = 16)

56. Define the following terms:

(i) Osmosis (ii) Osmotic pressure

57. Briefly explain the effects of each of the following on the osmotic pressure of a solution:

(i) Solute concentration (ii) Temperature of solution

58. What is the osmotic pressure of 0.0010-M solution of calcium chloride at 50°C? Assume complete dissociation of the salt.

(R = 0.0821dm^3 atm K^{-1} mol^{-1})

59. Calculate the temperature at which the osmotic pressure of 0.0100-M glucose solution would be 0.21 atm.

60. 0.50 g polystyrene, $[C_8H_8]_n$, was dissolved in 250.0 cm^3 of water to produce a solution whose osmotic pressure is 60.0 Pa at 27.0°C. Compute the molar mass of the polystyrene, hence calculate the number of styrene molecules in the polymer.

(R = 8.314 J K^{-1} mo1^{-1})

61. 25.0 g of a resin was dissolved in 150.0 cm^3 of petrol to produce an adhesive whose osmotic pressure is 0.103 atm at 27°C. What is the molecular mass of the resin?

(R = 0.082 atom dm^3 K^{-1} mol^{-1})

62. 0.20 g of polypropylene, $[C_3H_6]_n$, was dissolved in 50.0 cm^3 of an organic solvent to produce a solution whose osmotic pressure is 2.23 Torr at 27°C. Determine

(a) the molecular mass of the polymer;

(b) the number of monomer units in the polymer.

(H = 1, C = 12, R = 62.4 Torr K^{-1} mol^{-1})

63. 5.0 g of sucrose, $C_{12}H_{22}O_{11}$, was dissolved in 150.0 cm^3 of water at 25°C. What is the osmotic pressure of the solution?

(H = 1, C = 12, O = 16, R = 0.082 dm^3 atm K^{-1} mol^{-1})

64. The osmotic pressure of a solution containing 5.50 g of ethanoic acid in 150 cm^3 of benzene is 9.87 atm at 25°C. Calculate the degree of association of the acid in the solvent.

(R = 0.082 dm^3 atm K^{-1} mol^{-1}, M_2 = 60.0 g mol^{-1})

Conductance of solutions

65. Define the following terms:

(a) Conductivity (b) Molar conductivity (c) Strong electrolyte (d) Weak electrolyte (e) Non-electrolyte

66. Calculate the molar conductivity at infinite dilution of the following compounds:

(a) Potassium iodide, KI.

(l_a = 76.8 S cm^3 mol^{-1},l_c= 73.5 S cm^3 mol^{-1})

(b) Calcium carbonate, $CaCO_3$.

(l_a = 138.6 S cm^3 mol^{-1}, l_c = 119.0 S cm^3 mol^{-1})

(c) Silver bromide, AgBr.

(l_a = 78.1 S cm^3 mol^{-1}, l_c = 61.9 S cm^3 mol^{-1})

(d) Copper(II) sulphate, $CuSO_4$.

(l_a = 159.6 S cm^3 mol^{-1}, l_c = 107.2 S cm^3 mol^{-1})

(e) Copper(II) nitrate, $CuNO_3$.

(l_a = 71.5 S cm^3 mol^{-1}, l_c = 107.2 S cm^3 mol^{-1})

67. The resistance of a cell containing 0.0350-M solution of sulphuric acid is 50.0 Ω. Determine the molar conductance of the electrolyte, given that the cell constant is 0.301 cm^{-1}.

68. The molar conductance of 0.025-M solution of sodium hydroxide was measured to be 240 S cm^3 mol^{-1}, and the resistance, 45.8 W. Calculate

(a) the conductivity of the solution;

(b) the molar volume of the solution;

(c) the cell constant.

69. The resistance of a cell when it was filled with 0.043-M of solution A was 30.0 Ω, and its molar conductivity, 100.0 S cm^3 mol^{-1}. The cell was then emptied and filled with 0.0065 M of another solution B, and the new resistance was measured to be 50.0 Ω, calculate

(a) the cell constant;

(b) the molar conductivity of solution B.

70. 1.5 mol of carbonic acid was dissolved in 150.0 cm^3 of water at a certain temperature, and the molar conductance was measured to be 0.637 S cm^3 mol^{-1}. Calculate the ionization constant of the acid at this temperature.

(l_a = 138.6 S cm^3 mol^{-1}, l_c = 349.8 S cm^3 mol^{-1})

71. The dissociation constant of 0.500-M solution of ethanoic acid was measured to be 1.70 × 10^{-6} M^2 at a certain temperature. Calculate the molar conductivity and specific conductance of the acid at the given temperature.

(l_a= 349.8 S cm^3 mol^{-1}, l_c = 40.9 S cm^3 mol^{-1})

Answers

1. E   2. D
3. C   4. E
5. D   6. D
7. B   8. E
9. B   14. 51.5 gdm^{-3}, 0.486 M
15. 0.5 g   16. 0.12 M
17. 190 cm^3 18. 0.31 M
19. 7.0 g   20. 0.018 dm^3
21. 0.12 M   22. 3.05 cm^3
23. (b) 2.1 *m*   24. 7.2 *m*
26. yes   27. Just above 2930 dm^3
28. 7.0 × 10^{-10} M   29. 2.3 × 10^{-12} M^2
30. 8.6 × 10^{-9} M^2 31. 2.0 × 10^{-4} M, 0.029 gdm^{-3}
32. 4.7 × 10^{-6} M   34. 3.8 × 10^{-11} M
35. 3.9 Mm   36. 7.1 × 10^{-5} M
37. 0.063 M   38. 1.3 × 10^{-15} M
39. 3.2 × 10^{-8} M   40. 6.2 × 10^{-4} M
41. 0.010 M   42. 10 atm
43. 1.0 M   45. 68.9 kPa
46. 21.7 Torr   47. 757.7 mmHg
48. 230 g mol^{-1} 49. 85 g mol^{-1}
50. 0.404 K   51. (a) 51.2 kg mol^{-1} (b) 750
52. 2.02 kg mol^{-1}, 72   53. 100.037°C

54. 0.040°C 55. 0.12°C

58. 0.080 atm 59. 256 K

60. 83 kg mol^{-1}, 800 61. 40 kg mol^{-1}

62. (a) 34 kg mol^{-1} (b) 810 63. 2.4 atm

64. 67.6%

66. (a) 150.3 S cm^{3} mol^{-1} (b) 257.6 S cm^{3} mol^{-1} (c) 140.0 S cm^{3} mol^{-1} (d) 266.8 S cm^{3} mol^{-1}
(e) 178.7 S cm^{3} mol^{-1}

67. 172 S cm^{3} mol^{-1}

68. (a) 6.0 mS (b) 40 dm^{3} mol^{-1} (c) 0.27 cm^{-1}

69. (a) 0.13 cm^{-1} (b) 400 S cm^{3} mol^{-1}

70. 5.8 × 10^{-6} M^{3}

71. 0.719 S cm^{3} mol^{-1}, 3.60 × 10^{-4} S

8

Chapter Quantitative Analysis

Quantitative analysis is the determination of the amounts of substances. The two branches of quantitative analysis are volumetric analysis and gravimetric analysis.

8.1 VOLUMETRIC ANALYSIS

Volumetric analysis involves volume measurements. The method used in volumetric analysis is titration, which involves the addition of the standard solution of a substance, called the titrant, to a known volume of the solution of another substance of unknown concentration, called the analyte, until the reaction is just complete. The stage at which just the right amount of the titrant has been added to the analyte is called equivalence point. The different types of titrations include acid-base titration, redox titration and back titration.

8.1.1 Acid-base Titration

The equivalence point of a redox titration in which the reduced and oxidized forms of a reducing or oxidizing agent have different colours can be easily determined by the colour change of the oxidizing or reducing agent. On the other hand, acid and base solutions are usually colourless, and the equivalence point cannot be determined by merely looking at the reaction mixture. This problem is overcome by adding a suitable indicator to the base solution, which is normally held in a volumetric flask.

Indicators are dyes that change colours according to the pH of a solution in which they are dissolved. Examples include methyl orange, methyl red, phenolphthalein, thymol blue, litmus, phenol red, bromocresol green, etc. The equivalence point is usually recognized by the characteristic colour change of an indicator. For example, the colour of methyl orange changes to orange at equivalence point. Table. 8.1 is a list of common indicators and their pH range of colour change.

Table 8.1: Common acid-base indicators

Indicator	*pH range of colour change*	*Acid colour*	*Base colour*
2,6 Dinitrophenol	2.0−4.0	Colourless	Yellow
Bromocresol green	4.0−5.6	Yellow	Blue
Bromocresol purple	5.2−6.8	Yellow	Purple
Bromophenol blue	3.0−4.6	Yellow	Blue
Litmus	5.0−8.0	Red	Blue
Methyl orange	3.1−4.4	Red	Yellow
Methyl red	4.8−6.0	Red	Yellow
Methyl yellow	2.9−4.0	Red	Yellow
Picric acid	0.1−3.8	Colourless	Yellow
Thymol blue	1.2−2.8	Red	Yellow

The choice of indicator for an acid-base titration depends on the strengths of the acid and base, as given below:

Strong acid with strong base: The pH at equivalence point is usually neutral. Any indicator can be used.

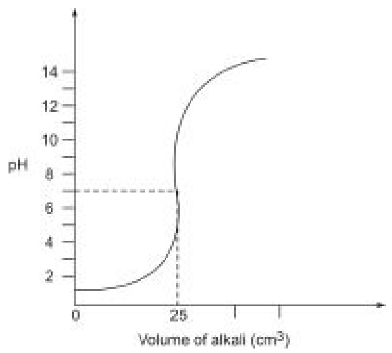


Figure 8.1 The pH curve for the titration of a strong acid with a strong base.

Strong acid with weak base: The pH at equivalence point is usually acidic. The suitable indicator is methyl orange.

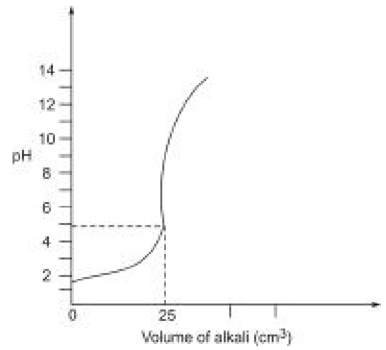


Figure 8.2 The pH curve for the titration of a strong acid with a weak base.

Weak acid with strong base: The pH at equivalence point is usually basic. The suitable indicator is phenolphthalein.

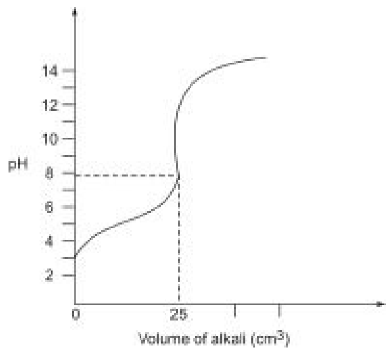


Figure 8.3 The pH curve for the titration of a weak acid with a strong base.

Weak acid with weak base: There is no suitable indicator.

The different numerical problems found in acid-base titration are illustrated below. It should be noted that similar calculations are encountered in acid-base and redox titrations.

8.1.1.1 Standardization and mole ratio

In acid-base titrations, the concentration of the analyte is determined from the volume of the titrant required to react with it, using the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$$

where C_A = The concentration of the acid.

C_B = The concentration of the base.

V_B = The reacting volume of the acid.

V_B = The reacting volume of the acid.

n_a = The number of moles of the acid needed to react with the base as given by the equation of reaction.

n_b = The number of moles of the base needed to react with the acid as given by the equation of reaction.

The above relation is based on the knowledge of the fact that the mole ratio of the reacting acid and base should be equal to that obtained from the stoichiometry of reaction. The relation is also applicable to redox titrations, in which the acid and base are replaced by oxidizing and reducing agents.

Example 1 0.15 M of sulphuric acid solution was titrated with 25.00 cm^3 of sodium hydroxide solution. The result is shown below:

Burrette reading	*1*	*2*	*3*	*4*
Final reading (cm^3)	50.00	28.50	50.00	29.10
Initial reading (cm^3)	28.50	8.50	29.90	8.90
Volume of acid used (cm^3)	21.50	20.00	20.10	20.20

Calculate the molar and mass concentrations of the base.

(H = 1.0, O = 16.0, Na = 23.0)

Solution The molarity or molar concentration of the base is calculated from the relation:

$$\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$$

The equation of reaction is

$$H_2SO_4(aq) + 2NaOH\ (aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

C_A = 0.15 M

The volume of acid used is the average of the three concordant values in the table, i.e.

$V_A = \frac{20.00\ \text{cm}^3 + 20.10\ \text{cm}^3 + 20.20\ \text{cm}^3}{3} = 20.10\ \text{cm}^3$

V_B = 25.00 cm^3

n_a = 1

n_b = 2

C_B = ?

Substituting we have

$$\frac{0.15\ \text{M} \times 20.10\ \cancel{\text{cm}^3}}{C_B \times 25.00\ \cancel{\text{cm}^3}} = \frac{1}{2}$$

Cross-multiplying we have

$C_B \times 25.00 = 6.0$ M

So $C_B = \frac{6.0\ \text{M}}{25.00}$

= 0.24 M

The mass concentration is obtained from the relation

$C = \frac{\rho}{M}$

$\therefore\ \rho = C \times M$

$M = (23.0 + 16.0 + 1.0)\ \text{g mol}^{-1} = 40.0\ \text{g mol}^{-1}$

$C = 0.24\ \text{mol dm}^{-3}$

ρ = ?

Substituting we have

$$\rho = 0.24\ \cancel{\text{mol}}\ \text{dm}^{-3} \times \frac{40.0\ \text{g}}{1\ \cancel{\text{mol}}}$$

$$= 9.6\ \text{g dm}^{-3}$$

Example 2 25.00 cm^3 of a 7.3-g dm^3 solution of sodium carbonate requires 30.50 cm^3 of a hydrochloric acid solution for complete reaction. Calculate the molar concentration of the acid solution.

(C = 12, O = 16, Na = 23)

Solution We have to apply the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$$

The equation of reaction is

$$2\text{HCl}(aq) + \text{Na}_2\text{CO}_3(aq) \rightarrow 2\text{NaCl}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(aq)$$

The molar concentration of the base is obtained from the relation

$$C = \frac{\rho}{M}$$

$M = [(23 \times 2) + 12 + (16 \times 3)]\ \text{g mol}^{-1} = 106\ \text{g mol}^{-1}$

$\rho = 7.3\ \text{g dm}^{-3}$

$C_B = ?$

Substituting we have

$$C_B = \frac{7.3\ \cancel{\text{g}} \times 1\ \text{mol}}{106\ \cancel{\text{g}} \times 1\ \text{dm}^3} = 0.069\ \text{M}$$

$V_a = 30.50\ \text{cm}^3$

$V_B = 25.00\ \text{cm}^3$

$n_a = 2$

$n_b = 1$

$C_A = ?$

Substituting we have

$$\frac{C_A \times 30.50\ \cancel{cm^3}}{0.069\ \text{M} \times 25.00\ \cancel{cm^3}} = \frac{2}{1}$$

Cross-multiplying we have

$C_A \times 30.50 = 3.5$ M

Then $C_A = \frac{3.5\ \text{M}}{30.50}$

$= 0.11$ M

Example 3 0.15 M of a mineral acid solution was titrated with a sodium carbonate solution containing 4.8 g of the alkali per dm^3 of solution. If 15.00 cm^3 is the acid just neutralized the salt, calculate the mole ratio of acid to base, and suggest what the acid could be.

(C = 12, O = 16, Na = 23)

Solution The amount of each substance is obtained from the relation

$$n = C \times V$$

For the acid we have

$C_A = 0.15$ mol dm^{-3}
$V_A = 15.00$ cm^3 = 0.015 dm^3
n_a = ?

Substituting we have

$$n_a = \frac{0.15\ \text{mol}}{\cancel{dm^3}} \times 0.015\ \cancel{dm^3}$$

$= 0.0023$ mol

The molar concentration of the base is obtained from the relation

$$C = \frac{\rho}{M}$$

$M = [(23 \times 2) + 12 + (16 \times 3)]$ g mol^{-1} = 106 g mol^{-1}
r = 4.8 g dm^{-3}
C_B = ?

Substituting we have

$$C_B = \frac{4.8\,\cancel{g} \times 1\,\text{mol}}{106\,\cancel{g} \times 1\,\text{dm}^3} = 0.045\ \text{mol dm}^{-3}$$

V_B = 25.00 cm^3 = 0.025 dm^3

n_b = ?

Substituting we have

$$n_b = \frac{0.045\,\text{mol}}{\cancel{\text{dm}^3}} \times 0.025\,\cancel{\text{dm}^3}$$

= 0.0011 mol

The mole ratio of acid to base is

$$\frac{n_a}{n_b} = \frac{0.0023\,\text{mol}}{0.0011\,\text{mol}} = \frac{2}{1}$$

Thus the mole ratio of acid to base is 2:1.

The acid is likely to be hydrochloric or nitric acid because monoprotic acids react with sodium carbonate in ratio 2:1.

$$2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

$$2HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2NaNO_3(aq) + H_2CO_3(aq) + CO_2(g)$$

Practice Problems

1. A nitric acid solution containing 9.80 g of the acid in 250.00 cm^3 of solutio titrated with 20.00 cm^3 of potassium hydroxide solution. If 14.00 cm^3 of th solution just neutralized the base, calculate the molar and mass concentratio the base.

   (H = 1, N = 14, O = 16, K 39) [*Answ* = 0.43 M, r = 24 g dm^{-3}]

2. A sulphuric acid solution was titrated with 25.00 cm^3 of 0.25-M soluti

sodium hydroxide. If 15.50 cm^3 of the acid just neutralized the base, calcula
molar and mass concentration of the acid.

(H = 1, O = 16, S
32)

[*Answer:* C_A = 0.20 M, r = 20 g dm^{-3}]

3. A is a solution of hydrochloric acid containing 0.63 g of the acid in 1000.0
of solution. B is 0.26-M alkali solution. If 30.00 cm^3 of A completely neutr
20.00 cm^3 of B, calculate the mole ratio of acid to base, and suggest what the
could be.

(H = 1.0, Cl
35.5)

[*Answer:* 1:1, NaOH or KOH]

8.1.1.2 Percentage purity

The percentage purity is calculated based on the knowledge that only the amount of the pure substance in the impure sample would take part in chemical reaction. Thus the concentration of the impure sample obtained from calculation is the concentration of the pure substance. The percentage purity or impurity can then be calculated as follows:

$$\text{Percentage purity} = \frac{\text{Mass of pure substance}}{\text{Mass of impure sample}} \times 100\%$$

$$\text{Percentage purity} = \frac{\text{Mass concentration of pure substance}}{\text{Mass concentration of impure sample}} \times 100\%$$

The percentage of impurity can also be obtained by subtracting the percentage purity from 100%, and vice versa, i.e.

Percentage purity = 100% − percentage of impurity
Percentage impurity = 100% − percentage of purity

Example 1 A is a solution containing 8.3 g dm^{-3} of impure ethanedioic acid. B is a 0.15-M sodium hydroxide solution. If 19.50 cm^3 of the acid just neutralizes 20.00 cm^3 of the base, calculate the percentage purity and impurity of the acid.

(H = 1.0, C = 12.0, O = 16.0)

Solution We must first obtain the molar concentration of the pure acid from the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$$

The equation of reaction is

$$H_2C_2O_4(aq) + 2NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$$

V_A = 19.50 cm^3
C_B = 0.15 M
V_B = 20.00 c
n_a = 1
n_b = 2
C_A = ?

Substituting we have

$$\frac{C_A \times 19.50\ \cancel{cm^3}}{0.15\ M \times 20.00\ \cancel{cm^3}} = \frac{1}{2}$$

Cross-multiplying we have

$C_A \times 39.00 = 3.0$ M

So $C_A = \frac{3.0\ M}{39.00} = 0.077$ M

Thus the molar concentration of the pure acid is 0.077 M. The mass concentration of the pure acid is obtained from the relation

$C = \frac{\rho}{M}$

$\therefore \rho = C \times M$
$M = [(1.0 \times 2) + (12.0 \times 2) + (16.0 \times 4)]\ g\ mol^{-1} = 90.0\ g\ mol^{-1}$
ρ = ?

Substituting we have

$\rho = 0.077\ \cancel{mol}\ dm^{-3} \times \frac{90.0\ g}{1\ \cancel{mol}}$

$= 6.9\ g\ dm^{-3}$

We can now determine the percentage purity of the acid from the relation

Percentage purity $= \frac{\text{Mass concentration of pure substance}}{\text{Mass concentration of impure sample}} \times 100\%$

Mass concentration of impure acid = 8.3 g dm^{-3}
Percentage purity = ?

Substituting we have

Percentage purity $= \frac{6.9\ \cancel{g}\ \cancel{dm^{-3}}}{8.3\ \cancel{g}\ \cancel{dm^{-3}}} \times 100\%$

= 83%

The percentage of impurity is obtained from the relation

Percentage impurity = 100% − % purity

Thus Percentage of impurity = 100% − 83%

= 17%

Alternatively, the percentage of impurity can be obtained from the relation

Percentage impurity $= \frac{\text{Mass concentration of impurity}}{\text{Mass concentration of the impure sample}}$

Mass concentration of impurity = 8.3 g dm^{-3} – 6.9 g dm^{-3} = 1.4 g dm^{-3}
Percentage of impurity = ?

Substituting we have

Percentage of impurity $= \frac{1.4\ \cancel{g}\ \cancel{dm^{-3}}}{8.3\ \cancel{g}\ \cancel{dm^{-3}}} \times 100\%$

= 17%

Example 2 A 25.00 cm^3 solution containing 6.9 g of impure anhydrous sodium carbonate was neutralized by 28.00 cm^3 of 0.10-M solution of sulphuric acid. Calculate the percentage purity of the salt.

(C = 12, O = 16, Na = 23)

Solution We have to obtain the molar concentration of the pure salt from the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$$

The equation of reaction is

$$H_2SO_4(aq) + Na_2CO_3(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(aq)$$

C_A = 0.10 M

V_A = 14.00 cm^3

V_B = 25.00 cm^3

n_a = 1

n_b = 1

C_B = ?

Substituting we have

$$\frac{0.10\ \text{M} \times 14.00\ \cancel{\text{cm}^3}}{C_B \times 25.00\ \cancel{\text{cm}^3}} = \frac{1}{1}$$

Cross-multiplying we have

$C_B \times 25.00$ = 1.4 M

$$C_B = \frac{1.4\ \text{M}}{25.00}$$

= 0.056 M

We can now determine the mass concentration of the pure base from the relation

$$C = \frac{\rho}{M}$$

$\therefore\ \rho = C \times M$

$M = [(23 \times 2) + 12 + (16 \times 3)]\ \text{g mol}^{-1} = 106\ \text{g mol}^{-1}$

ρ = ?

Substituting we have

$$\rho = 0.056\ \cancel{\text{mol}}\ \text{dm}^{-1} \times \frac{106\ \text{g}}{1\ \cancel{\text{mol}}}$$

= 5.9 g dm^{-3}

This is the mass of the pure base in 1000.00 cm^3 of solution. The percentage purity can now be determined from the relation

$$\text{Percentage purity} = \frac{\text{Mass concentration of pure substance}}{\text{Mass concentration of impure sample}} \times 100\%$$

Mass concentration of impure salt = 6.9 g dm^{-3}
Percentage purity = ?

Substituting we have

$$\text{Percentage purity} = \frac{5.9\ \cancel{g}\ \cancel{dm^{-3}}}{6.9\ \cancel{g}\ \cancel{dm^{-3}}} \times 100\%$$

$= 86\%$

Practice Problems

1. A 10.5-g dm^{-3} solution of impure ethanedioic acid was titrated with 0.20-M potassium hydroxide solution. If 44.00 cm^3 of the acid just neutralized 20.00 cm^3 of the base, calculate the percentage purity of the acid.
   (H = 1, C = 12, O = 16)
   [*Answer:* 77%]
2. 24.00 cm^3 of a 0.20-M solution of hydrochloric acid neutralizes 20.00 cm^3 of a solution containing 5.9 g of impure sodium carbonate per 250.00 cm^3 of solution. Calculate the percentage of impurity in the base.
   (H = 1, O = 16, Na = 23)
   [*Answer:* 46%]

8.1.1.3 Molar masses

The following examples illustrate how the molar masses of substances can be obtained from acid-base titration.

Example 1 22.50 cm^3 of 0.055-M solution of sulphuric acid completely neutralizes 25.00 cm^3 of a solution containing 5.6 g of an unknown base, XOH, per dm^3 of solution. Calculate the molar mass of the base. Hence determine the relative atomic mass of the element X.

(H = 1, O = 16)

Solution The very first step is to obtain the molarity of the base from the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$$

The equation of reaction is

$$H_2SO_4(aq) + 2XOH(aq) \rightarrow X_2SO_4(aq) + 2H_2O(1)$$

C_A = 0.055 M
V_A = 22.50 cm^3
V_B = 25.00 cm^3
n_a = 1
n_b = 2
C_B = ?

Substituting we have

$$\frac{0.055\ \mathrm{M} \times 22.50\ \cancel{\mathrm{cm^3}}}{C_B \times 25.00\ \cancel{\mathrm{cm^3}}} = \frac{1}{2}$$

Cross-multiplying we have

$C_B \times 25.00$ = 2.5 M

Thus $C_B = \frac{2.5\ \mathrm{M}}{25.00}$

= 0.10 M

The molar mass of the base is obtained from the relation

$C = \frac{\rho}{M}$

$\therefore\ M = \frac{\rho}{C}$

r = 5.6 g dm^{-3}
M = ?

Substituting we have

$M = \frac{5.6\ \mathrm{g}\ \cancel{\mathrm{dm^{-3}}}}{0.10\ \mathrm{mol}\ \cancel{\mathrm{dm^{-3}}}}$

= 56 g mol^{-1}

Thus the molar mass of the base is 56 g mol^{-1}. The relative atomic mass of X is obtained by equating the sum of the relative atomic masses of the constituent elements of the base to its relative molecular mass, i.e.

$X + 16 + 1 = 56$

So $X = 56 - 17$

$= 39$

This is the relative atomic mass of potassium; hence the base is potassium hydroxide, KOH.

Example 2 12.50 cm^3 of an uknown diprotic acid, H_2X, containing 14.7 g of the acid per dm^3 of solution completely neutralizes 25.00 cm^3 of a 0.15-M solution of sodium hydroxide. What is the molar mass of the acid?

Solution The very first step is to obtain the molarity of the acid from the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$$

The equation of reaction is

$$H_2X(aq) + 2NaOH(aq) \rightarrow Na_2X(aq) + 2H_2O(1)$$

$C_B = 0.15$ M

$V_A = 12.50$ cm^3

$V_B = 25.00$ cm^3

$n_a = 1$

$n_b = 2$

$C_A = ?$

Substituting we have

$$\frac{C_A \times 12.50 \cancel{cm^3}}{0.15 \text{ cm}^3 \times 25.00 \cancel{cm^3}} = \frac{1}{2}$$

Cross-multiplying we have

$C_A \times 25.00 = 3.8$ M

So $C_A = \frac{3.8 \text{ M}}{25.00}$

$= 0.15$ M

The molar mass of the acid is obtained from the relation

$$C = \frac{\rho}{M}$$

$$\therefore\ M = \frac{\rho}{C}$$

$\rho = 14.7\ \text{g dm}^{-3}$
$M = ?$

Substituting we have

$$M = \frac{14.7\ \text{g}\ \cancel{\text{dm}^{-3}}}{0.15\ \text{mol}\ \cancel{\text{dm}^{-3}}}$$

$= 98\ \text{g mol}^{-1}$

This is the molar mass of sulphuric acid, H_2SO_4.

Practice Problems

1. A is a solution of unknown monoprotic acid, HX, containing 7.3 g of the acid per dm^3 of solution. B is a 0.15-M sodium hydroxide solution. If 15.00 cm^3 of solution A neutralizes 20.00 cm^3 of solution B, determine:

(a) the molar mass of the acid;
(b) the relative atomic mass of the element X, and identify the acid.

(H = 1) [*Answers:* (a) 36.5 g mol^{-1} (b) 35.5, HCl]

2. 18.75 cm^3 of 0.20-M sulphuric acid solution neutralizes 25.00 cm^3 of the solution of an unknown base, XOH, containing 12.0 g of the base per dm^3 of solution. Determine:

(a) the molar mass of the base;
(b) the relative atomic mass of the element X, hence identify the base.

(H = 1, O = 16) [*Answers:* (a) 40 g mol^{-1} (b) 23, NaOH]

8.1.1.4 Number of molecules of water of crystallization

The mass of water of crystallization of a hydrated salt used acid-base titration is calculated based on the knowledge that the water of crystallization does not take part in reaction. The number of molecules of water of crystallization can be obtained from the following relations:

$$M = \frac{\rho}{C}$$

where M = Molar mass of hydrated salt.
ρ = Mass concentration of hydrated salt.
C = Molar concentration of the salt.

Alternatively, we can use the relation

$$\frac{\text{Mass concentration of anhydrous salt}}{\text{Molar mass of anhydrous salt}} = \frac{\text{Mass concentration of anhydrous salt}}{\text{Molar mass of anhydrous salt}}$$

Example 1 25.00 cm^3 of a solution containing 5.36 g of hydrated sodium carbonate, $Na_2CO_3.xH_2O$, in 250.00 cm^3 of solution was neutralized by 25.00 cm^3 of 0.075-M sulphuric acid solution. Determine:

(a) the number of molecules of water of crystallization in the hydrated salt;
(b) the percentage composition of water of crystallization.

(H = 1, C = 12, O = 16, Na = 23)

Solution

(a) The number of molecules of water of crystallization can be obtained from the relation

$$M = \frac{\rho}{C}$$

The molar concentration of the salt is obtained from the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$$

The equation of reaction is

$$H_2SO_4(aq) + Na_2CO_3(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$$

C_A = 0.075 M
V_A = 25.00 cm^3
V_B = 25.00 cm^3
n_a = 1

$n_b = 1$
$C_B = ?$

Substituting we have

$$\frac{0.075\ \text{M} \times 25.00\ \cancel{\text{cm}^3}}{C_B \times 25.00\ \cancel{\text{cm}^3}} = \frac{1}{1}$$

Cross-multiplying we obtain

$$C_B = 0.075\ \text{M}$$

The mass concentration of the hydrated salt is obtained from the relation

$\rho = \frac{m}{V}$

$m = 5.36\ \text{g}$
$V = 250.00\ \text{cm}^3 = 0.25\ \text{dm}^3$
$\rho = ?$

Substituting we have

$\rho = \frac{5.36\ \text{g}}{0.25\ \text{dm}^3} = 21.44\ \text{g dm}^{-3}$

$M = [(23 \times 2) + 12 + (16 \times 3) + x\,(16 + 2)]\ \text{g mol}^{-1} = (106 + 18x)\ \text{g mol}^{-1}$
$C = 0.075\ \text{mol dm}^{-3}$
$x = ?$

Substituting we have

$$(106 + 18x)\ \text{g mol}^{-1} = \frac{21\ \text{g}\ \cancel{\text{dm}^{-3}}}{0.075\ \text{mol}\ \cancel{\text{dm}^{-3}}}$$

Cross-multiplying we have

$0.075\ \cancel{\text{mol}} \times \frac{(106 + 18x)}{1\ \cancel{\text{mol}}} = 21.44\ \text{g}$

Thus $7.95\ \text{g} + 1.35x\ \text{g} = 21.44\ \text{g}$

Then 1.35x g = 21.44 g – 7.95 g = 13.49 g

So $x = \frac{13.49\,\cancel{g}}{1.35\,\cancel{g}}$

$= 10$

We can as well use the mass of the hydrated salt in the 250.00 cm^3 of solution, using the relation

$n = \frac{m}{M}$

$\therefore\ M = \frac{m}{n}$

$M = (106 + 18x)$ g mol^{-1}
$n = 0.019$ mol
$m = 5.36$ g
$x = ?$

Substituting we have

$$(106 + 18x)\ \text{g mol}^{-1} = \frac{5.36\ g}{0.019\ \text{mol}}$$

Cross-multiplying we have

$$0.19\,\cancel{\text{mol}} \times \frac{(106 \times 18x)}{1\,\cancel{\text{mol}}} = 5.36\ \text{g}$$

Then 2.01 g + 0.34x g = 5.36 g
Thus 0.34x g = 5.36 g – 2.01 g = 3.35 g

So $x = \frac{3.35\,\cancel{g}}{0.34\,\cancel{g}}$

$= 10$

Alternatively, we can apply the relation

$$\frac{\text{Mass concentration of hydrated salt}}{\text{Molar mass of hydrated salt}} = \frac{\text{Mass concentration of anhydrous salt}}{\text{Molar mass of anhydrous salt}}$$

The mass concentration of the anhydrous salt is obtained from the relation

$C = \frac{\rho}{M}$

$\therefore\ \rho = C \times M$

$M = [(23 \times 2) + 12 + (16 \times 3)]\ \mathrm{g\ mol^{-1}} = 106\ \mathrm{g\ mol^{-1}}$

$\rho = ?$

Substituting we have

$$r = 0.075\ \cancel{\mathrm{mol}}\ \mathrm{dm^{-3}} \times \frac{106\ \mathrm{g}}{1\ \cancel{\mathrm{mol}}} = 7.95\ \mathrm{g\ dm^{-3}}$$

Substituting into the above relation we have

$$\frac{21.44\ \mathrm{g\ dm^{-3}}}{[106 + 18x]\ \mathrm{g\ mol^{-1}}} = \frac{7.95\ \mathrm{g\ dm^{-3}}}{106\ \mathrm{g\ mol^{-1}}}$$

Cross-multiplying we have

$21.44\ \mathrm{g\ dm^{-3}} \times 106\ \mathrm{g\ mol^{-1}} = 7.95\ \mathrm{g\ dm^{-3}} \times (106 + 18x)\ \mathrm{g\ mol^{-1}}$

So $2272.64\ \mathrm{g^{2}\ dm^{-3}\ mol^{-1}} = 842.6\ \mathrm{g^{2}\ dm^{-3}\ mol^{-1}} + 143.1x\ \mathrm{g^{2}\ dm^{-3}\ mol^{-1}}$

Collecting like terms we have

$143.1x\ \mathrm{g^{2}\ dm^{-3}\ mol^{-1}} = 2272.64\ \mathrm{g^{2}\ dm^{-3}\ mol^{-1}} - 842.6\ \mathrm{g^{2}\ dm^{-3}\ mol^{-1}}$

$= 1430.04\ \mathrm{g^{2}\ dm^{-3}\ mol^{-1}}$

Thus $x = \frac{1430.04\ \cancel{\mathrm{g^{2}}}\ \cancel{\mathrm{dm^{-3}}}\ \cancel{\mathrm{mol^{-1}}}}{143.1\ \cancel{\mathrm{g^{2}}}\ \cancel{\mathrm{dm^{-3}}}\ \cancel{\mathrm{mol^{-1}}}}$

$= 10$

Thus the formula of the hydrated salt is $Na_2CO_3.10H_2O$.

(b) The percentage composition of water of crystallization is obtained from the relation

Percentage composition of water $= \frac{\text{Mass concentration of water}}{\text{Mass concentration of hydrated salt}} \times 100\%$

Mass of concentration water = Mass concentration of hydrated salt
– Mass concentration of anhydrous salt

So Mass concentration of water $= 21.44\ \mathrm{g\ dm^{-3}} - 7.95\ \mathrm{g\ dm^{-3}} = 13.49\ \mathrm{g\ dm^{-3}}$

Percentage composition of water = ?

Substituting we have

Percentage composition of water = $\frac{13.49\,\cancel{g}\,\cancel{dm^{-3}}}{21.44\,\cancel{g}\,\cancel{dm^{-3}}}$ × 100%

= 63%

Alternatively, we can use the masses of anhydrous and hydrated base in the 250.00 cm^3 of solution. In this case

Percentage composition of water = $\frac{\text{Mass of water of crystallization}}{\text{Mass of hydrated salt}}$ × 100%

Mass of water = Mass of hydrated base − Mass of anhydrous base
Mass of hydrated base = 5.36 g

The mass of the anhydrous base is obtained from the relation

$n = \frac{m}{M}$

$\therefore\ m = n \times M$

The amount of the anhydrous base is obtained from the relation

$n = C \times V$
$C = 0.075$ mol dm^{-3}
$V = 250.00$ cm^3 = 0.25 dm^3
$n = ?$

Substituting we have

$n = \frac{0.075\text{ mol}}{1\,\cancel{dm^{3}}} \times 0.25\,\cancel{dm^{3}} = 0.019\text{ mol}$

$M = 106$ g mol^{-1}
$m = ?$

Thus $m = 0.019\,\cancel{mol} \times \frac{106\text{ g}}{1\,\cancel{mol}} = 2.0\text{ g}$

So Mass of water of crystallization = 5.36 g – 2.0 g = 3.4 g

Percentage composition of water $= \frac{3.4\ \cancel{g}}{5.36\ \cancel{g}} \times 100\%$

= 63%

We can as well apply the relation

Percentage composition of water $= \frac{\text{Mass of water of crystallization in 1 mol of hydrated salt}}{\text{Molar mass of hydrated salt}}$

× 100%

Since there are 10 molecules of water of crystallization in 1 mol of the hydrated salt, then

Mass of water in 1 mol of hydrated salt = 10 × 18 g mol^{-1} = 180 g mol^{-1}

Molar mass of hydrated salt = (106 + 180) g mol^{-1} = 286 g mol^{-1}

Substituting we have

Percentage composition of water $= \frac{180\ \cancel{g}\ \cancel{mol^{-1}}}{286\ \cancel{g}\ \cancel{mol^{-1}}}$

= 63%

Example 2 A is 0.066-M solution of sulphuric acid. B is a 0.025-M solution of sodium carbonate containing 3.10 g of the hydrated salt per dm^3 of solution. If 18.90 cm^3 of A neutralizes 25.00 cm^3 of B, determine

(a) the number of molecules of water of crystallization in the hydrated salt;

(b) the percentage composition of water crystallization in the hydrated salt.

(H = 1, C = 12, O = 16, Na = 23)

Solution

(b) As usual, we can apply the relation

$M = \frac{\rho}{c}$

$M = (106 + 18x)\ \text{g mol}^{-1}$

$C = 0.025\ \text{mol dm}^{-3}$
$\rho = 3.10\ \text{g dm}^{-3}$
$x = ?$

Substituting we have

$$(106 + 18x)\ \text{g mol}^{-1} = \frac{3.1\ \text{g dm}^{-3}}{0.025\ \text{mol dm}^{-3}}$$

Cross-multiplying we have

$$0.25\ \cancel{\text{mol}}\ \text{dm}^{-3} \times \frac{(106 + 18x)\ \text{g}}{1\ \cancel{\text{mol}}} = 3.1\ \text{g dm}^{-3}$$

So $2.65\ \text{g dm}^{-3} + 0.45x\ \text{g dm}^{-3} = 3.1\ \text{g dm}^{-3}$
Then $0.45x\ \text{g dm}^{-3} = 3.10\ \text{g dm}^{-3} – 2.65\ \text{g dm}^{-3} = 0.45\ \text{g dm}^{-3}$

Thus $x = \frac{0.45\ \cancel{\text{g}}\ \cancel{\text{dm}^{-3}}}{0.45\ \cancel{\text{g}}\ \cancel{\text{dm}^{-3}}}$

$= 1$

Alternatively, we can apply the relation

$$\frac{\text{Mass concentration of hydrated salt}}{\text{Molar mass of hydrated salt}} = \frac{\text{Mass concentration of anhydrous salt}}{\text{Molar mass of anhydrous salt}}$$

The mass concentration of the anhydrous salt is obtained from the relation

$C = \frac{\rho}{M}$

$\therefore\ \rho = C \times M$
$C = 0.025\ \text{M}$
$M = [(23 \times 2) + 12 + (16 \times 3)]\ \text{g mol}^{-1} = 106\ \text{g mol}^{-1}$
$\rho = ?$

Substituting we have

$\rho = 0.025\ \cancel{\text{mol}}\ \text{dm}^{-3} \times \frac{160\ \text{g}}{1\ \cancel{\text{mol}}} = 2.65\ \text{g dm}^{-3}$

Molar mass of the hydrated salt $= (106 + 18x)\ \text{g mol}^{-1}$

We now substitute to obtain

$$\frac{3.10\ \text{g dm}^{-3}}{[106 + 18x]\ \text{g mol}^{-1}} = \frac{2.65\ \text{g dm}^{-3}}{106\ \text{g mol}^{-1}}$$

Cross-multiplying we have

$3.10\ \text{g dm}^{-3} \times 106\ \text{g mol}^{-1} = 2.65\ \text{g dm}^{-3} \times (106 + 18x)\ \text{g mol}^{-1}$

Then $328.6\ \text{g}^2\text{dm}^{-3}\text{mol}^{-1} = 280.9\ \text{g}^2\text{dm}^{-3}\text{mol}^{-1} + 47.7x\ \text{g}^2\text{dm}^{-3}\text{mol}^{-1}$

Collecting like terms we have

$47.7x\ \text{g}^2\text{dm}^{-3}\text{mol}^{-1} = 328.6\ \text{g}^2\text{dm}^{-3}\text{mol}^{-1} - 280.9\ \text{g}^2\text{dm}^{-3}\text{mol}^{-1} = 47.7\ \text{g}^2\text{dm}^{-3}\text{mol}^{-1}$

Thus $x = \frac{47.7\ \cancel{\text{g}^2}\ \cancel{\text{dm}^{-3}}\ \cancel{\text{mol}^{-1}}}{47.7\ \cancel{\text{g}^2}\ \cancel{\text{dm}^{-3}}\ \cancel{\text{mol}^{-1}}}$

$= 1$

Thus the formula of the hydrated salt is $Na_2CO_3.H_2O$.

(b) As usual, we can apply the relation

Percentage composition of water $= \frac{\text{Mass concentration of water of crystallization}}{\text{Mass concentration of hydrated salt}} \times 100\%$

Mass concentration of water = mass concentration of hydrated salt − mass concentration of anhydrous salt

Mass concentration of water $= 3.10\ \text{g dm}^{-3} - 2.65\ \text{g dm}^{-3} = 0.45\ \text{g dm}^{-3}$

We now substitute into the original equation to obtain

Percentage composition of water $= \frac{0.45\ \cancel{\text{g}}\ \cancel{\text{dm}^{-3}}}{3.10\ \cancel{\text{g}}\ \cancel{\text{dm}^{-3}}} \times 100\%$

$= 15\%$

Alternatively, we can apply the relation

Percentage composition of water = $\frac{\text{Mass of water of crystallization in 1 mol of hydrated salt}}{\text{Molar mass of hydrated salt}}$

Since there is 1 molecule of water of crystallization in 1 mol of the hydrated salt, then

Mass of water in 1 mol of hydrated salt = 18 g mol^{-1} = 18 g mol^{-1}

Molar mass of hydrated salt = (106 + 18) g mol^{-1} = 124 g mol^{-1}

Substituting we have

Percentage composition of water = $\frac{18\,\cancel{\text{g mol}^{-1}}}{124\,\cancel{\text{g mol}^{-1}}} \times 100\%$

= 15%

Practice Problems

1. A quantity of hydrated sodium carbonate was exposed to the atmosphere, after which it was dissolved in 300.00 cm^3 of distilled water. If 25.00 cm^3 of the solution reacts completely with 25.00 cm^3 of 0.10-M hydrochloric acid solution, determine the number of molecules of water crystallization in the salt, given that the solution contains 8.3 g of the hydrated salt.

   (H = 1, C = 12, O = 16, Na = 23) [*Answer:* 3]

2. 18.00 cm^3 of 0.010-M solution of sulphuric acid reacts completely with 20.00 cm^3 of 0.010-M sodium carbonate solution. If 2.5 g of the hydrated salt is present per dm^3 of solution, calculate:

(a) the mass concentration of the anhydrous salt;
(b) the percentage by mass of water of crystallization in the hydrated salt.

(H = 1, C = 12, O = 16, Na = 23) [*Answers:* (a) 1.1 g dm^{-1} (b) 58%]

8.1.1.5 Solubility of bases

The solubility of bases is calculated from the molar concentration of the base. Once the molar concentration is known, the solubility can be calculated from the first principle or dilution.

Example 1 20.50 cm^3 of 0.15-M hydrochloric acid solution neutralizes 25.00 cm^3 of a saturated solution of sodium hydroxide prepared at 25°C. Determine the molar and mass solubilities of the base at this temperature.

(H = 1, O = 16, Na = 23)

Solution We must start by calculating the molarity of the base from the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$$

The equation of reaction is

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

$C_A = 0.15$ M
$V_A = 20.50$ cm^3
$V_B = 25.00$ cm^3
$n_a = 1$
$n_b = 1$
$C_B = ?$

Substituting we have

$$\frac{0.15\ \mathrm{M} \times 20.50\ \cancel{\mathrm{cm^3}}}{C_B \times 25.00\ \cancel{\mathrm{cm^3}}} = \frac{1}{1}$$

Cross-multiplying we have

$C_B \times 20.50 = 3.08$ M

Then $C_B = \frac{3.08\ \mathrm{M}}{20.50}$

$= 0.15$ M

Since the solution is already saturated, then the solubility of the base at 25°C is equal to its molar concentration, i.e., 0.15 M.

The mass solubility is the mass concentration, which is obtained from the relation

$C = \frac{\rho}{M}$

$\therefore\ \rho = C \times M$
$M = (1 + 16 + 23)$ g mol^{-1} = 40 g mol^{-1}
$\rho = ?$

Substituting we have

$\rho = 0.15\,\cancel{\text{mol}}\ \text{dm}^{-3} \times \frac{40\ \text{g}}{1\,\cancel{\text{mol}}}$

$= 6\ \text{g dm}^{-3}$

Example 2 A sodium carbonate solution was prepared by making up 20.00 cm^3 of its saturated solution to 1000.00 cm^3 at 25°C. If 12.50 cm^3 of 0.25-M sulphuric acid completely neutralizes 25.00 cm^3 of the salt solution, calculate the molar and mass solubilities of the salt at 25°C.

(C = 12, O = 16, Na = 23)

Solution We begin by calculating the molar concentration of the base from the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$$

The equation of reaction is

$$Na_2CO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$$

$C_B = 0.25$ M

$V_A = 12.50$ cm^3

$V_B = 25.00$ cm^3

$n_a = 1$

$n_b = 1$

$C_B = ?$

Substituting we have

$$\frac{0.25\ \text{M} \times 12.50\ \cancel{\text{cm}^3}}{C_B \times 25.00\ \cancel{\text{cm}^3}} = \frac{1}{1}$$

Cross-multiplying we obtain

$C_B \times 25.00 = 3.13$ M

Then $C_B = \frac{3.13\ \text{M}}{25.00}$

$= 0.12$ M

This molar concentration should not be taken as the molar solubility of the base because the solution is not saturated. The molar concentration implies that

20.00 cm^3 of the solvent can dissolve 0.12 mol of the base at 25°C. Since solubility is normally reported per dm^3 of solution, then we need to find the maximum amount of the base that can be present in 1.0 dm^3 of the solution at the same temperature. Working from the first principle we have

$0.020\ dm^3 = 0.12\ mol$

$1.0\ dm^3 = x$

Thus $0.12\ mol \times 1.0\ dm^3 = 0.020\ dm^3 \times x$

Thus $x = \frac{0.12\ mol \times 1.0\ \cancel{dm^3}}{0.020\ \cancel{dm^3}}$

$= 6.0\ mol$

Since the maximum amount of the base that can be present in 1.0 dm^3 of the solution is 6.0 mol at 25°C, then the molar solubility of the base at the temperature is 6.0 M.

Alternatively, we can apply the dilution principle,

$C_1V_1 = C_2V_2$

$V_1 = 20.00\ cm^3 = 0.020\ dm^3$

$V_2 = 1000.00\ cm^3 = 1.0\ dm^3$

$C_2 = 0.12\ M$

$C_1 = ?$

Substituting we have

$C_1 \times 0.020\ dm^3 = 0.12\ M \times 1.0\ dm^3$

So $C_1 = \frac{0.12\ mol \times 1.0\ \cancel{dm^3}}{0.020\ \cancel{dm^3}}$

$= 6.0\ M$

The mass concentration is obtained from the relation

$C = \frac{\rho}{M}$

$\therefore\ \rho = C \times M$

$M = [(23 \times 2) + 12 + (16 \times 3)]\ g\ mol^{-1} = 106\ g\ mol^{-1}$

$\rho = ?$

Substituting we have

$$\rho = 6.0\,\cancel{\text{mol}}\ \text{dm}^{-3} \times \frac{106\ \text{g}}{1\,\cancel{\text{mol}}}$$

$= 640\ \text{g dm}^{-3}$

Practice Problems

1. 22.85 cm^3 of a 0.20-M hydrochloric acid solution neutralizes 20.00 cm^3 of a saturated solution of sodium hydroxide prepared at 25°C. Determine the molar solubility of the base at the specified temperature.
   (H = 1, O = 16, Na = 23) [*Answer:* 0.23 M]
2. A potassium hydroxide was prepared by making up 30.00 cm^3 of its saturated solution to 1000.00 cm^3 at 25°C. Calculate the mass solubility of the salt at 25°C, given that 28.50 cm^3 of 0.080-M sulphuric acid solution neutralizes 25.00 cm^3 of the base solution.
   (H = 1, O = 16, K = 39)
   [*Answer:* 340 g dm^{-3}]

8.1.1.6 The volume of gas evolved

Carbon dioxide is evolved when carbonates or hydrogencarbonates are treated with acids. The following examples illustrate the calculations involving the volumes of gases evolved during titration.

Example 1 25.50 cm^3 of 0.25-M nitric acid solution reacts completely with 20.00 cm^3 of sodium carbonate. Calculate the volume of carbon dioxide liberated at STP.

(Molar volume of a gases at STP = 22.4 $\text{dm}^3\ \text{mol}^{-1}$)

Solution The first step is to obtain the molarity of the base from the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$$

The equation of reaction is

$$Na_2CO_3(aq) + 2HNO_3(aq) \rightarrow 2NaNO_3(aq) + H_2O(l) + CO_2(g)$$

$C_A = 0.25$ M
$V_A = 25.50$ cm^3
$V_B = 20.00$ cm^3
$n_a = 2$
$n_b = 1$
$C_B = ?$

Substituting we have

$$\frac{0.25\ \text{M} \times 25.50\ \cancel{\text{cm}^3}}{C_B \times 20.00\ \cancel{\text{cm}^3}} = \frac{2}{1}$$

So $C_B \times 40.00 = 6.38$ M

Then $C_B = \frac{6.38\ \text{M}}{40.00}$

$= 0.16$ M

We now calculate the amount of the base from the relation

$n = C \times V$
$V = 20.00$ cm^3 $= 0.020$ dm^3
$n = ?$

Substituting we have

$$n = \frac{0.16\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 0.020\ \cancel{\text{dm}^3}$$

$= 0.0032$ mol

From the equation, 1 mol of the salt liberates 1 mol of carbon dioxide, then 0.0032 mol of the salt would also liberate 0.0032 mol of the gas. We know that the amount of a gas at STP is given by the relation

$$n = \frac{V}{22.4\ \text{dm}^3\ \text{mol}^{-1}}$$

$\therefore\ V = n \times 22.4$ dm^3 mol^{-1}
$V = ?$

Substituting we have

$V = 0.0032\,\cancel{\text{mol}} \times \dfrac{22.4\ \text{dm}^3}{1\,\cancel{\text{mol}}}$

$= 0.072\ \text{dm}^3$

Alternatively, we can obtain the volume from the first principle:

1.0 mol of carbon dioxide occupies a volume of 22.4 dm^3 at STP, then 0.0032 mol of the gas would occupy x at STP, i.e.

1.0 mol = 22.4 dm^3

0.0032 mol = x

Then $x \times 1.0$ mol = 22.4 $\text{dm}^3 \times 0.0032$ mol

So $x = \dfrac{22.4\ \text{dm}^3 \times 0.0032\,\cancel{\text{mol}}}{1.0\,\cancel{\text{mol}}}$

$= 0.072\ \text{dm}^3$

Example 2 30.00 cm^3 of 0.10-M sulphuric acid solution reacts completely with 25.00 cm^3 of anhydrous sodium carbonate. Calculate the volume of carbon dioxide liberated by the salt at STP.

(Molar volume of a gas at STP = 22.4 $\text{dm}^3\ \text{mol}^{-1}$)

Solution As usual, we have to begin by calculating the molarity of the base from the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$$

The equation of reaction is

$$H_2SO_4(aq) + Na_2CO_3(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(aq)$$

C_A = 0.10 M

V_A = 30.00 cm^3

V_B = 25.00 cm^3

n_a = 1

n_b = 1

C_B = ?

Substituting we have

$$\frac{0.10\ \text{M} \times 30.00\,\cancel{\text{cm}^3}}{C_B \times 25.00\,\cancel{\text{cm}^3}} = \frac{1}{1}$$

Cross-multiplying we have

$C_B \times 25.00\ \text{cm}^3 = 3.0\ \text{M}$

So $C_B = \frac{3.0\ \text{M}}{25.00}$

$= 0.12\ \text{M}$

The amount of the salt can now be obtained from the relation

$n = C \times V$

$V = 25.00\ \text{cm}^3 = 0.025\ \text{dm}^3$

$n = ?$

Substituting we have

$n = \frac{0.12\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 0.025\ \cancel{\text{dm}^3}$

$= 0.0030\ \text{mol}$

Finally, we can now obtain the volume of the gas from the relation

$n = \frac{V}{22.4\ \text{dm}^3\ \text{mol}^{-1}}$

$\therefore\ V = n \times 22.4\ \text{dm}^3\ \text{mol}^{-1}$

$V = ?$

We now substitute to obtain

$V = 0.0030\ \cancel{\text{mol}} \times \frac{22.4\ \text{dm}^3}{1\ \cancel{\text{mol}}}$

$= 0.067\ \text{dm}^3$

Alternatively, 1.0 mol of carbon dioxide occupies a volume of 22.4 dm^3 at STP, then 0.0030 mol of the gas would occupy x at STP, i.e.

1.0 mol $= 22.4\ \text{dm}^3$

0.0030 mol $= x$

Thus $x \times 1.0\ \text{mol} = 0.0030\ \text{mol} \times 22.4\ \text{dm}^3$

So $x = \frac{0.0030\ \cancel{\text{mol}} \times 22.4\ \text{dm}^3}{1\ \cancel{\text{mol}}}$

= 0.067 dm^3

Practice Problem

25.00 cm^3 of 0.15-M hydrochloric acid solution reacts completely with cm^3 of anhydrous sodium carbonate. Calculate the volume of carbon liberated at STP.

(Molar volume of gases at STP dm^3)

[*Answer:* 0.042 dm^3]

8.1.1.7 The mass of the salt and number of ions produced

The mass of a salt, or the number of ions produced by a substance, can be obtained by first calculating the amount of the substance present in the reacting mixture. Once this is done, we can proceed to work out the required mass from stoichiometry.

Example 1 28.00 cm^3 of a hydrochloric acid solution neutralizes 20.00 cm^3 of 0.25-M sodium hydroxide solution. Calculate

(a) the number of aqueous hydrogen ions per dm^3 of the acid solution;

(b) the mass of the salt that would be produced from 500.00 cm^3 of the base.

(H = 1.0, Na = 23.0, Cl = 35.5, $N_A = 6.02 \times 10^{23}$ mol^{-1})

Solution

(a) The first step is to obtain the molarity of the acid from the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_a}{n_b}$$

The equation of reaction is

$$HCl(aq) + 2NaOH(aq) \rightarrow NaCl(aq) + 2H_2O(l)$$

V_A = 28.00 cm^3

C_B = 0.25 M

V_B = 20.00 cm^3

n_a = 1

n_b = 2

C_A = ?

Substituting we have

$$\frac{C_A \times 28.00\ \cancel{\text{cm}^3}}{0.25\ \text{M} \times 20.00\ \cancel{\text{cm}^3}} = \frac{1}{2}$$

Cross-multiplying we obtain

$C_A \times 56.00 = 5.0$ M

So $C_A = \frac{5.0\ \text{M}}{56.00}$

$= 0.089$ M

This means that 1.0 dm^3 of the acid solution contains 0.18 mol of the acid. The acid dissociates as follows:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

According to the equation, 1 mol of the acid produces 1 mol of H^+, then 0.18 mol of the acid would also produce 0.18 mol of H^+. Now we know that

$$n = \frac{N}{6.02 \times 10^{23}\ \text{mol}^{-1}}$$

$\therefore N = n \times 6.02 \times 10^{23}\ \text{mol}^{-1}$

Substituting we have

$$N = 0.18\ \cancel{\text{mol}} \times \frac{6.02 \times 10^{23}}{1\ \cancel{\text{mol}}}$$

$= 1.1 \times 10^{23}$

Alternatively, from the first principle we have
1 mol of H^+ contains 6.02×10^{23} H^+, then 0.18 mol would contain N, i.e.

1 mol $= 6.02 \times 10^{23}$

0.18 mol $= N$

Then $N \times 1$ mol $= 1.1 \times 10^{23}$ mol

So $N = \frac{1.1 \times 10^{23} \cancel{\text{mol}}}{1 \cancel{\text{mol}}}$

$= 1.1 \times 10^{23}$

(b) The salt produced is sodium chloride, NaCl. To obtain the mass of the salt we must first obtain the amount of the base from the relation

$n = C \times V$

$C = 0.25 \text{ mol dm}^{-3}$

$V = 500.00 \text{ cm}^3 = 0.50 \text{ dm}^3$

$n = ?$

Substituting we have

$n = \frac{0.25 \text{ mol}}{1 \cancel{\text{dm}^3}} \times 0.50 \cancel{\text{dm}^3}$

$= 0.13 \text{ mol}$

According to the equation, 1 mole of sodium hydroxide produces 1 mol of sodium chloride, then 0.13 mol of the base would also produce 0.13 mol of the salt. The mass of the salt is determined from the relation

$n = \frac{m}{M}$

$\therefore\ m = n \times M$

$M = (23.0 + 35.5) \text{ g mol}^{-1} = 58.5 \text{ g mol}^{-1}$

$m = ?$

Substituting we have

$m = 0.13 \cancel{\text{mol}} \times \frac{58.5 \text{ g}}{1 \cancel{\text{mol}}}$

$= 7.6 \text{ g}$

Example 2 22.89 cm^3 of 0.15-M hydrochloric acid completely reacts with 25.00 cm^3 of sodium carbonate. Calculate:

(a) the number of sodium ions present in the reacting volume of the base;

(b) the mass of sodium chloride that would be obtained if the solution produced is evaporated to dryness.

(Na = 23.0, Cl = 35.5, N_A = 6.02×10^{23} mol^{-1})

Solution

(a) We must first obtain the molarity of the base from the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_A}{n_B}$$

The equation of reaction is

$$2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

C_A = 0.15 M

V_A = 22.89 cm^3

V_B = 25.00 cm^3

n_a = 2

n_b = 1

C_B = ?

Substituting we have

$$\frac{0.15\text{ M} \times 22.89\,\cancel{\text{cm}^3}}{C_B \times 25.00\,\cancel{\text{cm}^3}} = \frac{2}{1}$$

We now cross-multiply to obtain

$C_B \times 50.00$ = 3.43 M

So $C_B = \frac{3.43\text{ M}}{50.00}$

= 0.069 M

Next, we calculate the amount of the reacting base from the relation

$n = C \times V$

V = 25.00 cm^3 = 0.025 dm^3

n = ?

Substituting we have

$$n = \frac{0.069\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 0.025\ \cancel{\text{dm}^3}$$

$= 0.0017$ mol

Sodium carbonate dissociates as follows:

$$Na_2CO_3(aq) \rightarrow 2Na^+(aq) + CO_3^{2-}(aq)$$

From the equation, 1 mol of the base produces 2 mol of Na^+, then 0.0017 mol of the base would produce 0.0034 mol of the ion. Now we know that

$$n = \frac{N}{6.02 \times 10^{23}\ \text{mol}^{-1}}$$

$\therefore\ N = n \times 6.02 \times 10^{23}\ \text{mol}^{-1}$

Substituting we have

$$N = 0.0034\ \cancel{\text{mol}} \times \frac{6.02 \times 10^{23}}{1\ \cancel{\text{mol}}}$$

$= 2.0 \times 10^{21}$

(b) Sodium chloride would be produced as residue when the solution produced is evaporated to dryness. The amount of salt produced can be calculated from the amount of the base or acid. If we are to use the amount of the acid, then according to the equation, 2 mol of the acid produces 1 mol of the salt, then 0.0017 mol of the acid would produce 0.0034 mol of the salt. The mass of the salt is obtained from the relation

$$n = \frac{m}{M}$$

$\therefore\ m = n \times M$

$M = (23.0 + 35.5)\ \text{g mol}^{-1} = 58.5\ \text{g mol}^{-1}$

$m = ?$

Substituting we have

$$m = 0.0034\ \cancel{\text{mol}} \times \frac{58.5\ g}{1\ \cancel{\text{mol}}}$$

$= 0.20$ g

Practice Problems

1. 25.95 cm^3 of a 0.10-M nitric acid solution reacts completely with 20.00 cm^3 of a sodium hydroxide solution. Calculate:

(a) the number of aqueous sodium ions in 350.00 cm^3 of the solution of the base;

(b) the number of aqueous hydrogen ions contained in the reacting volume of the acid.

(N_A = 6.02 × 10^{23} mol^{-1}) [*Answers:* (a) 2.8 × 10^{22} (b) 1.6 × 10^{21}]

2. A is an ethanedioic acid solution. B is a 0.15-M potassium hydroxide solution. If 20.87 cm^3 of a solution A neutralizes 20.00 cm^3 of solution B, calculate the mass of the salt that would be produced by 750.00 cm^3 of the acid solution.

(C = 12, O = 16, K = 39) [*Answer:* 7.8 g]

8.1.2 Back Titration

Back titration is a form of titration in which a known amount of an excess reagent is added to an analyte, and the amount which remains unreacted is measured by titrating it with another reagent. The amount of the analyte is determined from the amount of the reagent that has been used up in reaction with the analyte.

The following steps are followed in calculating the amount of the analyte:

- Determine the amount of the reagent originally added to the analyte.
- Determine the amount of excess reagent by calculating the amount of it that has reacted with the neutralizing agent.
- Determine the amount of the reagent that reacted with the analyte by subtracting the amount of it in excess from the original amount of it added to the analyte.
- From stoichiometry, determine the amount of the analyte from the amount of the reagent that has reacted with it.

Example 1 An aqueous ammonia solution was added to 50.00 cm^3 of 0.20-M hydrochloric acid solution which was in excess. The resulting mixture was then neutralized completely by 25.00 cm^3 of 0.10-M sodium hydroxide solution. Determine the number of moles and mass of the analyte.

(H = 1, N = 14)

Solution We begin by calculating the amount of the acid added to the ammonia solution, using the relation

$n = C \times V$

$C = 0.20 \text{ mol dm}^{-3}$

$V = 50.00 \text{ cm}^3 = 0.050 \text{ dm}^3$

$n = ?$

Substituting we have

$$n = \frac{0.20 \text{ mol}}{1 \cancel{\text{dm}^3}} \times 0.050 \cancel{\text{dm}^3}$$

$= 0.010 \text{ mol}$

It should be well noted that not all this amount of the acid would react with ammonia since the acid is in excess. We now determine the amount of the excess acid as follows:

We first determine the amount of the sodium hydroxide solution, from the relation

$n = C \times V$

$C = 0.10 \text{ mol dm}^{-3}$

$V = 25.00 \text{ cm}^3 = 0.025 \text{ dm}^3$

$n = ?$

Substituting we have

$$n = \frac{0.10 \text{ mol}}{1 \cancel{\text{dm}^3}} \times 0.025 \cancel{\text{dm}^3}$$

$= 0.0025 \text{ mol}$

The equation of reaction is

$$\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

From the equation, 1 mol of the base requires 1 mol of the acid, then 0.0025 mol of the base would also require 0.0025 mol of the acid. Thus the amount of the excess acid is 0.0025 mol. We can now obtain the amount of the acid that reacted with the analyte from the relation

Amount of acid used up = Original amount of acid − Amount of the excess acid

So Amount of acid used up = 0.010 mol − 0.0025 mol = 0.0075 mol

Finally, we can now determine the amount of the analyte, ammonia from the above amount of the acid. The equation of reaction is

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(s)$$

From equation, 1 mol of HCl reacts with 1 mol of NH_3, then 0.0075 mol of HCl would also react with 0.0075 mol of NH_3. Thus the amount of the analyte is 0.0075 mol. The mass of the analyte is obtained from the relation

$n = \frac{m}{M}$

$\therefore\ m = n \times M$

$M = [14 + (1 \times 3)]\ \text{g mol}^{-1} = 17\ \text{g mol}^{-1}$

$m = ?$

Substituting we obtain

$m = 0.0075\,\cancel{\text{mol}} \times \frac{17\ \text{g}}{1\,\cancel{\text{mol}}}$

$= 0.13\ \text{g}$

Example 2 In an experiment to determine the amount of glucose present in a basic solution, a chemist adds 50.00 cm^3 of 0.10-M iodine solution to 20.00 cm^3 of the solution. The unreacted iodine is then titrated against 0.20-M solution of sodium thiosulphate. If the unreacted iodine requires 20.00 cm^3 of the thiosulphate solution for complete reaction, determine:

(a) the amount of the glucose present in the solution;

(b) the molar and mass concentrations of the glucose.

(H = 1, C = 12, O = 16)

Solution The amount of iodine[1] added to the analyte is obtained from the relation

$n = C \times V$

$C = 0.10\ \text{mol dm}^{-3}$

V = 50.00 cm^3 = 0.050 dm^3

n = ?

Substituting we have

$$n = \frac{0.10\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 0.050\ \cancel{\text{dm}^3}$$

= 0.0050 mol

We now determine the amount of the excess iodine as follows:
The amount of the sodium thiosulphate is determined as follows:

$n = C \times V$

C = 0.20 mol dm^{-3}

V = 20.00 cm^3 = 0.020 dm^3

n = ?

Substituting we have

$$n = \frac{0.20\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 0.020\ \cancel{\text{dm}^3}$$

= 0.0040 mol

The balanced redox equation for the reaction between iodine, present in solution as triiodide ions (I_3^-), and sodium thiosulphate is

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow 3I^-(aq) + S_4O_6^{2-}(aq)$$

Since the equation shows that 2 mol of $S_2O_3^{2-}$ react with 1 mol of I_3^-, then 0.0040 mol of $S_2O_3^{2-}$ would also react with 0.0020 mol of I_3^-. Thus the amount of the excess iodine is 0.0020 mol. The amount of iodine that reacted with the glucose is obtained as follows:

The amount of iodine used up = original amount of iodine – amount of excess iodine

So The amount of iodine used up = 0.0050 mol − 0.0020 mol = 0.0030 mol

The redox equation of reaction between iodine and the basic glucose solution is

$$C_6H_{12}O_6(aq) + I_3^-(aq) + 3OH^-(aq) \rightarrow C_6H_{12}O_7^-(aq) + 2H_2O(l) + 3I^-(aq)$$

---

[1] The solution is made by dissolving iodine in potassium iodide, KI, solution.

From the equation, 1 mo1 of I_3^- requires 1 mo1 of $C_6H_{12}O_6$, then 0.0030 mol of I_3^- would also require 0.0030 mol of $C_6H_{12}O_6$. Thus the amount of $C_6H_{12}O_6$ in the basic solution is 0.0030 mol. The molarity is obtained from the relation

$$C = \frac{n}{V}$$

$V = 20.00\ \text{cm}^3 = 0.020\ \text{dm}^3$
$C = ?$

Substituting we have

$$C = \frac{0.0030\ \text{mol}}{0.020\ \text{dm}^3}$$

$= 0.15\ \text{M}$

The mass concentration is obtained from the relation

$$C = \frac{\rho}{M}$$

$\therefore\ \rho = C \times M$
$M = [(12 \times 6) + (1 \times 12) + (16 \times 6)]\ \text{g mol}^{-1} = 180\ \text{g mol}^{-1}$
$\rho = ?$

Substituting we have

$$\rho = 0.15\ \text{mol dm}^{-3} \times \frac{180\ \text{g}}{1\ \cancel{\text{mol}}}$$

$= 27\ \text{g dm}^{-3}$

Practice Problem

A sample of calcium carbonate was dissolved in 50.00 cm^3 of 0.20-M sulphuric acid solution. The resulting mixture was then titrated against 0.10-M solution of sodium hydroxide. If 18.50 cm^3 of the base was neutralized by 15.50 cm^3 of the mixture, determine the mass of the calcium carbonate sample.

(C = 12, O = 16, Ca = 40) [*Answer:* 0.9 g]

8.2 GRAVIMETRIC ANALYSIS

Gravimetric analysis is the aspect of quantitative analysis concerned with mass measurements. Most times, the substance whose mass is required must first be converted to a form that can be weighed before its mass can be determined from calculation.

The following are the main steps involved in gravimetric analysis:

1. Precipitation of the analyte (the substance whose mass is to be determined) by an appropriate reagent.
2. Filtration of the precipitate, which is the compound formed between the analyte and the reagent.
3. Washing of the precipitate to remove impurities.
4. Drying the precipitate in a crucible to remove moisture.

Example 1 A sample of lead(II) chlorate was dissolved in water and treated with excess sodium chloride solution. The resulting precipitate was washed, dried and weighed to a constant mass of 0.705 g. Calculate the mass of lead in the original sample.

(Cl = 35.5, Pb = 207.2)

Solution The equation for the precipitation is

$$Pb^{2+}(aq) + 2Cl^{-}(aq) \rightarrow PbCl_2(s)$$

The mass of lead in the analyte is evidently the mass of lead in the precipitate. We can obtain this from the relation

$m = \frac{A_r}{M_r} \times$ mass of precipitate

$M_r = 207.2 + (35.5 \times 2) = 278.2$

$A_r = 207.2$

Mass of precipitate = 0.705 g

$m = ?$

Substituting we have

$m = \frac{207.2}{278.2} \times 0.705$ g

= 0.525 g

Alternatively, we can first obtain the number of moles of the precipitate:

$n = \frac{m}{M}$

$M = 278.2 \text{ g mol}^{-1}$

$n = ?$

Substituting we have

$n = \frac{0.705 \text{ g} \times 1 \text{ mol}}{278.2}$

$= 2.53 \times 10^{-3}$ mol

The above equation shows that the formation of 1 mol of $PbCl_2$ requires 1 mol of Pb^{2+}. Thus the amount of Pb^{2+} in the precipitate, which is equivalent to the amount of lead in the analyte, is 2.53×10^{-3} mol. Finally, we have to convert this amount of lead to mass, using the relation

$m = n \times M$

Thus $m = 2.53 \times 10^{-3} \cancel{\text{mol}} \times \frac{207.2 \text{ g}}{1 \cancel{\text{mol}}}$

$= 0.525$ g

Example 2 0.305 g of an impure sample of lead(II) nitrate was dissolved in water and titrated against 0.15-M solution of potassium iodide. Calculate the percentage purity of the lead(II) nitrate if the analyte required 5.84 cm^3 of the reagent for complete reaction.

(N = 14, O = 16, I = 126.9, Pb = 207.2)

Solution We must first determine the mass of lead in the precipitate, which is equivalent to the mass of lead in the analyte. The equation for the precipitation is

$$Pb^{2+}(aq) + 2I^{-}(aq) \rightarrow PbI_2(s)$$

The mass of the precipitate is not known. However, we can determine this from the amount of the reagent, KI, as follows:

$n = C \times V$

$C = 0.15 \text{ mol dm}^{-3}$

$V = 5.84 \text{ cm}^3 = 5.84 \times 10^{-3} \text{ dm}^3$

$n = ?$

Substituting we have

$$n = \frac{0.15\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 5.84 \times 10^{-3}\ \cancel{\text{dm}^3}$$

$= 8.76 \times 10^{-3}$ mol

From the above equation, 2 mol of KI produces 1 mol of PbI_2, then 8.76×10^{-3} mol of KI would produce 4.38×10^{-4} mol of PbI_2. We can now convert this to mass as follows:

$m = n \times M$

$M = [207.2 + (126.9 \times 2)]\ \text{g mol}^{-1} = 461.0\ \text{g mol}^{-1}$

$m = ?$

Substituting we have

$$m = 4.38 \times 10^{-4}\ \cancel{\text{mol}} \times \frac{461.0\ \text{g}}{1\ \cancel{\text{mol}}}$$

$= 0.202$ g

Thus the mass of lead in the precipitate and, of course, the analyte is

$$m = \frac{207.2}{461.0} \times 0.202\ \text{g}$$

$= 0.0908$ g

We now have to determine the mass of NO_3^- in order to know the mass of pure $Pb(NO_3)_2$. This can be done by first writing the equation for the dissociation of the analyte, i.e.

$$Pb(NO_3)_2(aq) \rightarrow Pb^{2+}(aq) + 2NO_3^-(aq)$$

From the equation, 1 mol of the analyte contains 2 mol of NO_3^-, then 4.38×10^{-4} mol of the analyte would contain 8.76×10^{-4} mol of NO_3^-. We must now convert this to mass, using the relation

$m = n \times M$

$M = [14 + (16 \times 3)]\ \text{g mol}^{-1} = 62\ \text{g mol}^{-1}$

$m = ?$

Substituting we have

$$m = 8.76 \times 10^{-4} \cancel{\text{mol}} \times \frac{62\ g}{1\ \cancel{\text{mol}}}$$

$= 0.054$ g

The mass of pure $Pb(NO_3)_2$ is the sum of the masses of Pb and NO_3^-, i.e

$$m = 0.0908 \text{ g} + 0.054 \text{ g} = 0.140 \text{ g}$$

Impurities add to the mass of the analyte to make it up to 0.305 g. The percentage purity is obtained from the relation

$$\text{Percentage purity} = \frac{\text{Mass of pure analyte}}{\text{Mass of impure analyte}} \times 100\%$$

Substituting we have

$$\text{Percentage purity} = \frac{0.140\ g}{0.305\ g} \times 100\%$$

$= 46\%$

Example 3 0.427 g of an unknown salt XBr_2 was dissolved in water and titrated with a solution of silver nitrate. The resulting precipitate was washed, dried and weighed to a constant mass of 0.540 g. Identify the salt from the relative atomic masses given below.

(Mg = 23.3, Ca = 40, Mn = 54.9, Br = 79.9, I = 126.9, Ba = 137.3)

Solution We can only identity the salt if the identify of the element X is known. This can be done by working out the atomic mass of X, and matching it up with the appropriate element in the list given above. We begin by first writing the equation of reaction:

$$XBr_2(aq) + 2AgNO_3(aq) \rightarrow 2AgBr(s) + X(NO_3)_2(aq)$$

The mass of bromine in the precipitate, AgBr, must be the same as that in the analyte. This is obtained from the relation

$$m = \frac{A_r}{M_r} \times \text{mass of the precipitate}$$

A_r = 79.9

M_r = 107.9 + 79.9 = 187.8

Mass of the precipitate = 0.540 g

m = ?

Substituting we have

$$m = \frac{79.9}{187.8} \times 0.54\ \text{g}$$

= 0.230 g

Alternatively, the mass of bromine in the precipitate can be obtained as follows:

We first obtain the amount of the precipitate in moles:

$$n = \frac{m}{M}$$

m = 0.540 g

M = 187.8 g mol^{-1}

n = ?

Substituting we have

$$n = \frac{0.540\ \cancel{\text{g}} \times 1\ \text{mol}}{187.8\ \cancel{\text{g}}}$$

= 2.88 × 10^{-3} mol

The equation for the formation of the precipitate is

$$\text{Ag}^+(aq) + \text{Br}^-(aq) \rightarrow \text{AgBr}(s)$$

Since the formation of 1 mol of AgBr requires 1 mol of Br$^-$, then 2.88 × 10^{-3} mol of the precipitate would contain 2.88 × 10^{-3} mol of Br$^-$. We can now convert this to mass as follows:

$m = n \times M$

M = 79.9 g mol^{-1} (molar mass of bromide ion)

m = ?

Substituting we have

$m = 2.88 \times 10^{-3}\,\cancel{\text{mol}} \times \frac{79.9\text{ g}}{1\,\cancel{\text{mol}}}$

$= 0.230\text{ g}$

The mass of bromine in the analyte is obtained from the relation

$m = \frac{2A_r}{M_r} \times \text{mass of analyte}$

$M_r = \text{X} + (2 \times 79.9) = \text{X} + 159.8$
$A_r = 79.9$
$m = 0.230\text{ g}$
Mass of analyte = 0.427 g
X = ?

Substituting we have

$$0.230\text{ g} = \frac{2 \times 79.9}{\text{X} + 159.8} \times 0.427\text{ g}$$

Cross-multiplying we obtain

$0.230\text{X g} + 36.754\text{ g} = 68.235\text{ g}$
So $0.230\text{X g} = 68.235\text{ g} - 36.754\text{ g} = 31.481\text{ g}$

Thus $\text{X} = \frac{31.481\,\cancel{\text{g}}}{0.230\,\cancel{\text{g}}}$

$= 137$

Alternatively, we can first obtain the amount of X from that of barium. The equation for the dissociation of the analyte is

$$\text{XBr}_2(aq) \rightarrow \text{X}^{2+}(aq) + 2\text{Br}^-(aq)$$

The equation shows that the analyte contains 2 mol of Br^- for every mol of X^{2+}. Thus the amount of X in analyte is 1.44×10^{-3} mol. The mass of X can be obtained by subtracting the mass of barium from the analyte, i.e.

$$m = 0.427\text{ g} - 0.230\text{ g} = 0.197\text{ g}$$

Finally, we can obtain the relative molecular mass of X from the relation

$n = \frac{m}{M}$

Thus $M = \frac{0.197\ \text{g}}{1.44 \times 10^{-3}\ \text{mol}}$

$= 137\ \text{g mol}^{-1}$

Thus the relative atomic mass of X is 137, which is the relative atomic mass of barium to three significant figures. Thus the salt is barium chloride, $BaCl_2$.

Practice Problems

1. Magnesium chloride was dissolved in water and titrated with silver nit precipitate was then washed, dried and weighed to a constant mass of 0.45 g

(a) the mass of chlorine in the analyte;
(b) the percentage composition of magnesium in the analyte.

35.5, Ag
107.9)
[*Answers:* (a) 0.11 g (b) 25%]

2. 0.922 g of a hydrated barium halide $BaX_2.nH_2O$ was dissolved in water an sulphuric acid. The resulting precipitate was then washed, dried and wei 0.680 g. Determine the number of molecules of water of crystallization in th a similar sample of the salt reduced by 34.2% when heated to a constant identity of the element X from the data given below.

(O = 16, Cl =35.5, Ni = 58.7, Br = 79.9, Ag = 107.9, I = 126.

SUMMARY

- Quantitative analysis is the determination of the amounts of substances.
- Volumetric analysis is the determination of the amounts of substances by volume measurement.
- Equivalence point refers to the point during titration at which the reaction is just complete. This is usually indicated by a colour change of an indicator.
- An indicator is a dye that changes colour according to the pH of the solution in which it is dissolved.
- The pH at equivalence point of the titration of a strong acid with a strong

base is usually neutral.

- The pH at equivalence point of the titration of a strong acid with a weak base is usually less than 7.
- The pH at equivalence point of the titration of a weak acid with a strong base is usually greater than 7.
- Back titration is a form of titration in which a known amount of an excess reagent is added to an analyte, and the unreacted reagent titrated with another reagent. The amount of the analyte is determined from the amount of the reagent that has been used up in reaction with the analyte.
- Gravimetric analysis is the determination of the amounts of substances by mass measurement.

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. The pH at the equivalence point of the titration of a strong acid with a weak base is usually

A. less than 7. B. greater than 7.

C. neutral. D. equal to 7.

E. greater than 5.

2. Consider the following indicators and their pH range for colour change:

Methyl red	4.8–6.0
Methyl orange	3.4–4.4
Phenolphthalein	8.2–10.0
Thymol blue	1.2–2.8
Bromocresol green	4.0–2.8

Which of the indicators is suitable for the titration of a weak acid with a strong base?

A. Phenolphthalein B. Methyl orange

C. Methyl red D. Thymol blue

E. Bromocresol green

3. Which of the following statements is/are true?

i. There is no suitable indicator for the titration of a weak base with a weak acid.

ii. The pH at the equivalence point of the titration of a strong acid with a strong base is less than 7.

iii. Indicators exhibit different colours in acidic and basic solutions.

iv. No indicator is required for all redox titrations.

A. i and ii B. i only

C. ii only D. i and iii

E. iii and iv

4. The point in a redox titration at which just the right amount of the reducing agent has been added to an oxidizing agent is called

A. Equivalence point B. Neutralization point

C. Termination point D. End point

E. Flash point

5. Which of the following is **NOT** a step in gravimetric analysis?

A. Identifying the right reagent.

B. Weighing of the precipitate.

C. Measuring the volume of the precipitate.

D. Drying the precipitate.

E. Filtration.

6. 15.50 cm^3 of 0.15-M nitric acid solution neutralizes 20.00 cm^3 of a potassium hydroxide solution. What is the molarity of the base solution?

A. 0.10 M B. 0.11 M

C. 0.12 M D. 0.20 M

E. 0.21 M

7. 30.00 cm^3 of 0.10-M solution of an oxidizing agent requires 25.00 cm^3 of a 0.060-M solution of a reducing agent for complete reaction. The mole ratio of the oxidizing agent to the reducing agent is

A. 1:1. B. 1:2.

C. 2:1. D. 3:1.

E. 1:3.

ESSAY TYPE QUESTIONS

Volumetric analysis

8. (a) Differentiate between volumetric and gravimetric analysis.

(b) Explain the role of an indicator in acid-base titration.

(c) Explain why is it necessary to take the pH range for colour change of an indicator into consideration before using it in an acid-base titration.

9. State the appropriate indicator(s) for each of the following acid-base titrations:

(a) Ethanoic acid with sodium hydroxide.
(b) Nitric acid and ammonia.
(c) Hydrochloric acid and sodium carbonate.
(d) Sulphuric acid and potassium hydroxide.
(e) Hydrochloric acid and sodium hydroxide.

10. Solution A is a 0.20-M solution of nitric acid, while solution B is a solution of anhydrous sodium carbonate. If 18.00 cm^3 of the acid solution just neutralizes 25.00 cm^3 of the base, calculate

(a) the molar concentration of the base;
(b) the volume of carbon dioxide liberated at STP.

(Molar volume of gases at STP = 22.4 $dm^3\ mol^{-1}$)

11. 18.50 cm^3 of a 0.15-M solution of nitric acid neutralizes 20.00 cm^3 of a potassium hydroxide solution. What is the molarity of the base? Hence determine the mass of the potassium nitrate produced.

(N = 14, O = 16, K = 39)

12. 25.00 cm^3 of 0.20-M sodium carbonate solution requires 30.00 cm^3 of a sulphuric acid solution for complete reaction. Calculate the mass concentration of the acid. Hence determine the number of the sodium ions produced.

(H = 1, O = 16, S = 32, $N_A = 6.02 \times 10^{23}\ mol^{-1}$)

13. 20.00 cm^3 of an ammonia solution was neutralized by 19.20 cm^3 of a 0.10-M solution of hydrochloric acid. What is the mass concentration of the ammonia solution? Hence determine the mass of the ammonium chloride produced.

(H = 1, N = 14, Cl = 35.5)

14. 25.00 cm^3 of oxalic acid, $H_2C_2O_4$, solution requires 18.00 cm^3 of a 0.15-M solution of potassium permanganate, $KMnO_4$, for complete reaction. Calculate the mass concentration of the reducing agent.

(H = 1.0, C = 12.0, O = 16.0)

15. 20.00 cm^3 of a 0.20-M iodine solution requires 18.50 cm^3 of a sodium thiosulphate, $Na_2S_2O_3$ for complete reaction. What is the molarity of the reducing agent?

16. A solution contains 6.50 g of impure sodium hydroxide per 250 cm^3 of

solution. Determine the percentage purity of the base if 20.00 cm^3 of the solution was neutralized by 22.00 cm^3 of 0.20-M sulphuric acid solution.

(H = 1, O = 16, Na = 23)

17. 5.00 g of anhydrous sodium carbonate was made up to 1.0 dm^3 of solution. 25.00 cm^3 of this solution was neutralized by 22.50 cm^3 of 0.100-M nitric acid solution. Calculate the percentage purity of the base? Hence determine the volume of carbon dioxide produced at STP.

(H = 1, C = 12, N = 14, O = 16, Na = 23, molar volume of gases at STP = 22.4 dm^3 mol^{-1})

18. 1.35 g of hydrated sodium carbonate, $Na_2CO_3.xH_2O$, was dissolved in 200.00 cm^3 of water. 25.00 cm^3 of the resulting solution neutralizes 27.30 cm^3 of 0.10-M hydrochloric acid solution, calculate

(a) the number of molecules of water of crystallization in the salt;

(b) the percentage composition of water in the salt.

(H = 1, C = 12, O = 16, Na = 23)

19. 1.50 g of sodium carbonate was dissolved in 150.00 cm^3 of water. Calculate the number of molecules of water of crystallization in the salt if 20.00 cm^3 of the resulting solution neutralized 18.50 cm^3 of 0.076-M nitric acid solution. Hence determine the percentage composition of water in the salt.

(H = 1, C = 12, O = 16, Na = 23)

20. A saturated solution of potassium hydroxide was prepared at 25°C. 25.00 cm^3 of this solution was completely neutralized by 20.00 cm^3 of a 0.10-M sulphuric acid solution. What is the solubility of the base at the specified temperature?

(H = 1, O = 16, K = 39)

21. A sodium hydroxide solution was prepared by making up 20.00 cm^3 of a saturated solution of the base to 1.0 dm^3 at 25°C. Calculate the molar solubility of the base, given that 20.00 cm^3 of the base solution requires 18.70 cm^3 of 0.10-M hydrochloric acid solution for complete neutralization.

22. A is a solution containing 1.4 g of hydrochloric acid in 150.00 cm^3 of solution. B is a

0.10 M solution of a base. What is the mole ratio of the acid to base if 10.00 cm^3 of the acid solution neutralized 25.00 cm^3 of the base.

(H = 1, Cl = 35.5)

23. A solution of anhydrous sodium carbonate contains 4.5 g of the salt in

550.00 cm^3 of solution. The salt solution was then titrated with a 0.11 M of an acid solution. What is the mole ratio of the acid to base if 20.00 cm^3 of the salt solution was completely neutralized by 28.00 cm^3 of the acid solution?

(C = 12, O = 16, Na = 23)

24. 21.10 cm^3 of 0.10-M hydrochloric acid solution completely neutralized 20.00 cm^3 of a solution containing 0.66 g of an unknown base, XOH, in 150.00 cm^3 of solution. Calculate the molar mass of the base. Hence determine the relative atomic mass of the element X.

25. 28.00 cm^3 of a solution containing 13.86 g of an unknown acid, HX, per dm^3 of solution neutralized 20.00 cm^3 of 0.12-M sodium carbonate solution. What is the molar mass of the acid? Hence identify the acid if possible.

26. A sample of calcium carbonate dissolved in 50.00 cm^3 of 0.25-M hydrochloric acid solution. Calculate the mass of the sample if the resulting solution requires 25.00 cm^3 of 0.10-M sodium hydroxide solution for neutralization.

(C = 12, O = 16, Ca = 40)

27. In an experiment to determine the concentration of glucose in a basic solution, a 25 cm^3 sample of the solution was added to 0.10 dm^3 of 0.20-M potassium iodide solution, which was in excess. What is the concentration of glucose in the solution if the resulting solution requires 20.00 cm^3 of 0.15-M sodium thiosulpate solution for complete reaction?

Gravimetric analysis

28. One of the compounds responsible for the permanent hardness of water is dissolved calcium sulphate, which can only be removed by a precipitating agent, such as sodium carbonate. Four samples of water, from different sources, were analysed by the addition of excess sodium carbonate to determine the level of dissolved calcium ions each sample. The final masses of the precipitates obtained were 0.225 g, 0.215 g, 0.350 g and 0.105 g. Assuming no other dissolved ions are present, calculate the mass of calcium in each sample.

(C = 12, O = 16, Ca = 40)

29. A sample of silver nitrate was dissolved in water and titrated with a potassium iodide solution. The resulting precipitate was washed, dried and weighed to a constant mass of 0.225 g. Calculate the percentage composition by mass of silver in the sample.

(N = 14, O = 16, Ag = 107.9, I = 126.9)

30. 0.191 g of impure magnesium chloride was dissolved in water and titrated against a solution of silver nitrate. The resulting precipitate was washed, dried and weighed to a constant mass of 0.500 g. What is the percentage purity of the salt?

(Mg = 24, Cl = 35.5, Ag = 107.9)

31. A sample of barium nitrate was dissolved in water, and titrated against a solution of ammonium sulphate, resulting in the formation of a 0.225-g precipitate. What is the percentage composition by mass of nitrogen in the sample?

(N = 14, O = 16, I = 126.9, Ba = 137)

32. 0.725 g of a hydrated copper(II) sulphate, $CuSO_4.xH_2O$, was dissolved in water and titrated with a solution of barium nitrate, yielding a 0.665-g precipitate. Calculate the number of molecules of water of crystallization in the salt.

(H = 1, O = 16, S = 32, Cu = 63.5, Ba = 137)

33. The maximum level of impurity allowed in sodium carbonate to be used for a particular reaction is 5%. A 0.493-g sample of the compound was dissolved in water and titrated with a solution of cobalt(II) chloride, yielding a 0.540-g precipitate. Assess if the sample is suitable for the intended use.

(C = 12, O = 16, Na = 23, Co = 58.9)

34. A 0.120-g sample of a salt, XBr_2, was dissolved in water, and titrated against a solution of silver nitrate. The resulting precipitate was filtered, washed and weighed to a constant mass of 0.226 g. Identify the salt, using the relative atomic masses given below. Hence determine the percentage composition by mass of the element X in the sample?

(Be = 9, Mg = 24, Ca = 40, Br = 79.9, Co = 58.9, Ag = 107.9, Ba = 137)

Answers

1. A 2. A 3. D 4. A

5. C 6. C 7. C

10. (a) 0.072 M (b) 40 cm^3

11. 0.14 M

12. 16 g mol^{-1}, 6.02 × 10^{21}

13. 0.096 M, 0.10 g
14. 24 gdm^{-3}
15. 0.43 M
16. 68%
17. 95.4%, 25.2 cm^{3}
18. (a) 1 (b) 15%
19. 10, 63%
20. 0.16 M or 9.0 gdm^{-3}
21. 4.7 M or 190 gdm^{-3}
22. 1:1
23. 2:1
24. 40 g mol^{-1}, 23
25. 81 g mol^{-1}, HBr
26. 0.5 g
27. 0.74 M
28. 0.09 g, 0.086 g, 0.14 g, 0.042 g
29. 63.2%
30. 86.9%
31. 10.7%
32. 5
33. yes
34. $CaBr_2$, 19.8%

9

Chapter

Thermodynamics

Thermodynamics is the science of interconversion of energy. The common terminologies used in thermodynamics are:

System: A system refers to a sample specified in the universe for study or consideration. There are different types of systems:

(i) Closed system: This is a system that does not allow for the exchange of matter between the system and its surroundings, such that matter is restricted within the system. However, such a system exchanges energy with the surroundings.

(ii) Open system: This is a system that exchanges both matter and energy with its surroundings. In other worΔS, such a system allows energy and matter to flow across its boundary.

(iii) Isolated system: This is a system that neither allows energy nor matter to transverse its boundary.

(iv) Homogeneous system: This is a system that is in one phase, i.e., it is uniform throughout.

(v) Heterogeneous system: This is a system consisting of more that one phase, i.e., it is not uniform throughout.

Boundary: The boundary of a system is the region that encloses the system, and separates it from its surroundings.

Surroundings: The surroundings of a system is the part of the universe beyond its boundary. The surroundings interact with the system when such is desired.

A universe: A universe consists of a system and its surroundings.

Property: A property refers to the characteristic or feature of a system which is observable at any instant of time. The different types of properties encountered in thermodynamics are:

(i) Extensive property: This is a property that depenΔS on the mass of a system. Examples include internal energy, weight, volume, and heat capacity.

(ii) Intensive property: This is a property that is independent of the mass of a system. For example, the density and specific heat capacity of a substance are constant, regardless of the mass under consideration.

(iii) Microscopic property: This is a property that is associated with the individual molecules of a system, e.g., velocity of a molecule, volume of a molecule, energy of a molecule, etc.

(iv) Macroscopic property: This is a property that is associated with the whole system, and it can be thought of as being the sum of the contributions of all the molecules that constitute the system. Examples include density, pressure, viscosity, volume, etc.

(v) State property: This is a property that is independent of the history of the system. In other worΔS, it is a property that does not depend on how a substance was prepared. Examples include internal energy, temperature, density, volume, etc.

State: The state of a system is a collection of macroscopic properties which partially or fully describe its characteristics at any specific time. When there is a change in any of such properties, then the system is said to undergo a change of state.

Thermodynamic process: A thermodynamic process occurs when a system undergoes a change of state. The different types of processes encountered in chemical thermodynamics are:

(i) Isothermal process: This is a process that occurs at constant temperature.

(ii) Isobaric process: This is a process that occurs at constant pressure.

(iii) Isochoric process: This is a process that occurs at constant volume.

These processes could be reversible or not. A process is said to be reversible if an alteration in its state can restore it to its original state after being taken through a series of equilibrium states, otherwise it is said to be irreversible.

Phase: Phase refers to the physical nature of a system. The three phases of matter include solid, liquid and gas. A system is said to be in one phase if it is uniform throughout its mass.

9.1 CALORIMETRY

Energy is defined as the ability to do work. Heat is one of the several forms of energy. Calorimetry is the experimental determination of heats of reactions. The SI unit of heat energy is joule (J). Another common unit used is calorie (Cal), which is related to the SI unit as follows

$$1 \text{ Cal} = 4.184 \text{ J}$$

The quantity of heat Q received or lost by a body is directly proportional to its mass and temperature change, i.e.

$$Q \; \mu \; m\Delta T$$

Introducing the constant of proportionality, we have

$$Q = mc\Delta T$$

where m = Mass of the substance.

c[1] = The specific heat capacity of the body.

ΔT = Temperature change in K or °C.

When a hot body is in contact with a colder body, heat flows from the hot body to the colder body until both bodies attain thermal equilibrium. This is termed the zeroth law of thermodynamics. From the principle of conservation of energy, we have

Heat gained by the colder body = Heat lost by the hot body

This statement holΔS true provided no heat is lost to the surroundings.

When heat is supplied to a system in the form of electrical energy, then the quantity of electrical energy supplied to the system is obtained from the relations

$$E = IVt \text{ or } E = I^2Rt \text{ or } E = \frac{V^2t}{R}$$

where I = Current

V = The potential difference

t = The time

R = The resistance

Since the electrical energy supplied to the system must be equal to the heat energy gained, then we have

$$E = IVt = I^2Rt = \frac{V^2t}{R} = mc\Delta T$$

Example 1 A copper ball of mass 2.0 kg was heated to a temperature of 100°C. It was then quickly transferred into a calorimeter of water. The final steady temperature of the mixture was 40°C, calculate the heat gained by the water; assuming the specific heat capacity of the calorimeter is negligible.

$$(c = 400 \text{ J kg}^{-1} \text{ K}^{-1})$$

Solution The fact that the specific heat capacity of the material of the calorimeter is negligible means that it gains no heat.

The energy balance is

Heat lost by the copper ball = Heat gained by water

The heat lost by the copper ball is obtained from the relation

$Q = mc(T_1 - T_2)$

$m = 2$ kg

$c = 400$ J kg^{-1} K^{-1}

$T_1 = 100°\text{C} + 273 \text{ K} = 373 \text{ K}$

$T_2 = 40°\text{C} + 273 \text{ K} = 313 \text{ K}$

$Q = ?$

Substituting we obtain

$$Q = \frac{2.0\,\cancel{\text{kg}} \times 400 \text{ J} \times [373 - 313]\,\cancel{\text{K}}}{1\,\cancel{\text{kg}} \times 1\,\cancel{\text{K}}}$$

Thus $Q = 2 \times 400 \text{ J} \times 60 \text{ K}$

$= 50$ kJ

Example 2 A piece of iron of mass 22 g at a temperature of 100°C was dropped into a calorimeter containing 10.5 g of water.

The steady final temperature of the mixture was 19.5°C. What is the initial temperature of the water?

$$(c\,(\text{iron}) = 0.45 \text{ J g}^{-1} \text{ K}^{-1},\ c\ (\text{water}) = 4.2 \text{ J g}^{-1} \text{K}^{-1})$$

Solution We have to start with the energy balance

Heat lost by iron = heat gained by water

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[1] The specific heat capacity of a substance is defined as the quantity of heat required to raise the temperature of a unit mass of the substance by a unit temperature. It is measured in J kg^{-1} K^{-1} or J g^{-1} K^{-1}. The heat required to raise the temperature of the entire sample of as substance is called heat capacity C. It's the product of the specific heat capacity of the substance and the mass of its sample under consideration, i.e. $C = mc$.

We are denoting the initial temperature of iron by T_1, initial temperature of water T_2, and the final steady temperature of the mixture by T_3. Thus

$m_i c_i (T_1 - T_3) = m_w c_w (T_3 - T_2)$

m_i = The mass of iron = 22 g

c_i = The specific heat capacity of iron = 0.45 J g^{-1} K^{-1}

m_w = The mass of water = 10.5 g

c_w = The specific heat capacity of water = 4.2 J g^{-1} K^{-1}

T_1 = The initial temperature of iron = 100°C + 273 K = 373 K

T_3 = The final steady temperature of the mixture = 19.5°C + 273 K = 292.5 K

T_2 = The initial temperature of water = ?

We now substitute to obtain

$$\frac{22\cancel{g} \times 0.45 \text{ j} \times (373 - 292.5)\cancel{K}}{1\cancel{g} \times 1\cancel{K}} = \frac{10.5\cancel{g} \times 4.2 \text{ j} \times (292.5 \text{ K} - T_2)}{1\cancel{g} \times 1 \text{ K}}$$

Thus 9.9 J × 80.5 $= \dfrac{44.1 \text{ J} \times (292.5 \text{ K} - T^2)}{1 \text{ K}}$

Then 796.95 J $= \dfrac{12899.25 \text{ j K} - 44.1T_2 \text{J}}{1 \text{ K}}$

Cross-multiplying we have

$$796.95 \text{ J K} = 12899.25 \text{ J K} - 44.1T_2 \text{ J}$$

We now collect like terms to obtain

$44.1T_2$ J = 12899.25 J K − 796.95 J K = 2102.3 J K

$T_2 = \dfrac{12102 \text{ J} \cancel{K}}{44.1 \cancel{J}}$

= 274 K

Example 3 250 g of water is heated through a temperature of 25°C. What is the heat gained by the system?

(c = 4.2 J g^{-1} K^{-1})

Solution This problem requires the direct application of the relation

$Q = mc\Delta T$

$m = 250$ g

$c = 4.2$ J $g^{-1}K^{-1}$

$\Delta T = 25°C = 25$ K

Finally, we now substitute to obtain

$$Q = \frac{250\,\cancel{g} \times 4.2\text{ J} \times 25\,\cancel{K}}{1\cancel{g} \times 1\cancel{K}}$$

= 26 kJ

Note that the numerical value of ΔT in °C is the same with that in K.

Example 4 A quantity of water at 10°C was heated by an electric heater. What is the mass of the water if it attained a temperature of 90°C after 10 min., given that the current and voltage supplied were 0.1 A and 240 V respectively?

($c = 4200$ J $kg^{-1}K^{-1}$)

Solution This is a case of conversion of electrical energy into heat energy. Since current and voltage are specified, then we have to apply the relation

$IVt = mc(T_2 - T_1)$

$I = 0.1$ A

$V = 240$ V

$t = 10$ min. = 10 × 60 s = 600 s

$c = 4200$ J $kg^{-1}K^{-1}$

$T_1 = 10°C + 273\text{ K} = 283\text{ K}$

$T_2 = 90°C + 273\text{ K} = 363\text{ K}$

$m = ?$

Substituting we have

$$0.1\text{ A} \times 240 \times \text{V } 600\text{ s} = \frac{m \times 4200\text{ J} \times (363 - 283)\cancel{K}}{1\cancel{K} \times 1\text{ kg}}$$

$$\text{So } 14400\text{ J} = \frac{m \times 4200\text{ J} \times 80}{1\text{ K}}$$

Cross-multiplying we obtain

$m \times 336000\ \text{J} = 14400\ \text{J K}$

$\therefore\ m = \frac{14400\ \cancel{\text{J}}\ \text{kg}}{336000\ \cancel{\text{J}}}$

$= 0.043\ \text{kg or } 43\ \text{g}$

Note that 1 A × 1 V × 1 s = 1 J.

Example 5 We are required to determine the heat of vaporization of seawater. What is the power rating of the heater that should be used in order to heat 200.0 g of the liquid from 10 to 100°C in 30 min.?

($c = 3900\ \text{J kg}^{-1}\,\text{K}^{-1}$)

Solution The key to solving this problem is to know the relationship between expended energy (work) and power. Power is defined as the work done (energy expended) per unit time, i.e.

$P = \frac{E}{t}$

$\therefore\ E = P \times t$

Since electrical energy is converted to heat, then

$P \times t = mc\,(T_2 - T_1)$

$t = 30 \times 60\ \text{s} = 1800\ \text{s}$

$m = 200.0\ \text{g} = 0.20\ \text{kg}$

$c = 3900\ \text{J kg}^{-1}\ \text{K}^{-1}$

$T_1 = 10°\text{C} + 273\ \text{K} = 283\ \text{K}$

$T_2 = 100°\text{C} + 273\ \text{K} = 373\ \text{K}$

$P = ?$

Substituting we have

$P \times 1800\ \text{s} = \frac{0.20\ \cancel{\text{kg}} \times 3900\ \text{J} \times (373 - 283)\ \cancel{\text{K}}}{1\ \cancel{\text{K}} \times 1\ \cancel{\text{kg}}}$

Thus $P \times 1800\ \text{s} = 780\ \text{J} \times 90 = 70200\ \text{J}$

So $P = \frac{70200\ \text{J}}{1800\ \text{s}}$

$= 39\ W^{2}$

Practice Problems

1. 500 J of heat raised the temperature of 10.0 g of water to 80°C. What was th

   $^{-1}$)

   [*Answer:* 68°C]

2. A solution of sodium hydroxide was added to dilute hydrochloric acid. The temperature recorded was 75°C. What was the heat gained during the reactio

   (Assume that the specific capacity of the solutio

3. An aluminium ball of mass 10.0 kg initially at a temperature of 80°C was dr final steady temperature of the mixture if the initial temperature of the water

   $^{-1}$)

4. A student heated 100.0 g of water initially at a temperature of 0°C for 1 ho the coils of the heater and current were 40.8 Ω and 0.10 A respectively?

   $^{-1}$)

   [Answer: 3.5°C]

9.2 HEAT (ENTHALPY CHANGE) OF PHYSICAL CHANGE

Matter can be changed from one state or phase to another by a change in temperature. For example, it is very easy to convert ice to liquid water by raising its temperature. The heat or enthalpy change ΔH of change of state is the heat required to convert a substance from one state to another at its transition temperature, without a corresponding change in temperature. The heat of change of state is also called latent heat.

Transition temperature is the temperature at which a substance changes from one state to another. Examples are the melting and boiling points of water, which are 0°C and 100°C respectively. Any heat supplied to a substance at its transition temperature does not bring about any rise in temperature. For an endothermic process like melting, heat is used for overcoming the intermolecular forces of attraction between the molecules of the substance. The temperature would only begin to rise after a complete change of state has occurred.

Different types of enthalpy change accompanying physical processes are explained below.

Heat of vaporisation: The heat of vaporisation ΔH_v is the amount of heat required to change one mole of a substance at its boiling point from the liquid to the gaseous state. The standard heat of vaporisation ΔH^o_v is the amount of heat required to change one mole of a pure substance at its normal boiling point (at 1 atm) from the liquid to the gaseous state.

In vaporisation, the ‘reactant’ is the liquid while the ‘product’ is the gas. Thus

$$\Delta H_v = H_g - H_l$$

At standard conditions we have

$$\Delta H^o_v = H^o_g - H^o_1$$

Heat of fusion: The heat of fusion ΔH_f is the amount of heat required to change one mole of a substance at its freezing point from the solid to the liquid state. The standard heat of fusion is the heat required to change one mole of a pure substance at its normal freezing point (at 1 atm) from the solid to the liquid state.

The ‘reactant’ in melting is the solid while the ‘product’ is the liquid. Thus

$$\Delta H_f = H_l - H_s$$

At standard conditions we have

$$\Delta H^o_f = \Delta H^o_1 - H^o_s$$

Heat of sublimation: The heat of sublimation ΔH_s is the heat required to change one mole of a substance directly from the solid to the gaseous state. The standard heat of sublimation ΔH^o_s is the heat required to change one mole of a pure substance directly from the solid to the gaseous state at 1 atm of pressure.

The ‘reactant’ in sublimation is the solid, while the vapour (gas) constitutes the ‘product’. Thus

$$\Delta H_s = H_g - H_s$$

As we will see shortly from Hess’s law[3], the enthalpy change of a particular reaction can be obtained from the enthalpy changes of reactions that can be combined in some ways to obtain the reaction. Thus we can safely conceive sublimation as the sum of melting and vaporisation processes. In this regard, the heat of sublimation becomes the sum of the heat of fusion and vaporisation, i.e.

$$\Delta H_s = \Delta H_f + \Delta H_v$$

---

[2] The SI unit of power is the watt (W). 1 W 1 J s^{-1}.

At standard conditions we have

$$\Delta H^{o}_{s} = \Delta H^{o}_{f} - \Delta H^{o}_{f}$$

Heat of freezing: The heat of freezing ΔH_{fr} is the quantity of heat that must be removed from one mole of a substance to change it from the liquid to the solid state at its freezing or melting point. The standard heat of freezing ΔH^{o}_{fr} is the quantity of heat that must be removed from a pure substance in order to change it from the liquid to the solid state at its normal freezing or melting point.

As the definition suggests, the heat of freezing is an exothermic process; the exact opposite of the heat of fusion. Thus

$$\Delta H_{fr} = -\,\Delta H_{f} = H_{s} - H_{l}$$

At standard conditions we have

$$\Delta H^{o}_{fr} = -\,\Delta H^{o}_{f} = H^{o}_{s} - H^{o}_{1}$$

Heat of condensation: The heat of condensation ΔH_{c} is the amount of heat that must be removed from or evolved by a substance in order to change it from the gaseous to the liquid state at its boiling point. The standard heat of condensation ΔH^{o}_{c} is the amount of heat that must be removed from or evolved by one mole of a pure substance in order to change it from the gaseous to the liquid state at its normal boiling point (at 1 atm).

Unlike vaporisation, condensation is an exothermic process. In fact, the heat of condensation is the exact opposite of the heat of vaporisation, i.e.

$$\Delta H_{c} = -\Delta H_{v} = H_{l} - \mathrm{H}_{\mathrm{g}}$$

At standard conditions we have

$$\Delta H^{o}_{c} = -\,\Delta H^{o}_{v} = H^{o}_{1} - H^{o}_{g}$$

Heat of solution: The heat of solution ΔH_{sol} is the heat absorbed or evolved when one mole of a substance is dissolved in water. The standard heat of solution ΔH^{o}_{sol} is the heat absorbed or evolved when one mole of a substance is dissolved in so much water that further dilution results in no detectable heat change.

Example 1 50.0 g of ethanol, C_2H_5OH, was vaporised in approximately 11 min. when a 50-Ω heater was used to heat the liquid at its boiling point. What is the heat of vaporisation of ethanol if the current is 1.0 A?

(H = 1, C = 12, O = 16)

[3] Hess' s law is treated in Section 9.3.

Solution The heat supplied by the heater was used to boil away 50.0 g of benzene at its boiling point. The heat supplied should be calculated from the relation

$Q = I^2RT$
$I = 1$ A
$R = 50$ W
$t = 11$ min. $= 11 \times 60$ s $= 660$ s
$Q = ?$

Substituting we have

$$Q = (1\ \text{A})^2 \times 50\ \text{W} \times 660\ \text{s} = 33\ \text{kJ}$$

We must now recall the definition of heat of vaporisation: the heat required to vaporise one mole of a substance. Thus the heat of vaporisation of the compound has to be calculated from the relation

$$\Delta H_{V} = \frac{\text{Quantity of heat supplied}}{\text{Amount of liquid vaporised}}$$

The amount of the liquid vaporised is obtained from the relation

$n = \frac{m}{M}$

$M = [(12 \times 2) + (1 \times 5) + 16 + 1]\ \text{g mol}^{-1} = 46\ \text{g mol}^{-1}$
$m = 50.0$ g
$n = ?$

Substituting we have

$$n = \frac{50.0\ \text{g} \times 1\ \text{mol}^{-1}}{46\ \cancel{\text{g}}} = 1.1\ \text{mol}$$

Finally, we now substitute into the above equation to obtain

$\Delta H_{V} = \frac{33\ \text{kJ}}{1.1\ \text{mol}}$

$= 30\ \text{kJ mol}^{-1}$

Example 2 85 g of ice at 0°C is dropped into a beaker of water. The mixture is then stirred continuously until all the ice is completely melted. Estimate the heat of fusion of water if the heat required to melt the ice completely was 25.85 kJ. What is the corresponding heat of freezing of water?

(H = 1, O = 16)

Solution 25.85 kJ of heat is required to melt the ice completely at 0°C. The heat of fusion is obtained from the relation

$$\Delta H_f = \frac{\text{Quantity of heat supplied}}{\text{Amount of ice melted}}$$

The amount of ice melted is obtained from the relation

$$n = \frac{m}{M}$$

$M = [(2 \times 1) + 16]\ \text{g mol}^{-1} = 18\ \text{g mol}^{-1}$
$m = 85\ \text{g}$
$n = ?$

Substituting we have

$$n = \frac{85\ \cancel{\text{g}} \times 1\ \text{mol}}{18\ \cancel{\text{g}}} = 4.7\ \text{mol}$$

Finally, we now substitute into the above equation to obtain

$$\Delta H_f = \frac{25.85\ \text{kJ}}{4.7\ \text{mol}}$$

$= 5.5\ \text{kJ mol}^{-1}$

As noted earlier, the heat of freezing is the opposite of the heat of fusion. All we need to do is to add the minus sign to this value to obtain

$$\Delta H_{fr} = -\,5.5\ \text{kJ mol}^{-1}$$

This means 5.5 kJ of heat has to be removed from one mole of water for freezing (solidification) to occur.

Example 3 The standard heat of sublimation of a substance is 57.5 kJ mol^{-1}. What is the standard heat of fusion of the substance if its standard heat of condensation is −42 kJ mol^{-1}?

Solution We have to apply the relation

$\Delta H^o_s = \Delta H^o_f + \Delta H^o_v$

$\therefore\ \Delta H^o_f = \Delta H^o_s - \Delta H^o_v$

$\Delta H^o_f = 57.5 \text{ kJ mol}^{-1}$

$\Delta H^o_v = -\Delta H^o_c = 42 \text{ kJ mol}^{-1}$

$\Delta H^o_f = ?$

Substituting we have

$\Delta H^o_f = 57.5 \text{ kJ mol}^{-1} - 42 \text{ kJ mol}^{-1}$

$= 15.5 \text{ kJ mol}^{-1}$

Example 4 Calculate the standard heat of sublimation of ice, given that its standard heats of fusion and vaporisation are 6.01 kJ mol^{-1} and 40.7 kJ mol^{-1} respectively.

Solution We have to apply the relation

$\Delta H^o_s = \Delta H^o_f + \Delta H^o_v$

$\Delta H^o_f = 6.01 \text{ kJ mol}^{-1}$

$\Delta H^o_v = 40.7 \text{ kJ mol}^{-1}$

$\Delta H^o_s = ?$

Substituting we have

$\Delta H^o_s = 6.01 \text{ kJ mol}^{-1} + 40.7 \text{ kJ mol}^{-1}$

$= 46.7 \text{ kJ mol}^{-1}$

Example 5 What quantity of heat is required to vaporise 2.50 dm^3 of water, given that the heat of vaporisation and density of water are 40.7 J mol^{-1} and 1 g cm^{-3} respectively?

(H = 1, O = 16)

Solution Since the heat of vaporisation would vaporise 1 mol of water, then the heat required to vaporise *n* mol of water is given by the equation

$$Q = n \times \Delta H_v$$

The amount of water is calculated as follows:
The density of a substance is given as

$$\rho = \frac{m}{V}$$

$\therefore\ m = r \times V$

$\rho = 1\ \text{g cm}^{-3}$

$V = 1000 \times 2.50\ \text{dm}^3 = 2500\ \text{cm}^3$

$m = ?$

We can now substitute to obtain

$$m = \frac{1\,\cancel{\text{g}} \times 2500\ \text{cm}^3}{1\,\cancel{\text{cm}^3}}$$

$= 2500$ g

In general, since the density of water is 1 g dm^{-3}, then the mass of x cm^3 of water is x g.

We can now work out the number of moles of water from the relation

$$n = \frac{m}{M}$$

$M = [(2 \times 1) + 16]\ \text{g mol}^{-1} = 18\ \text{g mol}^{-1}$

$n = ?$

Substituting we have

$$n = \frac{2500\,\cancel{\text{g}} \times 1\ \text{mol}}{18\,\cancel{\text{g}}} = 140\ \text{mol}$$

$\Delta H_v = 40.7\ \text{kJ mol}^{-1}$

$Q = ?$

Finally, we now substitute into the above relation to obtain

$$Q = 140\ \cancel{\text{mol}} \times \frac{40.7\ \text{kJ}}{1\,\cancel{\text{mol}}}$$

$= 57$ kJ

Practice Problems

1. 100.0 g of ammonia was vaporised by an electric heater when the current and voltage supplied were 0.24 A and 240 V respectively. What is the heat of vaporisation of ammonia if 25.5 g of the liquid was vaporised in 10 min. after it had reached its boiling point?

   (H = 1, N = 14)

   [Answer: 23 kJ mol^{-1}]
2. The heat of sublimation of a substance was experimentally determined to be 115 kJ mol^{-1}. What is the heat of freezing of the substance if its heat of vaporisation was determined to be 101 kJ mol^{-1}? [*Answer:* −14 kJ mol^{-1}]
3. What quantity of heat must be extracted from 50.00 cm^3 of sodium at its melting point of 98°C in order to freeze it completely? The heat of fusion of sodium is 2.6 kJ mol^{-1}.

   (Na = 11, r = 0.97 g cm^{-3}) [*Answer:* −11.4 kJ mol^{-1}]

9.3 HEAT (ENTHALPY CHANGE) OF REACTION

The heat, or enthalpy change of reaction, Δ*H* is the heat accompanying a chemical reaction. It is the difference between the heat contents (enthalpies) of reactants and products, i.e.

$$\Delta H = \sum H_p - \sum nH_r$$

where H_p = The enthalpy of products.

H_r = The enthalpy of reactants.

S is the Greek alphabet, sigma. It is used in mathematics to denote ‘summation of.’

A process (chemical or physical) that absorbs heat from its surroundings is called an endothermic process. In such a process, the heat contents of the products are greater than the heat contents of the reactants, and the heat of reaction is denoted with a plus sign. The reverse of this type of process is termed an exothermic process, denoted with a minus sign.

Since the heat of reaction is affected by several factors, then chemists have standard conditions under which it is measured. The value of Δ*H* obtained under these standard conditions is called the standard heat of reaction Δ*H*°. These conditions are:

- A temperature of 298 K.
- Normal atmospheric pressure, i.e. 1 atm.
- A concentration of 1 M for reactions involving aqueous solutions.

There are different types of heat of reaction, depending on the nature of the reaction under consideration.

Heat of formation: The heat of formation ΔH_f is the enthalpy change when one mole of a substance is formed from its elements. The standard heat of formation is the enthalpy change when one mole of a substance is formed from its elements under standard conditions.

Heat of neutralization: The heat of neutralization ΔH_n is the amount of heat evolved when one mole of hydrogen ions reacts with one mole of hydroxide ions to form one mole of water. The standard heat of neutralization ΔH^o_n is the quantity of heat evolved when one mole of hydrogen ions reacts with one mole of hydroxide ions, OH^-, to form one mole of water under standard conditions.

Heat of combustion: The heat of combustion ΔH_c is the heat evolved when one mole of a substance is burned completely in oxygen. The standard heat of combustion ΔH^o_n is the heat evolved when one mole of a substance is burned completely in oxygen under standard conditions.

Figure 9.1 Germain Henri Hess, Swiss-born Russian chemist (1802– 1850)

There are two ways of calculating heat of reaction. One of these methoΔS is to perform a relevant experiment, and calculate the heat of reaction from the data obtained. The second method is the theoretical approach of using Hess's law of constant heat summation. Hess's law states that the total enthalpy change of a chemical reaction is constant regardless of the route followed by the reaction, provided the conditions remain constant at the beginning and end of the reaction.

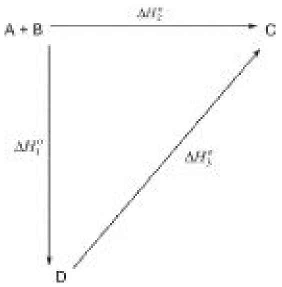
One way of using Hess's law is to calculate the standard heat of reaction as the algebraic difference between the sum of the standard heats of formation of the products and reactants:

$$\Delta H^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants})$$

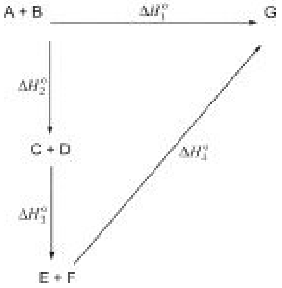
where ΔH° = The standard heat of reaction.
ΔH^o_f = The standard heat of formation.
n = Amount of reactants and products.

The standard enthalpies of formation of substances are given in thermodynamic tables. The enthalpies of formation of elements in their standard states are taken to be zero.

Hess's law can also be used to calculate the heat of reaction from the standard enthalpy changes of related reactions, which can be manipulated to give the desired reaction as their net reaction, e.g.



Then $\Delta H^o_2 = \Delta H^o_1 + \Delta H^o_3$



Then $\Delta H^o_1 = \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4$

With Hess's law, it is very easy to determine the heat of reaction by auditing or subtracting the heats of intermediate reactions. The intermediate reactions could be feasible or hypothetical. A hypothetical reaction is that which cannot be effected in practice, but given to help achieve a particular purpose. Our goal here is not to ascertain the feasibility of any intermediate reaction, but to be sure that the intermediate reactions can be manipulated to give the reaction whose enthalpy change is required. Once this is done, we can then calculate the desired enthalpy change by treating the heats of the intermediate reactions the same way the reactions were treated.

The following points summarise how the heat of reaction can be obtained from the heats of related reactions:

- When a reaction whose enthalpy change is required is the sum of the intermediate reactions, then the required heat of reaction is the sum of the heats of the intermediate reactions. For example, consider the reactions:

$$\mathrm{A + B \rightarrow C} \quad \Delta H^{o}_{1} \quad \mathrm{(I)}$$

$$\mathrm{C + D \rightarrow B + F} \quad \Delta H^{o}_{2} \quad \mathrm{(II)}$$

Adding the two equations we have

$$\mathrm{A + B \rightarrow C} \quad \Delta H^{o}_{1}$$

$$\mathrm{+\ C + D \rightarrow B + F} \quad \Delta H^{o}_{2}$$

$$\mathrm{A} + \cancel{\mathrm{B}} + \cancel{\mathrm{C}} + \mathrm{D} \rightarrow \cancel{\mathrm{C}} + \cancel{\mathrm{B}} + \mathrm{F} \quad \Delta H^{o}_{3}$$

Thus $\mathrm{A + D \rightarrow F} \quad \Delta H^{o}_{3} = \Delta H^{o}_{1} + \Delta H^{o}_{2}$

- When we subtract the intermediate reactions to obtain the reaction whose enthalpy change is required, then the required heat of reaction is obtained by subtracting the heats of the intermediate reactions. For example, consider the following reactions:

$$\mathrm{A + B \rightarrow C + F} \quad \Delta H^{o}_{1} \quad \mathrm{(I)}$$

$$\mathrm{A + B + F \rightarrow D} \quad \Delta H^{o}_{2} \quad \mathrm{(II)}$$

Subtracting Equation (I) from (II) we obtain

$$\mathrm{A + B \rightarrow C + F} \quad \Delta H^{o}_{1}$$

$$\mathrm{-\ A + B + F \rightarrow D} \quad \Delta H^{o}_{2}$$

$$\mathrm{-\ F \rightarrow C + F - D} \quad \Delta H^{o}_{3}$$

Thus $\mathrm{D \rightarrow C + 2F} \quad \Delta H^{o}_{3} = \Delta H^{o}_{1} + \Delta H^{o}_{2}$

- When we have to add and subtract series of intermediate reactions in order to obtain the reaction whose heat of reaction is required, then we must add and subtract the heats of the intermediate reactions in just the same way the reactions were added and subtracted. For example, consider the following reactions:

$$\mathrm{A + B \rightarrow C + F} \quad \Delta H^{o}_{1} \quad \mathrm{(I)}$$

$$\mathrm{A + B + F \rightarrow D} \quad \Delta H^{o}_{2} \quad \mathrm{(II)}$$

$$\mathrm{H \rightarrow I} \quad \Delta H^{o}_{3} \quad \mathrm{(III)}$$

Subtracting Equation (II) from (I) we obtain

$A + B \rightarrow C + F \quad \Delta H^{o}_{1}$

$- A + B + F \rightarrow D \quad \Delta H^{o}_{2}$

$-F \rightarrow C - D + F \quad \Delta H^{o}_{4} \quad \text{(IV)}$

Thus $D \rightarrow C + 2F \quad \Delta H^{o}_{4} = \Delta H^{o}_{1} + \Delta H^{o}_{2}$

Adding Equation (III) to (IV) we obtain

$H \rightarrow I \quad \Delta H^{o}_{3}$

$+ D \rightarrow C + 2F \quad \Delta H^{o}_{4}$

$H + D \rightarrow I + C + 2F \quad \Delta H^{o}_{5} \quad \text{(V)}$

Thus $\Delta H^{o}_{5} = \Delta H^{o}_{3} + \Delta H^{o}_{4} = \Delta H^{o}_{3} = \Delta H^{o}_{1} + \Delta H^{o}_{2}$

Hess’s law is based on the law of conservation of energy, which states that energy can neither be created nor destroyed, but can only be converted from one form to another. Thus during a chemical reaction the sum of the heat contents of the reactants and products is conserved.

Example 1 In a laboratory experiment to determine the heat of neutralization of sodium hydroxide and hydrochloric acid, 100.00 cm^3 of 0.50-M solutions of the two substances were mixed together. The initial temperature of the mixture was 25°C, while the final temperature of the reaction mixture was 28.4°C. Calculate the heat of neutralization.

(c (water) = 4.2 J $g^{-1} K^{-1}$, density of water = 1 g cm^{-3})

Solution We start by calculating the heat evolved by the reacting mixture:

$Q = m \times c \times (T_2 - T_1)$

$T_2 = 273\ K + 28.4°C = 301.4\ K$

The density of a substance is given by the relation

$r = \frac{m}{V}$

$\therefore\ m = r \times V$

$V = 200.00\ cm^3$

$r = 1\ g\ cm^{-3}$

$m = ?$

Substituting we have

$m = \frac{200.00\,\cancel{\text{cm}^3} \times 1\text{ g}}{1\,\cancel{\text{cm}^3}} = 200.00\text{ g}$

$c = 4.2\text{ J g}^{-1}\text{K}^{-1}$

$T_1 = 273\text{ K} + 25°\text{C} = 298\text{ K}$

$Q = ?$

We now substitute to obtain

$Q = \frac{200.00\,\cancel{\text{g}} \times 4.2\text{ J} \times (301.4 - 298)\,\cancel{\text{K}}}{1\,\cancel{\text{g}} \times 1\,\cancel{\text{K}}}$

Then $Q = 840\text{ J} \times 3.4 = 2856\text{ J}$

The next step is to work out the amounts of the reactants that evolved this quantity of heat:

$$n = C \times V$$

For HCl we have

$C = 0.50\text{ mol dm}^{-3}$

$V = 100.00\text{ cm}^3 = 0.100\text{ dm}^3$

$n = ?$

Substituting we obtain

$$n = \frac{0.50\text{ mol} \times 0.100\,\cancel{\text{dm}^3}}{1\,\cancel{\text{dm}^3}} = 0.050\text{ mol}$$

Alternatively, we can work from the first principle:

1000 cm^3 of 0.50-M solution of contains 0.50 mol, then 100 cm^3 will contain x, i.e.

$1000\text{ cm}^3 = 0.50\text{ mol}$

$100\text{ cm}^3 = x$

Thus $x \times 1000\text{ cm}^3 = 0.50\text{ mol} \times 100\text{ cm}^3$

$\therefore\ x = \frac{0.50\text{ mol} \times 100\,\cancel{\text{cm}^3}}{1000\,\cancel{\text{cm}^3}}$

$= 0.050\text{ mol}$

The amount of NaOH is also 0.050 mol because HCl and NaOH have equal concentration and volume. We can then proceed to say that 0.050 mol of HCl reacts with 0.050 mol of NaOH to evolve 2856 J of heat. The equation of reaction is

$$\mathrm{NaOH}(aq) + \mathrm{HCl}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

From the equation, 1 mol of NaOH reacts with 1 mol of HCl to form 1 mol of H_2O. Similarly, 0.050 mol of NaOH would react with 0.050 mol of HCl to form 0.050 mol of water. We must now calculate the heat of neutralization by recalling its definition: the heat evolved when 1 mol of an acid reacts with 1 mol of a base to produce 1 mol of water. Let this quantity of heat be *x*. Since the formation of 0.050 mol of water evolves 2856 J of heat, then the formation of 1 mol would evolve *x*, i.e.

$$x = \frac{2865\ \mathrm{J}}{0.050\ \mathrm{mol}}$$

$$= -57\ \mathrm{kJ\ mol^{-1}}$$

The minus sign shows that the reaction is exothermic, i.e. 57 kJ of heat is evolved during the reaction. This can be included in the equation as follows:

$$\mathrm{NaOH}(aq) + \mathrm{HCl}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)\ \Delta H = -57\ \mathrm{kJ\ mol^{-1}}$$

Example 2 The neutralization reaction between sulphuric acid and sodium hydroxide is represented as follows:

$$\mathrm{H_2SO_4}(aq) + 2\mathrm{NaOH}(aq) \rightarrow \mathrm{Na_2SO_4}(aq) + 2\mathrm{H_2O}(l)\ \Delta H = -114.2\ \mathrm{kJ}$$

Calculate the heat of neutralization.

Solution The key to this problem is to recall the definition of the heat of neutralization: the heat evolved when 1 mol of water is formed in a neutralization reaction. The above equation shows that the formation of 2 mol of water evolves 114.2 kJ of heat, then the formation of 1 mol would evolve *x*, i.e.

$$x = \frac{114.2\ \mathrm{kJ}}{2\ \mathrm{mol}}$$

$$= -57.1\ \mathrm{kJ\ mol^{-1}}$$

This is in agreement with the result obtained in the previous example. In general, the heats of neutralization of strong bases and strong aciΔS are approximately equal because they undergo complete ionization.

Example 3 What quantity of heat would be evolved when 20.0 g of sulphuric acid is completely neutralized by sodium hydroxide? The equation of reaction is

$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)\ \Delta H = -57.1\ \text{kJ mol}^{-1}$

(H = 1, O = 16, S = 32)

Solution We must start by calculating the amount of the acid:

$$n = \frac{m}{M}$$

$m = 20.0$ g

$M = [(2 \times 1) + 32 + (16 \times 4)]\ \text{g mol}^{-1} = 98\ \text{g mol}^{-1}$

$n = ?$

Substituting we obtain

$$n = \frac{20.0\ \cancel{g} \times 1\ \text{mol}}{98\ \cancel{g}} = 0.20\ \text{mol}$$

We now work out the amount of water that would be produced by this amount of the acid. From the equation, 1 mol of H_2SO_4 produces 2.0 mol of H_2O, then 0.20 mol of would produce x, i.e.

0.20 mol $= x$

1 mol $= 2$ mol

Thus $x \times 1\ \text{mol} = 0.20\ \text{mol} \times 2\ \text{mol}$

$$\therefore\ x = \frac{0.20\ \text{mol} \times 2\ \cancel{\text{mol}}}{1\ \cancel{\text{mol}}} = 0.40\ \text{mol}$$

Finally, we must now obtain the amount of heat change accompanying the production of this amount of water. From the equation, the production of 1 mol of H_2O evolves 57.1 kJ of heat, then the production of 0.40 mol would evolve x, i.e.

0.40 mol $= 57.1$ kJ

1 mol $= x$

Thus $x \times 1\ \text{mol} = 57.1\ \text{kJ} \times 0.40\ \text{mol}$

$$\therefore\ x = \frac{57.1\ \text{kJ} \times 0.40\ \cancel{\text{mol}}}{1\ \cancel{\text{mol}}}$$

$= 23$ kJ

Example 4 What is the heat of combustion of charcoal if 0.368 g of charcoal raises the temperature of 60.0 g of water by 50 K?

Solution We begin by calculating the quantity of heat required to raise the temperature of 60.0 g of water by 50 K:

$Q = m \times c \times \Delta T$

$\Delta T = 50\ \text{K}$

$m = 60.0\ \text{g}$

$c = 4.2\ \text{J g}^{-1}\text{K}^{-1}$

$Q = ?$

We will now substitute to obtain

$$Q = \frac{60.0\ \cancel{\text{g}} \times 4.2\ \text{J} \times 50\ \cancel{\text{K}}}{1\cancel{\text{g}} \times 1\cancel{\text{K}}} = 12.6\ \text{kJ}$$

We now calculate the amount of charcoal, an allotrope of carbon, burnt:

$n = \frac{m}{M}$

$m = 0.368\ \text{g}$

$M = 12\ \text{g mol}^{-1}$

$n = ?$

$\therefore\ n = \frac{0.368\ \cancel{\text{g}} \times 1\ \text{mol}}{12\cancel{\text{g}}} = 0.031\ \text{mol}$

This amount of charcoal raises the temperature of 60.0 g of water by 50 K. Thus 0.031 mol of charcoal evolves 12.6 kJ of heat. To obtain the heat of combustion of charcoal from this data, we have to recall the definition of the heat of combustion: the heat evolved when 1 mol of a substance is completely burnt in oxygen. If this is *x*, then

$x = \frac{12.6\ \text{kJ}}{0.031\ \text{mol}}$

$= -410\ \text{kJ mol}^{-1}$

The minus sign shows that combustion is an exothermic process.

Example 5 What is the enthalpy change for the reaction $2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)$?

$(\Delta H^{o}_{f}\ [\text{CO}_2(g)] = -393.5\ \text{kJ mol}^{-1},\ \Delta H^{o}_{f}\ [\text{CO}(g)] = -110.5\ \text{kJ mol}^{-1})$

Solution This problem illustrates how the standard heat of reaction is obtained from the standard heats of formation of reactants and products. Using Hess's law we have

$$\Delta H^o = \sum n\Delta H_f^o\,(\text{products}] - \sum n\Delta H_f^o\,(\text{reactants}]$$

There are 2 mol of the product, CO_2. Thus

$$\sum n\Delta H_f^o\,(\text{products}) = 2\text{ mol} \times \Delta H_f^o[CO_2\,(g)]$$

So $\sum n\Delta H_f^o\,(\text{products}) = 2\,\cancel{\text{mol}} \times \frac{(-393.5\text{ kJ})}{\cancel{1\text{mol}}} = -787\text{ kJ}$

There are 2 mol of CO and 1 mol of O_2. We must also remember that O_2 is in its standard state, making its ΔH^o_f to be zero. Thus

$$\sum n\Delta H_f^o\,(\text{reactants}) = 2\text{ mol} \times \Delta H_f^o[CO(g)]$$

So $\sum n\Delta H_f^o\,(\text{reactantz}) = 2\,\cancel{\text{mol}} \times \frac{(-110.5\text{ kJ})}{1\cancel{\text{mol}}} = -221\text{ kJ}$

Finally, we now substitute to obtain

$\Delta H^o = -787\text{ kJ} - (-221\text{ kJ}) = -787\text{ kJ} + 221\text{ kJ}$

$= -556\text{ kJ}$

Example 6 The combustion of methane is represented by the equation $CH_4(g) + O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$. What is the heat of combustion of the compound?

$(\Delta H^o_f\ [CH_4(g)] = -74.8\text{ kJ mol}^{-1}$, $\Delta H^o_f\ [CO_2(g)] = -393.5\text{ kJ mol}^{-1}$,

$\Delta H^o_f\ [H_2O(g)] = -241.8\text{ kJ mol}^{-1})$

Solution The heat of combustion of methane is the heat of reaction. We have to apply the relation

$$\Delta H^o = \sum n\Delta H_f^o\,(\text{products}) - \sum n\Delta H_f^o\,(\text{reactants})$$

The products contain 1 mol of $CO_2(g)$ and 2 mol of $H_2O(g)$. Thus

$$\sum n\Delta H_f^o\,(\text{products}) = 1\text{ mol} \times \Delta H_f^o[CO_2\,(g)] + 2\text{ mol} \times \Delta H_f^o[H_2O\,(g)]$$

Thus $\sum n\Delta H_f^o\,(\text{products}) = 1\text{ mol} \times x + 2\text{ mol} \times \Delta H_f^o[H_2O\,(l)]$

= −393.5 kJ − 483.6 kJ = −877.1 kJ

The reactants consist of 1 mol each of $CH_4(g)$ and $O_2(g)$. Thus

$\sum n\Delta H_f^\circ(\text{reactants})$ = 1 mol × ΔH^o_f $[CH_4(g)]$

Then $\sum n\Delta H_f^\circ(\text{reactants})$ = $1\,\cancel{\text{mol}} \times \frac{(-74.8\text{ kJ})}{1\,\cancel{\text{mol}}}$ −74.8 kJ

Finally, we now substitute to obtain

ΔH^o = −877.1 kJ − (−74.8 kJ)

= −877.1 kJ + 74.8 kJ

= −802.3 kJ

Since the equation involves the combustion of 1 mol of methane, then the heat of combustion of the compound is −802.3 kJ mol^{-1}.

Example 7 The neutralization reaction between calcium hydroxide and sulphuric acid is given by the equation

$$Ca(OH)_2(aq) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + 2H_2O(l)$$

What is the heat of formation of $CaSO_4(aq)$ if the heat of reaction is –111.67 kJ?

(ΔH^o_f $[Ca(OH)_2(aq)]$ = −1002.82 kJ mol^{-1}, ΔH^o_f $[H_2SO_4(aq)]$ = −909.27 kJ mol^{-1}, ΔH^o_f $[H_2O(l)]$ = −285.83 kJ mol^{-1})

Solution We have to apply the relation

$$\Delta H^o = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ[\text{reactants}]$$

Let the ΔH^o_f of $CaSO_4$ by *x*. The products consist of 1 mol of $CaSO_4(aq)$ and 2 mol of $H_2O(l)$. Thus

$$\sum n\Delta H_f^\circ(\text{products}) = 1\text{ mol} \times x + 2\text{ mol} \times \Delta H_f^\circ[H_2O(l)]$$

So $\sum n\Delta H_f^\circ(\text{products}) = 1\text{ mol} \times x + 2\,\cancel{\text{mol}} \times \frac{(-285.83\text{ kJ})}{1\,\cancel{\text{mol}}}$

= (1 mol × *x*) – 571.66 kJ

The reactants consist of 1 mol of $Ca(OH)_2(aq)$ and 2 mol of $HCl(aq)$. Thus

$\sum n\Delta H^\circ_f\text{(reactants)}$ = 1 mol × ΔH^o_f [$Ca(OH)_2(aq)$] + 1 mol × ΔH^o_f [$H_2SO_4\ (aq)$]

Thus $\sum n\Delta H^\circ_f\text{(reactants)} = 1\,\cancel{\text{mol}} \times \frac{(-1002.82\text{ kJ})}{1\,\cancel{\text{mol}}} + 1\,\cancel{\text{mol}} \times \frac{(-909.27\text{kJ})}{1\,\cancel{\text{mol}}}$

$= -\ 1002.82\text{ kJ} - 909.27\text{ kJ} = -\ 1912.14\text{ kJ}$

$\Delta H^o = -\ 111.67\text{ kJ}$

$x = ?$

We now substitute to obtain

$-111.67\text{ kJ} = (1\text{ mol} \times x - 571.66\text{ kJ}) - (-1912.09\text{ kJ})$

So $-111.67\text{ kJ} = 1\text{ mol} \times x - 571.66\text{ kJ} + 1912.09\text{ kJ}$

We now collect the like terms to obtain

$1\text{ mol} \times x = 571.66\text{ kJ} - 1912.09\text{ kJ} - 111.67\text{ kJ} = -1452.10\text{ kJ}$

$\therefore\ x = \frac{-1452.10\text{ kJ}}{1\text{ mol}}$

$= -1452.10\text{ kJ mol}^{-1}$

Example 8 The dissolution of calcium oxide is represented by the equation $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$. What is the heat of solution of calcium oxide?

(ΔH^o_f [$CaO(s)$] = −635.09 kJ mol^{-1}, ΔH^o_f [$H_2O(l)$)] = −285.83 kJ mol^{-1}, ΔH^o_f [$Ca(OH)_2(aq)$] = −1002.82 kJ mol^{-1})

Solution The heat of solution of $CaO(s)$ is the enthalpy change of the reaction. We have to apply the relation

$$\Delta H^o = \sum n\Delta H^\circ_f\text{(products)} - \sum n\Delta H^\circ_f\text{(reactants)}$$

The product consists of 1 mol of $Ca(OH)_2(aq)$. Thus

$\sum n\Delta H^\circ_f\text{(products]}$ = 1 mol × ΔH^o_f [$Ca(OH)_2(aq)$]

Then $\sum n\Delta H^\circ_f\text{(products]} = 1\,\cancel{\text{mol}} \times \frac{(-1002.82\text{ kJ})}{1\,\cancel{\text{mol}}}\ -1002.82\text{ kJ}$

The reactants consist of 1 mol each of $CaO(s)$ and $H_2O(l)$. Thus

$\sum n\Delta H^\circ_f\text{(reactants)}$ = 1 mol × ΔH^o_f [$CaO(s)$] + 1 mol × ΔH^o_f [$H_2O(l)$]

So $\sum n\Delta H^\circ_f\,(\text{reactants}) = 1\,\cancel{\text{mol}} \times \frac{(-635.09\text{ kJ})}{1\,\cancel{\text{mol}}} + 1\,\cancel{\text{mol}} \times \frac{(-285.83\text{ kJ})}{1\,\cancel{\text{mol}}}$

$= -635.09\text{ kJ} - 285.83\text{ kJ} = -920.92\text{ kJ}$

$\Delta H^\circ = ?$

Substituting we have

$\Delta H^\circ = -1002.82\text{ kJ} - (-920.92\text{ kJ})$

$= -1002.82\text{ kJ} + 920.92\text{ kJ}$

$= -81.90\text{ kJ}$

Since 1 mol of CaO was dissolved, then the standard heat of formation of the compound is −81.90 kJ mol^{-1}.

Example 9 Calculate the heat of formation of water vapour from liquid water from the information provided below.

$H_2(g) + ½O_2(g) \rightarrow H_2O(l)\quad \Delta H^\circ_c = -285.85\text{ kJ mol}^{-1}$

$H_2(g) + ½O_2(g) \rightarrow H_2O(g)\quad \Delta H^\circ_c = -241.82\text{ kJ mol}^{-1}$

Solution The equation for the formation of water vapour from liquid water is

$$H_2O(l) \rightarrow H_2O(g)\ \Delta H^\circ_f = ?$$

By applying Hess's law, we can obtain this equation by subtracting the first equation from the second:

$H_2(g) + ½O_2(g) \rightarrow H_2O(g)\quad \Delta H^\circ_2$

$- H_2(g) + ½O_2(g) \rightarrow H_2O(l)\quad \Delta H^\circ_1$

$\rightarrow H_2O(g) - H_2O(l)\quad \Delta H^\circ_3$

Thus $H_2O(l) \rightarrow H_2O(g)\quad \Delta H^\circ_3 = \Delta H^\circ_2 - \Delta H^\circ_1$

$\Delta H^\circ_1 = -285.85\text{ kJ mol}^{-1}$

$\Delta H^\circ_2 = -241.82\text{ kJ mol}^{-1}$

$\Delta H^\circ_3 = ?$

Substituting we have

$\Delta H^\circ_3 = -241.82\text{ kJ mol}^{-1} - (-285.85\text{ kJ mol}^{-1})$

$= -241.82\text{ kJ mol}^{-1} + 285.85\text{ kJ mol}^{-1}$

$= 44.03\text{ kJ mol}^{-1}$

Thus 44.03 kJ of heat must be supplied to 1 mol of water to form 1 mol of water vapour.

Example 10 Calculate the heat of formation of carbon dioxide from the heats of combustion of carbon and carbon monoxide as given below:

$C(s) + ½O_2(g) \rightarrow CO(g) \;\; \Delta H^o_c = -110.5 \text{ kJ mol}^{-1}$

$CO(g) + ½O_2(g) \rightarrow CO_2(g) \;\; \Delta H^o_c = -283 \text{ kJ mol}^{-1}$

Solution The equation for the formation of carbon dioxide from its standard elements is

$$C(s) + O_2(g) \rightarrow CO_2(g) \; \Delta H^o_f = ?$$

By applying Hess's law, we can easily obtain the heat of reaction, i.e., the heat of formation ΔH^o_f of carbon dioxide from the equations provided above, provided we can get a way of obtaining this equation from the equations. This is done by summing the two equations:

$C(s) + ½O_2(g) \rightarrow CO(g) \;\; \Delta H^o_1$

$+ \; CO(g) + ½O_2(g) \rightarrow CO_2(g) \;\; \Delta H^o_2$

$C(s) + \cancel{CO}(g) + O_2(g) \rightarrow \cancel{CO}(g) + CO_2(g) \;\; \Delta H^o_3$

Thus $C(s) + O_2(g) \rightarrow CO_2(g) \;\; \Delta H^o_3 = \Delta H^o_f = \Delta H^o_1 + \Delta H^o_2$

$\Delta H^o_1 = -110.5 \text{ kJ mol}^{-1}$

$\Delta H^o_f = -283 \text{ kJ mol}^{-1}$

$\Delta H^o_f = ?$

Substituting we have

$\Delta H^o_f = -110.5 \text{ kJ mol}^{-1} + (-283 \text{ kJ mol}^{-1})$

$= -110.5 \text{ kJ mol}^{-1} - 283 \text{ kJ mol}^{-1}$

$= -393.5 \text{ kJ mol}^{-1}$

Example 11 Calculate the heat of formation of butane from the information given below:

$C_4H_{10}(g) + 13/2O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g) \;\; \Delta H^o_c = -2878 \text{ kJ mol}^{-1}$

$\Delta H^o_f \, [CO_2(g)] = -393.51 \text{ kJ mol}^{-1}$

$\Delta H^o_f \, [H_2O(l)] = -285.83 \text{ kJ mol}^{-1}$

Solution The equation for the formation of butane from its standard elements, i.e., the reaction whose enthalpy change is required is

$4C(s) + 5H_2(g) \rightarrow C_4H_{10}(g) \;\; \Delta H^o_f = ? \;\; \text{(I)}$

We must now look for a way of obtaining this equation from the information given above. The equations for the last two data are not given, but we should have no problem with writing the equations for the formation of carbon dioxide and water, which are:

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^o_f = -393.51$ kJ mol^{-1} (II)

$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$ $\Delta H^o_f = -285.83$ kJ mol^{-1} (III)

To obtain the equation for the formation of butane we proceed as follows:
We first add 4 times Equation (II) to 5 times Equation:

$4 \times [C(s) + O_2(g) \rightarrow CO_2(g)]$ $\Delta H^o_f = -393.51$ kJ mol^{-1}

$+ 5 \times [H_2(g) + ½O_2(g) \rightarrow H_2O(g)]$ $\Delta H^o_f = - 285.83$ kJ mol^{-1}

$4C(s) + 5H_2(g) + 13/2O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$ $\Delta H^o_f = - 3003.19$ kJ mol^{-1} (IV)

Finally, we now subtract Equation (I) from (IV):

$4C(s) + 5H_2(g) + 13/2O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$ $\Delta H^o_f = - 3003.19$ kJ mol^{-1}

$- C_4H_{10}(g) + 13/2O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$ $\Delta H^o_f = - 2878$ kJ mol^{-1}

$4C(s) + 5H_2(g) \rightarrow C_4H_{10}(g)$ $\Delta H^o_f = - 125.19$ kJ mol^{-1}

Thus $4C(s) + 5H_2(g) \rightarrow C_4H_{10}(g)$ $\Delta H^o_f = - 125.19$ kJ mol^{-1}

So, the standard heat of formation of butane is −125.19 kJ mol^{-1}.

Example 12 Calculate the standard heat of combustion of benzene from the information given below:

$6C(s) + 3H_2(g) \rightarrow C_6H_6(l)$ $\Delta H^o_f = 49.00$ kJ mol^{-1} (I)

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^o_f = -393.51$ kJ mol^{-1} (II)

$H_2(g) + ½O_2(g) \rightarrow H_2O(g)$ $\Delta H^o_f = - 241.81$ kJ mol^{-1} (III)

Solution The equation for the combustion of benzene is

$C_6H_6(l) + 15/2O_2(g) \rightarrow 6CO_2(g) + 3H_2O(g)$ $\Delta H^o_c = ?$

To obtain this equation, we first add 6 times Equation (II) to 3 times Equation (III), i.e.

$6 \times [C(s) + O_2(g) \rightarrow CO_2(g)]$ $\Delta H^o_f = -393.51$ kJ mol^{-1}

$+ 3 \times [H_2(g) + ½O_2(g) \rightarrow H_2O(g)]$ $\Delta H^o_f = - 241.81$ kJ mol^{-1}

$3H_2(g) + 6C(s) + 15/2O_2(g) \rightarrow 6CO_2(g) + 3H_2O(g)$ $\Delta H^o_c = - 3086.52$ kJ mol^{-1} (IV)

Finally, we now subtract Equation (I) from (IV), i.e.

$3H_2(g) + 6C(s) + 15/2O_2(g) \rightarrow 6CO_2(g) + 3H_2O(g)$ $\Delta H^o_c = -3086.52$ kJ mol^{-1}

$-\ 6C(s) + 3H_2(g) \rightarrow C_6H_6\ (l)$ $\Delta H^o_f = 49.00$ kJ mol^{-1}

$15/2O_2(g) \rightarrow -\ C_6H_6\ (l) + 6CO_2(g) + 3H_2O(g)$ $\Delta H^o_c = -3135.52$ kJ mol^{-1}

Thus $C_6H_6(l) + 15/2O_2(g) \rightarrow 6CO_2(g) + 3H_2O(g\ \Delta H°_c)$ $= -3135.52$ kJ mol^{-1}

So, the standard heat of combustion[4] of benzene is −3135.52 kJ mol^{-1}.

Practice Problems

1. Zinc reacts with copper(II) sulphate according to the equation

   $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Zn(s)$ $\Delta H = -216$ kJ mol^{-1}

   What quantity of heat would be evolved when 5.0 g of zinc reacts with copper(II) sulphate?

   (Zn = 65) [*Answer:* 17 kJ]

2. The combustion of glucose in living tissues is represented by the equation

   $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$ $\Delta H = -2816$ kJ mol^{-1}

   What quantity of heat would be evolved when 200.0 g of glucose is burnt completely in oxygen?

   (H = 1, C = 12, O = 16) [*Answer:* 3100 kJ]

3. The dissolution of 10.0 g of ammonium nitrate, NH_4NO_3, absorbs 3287.5 J of heat. What is the heat of solution of the compound?

   (H = 1, N = 14, O = 16) [*Answer:* 26.3 kJ mol^{-1}]

4. The equation for the formation of methane is given below:

   $C(s) + 2H_2(g) \rightarrow CH_4(g)$ $\Delta H = -75$ kJ mol^{-1}

   What quantity of heat would be evolved when 20.0 g of methane is formed?

   (H = 1, C = 12) [*Answer:* 94 kJ]

5. Carbon and nitric acid react according to the equation

   $$C(s) + 4HNO_3(aq) \rightarrow 2H_2O(l) + 4NO_2(g) + CO_2(g)$$

   What is the enthalpy of formation of $HNO_3(aq)$ if 625.09 kJ of heat is evolved in the process?

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[4] As the equation shows, this refer to the situation in which the combusion reaction involves the formation of water vapour. The result for the combustion involving the formation of liquid water is –3276.55 kJ mol^{-1}.

(ΔH^o_f = [$CO_2(g)$] = −285.83 kJ mol^{-1},ΔH^o_f = [$NO_2(g)$] = 33.18 kJ mol^{-1},ΔH^o_f = [$CO_2(g)$] = −393.51 kJ mol^{-1}) [*Answer:* −207.36 kJ mol^{-1}]

6. The heats of combustion of methane, hydrogen and graphite (carbon) are given as follows:

$C(s) + O_2(g) \rightarrow CO_2(g)\ \Delta H^o_c = -393.51$ kJ mol^{-1} (I)

$H_2(g) + ½O_2(g) \rightarrow H_2O(l)\ \ \Delta H^o_c = -285.83$ kJ mol^{-1} (II)

$CH_4(g) + O_2(g) \rightarrow CO_2(g) + 2H_2O(l)\ \ \Delta H^o_c = -888.70$ kJ mol^{-1} (III)

Calculate the enthalpy of formation of methane.

[*Answer:* −75.17 kJ mol^{-1}]

9.3.1 Temperature Dependence of Heat of Reaction

Gustav-Robert Kirchhoff formulated a law that relates the heats of reaction at two different temperatures. This law, known as Kirchhoff's law, states that the difference in the enthalpies of a reaction at two different temperatures is the same as the difference in the enthalpies of heating the reactants and products through the same temperature difference at constant pressure.

Figure 9.2 Gustav-Robert Kirchhoff, German physicist (1824–1887).

To derive the Kirchhoff equation, we have to begin from the fundamental concept of enthalpy, ie

$$\Delta H = \sum H_P - \sum H_r \quad (9.1)$$

Since enthalpy varies with temperature, we can develop a differential relatilonship between enthalpy and temperature by differentiating Equation (9.1) at constant pressure:

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \left(\frac{\partial \sum H_P}{\partial T}\right)_P - \left(\frac{\partial \sum H_P}{\partial T}\right)_P \quad (9.2)$$

The molar heat capacity $C_{p,m}$ of a substance at constant pressure is defined as

$$C_{p,m} = \left(\frac{\partial H}{\partial T}\right)_p \quad (9.3)$$

Substituting Equation (9.3) into (9.2) we obtain

$$\left(\frac{\partial \Delta H}{\partial T}\right)_p = \sum C_{p,m} - \sum C_{p,m}$$

Thus $\left(\frac{\partial \Delta H}{\partial T}\right)_p = \mathrm{D}C_{p,m}$ (9.4)

We now change the partial derivative sign to exact differential to integrate Equation (9.4):

$$\frac{\mathrm{d}\Delta H}{\mathrm{d}T} = \mathrm{D}C_{p,m} \quad (9.5)$$

Cross-multiplying Equation (9.5) we have

$$\mathrm{d}\Delta H = \mathrm{D}C_{p,m}\mathrm{d}T \quad (9.6)$$

We can now integrate Equation (9.6) between the limits $\Delta H = \Delta H_{T1}$ at T_1 and $\Delta H = \Delta H_{T2}$ at T_2:

$$\int_{\Delta H_{T_1}}^{\Delta H_{T_2}} \mathrm{d}\Delta H = \int_{T_1}^{T_2} \Delta C_{p,m}\mathrm{d}T \quad (9.7)$$

We can be confronted with the following two situations:

- When the heat capacity $C_{p,m}$ over a particular temperature range, then $\mathrm{D}C_{p,m}$ comes out of the integral sign, such that integral becomes

  $$\Delta H_{T2} - \Delta H_{T1} = \mathrm{D}C_{p,m}(T_2 - T_1)$$

  So $\Delta H_{T2} = \Delta H_{T1} + \mathrm{D}C_{p,m}(T_2 - T_1)$ (9.8)

  Equation (9.8) is the Kirchhoff’s equation for the temperature dependence of heat of reaction at constant heat capacity.

- When $C_{p,m}$ is not constant, i.e., given as a function of temperature, then we can only integrate the left-hand side of Equation (9.7) to obtain

  $$\Delta H_{T2} = \Delta H_{T1} + \int_{T_1}^{T_2} \Delta C_{p,m}\mathrm{d}T \quad (9.9)$$

Since the standard enthalpies of reactions are usually specified at 298 K, then it is convenient to relate the enthalpy at any other temperature to that at 298 K because of data availability. We can now rewrite Equations (9.8) and (9.9) as follows:

$$\Delta H_{T2} = \Delta H^{o} + \mathrm{D}C_{p,m}(\mathrm{T}_2 - 298\ \mathrm{K}) \quad \text{when } T_2 > 298\ \mathrm{K}$$

$$\Delta H_{T2} = \Delta H^{o} + \int_{T_2}^{298\mathrm{K}} \Delta C_{p,m}\, \mathrm{d}T \quad \text{when } T_2 < 298\ \mathrm{K}$$

$$\Delta H_{T2} = \Delta H^{o} + \int_{298\mathrm{K}}^{T_2} \Delta C_{p,m}\, \mathrm{d}T \quad \text{when } T_2 > 298\ \mathrm{K}$$

where $\mathrm{D}C_p = \sum n C_{p,m}(\text{products}) - \sum n C_{p,m}(\text{reactants})$

n = Number of moles of a gas.

$C_{p,m}$ = Molar heat capacity at constant pressure.

Example 1 The standard heat of formation of water vapour is −241.81 kJ mol^{-1}. Determine the heat of formation of water at 100°C if the heat capacities at constant pressure of hydrogen, oxygen, and water vapour are 28.8 J K^{-1} mol^{-1}, 29.4 J K^{-1} mol^{-1} and 38.6 J K^{-1} mol^{-1} respectively for the given temperature range. The equation of reaction is

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g)$$

Solution Here, the molar heat capacities are given as constants. Thus we have to apply the relation

$$\Delta H_{T1} = \Delta H^{o} + \mathrm{D}C_{p,m}(T_2 - 298\ \mathrm{K})$$

$$\mathrm{D}C_p = \sum n C_{p,m}(\text{products}) - \sum n C_{p,m}(\text{reactants})$$

$$\sum n C_{p,m}(\text{products}) = 1\ \mathrm{mol} \times C_{p,m}(H_2O)$$

$$\text{So } \sum n C_{p,m}(\text{products}) = 1\cancel{\mathrm{mol}} \times \frac{38.6\ \mathrm{J\ K^{-1}}}{1\cancel{\mathrm{mol}}} = 38.6\ \mathrm{J\ K^{-1}}$$

$$\sum n C_{p,m}(\text{reactants}) = 1\ \mathrm{mol} \times C_{p,m}(H_2) + \tfrac{1}{2}\ \mathrm{mol} \times C_{p,m}(O_2)$$

$$\text{So } \sum n C_{p,m}(\text{reactants}) = 1\cancel{\mathrm{mol}} \times \frac{28.8\ \mathrm{J\ K^{-1}}}{1\cancel{\mathrm{mol}}} + 1/2\cancel{\mathrm{mol}} + \frac{28.8\ \mathrm{J\ K^{-1}}}{1\cancel{\mathrm{mol}}}$$

$$= 28.8\ \mathrm{J\ K^{-1}} + 14.7\ \mathrm{J\ K^{-1}} = 43.5\ \mathrm{J\ K^{-1}}$$

Substituting we have

$\mathrm{D}C_{p,m}$ = 38.6 J K^{-1} – 43.5 J K^{-1} = − 4.9 J K^{-1}

T_2 = 273 K + 100°C = 373 K

ΔH^o = − 241810 J

ΔH_{T2} = ?

Substituting we have

$$\Delta H_{T2} = -241810\ \mathrm{J} + \left(-\frac{4.9\ \mathrm{J}}{1\ \cancel{\mathrm{K}}}\right) \times (373 - 298)\ \cancel{\mathrm{K}}$$

Thus ΔH_{T2} = − 241810 J – 367.5 J

= − 242.2 kJ

Since only 1 mol of water vapour is formed, then the heat of formation at 100°C is − 242.2 kJ mol^{-1}.

Example 2 The standard enthalpy of formation of ammonia gas is −46.1 kJ mol^{-1}. At what temperature would its heat of formation become −50 kJ mol^{-1}. The molar heat capacity equations for the temperature range are given below:

$C_{p,m}$ (J K^{-1} mol^{-1})

$N_2(g)$	$27.9 + 4.18 \times 10^{-3} T$
$H_2(g)$	$29.6 + 2.31 \times 10^{-3} T$
$NH_3(g)$	$29.9 + 2.61 \times 10^{-3} T$

The equation of reaction $N_2(g) + 3/2H_2(g) \rightarrow NH_3(g)$.

Solution The molar heat capacities are not constant. Since $\Delta H_{T2} > \Delta H^o$, then T_2 > 298 K. Thus we have to apply the relation

$$\Delta H_{T2} = \Delta H^o + \int_{298\mathrm{K}}^{T_2} \Delta C_{p,m}\, \mathrm{d}T$$

$$\mathrm{D}C_p = \sum n C_{p,m}(\text{products}) - \sum n C_{p,m}(\text{reactants})$$

$$\sum n C_{p,m}(\text{products}) = 1\ \mathrm{mol} \times C_{p,m}\,(NH_3)$$

$$\text{Thus}\ \sum n C_{p,m}(\text{products}) = 1\ \cancel{\mathrm{mol}} \times \frac{(29.9 + 2.61 \times 10^{-3}\, T)\ \mathrm{J\ K^{-1}}}{1\ \cancel{\mathrm{mol}}}$$

$= 29.9 + 2.61 \times 10^{-3}\, T\ \mathrm{J\ K^{-1}}$

$\sum nC_{p,m}(\text{reactants})$ = 1 mol × $C_{p,m}(N_2)$ + 3/2mol × $C_{p,m}(H_2)$

So $\sum nC_{p,m}(\text{reactants})$ = $1\cancel{\text{mol}} \times \dfrac{[29.6 + 2.31\times10^{-3}T]\text{ J K}^{-1}}{1\cancel{\text{mol}}}$

$+ 3/2\ \cancel{\text{mol}} \times \dfrac{[29.6 + 2.31\times10^{-3}T]\text{ J K}^{-1}}{1\cancel{\text{mol}}}$

= 27.9 + 4.18 × 10^{-3} T J K^{-1} + 44.4 + 3.47×10^{-3} T J K^{-1}

= 72.3 + 7.65 × 10^{-3} T J K^{-1}

We now substitute to obtain

D$C_{p,m}$ = 29.9 + 2.61 × 10^{-3} T J K^{-1} − 72.3 + 7.65 × 10^{-3} T J K^{-1} = −42.4 − 5.04×10^{-3} T J K^{-1}

ΔH^o = − 46100 J

ΔH_{T2} = − 50000 J

T_2 = ?

Substituting we have

$$-50000 \text{ J} = -46100 \text{ J} + \int_{298K}^{T_2} (-42.4 - 5.04\times10^{-3}T) \text{ J K}^{-1}\, dT$$

For convenience we omit the units to obtain

$$\left[-42.4T - \frac{5.04\times10^{-3}T^2}{2}\right]_{298}^{T_2} = -50000 + 46100 = -3900$$

Then – 42.4T_2 – 2.52 × $10^{-3}T_2^2$ – (–12635.2 – 223.8) = − 3900

So – 42.4T_2 – 2.52 × $10^{-3}T_2^2$ + 12859 + 3900 = 0

Thus – 2.52 × $10^{-3}T_2^2$ + 42.4T_2 + 3900 = 0

We now have to solve this equation using the quadratic formula

$T_2 = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

a = − 2.52×10^{-3}, b = − 42.4, c = 16759

Substituting we have

$$T_2 = \frac{-(-42.4) \pm \sqrt{[-42.4]^2 - 4\left(-2.52\times10^{-3}\right)[16759]}}{2[-2.52\times10^{-3}]}$$

Then $T_2 = \frac{42.4 + \sqrt{1949.8}}{-5.04\times10^{-3}}$

So $T_2 = \frac{42.4 + 44.2}{-5.04\times10^{-3}}$ or $T_2 = \frac{42.4 - 44.2}{-5.04\times10^{-3}}$

$\therefore$ $T_2 = -17142.9$ K or $T_2 = 396.8$ K

Since the temperature cannot be negative, then our final answer should be 396.8 K.

Example 3 The heat of formation of hydrogen chloride is −92.3 kJ mol^{-1} at 25°C. Use the information given below to calculate the heat of formation at 500°C.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

$C_{p,m}$ (J K^{-1} mol^{-1})

$H_2(g)$ $27.8 + 3.4\times10^{-3}T$

$Cl_2(g)$ $34.8 + 2.4\times10^{-3}T$

$HCl(g)$ $28.1 + 3.5\times10^{-3}T$

Solution We have to apply the relation

$$\Delta H_{T2} = \Delta H^o + \int_{298\text{K}}^{T_2} \Delta n C_{p,m}\, dT$$

$$\text{D}C_p = \sum nC_{p,m}(\text{products}) - \sum nC_{p,m}(\text{reactants})$$

$$\sum nC_{p,m}(\text{products}) = 2 \text{ mol} \times C_{p,m} (\text{HCl})$$

Then $\sum nC_{p,m}(\text{products}) = 2\cancel{\text{mol}} \times \frac{[28.1 + 3.5\times10^{-3}T] \text{ J K}^{-1}}{1\cancel{\text{mol}}}$

$= 56.2 + 7.0 \times 10^{-3}\, T \text{ J K}^{-1}$

$\sum nC_{p,m}(\text{reactants}) = 1 \text{ mol} \times C_{p,m}(H_2) + 1 \text{ mol} \times C_{p,m}(Cl_2)$

So $\sum nC_{p,m}(\text{reactants})$ $= 1\,\cancel{\text{mol}} \times \dfrac{[27.8 + 3.4 \times 10^{-3}T)\ \text{J K}^{-1}}{1\,\cancel{\text{mol}}}$

$+ 1\,\cancel{\text{mol}} \times \dfrac{[34.8\ \ 2.4\ \ 10^{-3}T)\ \text{J K}^{-1}}{1\,\cancel{\text{mol}}}$

$= 27.8 + 3.4\times10^{-3}T$ J K^{-1} $+ 34.8 + 2.4\times10^{-3}T$ J K^{-1}

$= 62.6 + 5.8\times10^{-3}\ T$ J K^{-1}

We now substitute to obtain

D$C_{p,m}$ $= 56.2 + 7.0 \times 10^{-3}\ T$ J K^{-1} $- 62.6 + 5.8 \times 10^{-3}\ T$ J K^{-1}

$= -6.4 + 1.2 \times 10^{-3}\ T$ J K^{-1}

Since the equation involves the formation of 2 mol of the compound, then

ΔH^{o} $= 2 \times -92300$ J $= -184600$ J

T_1 $= 273$ K $+ 25°$C $= 298$ K

T_2 $= 273$ K $+ 500°$C $= 773$ K

ΔH_{T2} $= ?$

Substituting into the original equation we have

ΔH_{T2} $= -184600$ J $+ \int_{298\,\text{K}}^{773\,\text{K}}\left(-6.4 + 1.2\times10^{-3}T\right)\text{J K}^{-1}$

Thus ΔH_{T2} $= -184600$ J $+ \left[\left(-6.4T + \dfrac{1.2\times10^{-3}T^{2}}{2}\right)\text{J K}^{-1}\right]_{298\,\text{K}}^{773\,\text{K}}$

Then ΔH_{T2} $= -184600$ J $+ (-6.4 \times 773 + 6.0 \times 10\text{–}4 \times 773^{2})\dfrac{\text{J}}{1\,\cancel{\text{K}}} \times 1\,\cancel{\text{K}}$

$- (-6.4 \times 298 + 6.0 \times 10^{-4} \times 298^{2})\ \dfrac{\text{J}}{1\,\cancel{\text{K}}}\times 1\,\cancel{\text{K}}$

So ΔH_{T2} $= -184600$ J $- 4588.7$ J $+ 1853.9$ J

$= -187.3$ kJ

This is the heat change accompanying the formation of 2 mol of the compound. Since the heat of formation is expressed per mole, then

ΔH_{T2} $= \dfrac{-187.3\ \text{kJ}}{2\ \text{mol}}$

$= -93.7$ kJ mol^{-1}

Practice Problems

1. Calculate the heat of the reaction $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ at 400°C.

	ΔH^o_f(kJ mol^{-1})	$C_{p,m}$(J mol^{-1} K^{-1})
$CO(g)$	−110.53	29.2
$O_2(g)$		29.4
$CO_2(g)$	−393.51	37.2

[*Answer:* −285.49 kJ mol^{-1}]

2. The standard heat of formation of ammonia is −46.11 kJ mol^{-1}. At what temperature would its heat of formation be −40.34 kJ mol^{-1}?

	$C_{p,m}$ (J K^{-1}mol^{-1})
$N_2(g)$	$27.9 + 4.18\times10^{-3}T$
$H_2(g)$	$29.6 + 2.31\times10^{-3}T$
$NH_3(g)$	$29.9 + 2.61\times10^{-3}T$

[*Answer:* 280 K]

9.4 THE HEAT CAPACITIES OF GASES

The molar heat capacity C_m of a gas, measured in J K^{-1} mol^{-1}, is the temperature required to raise the temperature of 1 mole of the gas by 1 K. The heat capacities of gases vary markedly with temperature. For this reason, the heat capacities of gases are computed over a specific temperature range, which could be given as constants or in polynomial forms.

Some forms of polynomial equations in which the heat capacity of a gas could be expressed are:

$a + bT$

$a + bT + cT^2$

$a + bT + cT^2 + dT^3$

where a, b, c and d are constants that are different for each form of the equations.

The heat capacities of gases also vary with pressure and volume. The heat capacity measured at constant pressure is called isobaric (constant pressure) heat capacity $C_{p,m,}$ while that measured at constant volume is called the isochoric (constant volume) heat capacity $C_{v,m,}$ where $C_{p,m} > C_{v,m}$.

We will now derive the equations that relate the heat capacity of a gas and other thermodynamic properties. We begin from the relation

$$Q = mc\mathrm{D}T \quad (9.10)$$

Equation (9.10) can also be written in terms of n moles of a gas:

$$Q = nC_m\mathrm{D}T \quad (9.11)$$

where C is the molar heat capacity of a gas.

Now we write Equation (9.11) in the differential form

$$\mathrm{d}Q = nC_m\mathrm{d}T \quad (9.12)$$

Thus $C_m = \frac{\mathrm{d}Q}{n\mathrm{d}T}$ (9.13)

Since at constant pressure $\mathrm{d}Q = \Delta H$ (Section 9.6), then

$$C_{p,m} = \left(\frac{\mathrm{d}H}{n\mathrm{d}T}\right)_p \quad (9.14)$$

Thus the molar heat capacity of a gas at constant pressure is the change of enthalpy with temperature.

Similarly, at constant volume $\mathrm{d}Q = \mathrm{d}U$. Then

$$C_{v,m} = \left(\frac{\mathrm{d}U}{n\mathrm{d}T}\right)_v \quad (9.15)$$

Thus the molar heat capacity of a gas at constant volume is the change in internal energy with temperature. Equation (9.14) can be rearranged to obtain

$$\Delta H = nC_{p,m}\mathrm{d}T \quad (9.16)$$

We can now integrate Equation (9.16) between the limits $H = H_1$ at T_1 and $H = H_2$ at T_2, i.e.

$$\int_{H_1}^{H_2} \mathrm{d}H = \int_{T_1}^{T_2} nC_{p,m}\,\mathrm{d}T$$

Thus $H_2 - H_1 = \Delta H = n\int_{T_1}^{T_2} C_{p,m}\,\mathrm{d}T$ (9.17)

If the heat capacity is constant, then $C_{p,m}$ comes out of the integral and Equation (9.17) becomes

$\Delta H = nC_{p,m}\,(T_2 - T_1) = nC_{p,m}\Delta T$ (9.18)

Similarly, the same procedure can be repeated for Equation (9.15) to obtain

$\Delta U = \int_{T_1}^{T_2} C_{v,m}\,dT$ (9.19)

When $C_{v,m}$ is constant, then Equation (9.19) becomes

$\Delta U = nC_{v,m}\,(T_2 - T_1) = nC_{v,m}\mathrm{D}T$ (9.20)

We now derive the relationships between the two heat capacities and the universal gas constant R.

We begin from the first law of thermodynamics (Section 9.6) for an isobaric process:

$\Delta H = \Delta U + P\Lambda V$ (9.21)

The ideal gas equation for n moles of a gas is given as

$$PV = nRT$$

Since only the volume varies with temperature at constant pressure, then we can write

$P\mathrm{D}V = nR\Delta T$ (9.22)

The change in internal energy of an ideal gas is given by the equations

$\Delta U = \frac{3}{2}nR\Delta T$ for a monatomic gas. (9.23a)

$\Delta U = \frac{5}{2}\,nR\Delta T$ for a diatomic gas. (9.23b)

Substituting Equations (9.16), (9.22) and (9.23a) into (9.21) we obtain

$nC_{p,m}\Delta T = \frac{3}{2}\,nRT + nR\Delta T$

Thus $nC_{p,m}\Delta T = \frac{5}{2}\,nR\Delta T$

So $C_{p,m} = \frac{5/2nR\Delta T}{n\Delta T}$

$\therefore\ C_{p,m} = \frac{5}{2}R$ for a monatomic gas. (9.24)

Similarly, substituting Equations (9.16), (9.17) and (9.23b) into (9.21) we obtain

$nC_{p,m}\Delta T = \frac{5}{2}\ nR\Delta T + nR\Delta T$

Thus $nC_{p,m}\Delta T = \frac{7}{2}\ nR\Delta T$

So $C_{p,m} = \frac{7/2nR\Delta T}{n\Delta T}$

$\therefore\ C_{p,m} = \frac{7}{2}R$ for a diatomic gas. (9.25)

We now shift attention to isochoric (constant volume) process, for which the first law of thermodynamics becomes:

$\Delta Q = \Delta U$ (9.26)

Substituting Equations (9.11) and (9.23a) into (9.26) we obtain

$nC_{v,m}\Delta T = \frac{3}{2}\ nR\Delta T$

Then $C_{v,m} = \frac{3/2nR\Delta T}{n\Delta T}$

$\therefore\ C_{v,m} = \frac{3}{2}R$ for a monatomic gas. (9.27)

Similarly, substituting Equations (9.21) and (9.23b) into (9.26) we have

$nC_{v,m}\Delta T = \frac{5}{2}\ nR\Delta T$

Then $C_{v,m} = \frac{5/2nR\Delta T}{n\Delta T}$

$\therefore\ C_{v,m} = \frac{5}{2}R$ for a diatomic gas. (9.28)

The ratio $\frac{C_{p,m}}{C_{v,m}}$ is denoted with g, the Greek lower case letter gamma. For a monatomic gas:

$$g = \frac{5/2R}{3/2R}$$

$= 1.66$

For a diatomic gas:

$$g = \frac{7/2R}{5/2R}$$

$= 1.4$

Finally, we now derive the equation connecting $C_{p,m}$ $C_{v,m}$ and R by substituting Equations (9.18), (9.20) and (9.22) into (9.21):

$$nC_{p,m}\Delta T = nC_{v,m}\Delta T + nR\Delta T$$

Then $nC_{p,m}\Delta T - nC_{v,m}\Delta T = nR\Delta T$

So $(C_{p,m} - C_{v,m})\, n\Delta T = nR\Delta T$

Thus $C_{p,m} - C_{v,m} = \frac{nR\Delta T}{n\Delta T}$

$$C_{p,m} - C_{v,m} = R \quad (9.29)$$

This equation, called Mayer equation, is valid for all ideal gases.

Example 1 It requires 706.7 J of heat to raise the temperature of 814 g of carbon dioxide by 1 K at constant pressure. What is the molar heat capacity of the gas?

Solution The heat capacity C of a substance is the heat required to raise the temperature of any amount of it by 1 K or 1°C. Thus

$$C_{p,m} = \frac{C_p}{n}$$

The amount of the gas is obtained from the relation

$$n = \frac{m}{M}$$

$M = [12 + (16 \times 2)]\text{ g mol}^{-1} = 44\text{ g mol}^{-1}$
$m = 814\text{ g}$
$n = ?$

Substituting we have

$n = \frac{814\,\cancel{g} \times 1\,\text{mol}}{44\,\cancel{g}} = 18.5\,\text{mol}$

$C = 706.7\ \text{J K}^{-1}$

$C_{p,m} = ?$

Substituting into the original equation we have

$$C_{p,m} = \frac{706.7\ \text{J K}^{-1}}{18.5\ \text{mol}}$$

$= 38.2\ \text{J K}^{-1}\ \text{mol}^{-1}$

The molar heat capacity at constant volume is obtained from the relation

$C_{p,m} - C_{v,m} = R$

$\therefore\ C_{v,m} = C_{p,m} - R$

Thus $C_{v,m} = 38.2\ \text{J K}^{-1}\ \text{mol}^{-1} - 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$

$= 29.9\ \text{J K}^{-1}\ \text{mol}^{-1}$

Example 2 2.5 mol of a monatomic gas expanΔS reversibly when its temperature rises from 30 to 40°C against a constant atmospheric pressure of 1 atm. Calculate

(a) the change in internal energy of the system;
(b) the work done by the system;
(c) the enthalpy change of the process.

$$(R = 8.314\ \text{J K}^{-1}\,\text{mol}^{-1},\ C_{p,m} = \tfrac{5}{2} R)$$

Solution

(a) The change in internal energy is given by the relation

$\text{D}U = nC_{v,m}(T_1 - T_2)$

$C_{v,m} = \text{C}_{p,\text{m}} - R$

$C_{p,m} = \frac{5}{2} R$

$C_{v,m} = ?$

So $C_{v,m} = \frac{5}{2} R - R = \frac{3}{2} R$

Thus $C_{v,m} = \frac{3}{2} \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} = 12.471\ \text{J K}^{-1}\ \text{mol}^{-1}$

n = 2.5 mol
T_1 = 30°C + 273 K = 303 K
T_2 = 40°C + 273 K = 313 K
ΔU = ?

Substituting we obtain

$$\Delta U = 2.5\,\cancel{\text{mol}} \times \frac{12.471\ \text{J}}{1\,\cancel{\text{K}} \times 1\,\cancel{\text{mol}}} \times (313 - 303)\,\cancel{\text{K}}$$

$= 31\ \text{J} \times 10$
$= 310\ \text{J}$

(b) The work done in a reversible isobaric process is given by the equation

$w = P\text{D}V = nR(T_2 - T_1)$
n = 2.5 mol
R = 8.314 J K^{-1} mol^{-1}
T_1 = 303 K
T_2 = 313 K
n = ?

Substituting we obtain

$$w = 2.5\,\cancel{\text{mol}} \times \frac{8.314\ \text{J}}{1\,\cancel{\text{K}} \times 1\,\cancel{\text{mol}}} \times (313 - 303)\,\cancel{\text{K}}$$

$= 21\ \text{J} \times 10$
$= 210\ \text{J}$

(c) Since the process is isobaric, then we have to apply the relation

$$\Delta H = \Delta U + P\Delta V$$

From (a) and (b) we know that

ΔU = 310 J
$P\Delta V$ = 210 J
ΔH = ?

Substituting we have

ΔH = 310 J + 210 J

= 520 J

Alternatively, we can apply the relation

$\Delta H = nC_{p,m}(T_2 - T_1)$

$C_{p,m} = \frac{5}{2}R$

So $C_{p,m} = \frac{5}{2} \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$ = 20.785 J K^{-1} mol^{-1}

T_1 = 303 K

T_2 = 313 K

ΔH = ?

Substituting we obtain

$$\Delta H = 2.5\ \cancel{\text{mol}} \times \frac{20.785\ \text{J}}{1\ \cancel{\text{K}} \times 1\ \cancel{\text{mol}}} \times (313 - 303)\ \cancel{\text{K}}$$

= 52 J × 10

= 520 J

Example 3 The isobaric molar heat capacity of carbon dioxide within the temperature range of 273-1800 K is given by the equation $22.26 + 5.98 \times 10^{-2}\,T - 3.50 \times 10^{-5}\,T^2 + 7.47 \times 10^{-9}\,T^3$ J K^{-1} mol^{-1}. Compute the ΔH for 1 mol of the gas when heated through this temperature range.

(R = 8.314 J K^{-1} mol^{-1})

Solution Since $C_{p,m}$ is given in a polynomial form, then we have to apply the relation

$\Delta H = \int_{T_1}^{T_2} C_{p,m}\,dT$ (i.e. for 1 mol)

T_1 = 273 K

T_2 = 1800 K

$C_{p,m} = 22.26 + 5.98 \times 10^{-2}\,T - 3.50 \times 10^{-5}\,T^2 + 7.47 \times 10^{-9}\,T^3$ J K^{-1} mol^{-1}

ΔH = ?

Substituting we have

$$\Delta H = \int_{273\ \text{K}}^{1800\ \text{K}} (22.26 + 5.98 \times 10^{-2}\,T - 3.50 \times 10^{-5}\,T^2 + 7.47 \times 10^{-9}\,T^3)\ \text{J K}^{-1}\ \text{mol}^{-1}\,dT$$

Thus $\Delta H = \left[\left(22.26T + \frac{5.98 \times 10^{-2}T^2}{2} - \frac{3.50 \times 10^{-6}T^3}{3} + \frac{7.47 \times 10^{-9}T^4}{4}\right)\frac{\text{J mol}^{-1}}{1\text{ K}}\right]_{273\text{ K}}^{1500\text{ K}}$

So $\Delta H = (88508.3 - 8078.4)\ \frac{\text{J mol}^{-1}}{1\text{ K}}$

$= 80.4$ kJ mol^{-1}

Practice Problems

1. Through what temperature difference must 70.0 g of nitrogen gas be heated to increase its internal energy by 100 J?

$(C_{p,m} = \frac{7}{2}R = 8.314\text{ J K}^{-1}\text{mol}^{-1}$, N = l4) [*Answer:* 7 K or 7°C]

2. 1 mol of a diatomic gas expanΔS reversibly against a constant atmospheric pressure when its temperature rises by 15°C. Calculate

(a) the change in internal energy of the gas;
(b) the work done by the gas on the surroundings;
(c) the change in enthalpy of the gas.

$(C_{p,m} = \frac{7}{2}R,\ R = 8.314\text{ J K}^{-1}\text{ mol}^{-1})$

[*Answers:* (a) 310 J mol^{-1} (b) 120 J mol^{-1} (c) 440 J mol^{-1}]

3. The isochoric heat capacity of oxygen is given by the equation $19.66 + 1.3 \times 10^{-3}T$ J $\text{K}^{-1}\text{mol}^{-1}$. To what temperature must 1.50 mol the gas, initially at 0°C, be raised to increase its internal energy by 380 J?

[*Answer:* 292 K]

9.5 THERMODYNAMICS OF SOLUTIONS

Heat is either absorbed or evolved when a substance is dissolved in a solvent. This heat is called the heat or enthalpy change of solution ΔH_{sol}. The heat of solvation is the enthalpy change when the gaseous ions of a substance in solution are surrounded by molecules of the solvent. The heat of solvation is called heat of hydration ΔH_H when the solvent is water.

The heat of solution of a substance can be determined experimentally by calorimetry. An estimate of the heat of solution can also be made by summing up lattice enthalpy ΔH_L and heat of hydration of a substance:

$$\Delta H_{sol} = \Delta H_L + \Delta H_H$$

Whether dissolution would be exothermic or endothermic depenΔS on the values of ΔH_L and ΔH_H. For dissolution to be endothermic, the lattice energy must be greater than the heat of hydration. On the other hand, dissolution would be exothermic if the heat of hydration is greater than the lattice energy.

Example 1 In an experiment to determine the heat of solution of sodium hydroxide, a clean calorimeter was filled with 250 cm^3 of distilled water. A thermometer inserted into the water recorded a temperature of 5°C. 5.0 g of sodium hydroxide was then carefully weighed out, and added to the water. The mixture was stirred continuously with the thermometer until a final steady temperature of 10.2°C was recorded. What is the heat of solution of the base?

(H = 1.0, O = 16.0, Na = 23.0, $c = 4.2\ J\ K^{-1}\ g^{-1}$, density of water = 1.0 g cm^{-1})

Solution A rise in temperature implies that the dissolution is exothermic. Since the heat gained by the calorimeter is neglible, then the heat released by the base on dissolution equals the heat gained by the water. This is obtained from the relation

$$Q = mc\,(T_2 - T_1)$$

The density of the solution can be assumed to be equal to that of water. Since the density of water is 1.0 g cm^{-1}, it then follows that the mass the solution must be equal to its volume, i.e. m = 250 g. Other given data are

T_1 = 273 K + 5°C = 278 K

T_2 = 273 K + 10.2°C = 283.2 K

$c = 4.2\ J\ k^{-1}\ g^{-1}$

Q = ?

Substituting we obtain

$$Q = 250\,\cancel{g} \times \frac{4.2\ J}{1\,\cancel{K} \times 1\,\cancel{g}} \times (283.2 - 278)\,\cancel{K}$$

Thus $Q = 250 \times 4.2\ J \times 5.2 = 5460\ J$

Now we must remember that heat of solution is reported per mole. Thus, we must find the amount of heat that would be liberated when 1 mol of the base is dissolved. Consequently, the heat of solution is obtained from the relation

$$\Delta H_{sol} = \frac{Q}{n}$$

The number of moles of the base is obtained, using the relation

$n = \frac{m}{M}$

$M = (23.0 + 16.0 + 1.0)\ \text{g mol}^{-1} = 40.0\ \text{g mol}^{-1}$
$m = 5.0\ \text{g}$
$n = ?$

Substituting we obtain

$n = \frac{5.0\ \cancel{\text{g}} \times 1\ \text{mol}}{40.0\ \cancel{\text{g}}} = 0.125\ \text{mol}$

$\Delta H_{sol} = ?$

Finally, we now substitute into the above equation to obtain

$\Delta H_{sol} = \frac{5460\ \text{J}}{0.125\ \text{mol}}$

$= -43.7\ \text{kJ mol}^{-1}$

Alternatively, we can work from the first principle:

If 0.125 mol of the base liberates 5460 J of heat, then 1 mol would liberate x, i.e.

$0.125\ \text{mol} = 5460\ \text{J}$
$1\ \text{mol} = x$

So $0.125\ \text{mol} \times x = 1\ \text{mol} \times 5460\ \text{J}$

Thus $x = \frac{1\ \cancel{\text{mol}} \times 5460\ \text{J}}{0.125\ \cancel{\text{mol}}}$

$= 43.7\ \text{kJ}$

Thus the heat of solution of sodium hydroxide is $-43.7\ \text{kJ mol}^{-1}$. The minus sign shows that the dissolution is exothermic.

Example 2 The lattice enthalpy of potassium fluoride is $826\ \text{kJ mol}^{-1}$, while its heat of hydration is $-844\ \text{kJ mol}^{-1}$. Predict whether the dissolution of the salt would be exothermic or endothermic.

Solution A look at the two enthalpy changes suggests that the dissolution would be exothermic since the lattice enthalpy is lower than the heat of hydration. This is confirmed by calculating the heat of solution of the salt, using the relation

$\Delta H_{sol} = \Delta H_L + \Delta H_H$

$\Delta H_L = 826 \text{ kJ mol}^{-1}$

$\Delta H_H = -844 \text{ kJ mol}^{-1}$

$\Delta H_{sol} = ?$

Substituting we obtain

$\Delta H_{sol} = 826 \text{ kJ mol}^{-1} + (-844 \text{ kJ mol}^{-1})$

$\Delta H_{sol} = 826 \text{ kJ mol}^{-1} - 844 \text{ kJ mol}^{-1}$

$= -18 \text{ kJ mol}^{-1}$

The minus sign confirms that the dissolution is exothermic.

Example 3 Estimate the heat of solution of silver chloride if its lattice energy and heat of hydration are 916 kJ mol^{-1} and −850 kJ mol^{-1} respectively.

Solution As usual, we have to apply the relation

$\Delta H_{sol} = \Delta H_L + \Delta H_H$

$\Delta H_L = 916 \text{ kJ mol}^{-1}$

$\Delta H_H = -850 \text{ kJ mol}^{-1}$

$\Delta H_{sol} = ?$

Substituting we obtain

$\Delta H_{sol} = 916 \text{ kJ mol}^{-1} + (-850 \text{ kJ mol}^{-1})$

So $\Delta H_{sol} = 916 \text{ kJ mol}^{-1} - 850 \text{ kJ mol}^{-1}$

$= 66 \text{ kJ mol}^{-1}$

The positive value of the heat of solution shows that the dissolution would be endothermic.

Example 4 Calculate the heat hydration of silver ions from the data given below:

$Ag^+(g) + Cl^-(g) \rightarrow Ag^+(aq) + Cl^-(aq) \quad \Delta H^o_H = -850 \text{ kJ mol}^{-1}$

$Cl^-(g) \rightarrow Cl^-(aq) \quad \Delta H^o_H = -340 \text{ kJ mol}^{-1}$

Solution The equation of the process whose heat of hydration is required is

$$Ag^+(g) \rightarrow Ag^+(aq) \; \Delta H^o_H = ?$$

We can apply Hess’s law by subtracting the above equations to obtain this equation, as follows:

$\mathrm{Ag^+}(g) + \mathrm{Cl^-}(g) \rightarrow \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$ $\Delta H^o_H = -850\ \mathrm{kJ\ mol^{-1}}$

$-\ \mathrm{Cl^-}(g) \rightarrow \mathrm{Cl^-}(aq)$ $\Delta H^o_H = -340\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{Ag^+}(g) \rightarrow \mathrm{Ag^+}(aq)$ $\Delta H^o_H = -510\ \mathrm{kJ\ mol^{-1}}$

Thus the heat of hydration of silver ions is −510 kJ mol^{-1}, i.e.

$\Delta H^o_H = -850\ \mathrm{kJ\ mol^{-1}} - (-340\ \mathrm{kJ\ mol^{-1}})$

So $\Delta H^o_H = -850\ \mathrm{kJ\ mol^{-1}} + 340\ \mathrm{kJ\ mol^{-1}}$

$= -510\ \mathrm{kJ\ mol^{-1}}$

Example 5 Calculate the heat of hydration of fluoride ions from the information given below:

$\mathrm{Mg^{2+}}(g) + 2\mathrm{F^-}(g) \rightarrow \mathrm{Mg^{2+}}(aq) + 2\mathrm{F^-}(aq)$ $\Delta H^o_H = -2969\ \mathrm{kJ}$

$\mathrm{Mg^{2+}}(g) \rightarrow \mathrm{Mg^{2+}}(aq)$ $\Delta H^o_H = -2003\ \mathrm{kJ}$

Solution The equation of interest is

$\mathrm{F^-}(g) \rightarrow \mathrm{F^-}(aq)$ $\Delta H^o_H = ?$

This equation can be obtained by subtracting the second equation from the first:

$\mathrm{Mg^{2+}}(g) + 2\mathrm{F^-}(g) \rightarrow \mathrm{Mg^{2+}}(aq) + 2\mathrm{F^-}(aq)$ $\Delta H^o_H = -2969\ \mathrm{kJ}$

$-\ \mathrm{Mg^{2+}}(g) \rightarrow \mathrm{Mg^{2+}}(aq)$ $\Delta H^o_H = -2003\ \mathrm{kJ}$

$2\mathrm{F^-}(g) \rightarrow 2\mathrm{F^-}(aq)$ $\Delta H^o_H = -966\ \mathrm{kJ}$

Thus, the heat of hydration of 2 mol of fluoride ions is −966 kJ, i.e.

$\Delta H^o_H = 2929\ \mathrm{kJ} - (-2003\ \mathrm{kJ})$

So $\Delta H^o_H = 2969\ \mathrm{kJ} + 2003\ \mathrm{kJ} = -966\ \mathrm{kJ}$

Since the answer must be reported per mole of ions, then the heat of hydration of fluoride ions is

$\Delta H^o_H = \frac{-966\ \mathrm{kJ}}{2\ \mathrm{mol}}$

$= -483\ \mathrm{kJ\ mol^{-1}}$

Example 6 Use the information given below to calculate the heat of hydration of a gas consisting of 1 mol of calcium ions and 2 mol of chloride ions.

$\mathrm{Ca^{2+}}(g) \rightarrow \mathrm{Ca^{2+}}(aq)$ $\Delta H^o_H = -1657\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{Cl^-}(g) \rightarrow \mathrm{Cl^-}(aq)$ $\Delta H^o_H = -340\ \mathrm{kJ\ mol^{-1}}$

Solution The required equation is

$Ca^{2+}(g) + 2Cl^{-}(g) \rightarrow Ca^{2+}(aq) + 2Cl^{-}(aq)$ $\Delta H^{o}_{H} = ?$

This equation can be obtained by adding 2 times the second equation to the first, i.e.

$Ca^{2+}(g) \rightarrow Ca^{2+}\ (ag)$ $\Delta H^{o}_{H} = -1657$ kJ

$+2Cl^{-}(g) \rightarrow 2Cl^{-}(aq)$ $\Delta H^{o}_{H} = -680$ kJ

$Ca^{2+}\ (g) + 2Cl^{-}(g) \rightarrow Ca^{2+}(aq) + Cl^{-}(aq)$ $\Delta H^{o}_{H} = -2337$ kJ

Thus the heat of hydration of the gas is $\Delta H^{o}_{H} = -2337$ kJ, i.e.

$\Delta H^{o}_{H} = -\ 1657\ \text{kJ} + (-\ 680\ \text{kJ})$

So $\Delta H^{o}_{H} = -\ 1657\ \text{kJ} - 680\ \text{kJ}$

$= -\ 2337$ kJ

Practice Problems

1. In an experiment to determine the heat of solution of sodium chloride, 10.0 g of the salt was dissolved in 250 cm^{3} of distilled water in a calorimeter. Determine the heat of solution of the salt under the experimental conditions, given that the maximum temperatures recorded before and after the addition of the salt were 20°C and 20.5°C respectively.

   (Na =23.0, Cl = 35.5, $c = 4.2\ K^{-1}\ g^{-1}$, density of water = 1.0 g cm^{3})

   [*Answer:* 3.1 kJ mol^{-1}]

2. The lattice energy and heat of hydration of silver fluoride are 971 kJ mol^{-1} and −993 kJ mol^{-1} respectively. Estimate the heat of solution of the salt. [*Answer:* –22 kJ mol^{-1}]

3. Calculate the hydration energy of a gas containing 1 mol of silver ions and 1 mol of bromide ions, using the information given below.

   $Ag^{+}(g) \rightarrow Ag^{+}(aq)$ $\Delta H^{o}_{H} = -510$ kJ mol^{-1}

   $Br^{-}(g) \rightarrow Br^{-}(aq)$ $\Delta H^{o}_{H} = -309$ kJ mol^{-1}

   [*Answer:* −819 kJ mol^{-1}]

9.6 THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics states that energy can neither be created nor destroyed but can be converted from one form to another. Another way of stating this is to say that the total internal energy of a system is constant. The mathematical expression for the first law is

$Q = DU + w$

where Q = The heat absorbed or evolved by the system.

ΔU = The change in the internal energy of the system.

w = The work done on or by the system.

The following conventions are followed when dealing with this equation:

- Q is positive if the system absorbs heat, and negative if the system evolves heat.
- w is positive if work is done on the surroundings by the system, and negative if the surroundings does work on the system.

We will now see how the above equation is applied to different processes.

9.6.1 Isobaric Process

For a gaseous system undergoing an isobaric process, the heat output or input is the enthalpy change for the process, i.e.

$$Q = \Delta H \quad (9.30)$$

Work is defined as the product of force and distance travelled, i.e.

$$w = F \times l \quad (9.31)$$

Pressure is defined as the force per unit area, i.e.

$$P = \frac{F}{A}$$

Then $F = P \times A$ (9.32)

When a given volume of a gas moves through the distance *l*, its volume increases or decreases by the amount D*V*. The area of this distance is given by the relation

$$A = \frac{\Delta V}{l} \quad (9.33)$$

Substituting Equation (9.33) into (9.32) we have

$$F = P \times \frac{\Delta V}{l} \quad (9.34)$$

Substituting Equation (9.34) into (9.31) we obtain

$w = P \times \frac{\Delta V}{l} \times l$

Thus $w = P\mathrm{D}V = P(V_2 - \mathrm{V}_1)$ (9.35)

Thus, the work done in an isobaric process is the product of pressure and change in volume. Substituting Equations (9.30) and (9.35) into the original equation we obtain

$$\Delta H = \mathrm{D}U + P\mathrm{D}V$$

The relationship between the volume and temperature of a gas undergoing an isobaric process is given by Charles's law.

9.6.2 Isochoric Process

Since the volume remains constant, then $w = P\mathrm{D}V = 0$ for an isochoric gaseous system. Thus no work is done in an isochoric process. Substituting this into the original equation we have

$$Q = \mathrm{D}U = n\mathrm{C}_{v,\mathrm{m}}\mathrm{D}T$$

Thus the change in internal energy of a system is the same as its heat change at constant volume.

9.6.3 Isothermal Process

$\mathrm{D}U$ and ΔH are both functions of temperature. Thus they are both zero at constant temperature, i.e.

$$\Delta H = \mathrm{D}U = 0$$

The first law then reduces to

$Q = w = P\mathrm{D}V$ (9.36)

Thus the work done in an isothermal process is the same as the heat absorbed or evolved. Equation (9.37) can as well be written in the differential form as:

$\mathrm{d}w = P\mathrm{d}V$ (9.37)

From the ideal gas equation we know that

$P = \frac{nRT}{V}$ (9.38)

Substituting equation (9.38) into (9.37) we obtain

$\mathrm{d}w = \frac{nRT}{V}\mathrm{d}V$ (9.39)

For a system undergoing a reversible isothermal process, Equation (9.39) can be integrated within the limits $w = 0$ at V and $w = w$ at V_2, i.e.

$$\int_0^w dw = \int_{V_1}^{V_2} \frac{nRT}{V}\,\mathrm{d}V$$

Thus $w = nRT \int_{V_1}^{V_2} \frac{1}{V}\,\mathrm{d}V$

Then $w = nRT\,[\ln V]^{V2}_{V1}$

So $w = nRT\,[\ln V_2 - \ln V_1]$ (9.40)

Finally, we now apply the law of logarithms to Equation (9.40) to obtain

$$w = nRT \ln \left(\frac{V_2}{V_1}\right) = Q = P\mathrm{D}V \quad (9.41)$$

Since pressure is inversely proportional to volume, then Equation (9.41) can also be written as

$$w = nRT \left(\frac{P_1}{P_2}\right) = Q = P\mathrm{D}V \quad (9.42)$$

The relationship between pressure and volume undergoing an isothermal process is given by Boyle's law.

9.6.4 Adiabatic Process

The heat output or input of an adiabatic process is zero. Thus the first law reduces to

$\mathrm{D}U + w = 0$

So $w = -\mathrm{D}U = -nC_{v,m}\mathrm{D}T$ (9.43)

The P-V-T relationships of an adiabatic process can be obtained by writing Equation (9.43) in the differential form, as follows:

$P\mathrm{d}V + C_{v,m}\mathrm{d}T = 0$ (9.44)

We know that the ideal gas equation for 1 mol of a gas is given by

$PV = RT$ (9.45)

We now differentiate Equation (9.45) at constant pressure and volume to obtain

$P\mathrm{d}V + V\mathrm{d}P = R\mathrm{d}T$ (9.46)

Next, we divide Equation (9.45) by R to obtain

$$\mathrm{d}T = \frac{P\mathrm{d}V}{R} - \frac{V\mathrm{d}P}{R} \quad (9.47)$$

Substituting Equation (9.47) into (9.44) we have

$$P\mathrm{d}V + C_{v,m}\frac{P\mathrm{d}V}{R} + C_{v,m}\frac{V\mathrm{d}P}{R} = 0$$

Rearranging we obtain

$$P\mathrm{d}V\left(1+\frac{C_{v,m}}{R}\right) + C_{v,m}\frac{V\mathrm{d}P}{R} = 0 \quad (9.48)$$

We now substitute $R = C_{p,m} - C_{v,m}$ into Equation (9.49) to obtain

$$P\mathrm{d}V\left(1+\frac{C_{v}}{C_{p,m}-C_{v,m}}\right) + C_{v,m}\frac{V\mathrm{d}P}{C_{p,m}-C_{v,m}} = 0 \quad (9.49)$$

Equation (9.49) can be further simplified to obtain

$$C_{p,m}P\mathrm{d}V + C_{v,m}V\mathrm{d}P = 0 \quad (9.50)$$

Next, we divide Equation (9.48) by $C_{v,m}VP$, we obtain

$$\frac{\mathrm{d}V}{V} + \frac{\mathrm{d}P}{P} = 0 \quad (9.51)$$

where $g = \frac{C_{p,m}}{C_{v,m}}$

Integrating Equation (9.51) we obtain

$$\int\left(\gamma\frac{\mathrm{d}V}{V} + \frac{\mathrm{d}P}{P}\right) = \int 0$$

Thus $g \ln V + \ln P = \text{constant} \quad (9.52)$

So $PV^{g-1} = \text{constant}$ or $P_1V_1^{g} = P_2V_2^{g}$ or $\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma} \quad (9.53)$

We can also use the fact that PV/T is constant to obtain the following relationships from Equation (9.53):

$$TP^{(1-g)g} = \text{constant or } T_1P_1^{(1-g)g} = T_2P_2^{(1-g)g} \text{ or } \frac{T_2}{T_1} = \left(\frac{P_1}{P_2}\right)^{(1-\gamma)\gamma} \quad (9.54)$$

$$TP^{g-1} = \text{constant or } T_1V_1^{(g-1)} = T_2V_2^{(g-1)} \text{ or } \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad (9.55)$$

The differential form of the work done in an adiabatic process can be written as

$$\mathrm{d}w = P\mathrm{d}V \quad (9.56)$$

For adiabatic process we know that

$$PV^g = \text{constant or } PV^g = P_1V_1^g$$

$$\therefore\ P = P_1\left(\frac{V_1}{V}\right)^{\gamma}$$

Substituting into Equation (9.56) we have

$$\mathrm{d}w = P_1\left(\frac{V_1}{V}\right)^{\gamma} \mathrm{d}V \quad (9.57)$$

We now integrate Equation (9.57) within the limits $w = 0$ at V_1 and $w = w$ at V_2, i.e.

$$\int_0^w \mathrm{d}w = \int_{V_1}^{V_2} P_1\left(\frac{V_1}{V}\right)^{\gamma} \mathrm{d}V \quad (9.58)$$

Since PV^g is constant, then Equation (9.58) becomes

$$w = P_1V_1^g \int_{V_1}^{V_2} \frac{1}{V^{\gamma}} \mathrm{d}V$$

$$\text{Thus } w = P_1V_1^g \int_{V_1}^{V_2} V^{-g}\mathrm{d}V \quad (9.59)$$

So $w = P_1 V_1^{g} \left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V_1}^{V_2}$

Thus $w = \frac{P_1 V_1^{\gamma}\left(V_2^{1-\gamma} - V_1^{1-\gamma}\right)}{1-\gamma}$ (9.60)

Expanding equation (9.60) and using $P_1 V_1^{g} = P_2 V_2^{g}$, we now obtain

$w = \frac{P_2 V_2 - P_1 V_1}{1-\gamma}$ (9.61)

Substituting $PV = nRT$ into equation (9.61) we obtain

$w = \frac{nR(T_2 - T_1)}{1-\gamma} = -\mathrm{D}U = -nC_{v,m}\mathrm{D}T$ (9.62)

Equation (9.62) is the work done by n moles of an ideal gas undergoing a reversible adiabatic process.

Example 1 A system evolved 90 J of heat when 120 J of work was done on it. What is the change in its internal energy?

Solution We have to apply the relation

$Q = \mathrm{D}U + w$

$\therefore\ \mathrm{D}U = \mathrm{D}Q - w$

The fact that the system evolves heat means DQ is negative, and work being done on the system means w is negative. Thus

$\mathrm{D}Q = -90$ J

$w = -120$ J

$\mathrm{D}U = ?$

Substituting we have

$\Delta U = -90 \text{ J} - (-120 \text{ J})$

$= -90 \text{ J} + 120 \text{ J}$

$= 30 \text{ J}$

Example 2 The internal energy of a system increases by 40 J when the system does 250 J of work on its surroundings. Determine the amount of heat energy absorbed or evolved by the system.

Solution We have to apply the relation

$$Q = \Delta U + w$$

The work done is positive since the system does work on the surroundings. Thus

$\Delta U = 40$ J

$w = 250$ J

$Q = ?$

Substituting we have

$Q = 40 \text{ J} + 250 \text{ J}$

$= 290$ J

Thus 290 J of heat was absorbed by the system.

Example 3 The internal energy of a system increases by 20.0 J when it expanΔS from 20.0 dm^3 to 22.5 dm^3 against a constant pressure of 2.5×10^4 Pa. What is the enthalpy change of the system ?

Solution Since the gas expanΔS at constant pressure, then

$$\Delta H = \Delta U + P\Delta V$$

Since the gas expanΔS, then it follows that it does work on the surroundings. In other worΔS, the work done is positive.

$\Delta U = 20.0$ N m

$P = 2.5 \times 10^4 \text{ N m}^{-2}$

$V_1 = 20.0 \text{ dm}^3 = 20.0 \times 10^{-3} \text{ m}^3$

$V_2 = 22.5 \text{ dm}^3 = 22.5 \times 10^{-3} \text{ m}^3$

$\Delta H = ?$

We now substitute to obtain

$$\Delta H = 20.0 \text{ N m} + \left[\frac{2.5 \times 10^4 \text{ N}}{1 \text{ m}^2} \times \left(22.5 \times 10^{-3} - 20.0 \times 10^{-3}\right) \text{m}^3\right]$$

Thus $\Delta H = 20.0 \text{ N m} + 62.5 \text{ N m}$

$= 82.5$ J (N m)

Example 4 The enthalpy of a system increases by 50 kJ when its internal energy is increased by 113 kJ. What is the pressure of the system if the volume of the gas is reduced by 10 m^3 at constant pressure?

Solution We have to apply the relation

$$\Delta H = \Delta U + P\Delta V$$

$$\therefore\ P = \frac{\Delta H - \Delta U}{\Delta V}$$

The change in volume must be negative because the volume reduces (as the surroundings does work on the system). Thus the change in volume must be negative.

$\Delta U = 113$ kNm

$\Delta H = 50$ kNm

$\Delta V = -10 \text{ m}^3$

$P = ?$

Finally, we now substitute to obtain

$$P = \frac{(50 - 113)\text{ kNm}}{10\text{ m}^3}$$

$$\text{So } P = \frac{(-63\text{ kNm})}{10\text{ m}^3}$$

$$= 6.3\text{ kNm}^{-2}$$

Example 5 An ideal gas produces 150 kJ of heat after undergoing a reversible isochoric process. It then expanΔS from 15.7 to 50.0 dm^3 at a constant pressure of 101 kPa. Calculate

(a) the change in internal energy of the gas;
(b) the work done during the whole process;
(c) the enthalpy change of the system.

Solution

(a) We know that at constant volume

$$\text{D}U = \text{D}Q$$

Since the gas evolved 150 kJ of heat, then

$$\text{D}U = -150\text{ kJ}$$

The minus sign shows that the internal energy of the system decreases by 150 J.

(b) Since no work is done in an isochoric process, then the overall work done is given by

$w = P(V_2 - V_1)$

$P = 101 \text{ kNm}^{-2}$

$V_1 = 15.7 \text{ dm}^3 = 15.7 \times 10^{-3} \text{ m}^3$

$V_2 = 50.0 \text{ dm}^3 = 50.2 \times 10^{-3} \text{ m}^3$

$w = ?$

Substituting we have

$$w = \frac{101 \text{ kN}}{1 \text{ m}^2} \times (50.2 \times 10^{-3} - 15.7 \times 10^{-3}) \text{ m}^3$$

Thus $w = 101 \text{ kN} \times 34.3 \times 10^{-3} \text{ m}$

$= 3.46 \text{ kJ (kNm)}$

(c) For an isobaric process we have

$$\Delta H = \mathrm{D}U + P\mathrm{D}V$$

From the previous workings we know that

$\mathrm{D}U = -150 \text{ kJ}$

$w = 3.46 \text{ kJ}$

$\Delta H = ?$

Substituting we have

$\Delta H = -150 \text{ kJ} + 3.46 \text{ kJ}$

$= -147 \text{ kJ}$

Example 6 The reaction between hydrogen and oxygen to produce water vapour is given by the equation

$$H_2(g) + 2O_2(g) \rightarrow 2H_2O(g)$$

What is the work done at STP?

Solution The equation shows a decrease in the amount of species from the reactants to products. This implies that the reacting system is compressed by the surroundings, reducing its volume. Thus the work done should be negative. We know that for an isobaric process

$$w = P(V_2 - V_1)$$

Since the reaction took place at STP, then

$$P = 101325 \text{ N m}^{-2}$$

The volume of reactants (V_1) and the product (V_2) can be evaluated from the relation

$$V = n \times 22.4 \text{ dm}^3 \text{ mol}^{-1}$$

For the reactants we have

$n = (1 + 2) \text{ mol} = 3 \text{ mol}$

So $V_1 = 3\cancel{\text{mol}} \times \frac{22.4 \text{ dm}^3}{1\cancel{\text{mol}}}$

$= 67.2 \text{ dm}^3 = 67.2 \times 10^{-3} \text{ m}^{-3}$

For the product we have

$n = 2 \text{ mol}$

So $V_2 = 2\cancel{\text{mol}} \times \frac{22.4 \text{ dm}^3}{1\cancel{\text{mol}}}$

$= 44.8 \text{ dm}^3 = 44.8 \times 10^{-3} \text{ m}^3$

$w = ?$

Substituting we obtain

$w = \frac{101325 \text{ N}}{1 \text{ m}^2} \times (44.8 \times 10^{-3} – 67.2 \times 10^{-3}) \text{ m}^3$

Thus $w = 101325 \text{ N} \times (– 22.4 \times 10^{-3} \text{ m})$
$= −2.27 \text{ kJ}$

Thus the surroundings does 2.27 kJ of work on the system.

Example 7 2.5 mol of an ideal gas undergoes a reversible adiabatic expansion from 10.0 dm^3 at 30°C to a volume of 25 dm^3. Assuming the gas is monatomic, calculate

(a) the final temperature of the gas;
(b) the work done by the gas.

$$(R = 8.314 \text{ J K}^{-1} \text{mol}^{-1}, C_{v,m} = \tfrac{3}{2}R)$$

Solution The relationship between the temperature and volume of an ideal gas undergoing a reversible adiabatic process is given by the relation

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{1-\gamma}$$

T_1 = 30°C + 273 K = 303 K

V_1 = 10 dm^3

V_2 = 25 dm^3

g = 1.66

T_2 = ?

Substituting we have

$$\frac{T_2}{303\text{ K}} = \left(\frac{10\,\cancel{\text{dm}^3}}{25\,\cancel{\text{dm}^3}}\right)^{1.66-1}$$

Thus T_2 = 303 K × $(0.4)^{0.66}$

= 303 K × 0.546

= 165 K

(b) For a reversible adiabatic process we have

$w = -\text{D}U = -nC_{v,m}\,(T_2 - T_1)$

R = 8.314 J mol^{-1} K^{-1}

$C_{v,m} = \frac{3}{2}\,R = \frac{3}{2}$ = 12.471 J K^{-1} mol^{-1}

n = 2.5 mol

T_1 = 303 K

T_2 = 165 K

w = ?

Substituting we have

$$w = 2.5\,\cancel{\text{mol}} \times \frac{12.471\text{ J}}{1\,\cancel{\text{K}} \times 1\,\cancel{\text{mol}}} \times (163 - 303)\,\cancel{\text{K}}$$

Thus w = − 31 J × (–138)

= 4.3 kJ

Alternatively, we can apply the relation

$$w = \frac{nR(T_2 - T_1)}{1-\gamma}$$

Substituting we have

$w = \dfrac{2.5\,\cancel{\text{mol}} \times 8.314\ \text{J}(165 - 303)\cancel{\text{K}}}{(1 - 1.66) \times 1\,\cancel{\text{mol}} \times 1\,\cancel{\text{K}}}$

So $w = \dfrac{20.785\ \text{J} \times (-138)}{-0.66}$

Thus $w = \dfrac{-2868\ \text{J}}{-0.66}$

$= 4.3$ kJ

Example 8 1.5 mol of an ideal gas expanΔS from 20.0 to 32.5 dm^3 in a reversible isothermal process against a constant atmospheric pressure of 101 kPa. Calculate

(a) the work done by the gas;
(b) the temperature of the gas;
(c) the height to which the system would lift a load of 100.0 N.

(R = 8.314 J K^{-1}mol^{-1})

Solution

(a) The work done is given by the equation

$w = P(V_2 - V_1)$

$P = 101$ kNm^{-2}

$V_1 = 20$ dm^3 $= 20.0 \times 10^{-3}$ m^3

$V_2 = 32.5$ dm^3 $= 32.5 \times 10^{-3}$ m^3

$w = ?$

Substituting we have

$w = \dfrac{101\ \text{kN}}{1\ \text{m}^2} \times (32.5 \times 10^{-3} - 20.0 \times 10^{-3})\ \text{m}^3$

Then $w = 101\ \text{kN} \times 12.5 \times 10^{-3}$ m

$= 1.26$ kJ (kNm)

(b) The work done in an isothermal process at constant pressure is given as

$w = nRT \ln\left(\dfrac{V_2}{V_1}\right)$

$\therefore\ T = \dfrac{w}{nR \ln\left(\dfrac{V_2}{V_1}\right)}$

$w = 1260$ J
$R = 8.314$ J K^{-1} mol^{-1}
$V_1 = 20.0 \times 10^{-3}$ m^3
$V_2 = 32.5 \times 10^{-3}$ m^3
$n = 1.5$ mol
$T = ?$

Substituting we have

$$T = \frac{1260\,\cancel{\text{J}} \times 1\,\text{K} \times 1\,\cancel{\text{mol}}}{1.5\,\cancel{\text{mol}} \times 8.314\,\cancel{\text{J}} \times \ln\left(\dfrac{32.5 \times 10^{-3}\,\cancel{\text{m}^3}}{20.0 \times 10^{-3}\,\cancel{\text{m}^3}}\right)}$$

Thus $T = \frac{1260\ \text{K}}{12.471 \times 0.486}$

$= 208$ K

(c) Work and energy are similar concepts. Thus the work done in lifting a body through a height *h* can be equated to the potential energy, i.e.

$w = mgh$

$\therefore\ w = \frac{w}{mg}$

where *mg* is the weight of the load in N.

$w = 1260$ Nm
$mg = 100.0$ N
$h = ?$

Substituting we have

$$h = \frac{1260\,\cancel{\text{N}}\text{m}}{100.0\,\cancel{\text{N}}}$$

$= 13$ m

Example 9 The heat output of a reaction is 250 J when it undergoes a reversible isothermal process at a constant atmospheric pressure of 1 atm. What is the final volume of the gas if its initial volume is 10.0 dm^3?

Solution We have to apply the relation

$$w = P(V_2 - V_1)$$

For an isothermal process we know that

$$Q = w$$

Since heat is evolved, then Q must be negative, i.e.

$Q = -250$ J

$\therefore\ w = -250$ J = –250 Nm

$P = 1$ atm = 101325 Nm^{-2}

$V_1 = 10.0\ \text{dm}^3 = 10.0 \times 10^{-3}\ \text{m}^3$

$V_2 = ?$

Substituting we have

$-250\ \text{N m} = \frac{101325\ \text{N}}{1\text{m}^2} \times (V_2 - 10.0 \times 10^{-3}\ \text{m}^3)$

Then $-250\ \text{N m} = \frac{101325 V_2\ \text{N}}{1\text{m}^2} - \left[\frac{101325}{1\text{m}^2} \times 10.0 \times 10^{-3}\ \text{m}^3\right]$

So $-250\ \text{N m} = \frac{101325 V_2\ \text{N}}{1\text{m}^2} - 1013.25\ \text{N m}$

Collecting like terms we have

Thus $\frac{101325 V_2 \cancel{\text{N}}}{1\text{m}^2} = -250\ \text{N m} + 1013.25\ \text{N m} = 763\ \text{N m}$

Cross-multiplying we have

$101325 V_2 \text{N} = 763\ \text{N m}^3$

$\therefore\ V_2 = \frac{763 \cancel{\text{N}}\text{m}^3}{101325 \cancel{\text{N}}}$

$= 7.53 \times 10^{-3}\ \text{m}^3 = 7.53\ \text{dm}^3$

Example 10 The pressure of 15 dm^3 of a diatomic gas increased from 101 kPa to 150 Kpa when it undergoes a reversible adiabatic process. What is the final volume of the gas?

Solution The *P-V* relationship of a reversible adiabatic process is given by the equation

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

For a diatomic gas γ = 1.4

$P_1 = 101$ kPa

$V_1 = 15$ dm^3

$P_2 = 150$ kPa

$V_2 = ?$

Substituting we obtain

$$\frac{150\ \cancel{\text{kPa}}}{101\ \cancel{\text{kPa}}} = \left(\frac{15\ \text{dm}^3}{V_2}\right)^{1.4}$$

Thus $1.485 = \left(\frac{15\ \text{dm}^3}{V_2}\right)^{1.4}$

So $1.485^{\frac{1}{1.4}} = \frac{15\ \text{dm}^3}{V_2}$

Cross-multiplying we obtain

$V_2 \times 1.33 = 15$ dm^3

$\therefore\ V_2 = \frac{15\ \text{dm}^3}{1.33}$

$= 11$ dm^3

Practice Problems

1. The internal energy of a system increases by 50.0 J. What is the heat absorbed when the system does 105.8 J of work on the surroundings?
[*Answer:* 156 J]
2. A system has 250 J of work done on it by the surroundings. Determine the internal energy change of the system if its heat output is 50 J.
[*Answer:* 200 J]
3. A gas expanΔS when its internal energy changes by 700.0 J at a constant pressure of 101 kPa.

(a) What is the change in its volume if its enthalpy change is 250 J?
(b) Calculate the new volume of the gas if its original volume is 11.5 dm^3.

[*Answers:* (a) 9.4 dm^3 (b) 20.9 dm^3]

4. The heat output of 1 mol of a diatomic gas is 150 J when its temperature changes to 300 K at constant volume.
What is the initial temperature of the gas?

(R = 8.314 J K^{-1} mol^{-1}) [*Answer:* 307 K]

5. The volume of a system increases by 15 dm^3 when it undergoes a reversible isothermal process at a constant pressure of 1.5 atm. Calculate

(a) the change in internal energy of the system;
(b) the work done by the system.

[*Answers:* (a) 0 (b) 2.3 kJ]

6. 1.5 mol of an ideal monatomic gas initially at 0°C and 500 mmHg was taken through a reversible adiabatic process during which its pressure increases by 260 mmHg. If the initial volume of the gas is 12.5 dm^3, calculate

(a) the final temperature of the gas;
(b) the work done during the process.

(R = 8.314 J K^{-1} mol^{-1}) [*Answer:* (a) 432 K (b) −3.0 kJ]

9.7 THE SECOND LAW OF THERMODYNAMICS

There are different ways of stating the second law of thermodynamics. We will state it here as follows: A process would only occur spontaneously if there is an increase in the overall or total entropy of the universe.

A spontaneous change or process is that which has the natural tendency to occur at any rate without being driven by any external forces. For example, it is inconceivable that water would flow uphill without any external force supply. This is a common example of a non-spontaneous process. On the other hand, the flow of water downhill is spontaneous.

The second law of thermodynamic is of extreme importance in chemistry as it helps explain a wide range of phenomena. In addition, it helps in predicting the behaviour of a system under different conditions, such as if a process would occur or not, or when equilibrium would be achieved. All this is possible by the quantitative treatment and interpretation of two important concepts: entropy and Gibb’s free energy. These two important concepts are now treated, in turn, below.

9.7.1 Entropy

Entropy *S*, measured in J K^{-1}, is a measure of the degree of disorderliness or randomness of a system. The more disorderly a system, the higher its entropy, and vice versa. The standard molar entropy of a substance, measured in J K^{-1} mol^{-1}, is the entropy of 1 mol of a substance at 1 atm. Entropy is lowest in soliΔS, followed by liquiΔS, and highest in gases because of the very high degree of freedom of the molecules.

Entropy is a function of enthalpy change. When a system loses heat, then there is a decrease in the disorderliness of the system, while the reverse occurs during an endothermic process.

In general, the entropy change Δ*S* of a system is given by the relation

$$\Delta S = S_2 - S_1$$

where S_1 = The initial entropy of the system.

S_2 = The final entropy of the system.

Like standard heat of reaction, Hess's law can also be used to calculate the standard entropy change of a reaction. Thus the standard entropy change of a reaction is the algebraic difference between the total standard entropy of the products and the reactants:

$$\Delta S^o = \sum nS^\circ (\text{products}] - \sum nS^\circ [\text{reactants}]$$

where *n* and S^o are the amount and standard entropy, respectively, of each specie taking place in the reaction.

As the entropy of a system is altered, a corresponding but opposite change occurs to the entropy of its surroundings. In an exothermic reaction, the heat released decreases the entropy of the system, but it is used to increase the disorder of the surroundings, i.e., increasing its entropy. The reverse of this process holΔS for an endothermic process. The change in the entropy of the surroundings ΔS_{surr} is proportional to the heat output of a system and inversely proportional to the absolute temperature, i.e.

$$\Delta S_{surr} = -\frac{\Delta H}{T} \text{ (at constant pressure)} \quad (9.63)$$

The total entropy change of a system and its surroundings is called the total or overall entropy, or the entropy of the universe ΔS_T:

$$\Delta S_T = \Delta S + \Delta S_{surr} \quad (9.64)$$

This equation is of great importance as it helps to predict the feasibility of processes, as follows:

If $\Delta S_T < 0$, then process is not spontaneous.
If $\Delta S_T = 0$, then process is at equilibrium or reversible.
If $\Delta S_T > 0$, then process is spontaneous but not reversible.

Substituting Equation (9.63) into (9.64) we obtain

$$\Delta S_T = \Delta S - \frac{\Delta H}{T} \quad (9.65)$$

Since $\Delta S_T = 0$ for a reversible system, then Equation (9.65) becomes

$$\Delta S - \frac{\Delta H}{T} = 0$$

So $\Delta S = \frac{\Delta H}{T}$ (9.66)

Equation (9.66) is used for calculating the change in the entropy of a reversible system at equilibrium, such as phase transition, i.e., change of state.

We can proceed from Equation (9.66) to see how entropy varies with pressure, volume and temperature. We know that the first law is given as

$$\Delta H = DU + P\Delta U \quad (9.67)$$

Also, we know from Equation (9.67) that

$$\Delta H = T\Delta S$$

Substituting this into Equation (9.68) and dividing through by T we obtain

$$\Delta S = \frac{\Delta U}{T} + \frac{P\Delta V}{T}$$

For instantaneous change we have

$$\Delta S = \frac{dU}{T} + \frac{PdV}{T} \quad (9.68)$$

The ideal gas equation for n moles of a gas is

$$PV = nRT$$

$$\therefore P = \frac{nRT}{V} \quad (9.69a)$$

The instantaneous change in the internal energy of a gas is given as

$$dU = nC_{v,m}dT \quad (9.69b)$$

Substituting Equations (9.69a) and (9.69b) into (9.68) we have

$$\Delta S = nC_{v,m}\frac{dT}{T} + nR\frac{dV}{V} \quad (9.70)$$

We now integrate Equation (9.70) within the limits $S = S_1$ at T_1, V_1 and $S = S_2$ at T_2, V_2, i.e.

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2}\frac{1}{T}\,dT + \int_{V_1}^{V_2}\frac{1}{V}\,dT \quad (9.71)$$

Thus $S_2 - S_2 = \Delta S = \ln[T]_{T_1}^{T_2} + \ln[V]_{V_1}^{V_2}$

So $\Delta S = \ln T_2 - \ln T_1 + \ln V_2 - \ln V_1$

Then $\Delta S = \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right) \quad (9.72)$

Writing Equation (9.72) in terms of common logarithms we have

$$\Delta S = 2.3003nC_{v,m}\log\frac{T_2}{T_1} + 2.3003nR\log\frac{V_2}{V_1} \quad (9.73)$$

Equations (9.72) and (9.73) relate the entropy change of n moles of an ideal gas undergoing a reversible process with temperature and volume. The entropy change with temperature and pressure can be obtained from Equation (9.72) or (9.73) to be:

$$\Delta S = nC_{p,m}\ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1} \quad (9.74)$$

In terms of common logarithms we have

$$\Delta S = 2.303nC_{p,m}\log\frac{T_2}{T_1} - 2.3003nR\log\frac{V_2}{V_1} \quad (9.75)$$

Example 1 Calculate the standard entropy change of the reaction $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$.

($S^o[CO(g)]$ = 197.67 J K^{-1} mol^{-1}, $S^o[O_2(g)]$ = 205.14 J K^{-1} mol^{-1}, $S^o[CO_2(g)]$ = 213.74 J K^{-1} mol^{-1})

Solution We have to apply the equation

$$\Delta S^o = \sum nS^\circ(\text{products}] - \sum nS^\circ(\text{reactants})$$

The only product is 2 mol of $CO_2(g)$. Thus

$\sum nS^\circ(\text{products}]$ = 2 mol × $S^o[CO_2(g)]$

So $\sum nS^\circ(\text{products}] = 2\cancel{\text{mol}} \times \frac{205.14\ \text{J K}^{-1}}{1\cancel{\text{mol}}} = 410.28\ \text{J K}^{-1}$

The reactants consist of 2 mol of $CO(g)$ and 1 mol of $O_2(g)$. Then

$\sum nS^\circ(\text{reactants})$ = 2 mol × $S^o[CO(g)]$ + 1 mol × $S^o[O_2(g)]$

So $\sum nS^\circ(\text{reactants}) = 2\cancel{\text{mol}} \times \frac{197.67\ \text{J K}^{-1}}{1\cancel{\text{mol}}} + 1\cancel{\text{mol}} \times \frac{213.74\ \text{J K}^{-1}}{1\cancel{\text{mol}}}$

= (395.34 + 213.74) J K^{-1} = 609.08 J K^{-1}

ΔS^o = ?

Finally, we now substitute to obtain

ΔS^o = 609.08 J K^{-1} – 410.28 J K^{-1}

= 198.80 J K^{-1}

The positive value of ΔS^o shows that the entropy of the system increases as the product is formed.

Example 2 Calculate the entropy change accompanying the combustion of methane if the equation of reaction is given below:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

($S^o[CH_4(g)]$ = 186.3 J K^{-1} mol^{-1}, $S^o[O_2(g)]$ = 205.1 J K^{-1} mol^{-1}, $S^o[CO_2(g)]$ = 213.7 J K^{-1} mol^{-1}, $S^o[H_2O(g)]$ = 188.8 J K^{-1} mol^{-1})

Solution

We have to apply the relation

$$\Delta S^o = \sum nS^\circ(\text{reactants}] - \sum nS^\circ(\text{reactants}]$$

The products consist of 1 mol of $CO_2(g)$ and 2 mol of $H_2O(g)$. Thus

$\sum nS^\circ(\text{reactants}]$ = 1 mol × $S^o[CO_2(g)]$ + 2 mol × $S^o[H_2O(g)]$

Then $\sum nS^\circ(\text{reactants}) = 1\cancel{\text{mol}} \times \frac{197.67\ \text{J K}^{-1}}{1\cancel{\text{mol}}} + 2\cancel{\text{mol}} \times \frac{188.8\ \text{J K}^{-1}}{1\cancel{\text{mol}}}$

$= 213.7\ \text{J K}^{-1} + 377.6\ \text{J K}^{-1} = 591.3\ \text{J K}^{-1}$

The reactants consist of 1 mol of $CH_4(g)$ and 2 mol of $O_2(g)$. Thus

$\sum nS^\circ(\text{products}) = 1\ \text{mol} \times S^o[CH_4(g)] + 2\ \text{mol} \times S^o[O_2(g)]$

Then $\sum nS^\circ(\text{products}) = 1\cancel{\text{mol}} \times \frac{186.3\ \text{J K}^{-1}}{1\cancel{\text{mol}}} + 2\cancel{\text{mol}} \times \frac{20.5\ \text{J K}^{-1}}{1\cancel{\text{mol}}}$

$= 186.3\ \text{J K}^{-1} + 410.2\ \text{J K}^{-1} = 596.5\ \text{J K}^{-1}$

$\Delta S^o = ?$

Substituting we now obtain

$\Delta S^o = 591.3\ \text{J K}^{-1} - 596.5\ \text{J K}^{-1}$

$= -5.2\ \text{J K}^{-1}$

The negative value of entropy change shows that the entropy of the system decreases as the products are formed.

Example 3 The last stage of the production of nitric acid by the Ostwald process involves the disproportionation of nitrogen oxide in water:

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

Calculate the standard molar entropy of nitric acid if the entropy of the reacting system decreases by 286.6 J K^{-1} as the products are formed.

($S^o[NO_2(g)] = 240.1\ \text{J K}^{-1}\text{mol}^{-1}$, $S^o[H_2O(l)] = 69.9\ \text{J K}^{-1}\text{mol}^{-1}$, $S^o[NO(g)] = 210.8\ \text{J K}^{-1}\text{mol}^{-1}$)

Solution As usual, we have to apply the relation

$$\Delta S^o = \sum nS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})$$

The products consist of 2 mol of $HNO_3(aq)$ and 1 mol $NO(g)$. Thus

$$\sum nS^\circ(\text{products}) = 2\ \text{mol} \times S^o[HNO_3(aq)] + 1\ \text{mol} \times S^o[NO(g)]$$

Let $S^o[HNO_3(aq)]$ be x.

So $\sum nS^\circ(\text{products}) = 2\ \text{mol} \times x + 1\cancel{\text{mol}} \times \frac{210.8\ \text{J K}^{-1}}{1\cancel{\text{mol}}}$

$= 2x \text{ mol} + 210.8 \text{ J K}^{-1}$

The reactants consist of 3 mol of $NO_2(g)$ and 1 mol of $H_2O(l)$. Thus

$$\sum nS^{o}(\text{reactants}) = 3 \text{ mol} \times S^{o}[NO_2(g)] + 1 \text{ mol} \times S^{o}[H_2O(l)]$$

Then $\sum nS^{o}(\text{reactants}) = 3\cancel{\text{mol}} \times \frac{240.1 \text{ J K}^{-1}}{1\cancel{\text{mol}}} + 1\cancel{\text{mol}} \times \frac{69.9 \text{ J K}^{-1}}{1\cancel{\text{mol}}}$

$= 720.3 \text{ J K}^{-1} + 69.9 \text{ J K}^{-1} = 790.2 \text{ J K}^{-1}$

Since the entropy decreases, then

$$\Delta S^{o} = -286.6 \text{ J K}^{-1}$$

Substituting we have

$-286.6 \text{ J K}^{-1} = 2x \text{ mol} + 210.8 \text{ J K}^{-1} - 790.2 \text{ J K}^{-1}$

Thus $2x \text{ mol} = 790.2 \text{ J K}^{-1} - 210.8 \text{ J K}^{-1} - 286.6 \text{ J K}^{-1} = 292.8 \text{ J K}^{-1}$

$\therefore\ x = \frac{292.8 \text{ J K}^{-1}}{2 \text{ mol}}$

$= 146.4 \text{ J K}^{-1} \text{ mol}^{-1}$

Example 4 Calculate the ΔS for the conversion of 1 mol of water to ice at 0^{o}C, given that the heat of fusion of water is 333.55 J g^{-1}.

(H = 1, O = 16)

Solution Since the conversion of ice to water is an endothermic process, then ΔH must be positive. In other worΔS, the conversion of ice to water leaΔS to an increase in entropy. Thus

$$\Delta S = \frac{\Delta H}{T}$$

The total heat absorbed during the phase transition is calculated from the relation

$$\Delta H = m \times \Delta H_f$$

The mass of 1 mol of $H_2O(g)$ is its molar mass, i.e.

$m = M = [(1 \times 2) + 16] \text{ g mol}^{-1} = 18 \text{ g mol}^{-1}$

$\therefore\ \Delta H = 18 \cancel{\text{g}} \text{ mol}^{-1} \times \frac{333.55 \text{ J}}{1\cancel{\text{g}}} = 6003.9 \text{ J mol}^{-1}$

T = 273 K + 0°C = 273 K

ΔS = ?

Substituting we have

$$\Delta S = \frac{6003.9 \text{ J mol}^{-1}}{273 \text{ K}}$$

= 22.0 J K^{-1} mol^{-1}

Alternatively, we can apply the relation

$$\Delta S^o = S^o_2 - S^o_1$$

The standard molar entropies of water and ice at 0°C are 65.2 J K^{-1} mol^{-1} and 43.2 J K^{-1} mol^{-1}. Thus

ΔS^o = 65.2 J K^{-1} mol^{-1} – 43.2 J K^{-1} mol^{-1}

= 22.0 J K^{-1} mol^{-1}

Example 5 The entropy change accompanying the conversion of 1 mol of water to water vapour at 100°C is 109.1 J K^{-1} mol^{-1}. What is the molar heat of vaporisation of water?

Solution ΔH should be positive since heat is absorbed, i.e., the entropy increases. Thus

$$\Delta S = \frac{\Delta H_v}{T_b}$$

$\therefore$ $\Delta H_v = T_b \Delta S$

ΔS = 110.1 J K^{-1} mol^{-1}

T_b = 273 K + 100°C = 373 K

ΔH_v = ?

Substituting we have

$$\Delta H_v = 373 \cancel{\text{K}} \times \frac{110.1 \text{ J mol}^{-1}}{1 \cancel{\text{K}}}$$

= 41.1 kJ mol^{-1}

Example 6 Show that the change of entropy with temperature and pressure of a system undergoing a reversible process can be given by the equation

$$\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} - \frac{P_2}{P_1}$$

Solution

We have to begin from the equation

$$\Delta S = nC_{p,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \quad (9.76)$$

The general gas equation is given as follows:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore \frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1} \quad (9.77)$$

Substituting Equation (9.77) into (9.76) we obtain

$$\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1T_2}{P_2T_1}$$

Thus $\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} + nR \ln \frac{T_2}{T_1}$ (9.78)

Using $R = C_{p,m} - C_{v,m}$ in Equation (9.78) we obtain

$$\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} + n (C_{p,m} - C_{v,m}) \ln \frac{T_2}{T_1} \quad (9.79)$$

Thus $\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} + nC_{p,m} \ln \frac{T_2}{T_1} - nC_{v,m} \ln \frac{T_2}{T_1}$

So $\Delta S = nC_{p,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$ (9.80)

or $\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$ (9.81)

Example 7 1 mol of an ideal diatomic gas at a temperature of 25°C expanΔS reversibly from 10.0 to 17 dm^3. Calculate the entropy change of the process if the final temperature of the gas is 15°C.

(R = 8.314 J K^{-1} mol^{-1})

Solution We have to apply equation (9.81) for 1 mol of a gas

$$\Delta S = C_{v,m} \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

For an ideal diatomic gas we have

$$C_{v,m} = \frac{5}{2} R$$

R = 8.314 J K^{-1} mol^{-1}

Thus $C_{v,m} = \frac{5}{2} \times 8.314$ J K^{-1} mol^{-1} = 20.785 J K^{-1} mol^{-1}

T_1 = 273 K + 25°C = 298 K
T_2 = 273 K + 30°C = 303 K
V_1 = 10.0 dm^3
V_2 = 15 dm^3
ΔS = ?

Substituting we obtain

$$\Delta S = 20.785 \text{ J K}^{-1}\text{mol}^{-1} \times \ln \frac{303 \cancel{\text{K}}}{298 \cancel{\text{K}}} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \frac{15 \cancel{\text{dm}^3}}{10.0 \cancel{\text{dm}^3}}$$

So ΔS = 20.785 J K^{-1} mol^{-1} × 0.02 + 8.314 J K^{-1} mol^{-1} × 0.4
Then ΔS = 0.42 J K^{-1} mol^{-1} + 3.3 J K^{-1} mol^{-1}
= 3.4 J K^{-1} mol^{-1}

Example 8 2.5 mol of an ideal monatomic gas initially at 25°C and 101 kPa undergoes a reversible process to 10°C and 55 kPa. What is the entropy change of the gas?

(R = 8.314 J K^{-1} mol^{-1})

Solution We have to apply the relation

$$\Delta S = nC_{p,m} \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$$

For a monatomic gas we have

$C_{p,m} = \frac{5}{2} R$

$R = 8.314 \text{ J K}^{-1} \text{mol}^{-1}$

Thus $C_{p,m} = \frac{5}{2} \times 8.314 \text{ J K}^{-1} \text{mol}^{-1} = 20.785 \text{ J K}^{-1} \text{ mol}^{-1}$

$T_1 = 273 \text{ K} + 25°\text{C} = 298 \text{ K}$

$T_2 = 273 \text{ K} + 10°\text{C} = 283 \text{ K}$

$P_1 = 101 \text{ kPa}$

$P_2 = 55 \text{ kPa}$

$\Delta S = ?$

Substituting we obtain

$$\Delta S = 2.5 \cancel{\text{mol}} \times \frac{20.785 \text{ J K}^{-1}}{1 \cancel{\text{mol}}} \times \text{In} \frac{283 \cancel{\text{K}}}{298 \cancel{\text{K}}} - 2.5 \text{ mol} \times \frac{8.314 \text{ J K}^{-1}}{1 \cancel{\text{mol}}} \times \text{In} \frac{55 \cancel{\text{kPa}}}{101 \cancel{\text{kPa}}}$$

So $\Delta S = 51.96 \times (-0.05) \text{ J K}^{-1} - 20.785 \times 0.6 \text{ J K}^{-1}$

Thus $\Delta S = -2.6 \text{ J K}^{-1} - 12.5 \text{ J K}^{-1}$

$= -15.1 \text{ J K}^{-1}$

Example 9 The entropy of 2.5 mol of an ideal gas initially at 27°C increases by 15.5 J K^{-1} when it expanΔS at constant pressure. What is the final temperature of the gas?

$$(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1},\ C_{p,m} = \tfrac{5}{2} R)$$

Solution We have to apply the equation

$$\Delta S = nC_{p,m} \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$$

Since pressure is constant, then $P_1 = P_2$. The above equation then reduces to

$\Delta S = nC_{p,m} \ln \frac{T_2}{T_1}$

$C_{p,m} = \frac{5}{2} R$

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

So $C_{p,m} = \frac{5}{2} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 20.785 \text{ J K}^{-1} \text{ mol}^{-1}$

The entropy change must be assigned a positive sign because the entropy increases. Thus

$\Delta S = 15.5 \text{ J K}^{-1}$

$T_1 = 273 \text{ K} + 27°\text{C} = 300 \text{ K}$

$n = 2.5 \text{ mol}$

$T_2 = ?$

Substituting we have

$$15.5 \text{ J K}^{-1} = 2.5 \cancel{\text{mol}} \times \frac{20.785 \text{ J K}^{-1}}{1 \cancel{\text{mol}}} \times \ln \frac{T_2}{300 \text{ K}}$$

$$\text{So } 15.5 \text{ J K}^{-1} = 52 \text{ J K}^{-1} \times \ln \frac{T_2}{300 \text{ K}}$$

$$\text{Thus } \ln \frac{T_2}{303 \text{ K}} = \frac{15.5 \cancel{\text{J}} \cancel{\text{K}^{-1}}}{52 \cancel{\text{J}} \cancel{\text{K}^{-1}}} = 0.30$$

Taking the natural antilogarithm of both sides yielΔS

$$\frac{T_2}{300 \text{ K}} = e^{0.30} = 1.35$$

Cross-multiplying we have

$T_2 = 1.35 \times 300 \text{ K}$

$= 405 \text{ K}$

Example 10 1 mol of an ideal gas initially at 27°C undergoes a reversible change at constant volume. Calculate the entropy change if the final temperature of the gas is 0°C.

$(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, C_{v,m} = \frac{3}{2} R)$

Solution The applicable equation for entropy change for 1 mol of a gas is

$$\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

Since the process is isochoric, i.e., occurring at constant volume, then $V_1 = V_2$. The above equation then reduces to

$\Delta S = C_{v,m} \ln \frac{T_2}{T_1}$

$C_{v,m} = \frac{3}{2} R$

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Thus $C_{v,m} = \frac{3}{2} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$

$T_1 = 273 \text{ K} + 27°\text{C} = 300 \text{ K}$

$T_2 = 273 \text{ K} + 0°\text{C} = 273 \text{ K}$

$\Delta S = ?$

Substituting we have

$\Delta S = 12.471 \text{ J K}^{-1}\text{mol}^{-1} \times \frac{273 \cancel{\text{K}}}{300 \cancel{\text{K}}}$

So $\Delta S = 12.471 \text{ J K}^{-1} \text{ mol}^{-1} \times (-0.94)$

$= -1.2 \text{ J K}^{-1} \text{ mol}^{-1}$

Example 11 10 mol of an ideal gas undergoes a reversible change at constant temperature. Calculate the initial volume of the gas if its volume and entropy decrease to 2.0 dm^3 and 25.5 J K^{-1} respectively.

($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

Solution We have to apply the equation

$$\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

Since the process is isothermal, then $T_1 = T_2$. The above equation then reduces to

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

The entropy change must be assigned a minus sign because the entropy decreases. Thus

$\Delta S = -25.5 \text{ J K}^{-1}$

$V_2 = 2.0 \text{ dm}^3$

$n = 10 \text{ mol}$

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$V_1 = ?$

Substituting we have

$$-25.5 \text{ J K}^{-1} = 10\cancel{\text{mol}} \times \frac{8.314 \text{ J K}^{-1}}{1\cancel{\text{mol}}} \times \ln \frac{2.0 \text{ dm}^3}{V_1}$$

$$\text{Then } -25.5 \text{ J K}^{-1} = 8.314 \text{ J K}^{-1} \times \ln \frac{2.0 \text{ dm}^3}{V_1}$$

$$\text{Thus } \ln \frac{2.0 \text{ dm}^3}{V_1} = \frac{25.5 \cancel{\text{J}} \cancel{\text{K}^{-1}}}{83.14 \cancel{\text{J}} \cancel{\text{K}^{-1}}} = -0.31$$

Taking the natural antilogarithms of both sides we obtain

$$\frac{2.0 \text{ dm}^3}{V_2} = e^{-0.31} = 0.73$$

Cross-multiplying we obtain

$V_1 \times 0.73 = 2.0 \text{ dm}^3$

$$\therefore \; V_1 = \frac{2.0 \text{ dm}^3}{0.73}$$

$= 2.7 \text{ dm}^3$

Practice Problems

1. Calculate the standard entropy of the reaction

$$H_2(g) + 2O_2(g) \rightarrow 2H_2O(g)$$

($S^o[H_2(g)] = 130.68 \text{ J K}^{-1} \text{ mol}^{-1}$, $S^o[O_2(g)] = 205.14 \text{ J K}^{-1} \text{ mol}^{-1}$, $S^o[H_2O(g)] = 188.83 \text{ J K}^{-1} \text{mol}^{-1}$) [*Answer:* -163.30 J K^{-1}]

2. Calculate the change in entropy of 155 g of ethanol when it vaporises at 78°C.

   (H = 1, C = 12, O = 16, ΔH = 43.5 kJ mol^{-1}) [*Answer:* 418 J K^{-1}]

3. 1 mol of an ideal diatomic gas undergoes a reversible process at STP Calculate the entropy change of the system if the final temperature and pressure of the gas are 50°C and 1.5 atm respectively.

   (R = 8.314 J K^{-1} mol^{-1}) [*Answer:* 1.5 J K^{-1} mol^{-1}]

4. 2.5 mol of an ideal gas undergoes a reversible isobaric process at 0°C to a temperature of 27°C. What is the entropy change of the gas?

   (R = 8.314 J K^{-1} mol^{-1}, $C_{p,m} = \frac{5}{2} R$) [*Answer:* 4.9 J K^{-1}]

5. 1 mol of an ideal gas undergoes a reversible isothermal process at 760 mmHg. Calculate the final pressure of the gas if its entropy increases by 5.4 J K^{-1} mol^{-1}.

   (R = 8.314 J K^{-1} mol^{-1}) [*Answer:* 400 mm Hg]

9.7.1.1 Entropy of mixing

If two gases at the same initial pressure are mixed, then the entropy of mixing ΔS_M is defined as

$$\Delta S_M = -R(n_1 x_1 \ln x_1 + n_2 x_2 \ln x_2)$$

where n_1 = The number of moles of gas 1.

n_2 = The number of moles of gas 2.

x_1 = The mole fraction of gas 1.

x_2 = The mole fraction of gas 2.

R = Universal gas constant.

Example 50.0 g of nitrogen and 56 g of carbon dioxide were mixed to form a mixture of ideal gases after the partition separating them was removed. Calculate the entropy of mixing if both gases were at the same initial pressure.

(R = 8.314 J K^{-1} mol^{-1}, C = 12, N = 14)

Solution We have to apply the relation

$$\Delta S_M = -R(n_1 x_1 \ln x_1 + n_2 x_2 \ln x_2)$$

The number of moles of each gas is obtained from the relation

$$n = \frac{m}{M}$$

For nitrogen we have

$m = 50.0$ g

$M = (14 \times 2)$ g mol^{-1} = 28 g mol^{-1}

$n_1 = ?$

Substituting we have

$$n_1 = \frac{50.0\,\cancel{g} \times 1\,\text{mol}}{28\,\cancel{g}} = 1.8\ \text{mol}$$

For carbon dioxide we have

$m = 56$ g

$M = [12 + (16 \times 2)]$ g mol^{-1} = 44 g mol^{-1}

$n_2 = ?$

Substituting we have

$$n_2 = \frac{56\,\cancel{g} \times 1\,\text{mol}}{44\,\cancel{g}} = 1.3\ \text{mol}$$

$n_t = n_1 + n_2$

So $n_t = 1.8\ \text{mol} + 1.3\ \text{mol} = 3.1\ \text{mol}$

The mole fraction of each component is obtained from the relation

$$x = \frac{n_1}{n_t}$$

For nitrogen we have

$$x_1 = \frac{1.8\,\cancel{\text{mol}}}{3.1\,\cancel{\text{mol}}}$$

$= 0.58$

Since the total mole fraction must be 1, then

$x_2 = 1.0 - 0.58 = 0.42$

$R = 8.314$ J K^{-1} mol^{-1}

$\Delta S_M = ?$

We now substitute to obtain

$$\Delta S_M = \frac{8.314\ \text{J K}^{-1}}{1\ \text{mol}} \times (1.8\ \text{mol} \times 0.58 \times \text{In } 0.58 + 1.3\ \text{mol} \times 0.42 \times \text{In } 0.42)$$

So $\Delta S_M = \frac{8.314\ \text{J K}^{-1}}{1\ \text{mol}} \times [1.8\ \text{mol} \times 0.58 \times (-0.54) + 1.3\ \text{mol} \times 0.42 \times (-0.87)]$

Then $\Delta S_M = \frac{8.314\ \text{J K}^{-1}}{1\ \text{mol}} \times (-0.56\ \text{mol} - 0.48\ \text{mol})$

Thus $\Delta S_M = \frac{8.314\ \text{J K}^{-1}}{1\ \cancel{\text{mol}}} \times (-0.56\ \cancel{\text{mol}}) - \frac{8.314\ \text{J K}^{-1}}{1\ \cancel{\text{mol}}} \times (-0.48\ \cancel{\text{mol}})$

So $\Delta S_M = 4.6\ \text{J K}^{-1} + 4.0\ \text{J K}^{-1}$

$= 8.6\ \text{J K}^{-1}$

Practice Problem

Calculate the entropy of mixing of 2 mol of nitrogen and 1 mol of hydrogen, assuming the gases do not react and were at the same initial pressure.

[*Answer:* 7.2 J K^{-1}]

9.7.2 Gibb's Free Energy

The Gibb's free energy G of a system is the energy available for doing work. The values of the free energy change (or simply free energy) ΔG have the following implications:

If $\Delta G > 0$, then the process is not feasible (spontaneous).
If $\Delta G < 0$, then the process is feasible (spontaneous).
If $\Delta G = 0$, then the process is at equilibrium.

Figure 9.3 Josiah Willard Gibbs, American physicist and chemist (1839–1903)

The relationship between the ΔG of a process and its ΔS can be obtained from

ΔS_T, as follows:

$$\Delta S_T = \Delta S - \frac{\Delta H}{T} \quad (9.82)$$

We now multiply equation (9.82) by $-T$ to obtain

$$-T\Delta S_T = \Delta H - T\Delta S$$

The term $-T\Delta S_T$ is defined as the change in the free energy ΔG of the system. Thus

$$\Delta G = \Delta H - T\Delta S \quad (9.83)$$

At standard conditions we have

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

ΔG^o is the standard free energy of the process. Using Hess's law, the standard free energy change of reaction is calculated in just the same way as the standard heat of reaction:

$$\Delta G^o = \sum n\Delta G_f^o(\text{products}) - \sum n\Delta G_f^o(\text{reactants}) \quad (9.84)$$

ΔG^o_f is the standard free energy of formation of a substance. The standard free energy of formation of a substance in the standard free energy of reaction for the formation of one mole of the substance from its elements at standard conditions. Like standard heat of formation, the standard free energy of formation of elements in their standard states is zero.

The free energy of a reacting system is related to its composition by the relation

$$\Delta G = RT \ln \frac{Q}{K} \quad (9.85)$$

where Q = Reaction quotient.

K^5 = Equilibrium constant.

Equation (9.85) can also be written as:

$$\Delta G = RT \ln Q - RT \ln K \quad (9.86)$$

Since Q is unity at standard conditions, then the above equation then becomes

$$\Delta G^o = -RT \ln K \quad (9.87)$$

This equation relates the standard free energy of a process to its equilibrium constant. The free energy at any other conditions can be obtained by substituting Equation (9.88) into (9.87) to obtain

$$\Delta G = \Delta G^o + RT \ln Q \quad (9.88)$$

Example 1 Calculate the standard free energy of the reaction $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$.

(ΔG^o_f [$CH_4(g)$] = −50.7 kJ mol^{-1}, ΔG^o_f [$CO_2(g)$] = −394.4 kJ mol^{-1}, ΔG^o_f [$H_2O(g)$] = −228.6 kJ mol^{-1})

Solution We have to apply the relation

$$\Delta G^o = \sum n\Delta G^o_f\,(\text{products}) - \sum n\Delta G^o_f\,(\text{reactants})$$

The products consist of 1 mol of $CO_2(g)$ and 2 mol of $H_2O(g)$. Thus

$$\sum n\Delta G^o_f\,(\text{products}) = 1\text{ mol} \times \Delta G^o_f\,[CO_2(g)] + 2\text{ mol} \times \Delta G^o_f\,[H_2O(g)]$$

Then $\sum n\Delta G^o_f\,(\text{products}) = 1\cancel{\text{mol}} \times \frac{(-394.4\text{ kJ})}{1\text{ mol}} + 2\cancel{\text{mol}} \times \frac{(-228.6\text{ kJ})}{1\text{ mol}}$

$$= -394.4\text{ kJ} - 457.2\text{ kJ} = -851.6\text{ kJ}$$

The reactants consist of 1 mol each of $CH_4(g)$ and $O_2(g)$. Thus

$$\sum n\Delta G^o_f\,(\text{products}) = 1\text{ mol} \times \Delta G^o_f\,[CH_4(g)] + 2\text{ mol} \times 0$$

So $\sum n\Delta G^o_f\,(\text{products}) = 1\cancel{\text{mol}} \times \frac{(-394.4\text{ kJ})}{1\text{ mol}} = -50.7\text{ kJ}$

ΔG^o = ?

We now substitute to obtain

$$\Delta G^o = -851.6\text{ kJ} - (-50.7\text{ kJ})$$
$$= -851.6\text{ kJ} + 50.7\text{ kJ}$$
$$= -800.9\text{ kJ}$$

The negative value of ΔG^o shows that the reaction is spontaneous at standard conditions. But the reverse process, i.e., the decomposition of water into its elements, is not because the ΔG^o would be 800.9 kJ. In other wor∆S, the reverse process will require energy to drive it.

Example 2 Nitrogen dioxide dissolves in water in the presence of air to form

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[5] The equilibrium constant of a reaction is its reaction quotient measured or calculated at equilibrium. Chemical equilibrium is treated in Chapter 11.

nitric acid, as follows:

$$4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$$

Determine the standard free energy of formation of nitric acid, given that the standard free energy of the reaction is −176.2 kJ.

$$(\Delta G^o_f[NO_2(g)] = 51.3 \text{ kJ mol}^{-1},\ \Delta G^o_f\,[H_2O(l)] = -237.1 \text{ kJ mol}^{-1})$$

Solution We have to apply the relation

$$\Delta G^o = \sum n\Delta G^o_f\,(\text{products}) - \sum n\Delta G^o_f\,(\text{reactants})$$

The product is 4 mol of $HNO_3(aq)$. Thus

$$\sum n\Delta G^o_f\,[\text{products}] = 4 \text{ mol} \times \Delta G^o_f\,[HNO_3(aq)]$$

Let $\Delta G^o_f\,[HNO_3(aq)]$ be x. Then

$$\sum n\Delta G^o_f\,[\text{products}] = 4 \text{ mol} \times x = 4x \text{ mol}$$

The reactants consist of 4 mol of $NO_2(g)$, 2 mol of $H_2O(l)$ and 1 mol of $O_2(g)$. Thus

$$\sum n\Delta G^o_f\,[\text{reactants}] = 4 \text{ mol} \times \Delta G^o_f\,[NO_2(g)] + 2 \text{ mol} \times \Delta G^o_f\,[H_2O(l)] + 1 \text{ mol} \times 0$$

So $\sum n\Delta G^o_f\,[\text{reactants}] = 4\cancel{\text{mol}} \times \dfrac{51.3 \text{ J}}{1 \text{ mol}} + 2 \text{ mol} \times \dfrac{(-237.1 \text{ kJ})}{1\cancel{\text{mol}}}$

$= 205.2 \text{ kJ} + (-474.2) \text{ kJ} = 205.2 \text{ kJ} - 474.2 \text{ kJ} = -269.0 \text{ kJ}$

$\Delta G^o = -176.2 \text{ kJ}$

We now substitute to obtain

$-176.2 \text{ kJ} = 4x \text{ mol} - (-269.0 \text{ kJ})$

Thus $4x \text{ mol} = -176.2 \text{ kJ} - 269.0 \text{ kJ} = -445.2 \text{ kJ}$

$\therefore\ x = \dfrac{445.2 \text{ kJ}}{4 \text{ mol}}$

$= -111.3 \text{ kJ mol}^{-1}$

Example 3 Calculate the standard free energy of the combustion of methane from the data given below:

	ΔH^o_f (kJ mol^{-1})	S^o (J K^{-1} mol^{-1})
$CH_4(g)$	−74.8	186.3
$O_2(g)$	0	205.1
$CO_2(g)$	−393.5	213.7
$H_2O(g)$	−241.8	188.8

Solution We have to apply the relation

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

We must, of course, write the equation of reaction:

$$CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g)$$

As usual, ΔH^o must be obtained from the relation

$$\Delta H^o = \sum n\Delta H^o_f\,(\text{products}] - \sum n\Delta H^o_f\,[\text{reactants}]$$

The reactants consist of 1 mol of $CO_2(g)$ and 2 mol of $H_2O(g)$. Thus

$$\sum n\Delta H^o_f\,(\text{products}] = 2\text{ mol} \times \Delta H^o_f\,[H_2O(g)] + 1\text{ mol} \times \Delta H^o_f[CO_2(g)]$$

Then $\sum n\Delta H^o_f\,(\text{products}] = 2\,\cancel{\text{mol}} \times \frac{(-241.8\text{ kJ})}{1\,\cancel{\text{mol}}} + 1\,\cancel{\text{mol}} \times \frac{(-73.8\text{ kJ})}{1\,\cancel{\text{mol}}}$

$= -483.6\text{ kJ} + (-393.5)\text{ kJ} = -483.6\text{ kJ} - 393.5\text{ kJ} = -877.1\text{ kJ}$

The reactants consist of 1 mol of $CH_4(g)$ and 2 mol of $O_2(g)$. Thus

$$\sum n\Delta H^o_f\,(\text{reactants}) = 1\text{ mol} \times \Delta H^o_f[CH_4(g)] + 2\text{ mol} \times 0$$

So $\sum n\Delta H^o_f\,(\text{reactants}) = 1\,\cancel{\text{mol}} \times \frac{(-73.8\text{ kJ})}{1\,\cancel{\text{mol}}} = -73.8\text{ kJ}$

$\Delta H^o = ?$

Substituting we have

$$\begin{aligned}\Delta H^o &= -877.1\text{ kJ} - (-73.8)\text{ kJ}\\ &= (-877.1 + 73.8)\text{ kJ}\\ &= -803.3\text{ kJ}\end{aligned}$$

We must also work out ΔS^o from the relation

$$\Delta S^o = \sum nS^o\,(\text{products}] - \sum nS^o\,(\text{reactants})$$

However, we need not show the details here because ΔS^o has been found to be -5.2 J K^{-1} for the same reaction in Example 2 of Section 9.7.1.

T = 298 K (at standard conditions)

ΔG^o = ?

Finally, we now substitute to obtain

$$\Delta G^o = -803300\ \text{J} - 298\ \cancel{\text{K}} \times \frac{(-5.2\ \text{J})}{1\cancel{\text{K}}}$$

Thus $\Delta G^o = -803300\ \text{J} + 1549.6\ \text{J}$

$= -802\ \text{kJ}$

Example 4 Calculate the free energy of a reaction at 300 K when

(a) $\Delta H = -1.5$ kJ, $\Delta S = 5.0\ \text{J K}^{-1}$

(b) $\Delta H = -1.5$ kJ, $\Delta S = -5\ \text{J K}^{-1}$

Solution

(a) We have to use the relation

$\Delta G = \Delta H - T\Delta S$

ΔH = 1500 J

$\Delta S = 5.0\ \text{J K}^{-1}$

T = 300 K

ΔG = ?

Substituting we obtain

$$\Delta G = 1500\ \text{J} - 300\ \cancel{\text{K}} \times \frac{5.0\ \text{J}}{\cancel{\text{K}}}$$

Then $\Delta G = 1500\ \text{J} - 1500\ \text{J}$

$= 0$

The fact that $\Delta G = 0$ shows that the system is at equilibrium at the given conditions.

(b) We have to apply the relation

$\Delta G = \Delta H - T\Delta S$

ΔH = 1500 J

$\Delta S = -5.0\ \text{J K}^{-1}$

T = 300 K

Substituting we have

$$\Delta G = 1500\ \text{J} - \cancel{\text{K}} \times \frac{(-1.5\ \text{J})}{1\,\cancel{\text{K}}}$$

So $\Delta G = 1500\ \text{J} + 1500\ \text{J}$

$= 3\ \text{kJ}$

The positive value of ΔG shows that the reaction is not spontaneous at the specified conditions.

Example 5 The Haber process for the production of ammonia is represented by the equation:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

What is the minimum temperature at which the reaction can occur?

	ΔH^o_f (kJ mol^{-1})	S^o(J K^{-1} mol^{-1})
$NH_3(g)$	−46.1	192.5
$N_2(g)$	0	191.6
$H_2(g)$	0	130.7

Solution We have to use the relation

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Since ΔG must be negative for the reaction to be feasible, then the minimum temperature is the temperature at which ΔG changes from positive to negative. If we assume that ΔS and ΔH are independent of temperature, then this correspon∆S to the equilibrium temperature, i.e., the temperature at which $\Delta G^o = 0$. Thus

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

We have to work out ΔH^o from the relation

$$\Delta H^o = \sum n\Delta H^\circ_f\,[\text{products}] - \sum n\Delta H^\circ_f\,[\text{reactants}]$$

The product is 2 mol of $NH_3(g)$. Thus

$$\sum n\Delta H^\circ_f\,[\text{products}] = 2\ \text{mol} \times \Delta H^o_f[NH_3(g)]$$

Then $\sum n\Delta H_f^\circ\text{[products]} = 2\,\cancel{\text{mol}} \times \frac{(-46.1\text{ kJ})}{1\,\cancel{\text{mol}}} = -\,92.2\text{ kJ}$

The reactants consist of 1 mol of $N_2(g)$ and 3 mol of $H_2(g)$, which are both elements in their standard states. Thus

$$\sum n\Delta H_f^\circ\text{(reactants)} = 0$$

Substituting we have

$$\Delta H^o = -92.2\text{ kJ} - 0 = -92.2\text{ kJ}$$

Similarly, we have to obtain ΔS^o from the relation

$\Delta S^o = \sum nS^\circ\text{(products)} - \sum nS^\circ\text{(products)}$

$\sum nS^\circ\text{(products)} = 2\text{ mol} \times \Delta S^o[NH_3(g)]$

Then $\sum nS^\circ\text{(products)} = 2\,\cancel{\text{mol}} \times \frac{192.5\text{ J K}^{-1}}{1\,\cancel{\text{mol}}} = 385.0\text{ J K}^{-1}$

$\sum nS^\circ\text{(reactants)} = 1\text{ mol} \times \Delta S^o[N_2(g)] + 3\text{ mol} \times \Delta S^o[H_2(g)]$

Then $\sum nS^\circ\text{(reactants)} = 1\,\cancel{\text{mol}} \times \frac{191.6\text{ J K}^{-1}}{1\text{ mol}} + 3\,\cancel{\text{mol}} \times \frac{130.7\text{ J K}^{-1}}{1\text{ mol}}$

$= 191.6\text{ J K}^{-1} + 392.1\text{ J K}^{-1} = 583.7\text{ J K}^{-1}$

Substituting we have

$\Delta S^o = 385.0\text{ J K}^{-1} - 583.7\text{ J K}^{-1} = -198.7\text{ J K}^{-1}$

$T = ?$

Finally, we now substitute to obtain

$T = \frac{-92200\,\cancel{\text{J}} \times 1\text{ K}}{-198.7\,\cancel{\text{J}}}$

$= 464$ K or 191°C.

Thus the reaction would be feasible above 191°C, i.e. ΔG would have become negative.

Example 6 The K_p for the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$ is 794 at 25°C . What is the free energy of the reaction at the same temperature when the partial pressures of hydrogen, iodine and hydrogen are 0.2 atm, 0.3 atm and 0.9 atm respectively?

$$(R = 8.314 \text{ J K}^{-1} \text{mol}^{-1})$$

Solution We have to apply the relation

$$\Delta G = \Delta G^o + RT \ln Q$$

We have to work out ΔG^o from the relation

$\Delta G^o = -RT \ln K$
$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
$T = 273 \text{ K} + 25°\text{C} = 298 \text{ K}$
$K = 794$
$\Delta G^o = ?$

Substituting we have

$$\Delta G^o = 1 \cancel{\text{mol}} \times \frac{8.314 \text{ J}}{1 \cancel{\text{mol}} \times 1 \cancel{\text{K}}} \times 298 \cancel{\text{K}} \times \ln 794$$

$$= -2477.572 \text{ J} \times 6.68 = -16.6 \text{ kJ}$$

The $Q_p{}^6$ of the reaction is given

$$Q_p = \frac{(P_{\text{HI}})^2}{P_{\text{H}_2} \times P_{\text{I}_2}}$$

$P_{HI} = 0.9 \text{ atm}$
$P_{H2} = 0.2 \text{ atm}$
$P_{I2} = 0.3 \text{ atm}$
$Q_p = ?$

Substituting we have

$$Q_p = \frac{(0.9 \text{ atm})^2}{0.2 \text{ atm} \times 0.3 \text{ atm}}$$

Thus $Q_p = \dfrac{0.81 \cancel{\text{atm}^2}}{0.06 \cancel{\text{atm}^2}} = 13.5$

$\Delta G = ?$

Finally, we now substitute into the original equation to obtain

$$\Delta G = -16.6\text{ kJ} + 1\,\cancel{\text{mol}} \times \frac{8.314\text{ J}}{1\,\cancel{\text{mol}} \times 1\,\cancel{\text{K}}} \times 300\,\cancel{\text{K}} \times \ln 13.5$$

So $\Delta G = -16.6\text{ kJ} + 2477.572\text{ J} \times 2.60$

$= -16.6\text{ kJ} + 6.44\text{ kJ}$

$= -10.2\text{ kJ}$

Practice Problems

1. Calculate the standard free energy of the reaction $CaCO_3(g) \rightarrow CaO(s) + CO_2(g)$.

   (ΔG^o_f [$CaCO_3(g)$] = −1128.80 kJ mol^{-1}, ΔG^o_f [$CaO(s)$] = −604.03 kJ mol^{-1}, ΔG^o_f= [$CO_2(g)$] = −394.36 kJ mol^{-1}) [*Answer:* 130.40 kJ]

2. Calculate the standard free energy change of the reaction $2C_2H_2(g) + 5O_2(g) \rightarrow 2H_2O(g) + 4CO_2(g)$ from the data given below.

	ΔH^o_f (kJ mol^{-1})	S^o(J K^{-1}mol^{-1})
$C_2H_2(g)$	226.73	200.94
$O_2(g)$	0	205.14
$CO_2(g)$	−393.51	213.74
$H_2O(g)$	−241.82	188.83

[*Answer:* 2453.04 kJ]

3. The free energy of a reacting system is −255 kJ mol^{-1}. What is the temperature of the system if the entropy change is 148 J K^{-1}? [*Answer:* 27°C]

4. The K_p of the reaction $H_2(g) + Cl_2(g)$ dk $2HCl(g)$ is 9.7×10^{31} at 298 K. What is the free energy of the reaction at 27°C when the partial pressures of hydrogen chloride, hydrogen and chlorine are 1.1 Torr, 0.5 Torr, and 0.5 Torr respectively?

   (R = 8.314 J K^{-1} mol^{-1}) [*Answer:* −178.5 kJ]

5. The decomposition of calcium carbonate is given by $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. Assuming entropy change and heat of reaction are independent of temperature, predict the temperature at which the reaction is likely to occur?

	ΔH^o_f(kJ mol^{-1})	S^o (J K^{-1}mol^{-1})

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[6] The Q_p of the reaction $aA(g) + bB(g)$ fi $cC(g) + dD(g)$ is $\frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b}$. See Chapter 11 for more details.

$CaCO_3(s)$	−1206.90	92.96
$CaO(s)$	−635.09	39.75
$CO_2(g)$	−393.51	213.74

[*Answer:* Above 1110 K]

9.7.2.1 Free energy and temperature

The variation of free energy with temperature at constant pressure is given by the Gibbs-Helmholtz equation

$$\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = \Delta H_1\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

where ΔG_2 = The free energy at absolute temperature T_2.
ΔG_1 = The free energy at absolute temperature T_1.
ΔH_1 = The reaction enthalpy at temperature T_1.

It should be noted that the above equation is only valid for a small temperature range.

Figure 9.4 Herman von Helmholtz, German physicist (1821–1894).

Example 1 Calculate the Gibb's free energy for the formation of water at 37°C, given that the standard free energy and heat of formation are −237.1 kJ mol^{-1} and −285.8 kJ mol^{-1} respectively.

Solution We have to apply the relation

$$\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = \Delta H_1\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

We use the values at standard conditions as the initial values. Thus

$\Delta G_1 = -237.1 \text{ kJ mol}^{-1}$

$\Delta H_1 = -285.8 \text{ kJ mol}^{-1}$

$T_1 = 273 \text{ K} + 25°\text{C} = 298 \text{ K}$

$T_2 = 273 \text{ K} + 37°\text{C} = 310 \text{ K}$

$\Delta G_2 = ?$

Substituting we have

$$\frac{\Delta G_2}{310 \text{ K}} - \frac{[-237.1 \text{ kJ mol}^{-1})}{298 \text{ K}} = -285.8 \text{ kJ mol}^{-1}\left(\frac{1}{310 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

So $\dfrac{\Delta G_2}{310 \text{ K}} + \dfrac{0.796 \text{ kJ mol}^{-1}}{1 \text{ K}} = -285.8 \text{ kJ mol}^{-1} \times \left(\dfrac{1.3 \times 10^{-4}}{1 \text{ K}}\right)$

Then $\dfrac{\Delta G_2}{310 \text{ K}} = \dfrac{0.037 \text{ kJ mol}^{-1}}{1 \text{ K}} - \dfrac{0.796 \text{ kJ mol}^{-1}}{1 \text{ K}}$

Thus $\dfrac{\Delta G_2}{310 \text{ K}} = \dfrac{0.759 \text{ kJ mol}^{-1}}{1 \text{ K}}$

Cross-multiplying we obtain

$\Delta G_2 = \dfrac{0.759 \text{ kJ mol}^{-1}}{1 \cancel{\text{K}}} \times 310 \cancel{\text{K}}$

$= -240 \text{ kJ mol}^{-1}$

Example 2 Calculate the free energy of water vapour at 110°C, given that the molar heat of vaporization of water is 40.7 kJ mol^{-1}.

Solution We have to apply the relation

$$\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = \Delta H_1\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Water is at equilibrium with its vapour at 100°C . Thus the free energy at 100°C is 0. If we define all initial values at this temperature, then

$\Delta G_1 = 0$

$\Delta H_1 = 4.7 \text{ kJ mol}^{-1}$

$T_1 = 273 \text{ K} + 100°\text{C} = 373 \text{ K}$

$T_2 = 273 \text{ K} + 110°\text{C} = 383 \text{ K}$

$\Delta G_2 = ?$

Substituting we have

$$\frac{\Delta G_2}{383\text{ K}} - 0 = 40.7\text{ kJ mol}^{-1}\left(\frac{1}{383\text{ K}} - \frac{1}{373\text{ K}}\right)$$

Then $\frac{\Delta G_2}{383\text{ K}} = 40.7\text{ kJ mol}^{-1} \times \left(\frac{7.00\times10^{-5}}{1\text{ K}}\right)$

Thus $\frac{\Delta G_2}{383\text{ K}} = \frac{0.00285\text{ kJ mol}^{-1}}{1\text{ K}}$

Cross-multiplying we have

$$\Delta G_2 = \frac{0.00285\text{ kJ mol}^{-1}}{1\cancel{\text{K}}} \times 383\ \cancel{\text{K}}$$

$$= -1.09\text{ kJ mol}^{-1}$$

Practice Problems

1. The standard free energy and enthalpy change of a reaction are −130.41 kJ mol^{-1} and −178.3 kJ mol^{-1} respectively. What is the change is the free energy of the reaction at 70°C? [*Answer:* −123 kJ mol^{-1}]
2. The free energy of a reaction are 12.95 kJ mol^{-1} and 19.91 kJ mol^{-1} at 25°C and 75°C respectively. Calculate the standard enthalpy change of the reaction.

[*Answer:* −28.6 kJ mol^{-1}]

9.7.2.2 Variation of Gibb's free energy with pressure and volume

At constant temperature, the free energy change of a system varies with pressure and volume, as follows:

$$\Delta G = G_2 - G_1 = nRT\ \ln\left(\frac{P_2}{P_1}\right) = nRT\ \ln\left(\frac{V_1}{V_2}\right)$$

where n = The number of moles of the gas.

P_1 = The initial pressure of the system.

P_2 = The final pressure of the system.

V_1 = The initial volume of the system.

V_2 = The final volume of the system.

R = Universal gas constant.

Example 1 The free energy of a system is related to enthalpy and entropy as follows:

$$G = H - TS$$

Show that the free energy change of a system is related to pressure by the equation

$$\Delta G = nRT \ln\left(\frac{P_2}{P_1}\right)$$

Solution We have to start by writing the equation for free energy in the differential form, as follows:

$\mathrm{d}G = \Delta H - T\Delta S - S\mathrm{d}T$ (9.89)

We now proceed by using appropriate substitutions for ΔH and ΔS. From the first law, we know that

$\Delta H = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P$ (9.90)

$\mathrm{d}U = \mathrm{d}Q - P\mathrm{d}V$ (9.91)

The entropy change for a reversible process is given as

$\Delta S = \frac{\mathrm{d}Q}{T}$

Thus $\mathrm{d}Q = T\Delta S$ (9.92)

Substituting Equation (9.92) into (9.91) we obtain

$\mathrm{d}U = T\Delta S - P\mathrm{d}V$ (9.93)

Substituting Equation (9.93) into (9.90) we obtain

$\Delta H = T\Delta S - P\mathrm{d}V + P\mathrm{d}V + V\mathrm{d}P$

So $\Delta H = T\Delta S + V\mathrm{d}P$ (9.94)

Substituting Equation (9.94) into (9.89) we obtain

$\mathrm{d}G = T\Delta S + V\mathrm{d}P - T\Delta S - S\mathrm{d}T$

So $\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T$ (9.95)

Since at constant temperature $\mathrm{d}T = 0$, then Equation (9.95) reduces to

$\mathrm{d}G = V\mathrm{d}P$ (9.96)

For an ideal gas we have

$$V = \frac{nRT}{P} \quad (9.97)$$

Substituting this into Equation (9.97) we obtain

$$dG = \frac{nRT}{P}\,dP \quad (9.98)$$

We can now integrate Equation (9.98) within the limits $G = G_1$ at P_1 and $G = G_2$ at P_2:

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} \frac{nRT}{P}\,dT$$

Since n, R and T are constant, then we have

$$\Delta G = G_2 - G_1 = nRT \int_{P_1}^{P_2} dP \quad (9.99)$$

Finally, we now arrive at the equation

$$\Delta G = G_2 - G_1 = nRT \ln\left(\frac{P_2}{P_1}\right) \quad (9.100)$$

Since pressure is inversely proportional to volume, then Equation (9.100) can also be written as

$$\Delta G = G_2 - G_1 = nRT \ln\left(\frac{V_1}{V_2}\right) \quad (9.101)$$

Example 2 2.5 mol of an ideal gas initially at 760 mmHg undergoes a reversible process at a constant temperature of 28°C. Calculate the change in free energy of the gas, given that the final pressure of the gas is 550 mmHg.

($R = 8.314$ J K^{-1} mol^{-1})

Solution We have to apply the relation

$$\Delta G = G_2 - G_1 = RT \ln\left(\frac{P_2}{P_1}\right)$$

$n = 2.5$ mol

$R = 8.314$ J K^{-1} mol^{-1}

T = 273 K + 28°C = 301 K

P_1 = 760 mmHg

P_2 = 550 mmHg

ΔG = ?

Substituting we have

$$\Delta G = 2.5\,\cancel{\text{mol}} \times \frac{8.314\ \text{J}}{1\,\cancel{\text{mol}} \times 1\,\cancel{\text{K}}} \times 301\,\cancel{\text{K}} \times \left(\frac{550\ \cancel{\text{mmHg}}}{760\ \cancel{\text{mmHg}}}\right)$$

Thus $\Delta G = 6235.5\ \text{J} \times (-0.32)$

$= -2.0\ \text{kJ}$

Example 3 1 mol of an ideal gas undergoes a reversible isothermal compression from 50.0 to 37.8 dm^3 at 30°C. Calculate the free energy change of the gas.

($R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$)

Solution The applicable equation for 1 mol of a gas is

$$\Delta G = RT \ln\left(\frac{V_1}{V_2}\right)$$

R = 8.314 J K^{-1} mol^{-1}

T = 273 K + 30°C = 303 K

V_1 = 50.0 dm^3

V_2 = 37. 8 dm^3

ΔG = ?

Substituting we have

$$\Delta G = \frac{8.314\ \text{J mol}^{-1}}{1\,\cancel{\text{K}}} \times 303\,\cancel{\text{K}} \times \ln\left(\frac{50.0\ \cancel{\text{dm}^3}}{37.8\ \cancel{\text{dm}^3}}\right)$$

Thus $\Delta G = 2519.1\ \text{J mol}^{-1} \times 0.28$

$= 710\ \text{kJ mol}^{-1}$

It is obvious from the positive value of ΔG that the compression is not spontaneous. It has to be driven by an external force, such as the application of pressure.

Example 4 1.5 mol of an ideal gas initially at 101 kPa undergoes a reversible change at a constant temperature of 35°C. What is the final pressure of the gas, given that the free energy change is −650 J?

(R = 8.314 J K^{-1} mol^{-1})

Solution We have to apply the relation

$$\Delta G = RT \ln \left(\frac{P_2}{P_1}\right)$$

n = 1.5 mol

R = 8.314 J K^{-1} mol^{-1}

T = 273 K + 35°C = 308 K

P_1 = 101 kPa

ΔG = –650 J

P_2 = ?

Substituting we have

$$-650 \text{ J} = 1.5 \cancel{\text{mol}} \times \frac{8.314 \text{ J}}{1 \cancel{\text{mol}} \times 1 \cancel{\text{K}}} \times 308 \cancel{\text{K}} \times \left(\frac{P_2}{101 \text{ kPa}}\right)$$

So $-650 \text{ J} = 3841 \text{ J} \times \left(\frac{P_2}{101 \text{ kPa}}\right)$

Then $\left(\frac{P_2}{101 \text{ kPa}}\right) = \frac{650 \cancel{\text{J}}}{3841 \cancel{\text{J}}} = -0.17$

Taking the natural antilogarithms of both sides we have

$$\frac{P_2}{101 \text{ kPa}} = e^{-0.17} = 0.84$$

Finally, we now cross-multiply to obtain

P_2 = 101 kPa × 0.84

= 85 kPa

Practice Problems

1. 3.5 mol of an ideal gas undergoes a reversible isothermal process at 40°C. What is the free energy change of the gas if its pressure reduces from 1.0 to 0.70 atm? Hence calculate the final volume of the gas, given that its initial

volume is 25.0 dm^3

(R = 8.314 J K^{-1} mol^{-1}) [*Answers:* 3.3 kJ, 36 dm^3]

2. 2.0 mol of an ideal gas undergoes a reversible isothermal process at 35°C. The free energy change of the process is –2.82 kJ. What is the initial volume of the gas if its final volume is 22.5 dm^3?

(R = 8.314 J K^{-1} mol^{-1}) [*Answer:* 13 dm^3]

9.7.2.3 Gibb's free energy change of mixing

When two gases mix to form a mixture of ideal gases, then the Gibbs's free energy change of mixing ΔG_M is given as

$$\Delta G_M = nRT\,(x_1 \ln x_1 + x_2 \ln x_2)$$

where n = The total number of moles of the gases.

T = The absolute temperature.

x = The mole fraction of a gas.

R = Universal gas constant.

The above relation is valid provided the two gases are at the same initial pressure.

Example 1 1.0 mol of a gas A mixes with 2.0 mol of another gas B to form a mixture of ideal gases at 27°C. What is the free energy change of mixing if the two gases were at the same initial pressure?

(R = 8.314 J K^{-1} mol^{-1})

Solution We have to apply the relation

$$\Delta G_M = nRT\,(x_A \ln x_A + x_B \ln x_B)$$

The mole fraction of each gas is obtained from the relation

$$x = \frac{n_i}{n_t}$$

n_t = 1.0 mol + 2.0 mol = 3.0 mol

For gas A we have

$$x_A = \frac{1.0\ \text{mol}}{3.0\ \text{mol}} = 0.33\ \text{mol}$$

For gas B we have

$$x_B = \frac{2.0\ \text{mol}}{3.0\ \text{mol}} = 0.67$$

Alternatively,

$x_B = 1.0 - 0.33 = 0.67$

$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$

$T = 273\ \text{K} + 29°\text{C} = 302\ \text{K}$

$\Delta G_M = ?$

Substituting we have

$$\Delta G_M = 3.0\,\cancel{\text{mol}} \times \frac{8.314\ \text{J}}{1\,\cancel{\text{mol}} \times 1\,\cancel{\text{K}}} \times 302\,\cancel{\text{K}} \times (0.33 \ln 0.33 + 0.67 \ln 0.67)$$

So $\Delta G_M = 7482.6\ \text{J} \times [0.33(-1.1) + 0.67(-0.40)]$

Then $\Delta G_M = 7482.6\ \text{J} \times (-0.36 - 0.27)$

Thus $\Delta G_M = 7482.6\ \text{J} \times (-0.63)$

$= -4.7\ \text{kJ}$

Example 2 1.5 mol of a gas A mixes with an equal amount of another gas B to form a mixture of ideal gases at a certain temperature. Assuming the two gases were at the same initial pressure, calculate the temperature of the mixture if the free energy change of mixing is –5.2 kJ.

($R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$)

Solution We have to apply the relation

$$\Delta G_M = nRT\,(x_A \ln x_A + x_B \ln x_B)$$

The mole fraction of each gas is obtained from the relation

$$x = \frac{n_i}{n_t}$$

$n_t = 1.5\ \text{mol} + 1.5\ \text{mol} = 3.0\ \text{mol}$

$$x_A = x_B = \frac{1.5\,\cancel{\text{mol}}}{3.0\,\cancel{\text{mol}}} = 0.50$$

$DG_M = -5200\ \text{J}$

$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$

$T = ?$

We now substitute to obtain

$$-5200\ \text{J} = 3.0\ \cancel{\text{mol}} \times \frac{8.314\ \text{J K}^{-1}}{1\ \cancel{\text{mol}}} \times T \times (0.50\ln 0.50 + 0.50\ln 0.50)$$

So $-5200\ \text{J} = 24.942\ T\ \text{J K}^{-1} \times [0.50(-0.69) + 0.50(-0.69)]$
Then $-5200\ \text{J} = 24.942\ T\ \text{J K}^{-1} \times (-0.35 - 0.35)$
Thus $-5200\ \text{J} = 24.942\ T\ \text{J K}^{-1} \times (-0.70)$
So $-5200\ \text{J} = 17.46\ T\ \text{J K}^{-1}$

$$\therefore\ T = \frac{5200\ \cancel{\text{J}} \times 1\ \text{K}}{17.46\ \cancel{\text{J}}}$$

$$= 300\ \text{K}$$

Practice Problems

1. 110 g of carbon dioxide mixes with 48 g of oxygen to form an ideal mixture of gases at a temperature of 30°C. Calculate the Gibb's free energy change of mixing, given that the two gases were at the same initial pressure.
   (R = 8.314 J K^{-1} mol^{-1}, C = 12, O = 16) [*Answer:* – 6.7 kJ]
2. The Gibb's free energy change of mixing of 1.0 mol of a gas and 1.5 mol of another gas is −2.5 kJ. What is the temperature of the mixture assuming the two gases were initially at a pressure of l atm?
   (R = 8.314 J K^{-1} mol^{-1}) [*Answer:* 180 K]

9.8 EFFICIENCY

Not all the heat supplied to a system is converted to useful work. Efficiency h is a measure of the amount of the heat supplied to a system that is converted to useful work. A highly efficient system is one that converts a high amount of the heat supplied to it to useful work.

An important implication of the second law is that no system can be 100 per cent efficient. In other worΔS, it is impossible to construct a machine that will draw heat from a heat reservoir, and convert all to equivalent amount of work. Efficiency, which is usually expressed in percentage, is given by the relation

$$h = \frac{Q_2 - Q_1}{Q_2} \times 100\% = \frac{T_2 - T_1}{T_2} \times 100\%$$

where Q_1 = The heat converted to other forms of energy.

Q_2 = The heat supplied to the system.

T_1 = The absolute temperature at which heat is converted into other forms of energy.

T_2 = The absolute temperature at which heat is supplied to the system.

Since work and energy are similar concepts, then the work done w is given by the equation

$$w = Q_2 - Q_1$$

Consequently, we can as well write the above equation as follows:

$$h = \frac{w}{Q_2} \times 100\%$$

Example 1 An engine was supplied with 150 J of heat energy. How much useful work was done if 10 J of heat was used to heat up the engine? Hence determine the efficiency of the engine.

Solution The work done by the engine is given by the equation

$w = Q_2 - Q_1$

$Q_2 = 150$ J

$Q_1 = 10$ J

$w = ?$

Thus $w = 150\text{ J} - 10\text{ J}$

$= 140$ J

The efficiency is calculated from the relation

$$h = \frac{w}{Q_2} \times 100\%$$

Substituting we have

$$h = \frac{140\,J}{150\,J} \times 100\%$$

$= 93\%$

Example 2 Calculate the efficiency of an engine operating between 100°C and 10°C. How does this compare to that working between 120°C and 5°C?

Solution We have to apply the relation

$$h = \frac{T_2 - T_1}{T_2} \times 100\%$$

For the first case we have

T_1 = 273 K + 10°C = 283 K

T_2 = 273 K + 100°C = 373 K

h = ?

Substituting we have

$$h = \frac{(373 - 283)\,\cancel{K}}{373\,\cancel{K}} \times 100\%$$

So $h = \frac{90}{373} \times 100\%$

= 20 %

For the second case we have

T_1 = 273 K + 5°C = 278 K

T_2 = 273 K + 120°C = 393 K

h = ?

Substituting we have

$$h = \frac{(393 - 278)\,K}{393\,K} \times 100\%$$

So $h = \frac{115}{393} \times 100\%$

= 29%

The second system is obviously more efficient than the first. One important conclusion we can draw from this is that, the greater the temperature difference between the temperature of the 'source' (T_2) and that of the sink (T_1), the higher the efficiency of a system.

Example 3 Calculate the work done by a system operating between 150°C and 50°C if it was supplied with 150 J of heat.

Solution We have to apply the relation

$$\frac{w}{Q_2} \times 100\% = \frac{T_2 - T_1}{T_2} \times 100\%$$

It then follows that

$w = \frac{Q_2(T_2 - T_1)}{T_2}$

$Q_2 = 150$ J

$T_1 = 273$ K + 50°C = 323 K

$T_2 = 273$ K + 150°C = 423 K

$w = ?$

Substituting we have

$w = \frac{150\ \text{J}(423 - 323)\ \cancel{\text{K}}}{423\ \cancel{\text{K}}}$

Thus, $w = \frac{150\ \text{J} \times 100}{423}$

= 35 J

Example 4 The efficiency of an engine operating between 110°C and an unknown temperature *T* is 23.3%. Calculate *T*.

Solution We have to apply the relation

$h = \frac{T_2 - T_1}{T_2} \times 100\%$

h = 23.3%

$T_2 = 273$ K + 110°C = 383 K

$T_1 = ?$

Substituting we have

$23.3\% = \frac{383\ \text{K} - T_1}{383\ \text{K}} \times 100\%$

Then $\frac{23.3}{100} = \frac{383\ \text{K} - T_1}{383\ \text{K}}$

Cross multiplying we have

$8923.9\ \text{K} = 38300\ \text{K} - 100T_1$

So $-100T_1 = 8923.9\ \text{K} - 38300\ \text{K} = -29376\ \text{K}$

$\therefore\ T = \frac{-29376\ \text{K}}{-100}$

$= 294$ K

Practice Problems

1. What is the maximum efficiency of an engine that draws in 250 J of heat and ‘loses’ 15 J of heat? [*Answer:* 94%]
2. A Carnot engine draws in 150 J of heat and does 120 J of work. What is the temperature of the ‘source’ if the temperature of the ‘sink’ is 10°C? [*Answer:* 1400 K]

SUMMARY

- A thermodynamic system refers to a sample specified in the universe for study or consideration.
- A property is the characteristic of a system which is observable at any point in time.
- The state of a system refers to the collection of macroscopic properties which partially or fully describe its characteristics at any point in time.
- A thermodynamic process occurs when a system undergoes a change of state. Types of process include isothermal, isobaric, isochoric and adiabatic processes.
- The measurement of heat is called calorimetry. The heat absorbed or evolved by a body is calculated, using the relation

$$Q = mc\Delta T$$

- Electrical energy is given by the relations

$$E = IVt \text{ or } E = I^2Rt \text{ or } E = \frac{V^2t}{R}$$

- The heat or enthalpy change of a reaction is the heat evolved or absorbed during a chemical reaction. A reaction in which heat is evolved is called exothermic reaction, while that in which heat is absorbed is called endothermic reaction.
- Hess’s law of constant heat summation states that the total enthalpy change of

a chemical reaction is constant, regardless of the route by which the chemical change occurs, provided the temperature and pressure remain constant.

- The standard heat or enthalpy change of a reaction is obtained from the relation

$$\Delta H = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants})$$

- The temperature dependence of heat of reaction is given by Kirchhoff’s law:

$$\Delta H_{T2} = \Delta H_{T1} + \Delta n\mathrm{C}_{p,\mathrm{m}}(T_2 - T_1) \text{ or } \Delta H_{T2} = \Delta H_{T1} + \int_{T_1}^{T_2} \Delta n\mathrm{C}_{p,\mathrm{m}}\,\mathrm{d}T$$

- The molar heat capacity of a gas is the heat required to raise the temperature of 1 mole of the gas by 1 K.
- The heat capacity of a gas at constant volume is related to its change in internal energy by the relation

$$\Delta U = \int_{T_1}^{T_2} \Delta n\mathrm{C}_{p,\mathrm{m}}\,\mathrm{d}T \text{ or } \Delta U = nC_{v,m}(T_2 - T_1) = nC_{v,m}\Delta T$$

- The heat capacity of a gas at constant pressure is related to its enthalpy change by the relation

$$\Delta H = \int_{T_1}^{T_2} \Delta n\mathrm{C}_{p,\mathrm{m}}\,\mathrm{d}T \text{ or } \Delta H = nC_{p,m}(T_2 - T_1) = nC_{p,m}\Delta T$$

- The first law of thermodynamics state the total internal energy of a system is constant, i.e.

$$Q = \Delta U + w$$

- The first law for an adiabatic process is given as

$$\Delta H = \Delta U + P\Delta V$$

- The first law for an isochoric process is given as

$$Q = \Delta U = nC_{v,m}\Delta T$$

- The first law for an isothermal process is given as

$$Q = w = P\mathrm{d}V = nRT \ln\left(\frac{V_2}{V_1}\right) = nRT \ln\left(\frac{P_1}{P_2}\right)$$

- The first law for an adiabatic process is given as

$$w = \frac{nR(T_2 - T_1)}{1-\gamma} = -\mathrm{D}U = -nC_{v,m}\mathrm{D}T$$

- The second law of thermodynamics states that a process would only occur spontaneously if there is an increase in the overall or total entropy of the universe.
- Entropy is a measure of the degree of disorderliness or randomness of a system. The entropy change of a system is obtained from the relation

$$\Delta S = S_1 - S_2$$

- The standard entropy change of a reaction is calculated from the relation

$$\Delta S^o = \sum nS^o(\text{products}) - \sum nS^o(\text{reactants})$$

- The entropy change for a reversible system at equilibrium is given as

$$\Delta S = \frac{\Delta H}{T}$$

- The variation of entropy with temperature and volume is given by the relation

$$\Delta S = nC_{v,m}\ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$$

- The variation of entropy with temperature and pressure is given by the relation

$$\Delta S = nC_{p,m}\ln\frac{T_2}{T_1} - nRT\ln\frac{P_2}{P_1}$$

- The entropy of mixing is defined as

$$\Delta S_M = -R(n_1x_1\ln x_1 + n_2x_2\ln x_2)$$

- Gibb’s free energy is the energy available for doing work in a system. The change in free energy is given by the relation

$$\mathrm{D}G = G_2 - G_1$$

- The standard free energy of a reaction is given by the relation

$$\Delta S^o = \sum n\Delta G_f^o(\text{products}) - \sum n\Delta G_f^o(\text{reactants})$$

- The free energy change of a system is related to entropy change and heat of reaction by the relation

$$\mathrm{D}G = \Delta H - T\Delta S$$

- The composition or concentration dependence of free energy is given by the relation

$$\mathrm{D}G = \mathrm{D}G^{o} + RT\ \ln Q$$

- The relationship between standard free energy change and equilibrium constant is given by the relation

$$\mathrm{D}G^{o} = -RT\ \ln K$$

- The variation of free energy change with temperature at constant pressure is given by the Gibbs-Helmholtz equation

$$\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = \Delta H_1 \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- The variation of free energy with pressure is given by the relation

$$\mathrm{D}G = G_2 - G_1 = nRT\ \ln \left(\frac{P_2}{P_1}\right) = nRT\ \ln \left(\frac{V_1}{V_2}\right)$$

- The free energy of mixing is given by the relation

$$\mathrm{D}G_M = nRT(x_1 \ln x_1 + x_2 \ln x_2)$$

- Efficiency is the measure of the amount of heat converted to useful work compared to the amount of heat supplied to a system. Efficiency is given by the relation

$$\mathrm{h} = \frac{Q_2 - Q_1}{Q_2} \times 100\% \text{ or } \mathrm{h} = \frac{T_2 - T_1}{T_2} \times 100\% \text{ or } \mathrm{h} = \frac{w}{Q_2} \times 100\%$$

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. What quantity of heat is evolved when 2.0 kg of water is cooled from 100°C to 55.5°C?

A. 219 kJ B. 300 kJ
C. 350 kJ D. 370 kJ
E. 380 kJ

$$(c = 4200 \text{ J kg}^{-1} \text{K}^{-1})$$

2. 50.0 g of copper at 100°C was dropped into a quantity of cold water at 0°C.

Calculate the mass of the water assuming that the container is of negligible specific heat capacity. The final temperature of the mixture is 50°C.

A. 4.7 g B. 4.8 g
C. 5.0 g D. 9.0 g
E. 10.0 g

($c(H_2O) = 4200$ J kg^{-1} K^{-1}, $c(Cu) = 400$ J kg^{-1} K^{-1})

3. An electric heater was used to heat 300 g of benzene. The heating was continued until 156 g of the compound was vaporized. What is the enthalpy change of vaporization of benzene if the vaporization required 60.4 kJ of heat?

A. 18.0 kJ mol^{-1} B. 30.2 kJ mol^{-1}
C. 33.0 kJ mol^{-1} D. 52.0 kJ mol^{-1}
E. 40.1 kJ mol^{-1}

(C = 12, H = 1)

4. The standard enthalpy change of vaporization of a substance is 29.10 kJ mol^{-1}. What is its standard enthalpy of sublimation if its standard enthalpy change of freezing is −35.56 kJ mol^{-1}?

A. 6.46 kJ mol^{-1} B. 32.20 kJ mol^{-1}
C. 55.28 kJ mol^{-1} D. 64.66 kJ mol^{-1}
E. 80.22 kJ mol^{-1}

5. The heat capacity of a gas at constant volume is defined as

A. $C_{v,m} = \frac{dH}{dT}$ B. $C_{v,m} = \frac{dU}{dT}$

C. $C_{v,m} = \frac{dH}{dP}$ D. $C_{v,m} = \frac{dQ}{dT}$

E. $C_{v,m} = \frac{dH}{dQ}$

6. The correct heat capacity of a diatomic gas at constant pressure is

A. 8.314 J K^{-1} mol^{-1} B. 12.5 J K^{-1} mol^{-1}
C. 20.8 J K^{-1} mol^{-1} D. 28.0 J K^{-1} mol^{-1}
E. 29.1 J K^{-1} mol^{-1}

7. Which of the following is true about the reaction $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$?

A. Work is done on the surroundings.

B. Work is done on the reacting system.

C. The work done is negative.

D. The work done is positive.

E. No work is done.

8. The difference in initial and final temperatures of an isothermal process is always

A. 0 B. 1

C. negative D. positive

E. None of the above

9. An exothermic reaction is always accompanied by

A. decrease in enthalpy of a system.

B. increase in enthalpy of the surroundings.

C. increase in the enthalpy of a system.

D. A and B.

E. B and C.

10. Which of the following implies if the total entropy is negative?

A. Spontaneity of a process.

B. Process not spontaneous.

C. Process is spontaneous but irreversible.

D. Process is highly spontaneous.

E. Process occurs at an extremely slow rate.

11. What is the standard entropy change accompanying the freezing of 1 mol of methanol at its melting point of 175.5 K?

A. −22.2 J K^{-1} mol^{-1} B. −21.2 J K^{-1} mol^{-1}

C. 18.0 J K^{-1} mol^{-1} D. −18.0 J K^{-1} mol^{-1}

E. 22.2 J K^{-1} mol^{-1}

$$(\Delta H^{o}_{m} = 3.16 \text{ kJ mol}^{-1})$$

12. Calculate the change in internal energy of 1 mol of a diatomic gas when its temperature increases by 15.0°C.

A. 59 J mol^{-1} B. 60 J mol^{-1}

C. 62 J mol^{-1} D. 84 J mol^{-1}

E. 312 J mol^{-1}

$$(C_{v,m} = 5/2\, R,\ R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$

13. What is the entropy change of 1 mol of benzene when it vaporises, given that its standard heat of vaporisation and boiling point are 30.8 kJ mol^{-1} and

80.3°C respectively?

A. −151 J K^{-1} mol^{-1} B. −87.2 J K^{-1} mol^{-1}

C. 87.2 J K^{-1} mol^{-1} D. 102 J K^{-1} mol^{-1}

E. 151 J K^{-1} mol^{-1}

14. What is the standard enthalpy change of the reaction $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$?

A. −383.88 kJ B. −380.50 kJ

C. −350.00 kJ D. −300.20 kJ

E. −196.10 kJ

($\Delta H^o_f [H_2O_2(l)] = -187.78$ kJ mol^{-1}, $\Delta H^o_f [H_2O(g)] = -285.83$ kJ mol^{-1})

15. Calculate the heat of formation of aluminium oxide from the reaction given below:

$Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(g)$ $\Delta H = –3351.4$ kJ

A. −6702.8 kJ mol^{-1} B. −3351.4 kJ mol^{-1}

C. −3215.5 kJ mol^{-1} D. −1675.7 kJ mol^{-1}

E. −1115.8 kJ mol^{-1}

16. What amount of heat would be evolved when chlorine reacts with 10.0 g of aluminium. The equation of reaction is:

$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$ $\Delta H = -704.2$ kJ mol^{-1}

A. −316 kJ B. −261 kJ

C. −251 kJ D. −200 kJ

E. −151 kJ

(Al = 27)

17. The combustion of glucose is given by the equation:

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$ $\Delta H = -2816$ kJ mol^{-1}

What amount of glucose would evolve 2500 kJ of heat?

A. 0.50 mol B. 0.89 mol

C. 0.90 mol D. 1.1 mol

E. 1.5 mol

18. 1 mol of sodium hydroxide dissolves in water to liberate 43 kJ of heat. What amount of heat would be evolved when 20.0 g of sodium hydroxide is dissolved in water?

A. 20.5 kJ B. 20.8 kJ

C. 21.5 kJ D. 22.5 kJ

E. 43.0 kJ

(H = 1.0, O = 16.0, Na = 23.0)

19. The relative efficiency of two engines operating between 110°C 10°C and 150°C, 40°C is

A. 1.0 B. 1.1
C. 1.5 D. 1.7
E. 2.1

20. What is the standard entropy change of the reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$?

(S^o[NO(g)] = 210.7 J K^{-1} mol^{-1}, S^o[$NO_2(g)$] = 239.9 J K^{-1} mol^{-1}, S^o[$O_2(g)$ = 205.14
J K^{-1} mol^{-1}]

A. −60.0 J K^{-1} mol^{-1} B. −58.4 J K^{-1} mol^{-1}
C. 58.4 J K^{-1} mol^{-1} D. 60.0 J K^{-1} mol^{-1}
E. None of the above

21. If the D*G* of a reaction is zero, then the reaction is

A. spontaneous. B. at equilibrium.
C. reversible. D. irreversible.
E. not feasible.

22. What is the enthalpy change accompanying the freezing of 117 g of benzene?

A. −21.5 J B. −14.8 kJ
C. −9.9 kJ D. 9.9 kJ
E. 14.8 kJ

(H =1, C = 12, ΔH_f = 9.87 kJ mol^{-1})

ESSAY TYPE QUESTIONS

Calorimetry

23. An iron ball of mass 15 g at 90.0°C was dropped into a vessel 20.0 g of water initially at a temperature of 10.0°C. What is the final steady temperature of the mixture, assuming the vessel is of negligible specific heat capacity?

($c(H_2O) = 4.2\ J\ K^{-1}\ g^{-1}$, $c(iron) = 0.45\ J\ K^{-1}\ g^{-1}$)

24. 51 g of charcoal raises the temperature of 50.0 g of water by 49.8 K during a laboratory experiment to determine the heat of combustion of charcoal. What is the heat of combustion of the substance?

(C = 12, $c = 4.2\ J\ K^{-1}\ g^{-1}$)

25. What is the power rating of the heater required to raise the temperature of 500.0 g of water at 0°C to 100°C within 4 minutes?

($c = 4200\ J\ kg^{-1} K^{-1}$)

26. A quantity of water was heated with a heater rated 50.0 W. What is the mass of the water if it was heated through the temperature difference of 20.0°C in 50 minutes?

($c = 4200\ J\ kg^{-1}\ K^{-1}$)

Enthalpy change of physical change

27. 500.0 g of helium was heated to its boiling point of −268.8°C by an electric heater when the current and voltage supplies were 0.10 A and 240 V respectively. The heating was continued, and it was found that 162 g of the liquid vaporized under 2.2 minutes. Calculate its heat of vaporization.

(He = 4.0)

28. The heat of vaporization of a substance is 58 kJ mol^{-1}. What is its heat of sublimation if its heat of freezing is −16 kJ mol^{-1}?

29. What amount of heat is required to melt 100.0 g of iodine completely, given that its heat of fusion is 15.5 kJ mol^{-1}?

(I = 127)

30. The heat of vaporization of argon is 6.5 kJ mol^{-1}. How much heat is required to vaporize 250.0 cm^3 of the gas if its density is 1.66 gcm^{-3}.

(Ar = 40.0)

Enthalpy change of reaction

31. Define the following terms:
    (a) Heat of reaction.
    (b) Standard heat of combustion.
    (c) Standard heat of neutralization.
    (d) Standard heat of solution.
    (e) Exothermic reaction and endothermic reactions.

32. Calculate the standard heat of formation of butane from the information given below:

$$C_4H_{10}(g) + 13/2O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g) \quad \Delta H^o_f = -2878 \text{ kJ mol}^{-1}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^o_f = -393.5 \text{ kJ mol}^{-1}$$

$$H_2(g) + 1/2O_2(g) \rightarrow H_2O(g) \quad \Delta H^o_f = -241.8 \text{ kJ mol}^{-1}$$

33. Fluorine displaces bromine from potassium bromide as follows:

$$2KBr(s) + F_2(g) \rightarrow 2KF(s) + Br_2(g)$$

Calculate the standard heat of the reaction from the information given below:

$$2KBr(s) + Cl_2(g) \rightarrow 2KCl(s) + Br_2(g) \quad \Delta H^o = -55.0 \text{ kJ}$$

$$2KCl(s) + F_2(g) \rightarrow 2KF(s) + Cl_2(g) \quad \Delta H^o = -261.0 \text{ kJ}$$

34. The combustion of butane is given by the following equation:

$$C_4H_{10}(g) + 13/2O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g) \quad \Delta H = -2878 \text{ kJ mol}^{-1}$$

What amount of heat would be evolved when 100.0 g of butane is burnt completely in oxygen?

(H = 1, C = 12)

35. The combustion of ethane is represented by the equation $C_2H_2(g) + 5/2O_2(g) \rightarrow H_2O(g) + 2CO_2(g)$. What is the heat of combustion of the compound?

(ΔH^o_f [$C_2H_2(g)$] = 226.73 kJ mol^{-1}, ΔH^o_f [$H_2O(g)$] = −241.82 kJ mol^{-1},ΔH^o_f [$CO_2(g)$] = −393.51 kJ mol^{-1})

36. Aluminium reacts with chlorine according to the equation

$$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s) \; \Delta H = -1408.4 \text{ kJ}$$

Calculate the standard heat of formation of aluminium chloride.

37. Calculate the heat of formation of methane from the following data:

$$\Delta H^o_c\, [CH_4(g)] = -890 \text{ kJ mol}^{-1}$$

$$\Delta H^o_c\, [H_2(g] = -285.8 \text{ kJ mol}^{-1}$$

$$\Delta H^o_c\, [C(s)] = -393.5 \text{ kJ mol}^{-1}$$

38. (a) Derive the Kirchhoff's equation.

(b) Calculate the heat of formation of ammonia at 300°C. The equation of reaction is

$$N_2(g) + 3H_2(g) \text{ fi } 2NH_3(g)$$

	ΔH^o (kJ mol^{-1})	$C_{p,m}$ (J K^{-1} mol^{-1})
$NH_3(g)$	−46.1	35.65
$N_2(g)$	0	29.12
$H_2(g)$	0	28.83

39. The standard heat of the reaction $CO(g) + O_2(g) \rightarrow CO_2(g)$ is −566 kJ. At what temperature would the heat of reaction be –600 kJ?

	$C_{p,m}$ (J K^{-1} mol^{-1})
$O_2(g)$	$25.6 + 1.32 \times 10^{-2} T$
$CO(g)$	$26.6 + 0.76 \times 10^{-2} T$
$CO_2(g)$	$26.4 + 4.26 \times 10^{-2} T$

The heat capacities of gases

40. (a) Show that the $C_{p,m}$ of a diatomic gas is given by $\frac{7}{2}R$.

(b) Show that the $C_{v,m}$ of a monatomic gas is given by $\frac{3}{2}R$.

41. 3.0 mol of a diatomic gas expanΔS reversibly when its temperature rises by 20.0°C at a constant pressure of 120 kPa. Calculate

(a) the change in internal energy of the gas;

(b) the work done by the system;

(c) the enthalpy change of the system.

(R = 8.314 J K^{-1} mol^{-1}

42. It requires 72.8 J of heat to raise the temperature of 140 g of argon by 1 K. What is its molar heat capacity?

(Ar = 39.95)

Thermodynamics of solutions

43. The heat of solution of sodium chloride is 3.8 kJ mol^{-1}. What amount of heat would be absorbed when 50.0 g of sodium chloride is dissolved in water?

(Na = 23, Cl = 35.5)

44. In a laboratory experiment to determine the heat of solution of aluminium chloride, 10.0 g of the salt was dissolved in 250 cm^3 of water. The maximum temperatures recorded before and after the dissolution were 10.0°C and 33.5°C respectively. Determine the heat of solution of the salt.

(Al = 27.0, Cl = 35.5, c = 4.2 J K^{-1} g^{-1}, density of water = 1.0 g cm^{-3})

45. In a laboratory experiment to determine the heat of solution of calcium hydroxide, 5.0 g of the base was added to 200.0 cm^3 of water in a calorimeter. The maximum temperatures recorded before and after the dissolution were 10.0°C and 11.3°C respectively. What is the heat of solution of the base?

(C = 12.0, O = 16.0, Ca = 40.0, c = 4.2 J K^{-1} g^{-1}, density of water = 1.0 g cm^{-3})

46. The lattice energy and heat of hydration of potassium chloride are 717 kJ mol^{-1} and −701 kJ mol^{-1} respectively. Estimate the heat of solution of the salt.

47. The lattice energy and heat of hydration of magnesium chloride are 2524 J mol^{-1} and −2365 J mol^{-1} respectively. Estimate the heat of solution of the salt, and state whether the dissolution would be endothermic or exothermic.

48. The heat of solution of sodium fluoride is estimated to be 2.0 kJ mol^{-1}. Calculate the hydration energy of the salt if its lattice enthalpy is 929 kJ mol^{-1}.

49. Calculate the hydration energy of a gas consisting of 1 mol of silver ions and 1 mol of iodide ions, using the information given below.

$Ag^+(g) \rightarrow Ag^+(aq)$ $\Delta H^o_H = -510$ kJ mol^{-1}

$I^-(g) \rightarrow I^-(aq)$ $\Delta H^o_H = -296$ kJ mol^{-1}

50. Calculate the hydration energy of a gas containing 1 mol of aluminium ions and 3 mol of chloride ions.

$Al^{3+}(g) \rightarrow Al^{3+}(aq)$ $\Delta H^o_H = -4797$ kJ mol^{-1}

$Na^+(g) + Cl^-(g) \rightarrow Na^+(aq) + Cl^-(aq)$ $\Delta H^o_H = -784$ kJ mol^{-1}

$Na^+(g) \rightarrow Na^+(aq)$ $\Delta H^o_H = -444$ kJ mol^{-1}

51. Calculate the hydration energy of hydrogen ions from the information given below.

$H^+(g) + I^-(g) \rightarrow H^+(aq) + I^-(aq)$ $\Delta H^o_H = -1426$ kJ mol^{-1}

$Li^+(g) + I^-(g) \rightarrow Li^+(aq) + I^-(aq)$ $\Delta H^o_H = -854$ kJ mol^{-1}

$Li^+(g) \rightarrow Li^+(aq)$ $\Delta H^o_H = -558$ kJ mol^{-1}

52. Calculate the hydration energy of potassium ions from the information given below.

$K^+(g) + Br^-(g) \rightarrow K^+(aq) + Br^-(aq)$ $\Delta H^o_H = -670$ kJ mol^{-1}

$Na^+(g) + Br^-(g) \rightarrow Na^+(aq) + Br^-(aq)$ $\Delta H^o_H = -753$ kJ mol^{-1}

$Na^+(g) \rightarrow Na^+(aq)$ $\Delta H^o_H = -444$ kJ mol^{-1}

The first law of thermodynamics

53. (a) State the first law of thermodynamics.

(b) A system does 50 J of work when it absorbs 120 J of heat from its surroundings. What is the change in its internal energy?

(c) How would the internal energy be affected if the surroundings do 50 J of work on the above system?

54. A gas expanΔS when its internal energy increases by 50.0 J at a constant pressure of 12310 N m^{-2}. Calculate

(a) the change in its volume when the increase in enthalpy is 250 J,

(b) the new volume of the gas if its initial volume is 5.0 dm^3.

55. Show that PV^g is constant for a reversible adiabatic process.

56. An ideal gas evolves 200.0 J of heat at constant volume. It then expanΔS from 15.0 dm^3 to 20.0 dm^3 at a constant pressure of 880 Torr . Calculate

(a) the work done;

(b) the enthalpy change.

57. The equation for the combustion of propane is $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$. Calculate the work done on the surroundings at STP

(Molar volume of gases at STP = 22.4 dm^3 mol^{-1})

58. 5.0 moles of an ideal gas undergoes a reversible adiabatic expansion from 10.0 dm^3 at 15°C to 12.5 dm^3. Assuming the gas is diatomic, calculate

(a) the final temperature of the gas;

(b) the work done by the gas.

(R = 8.314 J K^{-1}mol^{-1})

59. 1.5 mol of an ideal gas undergoes a reversible isothermal expansion from 10.0 to 15.0 dm^3 against a constant external pressure of 760 mmHg. Calculate

(a) the work done by the gas;

(b) the operating temperature;

(c) the height to which the system would lift a mass of 2.0 kg.

(R = 8.314 J K^{-1} mol^{-1}, g = 10 ms^{-2})

60. The heat supplied to a system when it undergoes a reversible isothermal process at a constant pressure of 1.5 atm is 1.0 kJ. What is the final volume

of the gas if its initial volume is 15 dm^3?

61. 10.0 dm^3 of an ideal monatomic undergoes a reversible adiabatic process. What is the final pressure of the gas if its final volume and initial pressure are 8.0 dm^3 and 1.0 atm respectively?

62. An ideal monatomic gas at 27°C and 1.5 atm undergoes a reversible adiabatic process. What is the final pressure of the gas if its final temperature is 42°C?

63. 20.0 dm^3 of an ideal diatomic gas undergoes a reversible adiabatic process. What would be the final volume of the gas if its temperature is halved?

The second law of thermodynamics

64. What is the change in entropy of the reaction $C_2H_2(g) + 5/2O_2(g) \rightarrow H_2O(g) + 2CO_2(g)$?

($S^o[C_2H_2(g)] = 200.9$ J K^{-1} mol^{-1}, $S^o[O_2(g)] = 205.1$ J K^{-1} mol^{-1}, $S^o[H_2O(g)] =$ 188.7 J K^{-1} mol^{-1}, $S^o[CO_2(g)] = 213.7$ J K^{-1} mol^{-1})

65. Methanol burns in oxygen according to the equation $CH_3OH(l) + 3/2O_2(g) \rightarrow 2H_2O(l) + CO_2(g)$? Calculate the entropy of methanol given that the entropy change of the reaction is 226.6 J K^{-1}.

($S^o[O_2(g)] = 205.1$ J K^{-1} mol^{-1}, $S^o[H_2O(l)] = 69.9$ J K^{-1} mol^{-1}, $S^o[CO_2(g)] = 213.7$ J K^{-1} mol^{-1})

66. (a) Calculate the entropy change of a reversible system whose enthalpy change is 4.15 kJ at 100°C.

(b) The entropy change of a reversible system is −39.4 J K^{-1} at −20°C. What is the enthalpy change of the system?

67. (a) Show that the total entropy of the universe is given by the equation

$$\Delta S_T = \Delta S + \Delta S_{surr.}$$

where ΔS = The change in entropy of the system.

$\Delta S_{surr.}$ = The entropy change of the surroundings.

ΔS_T = The total entropy change.

(b) What are the implications of ΔS_T for a reacting system?

68. Derive the equation which relates entropy change to temperature and volume.

69. 2.5 mol of ideal diatomic gas at 25°C is compressed reversibly to two-thirΔS initial volume. Calculate the entropy change of the gas if its final

temperature is 35°C.

$(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$

70. 1.5 mol of an ideal monatomic gas at 120 kPa and 30°C undergoes a reversible compression to 35°C. What is the final pressure of the gas if its entropy decreases by 12.5 J K^{-1}?

$(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$

71. 1.0 mol of an ideal diatomic gas undergoes a reversible isochoric process at 30°C. What is the final temperature of the gas if its entropy increases by 3.45 J K^{-1}?

$(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$

72. 2.5 mol of an ideal monatomic gas initially at 27°C and 780 mmHg undergoes a reversible isothermal process. What is the final pressure of the gas if its entropy decreases by
2.5 J K^{-1}?

$(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$

73. The entropy change of 5.00 mol of an ideal diatomic gas initially at 10°C and 760 mmHg is 5.83 J K^{-1} when it undergoes a reversible isobaric process. What is the final temperature of the gas?

74. (a) What is free energy. Explain its implications for a reacting system?

(b) What is entropy? State whether the entropy has increased or decreased in each of the following cases:

(i) $H_2O\,(l) \rightarrow H_2O(g)$ (ii) $Al(g) \rightarrow Al(s)$ (iii) $H_2O(g) \rightarrow H_2O(l)$ (iv) $Ca(g) \rightarrow Ca(s)$ (v) $HCl(g) \rightarrow HCl(aq)$

75. Calculate the free energy of the reaction $CH_3OH(l) + 3/2O_2(g) \rightarrow 2H_2O(l) + CO_2(g)$.

$(DG^o_f\,[CH_3OH(l)] = -166.2 \text{ kJ mol}^{-1}, DG^o_f\,[H_2O(l)] = -237.2 \text{ kJ mol}^{-1}, DG^o_f\,[CO_2(g)] = -394.4 \text{ kJ mol}^{-1})$

76. The heat of fusion of ethanol is 4.60 kJ mol^{-1}. Calculate the temperature at which its free energy would be 1.45 kJ mol^{-1}, if its melting point is −114.3°C.

77. The equation for the combustion of 1 mol of methane is $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$. Calculate the free energy of the reaction at 65°C given that the standard heat of combustion is −890.4 kJ mol^{-1}.

$(DG^o_f[CH_4(g)] = -50.72 \text{ kJ mol}^{-1}, DG^o_f[CO_2(g)] = -394.36 \text{ kJ mol}^{-1}, DG^o_f$

[$H_2O(l)$] = −237.13 kJ mol^{-1}).

78. Calculate the heat of vaporization of benzene if its free energy is −3.923 kJ mol^{-1} at
398.3 K. The boiling point of benzene is 353.3 K.

79. Show that the Gibb's free energy of an ideal gas undergoing a reversible isothermal process is related to pressure by the equation

$$\Delta G = -nRT \ln\left(\frac{P_1}{P_2}\right)$$

80. 6.0 g of helium initially at 1.0 atm and 30°C undergoes a reversible isothermal process. Calculate the free energy of the gas, given that its final pressure is 0.75 atm. The gas should be assumed to be ideal.

(He = 4.0, R = 8.314 J K^{-1} mol^{-1})

81. 1.5 mol of an ideal gas having an initial volume of 25.0 dm^3 undergoes a reversible isothermal process during which its volume reduces to 15.0 dm^3. What is the free energy of the gas if its temperature is 28°C?

(R = 8.314 J K^{-1} mol^{-1})

82. The free energy of 1 mol of an ideal gas when it undergoes a reversible isothermal process at 35°C is −2.57 kJ mol^{-1}. Calculate the final volume of the gas if its initial volume is 27.0 dm^3.

(R = 8.314 J K^{-1} mol^{-1})

83. 2.5 mol of an ideal gas undergoes a reversible isothermal compression at 27°C to one-third its initial pressure. What is the initial pressure of the gas if its free energy and final pressure are −3.5 kJ and 1.5 atm respectively?

(R = 8.314 J K^{-1} mol^{-1})

84. Two gases A and B initially at the same pressure mix to form a mixture of ideal gases at 30°C. What is the free energy of mixing, given that 1.5 mol of A and 1.0 mol of B are involved in the mixing?

(R = 8.314 J K^{-1} mol^{-1})

85. The Gibb's free energy of mixing when 1.50 mol of a gas mixes with 2.50 mol of another gas is −4.5 kJ. What is the temperature of the mixture, given that the two gases were initially at the same pressure?

(R = 8.314 J K^{-1} mol^{-1})

86. The free energy of mixing of two gases that were originally at the same pressure is −2.57 kJ. What is the total number of moles of the gases, given

that one of them has a mole fraction 0.387? The temperature of the mixture is 32°C.

(R = 8.314 J K^{-1} mol^{-1})

87. The enthalpy change of a reaction is −99.16 kJ at 30°C. Calculate the free energy of the system when

(a) the entropy change is 271 J mol^{-1};

(b) the entropy change is −271 J mol^{-1}.

88. Calculate the standard entropy change of the reaction $CH_3OH(l) + 3/2O_2(g) \rightarrow 2H_2O(l) + CO_2(g)$ from the information given below:

	DG^o_f(kJ mol^{-1})	ΔH^o_f(kJ mol^{-1})
$CH_3OH(l)$	−166.3	−238.7
$O_2(g)$	0	0
$CO_2(g)$	−394.4	−393.5
$H_2O(l)$	−237.1	−285.8

89. Calculate the entropy of mixing when 1.0 mol of a gas mixes with 2.0 mol of another gas to form a mixture of ideal gases, given that both gases were initially at the same pressure.

(R = 8.314 J K^{-1} mol^{-1})

90. Calculate the entropy of mixing when 22.0 g of carbon dioxide mixes with 48.0 g of oxygen to form a mixture of ideal gases. The gases should be assumed to be at the same initial pressure.

(R = 8.314 J K^{-1} mol^{-1}, C = 12, O = 16)

91. Derive the relation

D$G = \Delta H - T\Delta S$

where DG = The free energy change.

ΔH = The enthalpy change

ΔS = The entropy change.

T = The absolute temperature.

92. Predict the temperature at which the reaction $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ is likely to occur.

	ΔH^o_f (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})
$CaCO_3(s)$	−365.56	151.08
$CaO(s)$	82.05	219.85
$H_2O(g)$	−241.82	188.83

Efficiency

93. (a) What is efficiency?

(b) Calculate the efficiency of each of the engines operating within the following temperatures:

(i) 110°C and 10°C (ii) 80°C and 12°C (iii) 150°C and 25°C (iv) 150°C and 10°C (v) 120°C and 20°C.

94. 2500 J of heat was supplied to a system. If 10% of this heat was expended on heating up the system, calculate

(a) the heat lost by the system;

(b) the work done by the system;

(c) the maximum efficiency of the system.

95. (a) The efficiency of an engine is 75%. What is the heat supplied to the system if 150 J of heat was lost?

(b) The work done by a machine is 250 J. What is the heat supplied to the machine if it operates between 111 °C and 5°C?

Answers

1. D 2. B 3. B 4. D 5. B 6. E
7. E 8. A 9. D 10. B 11. C 12. E
13. C 14. E 15. C 16. B 17. B 18. C
19. A 20. E 21. B 22. B
23. 16°C
24. 2.5 kJ mol^{-1}
25. 900 W
26. 1.8 kg
27. 80 J mol^{-1}
28. 74 kJ mol^{-1}
29. 6.10 kJ mol^{-1}
30. 67.4 kJ mol^{-1}
32. 95 kJ mol^{-1}
33. −316 kJ
34. 5000 kJ
35. −1255.57 kJ mol^{-1}
36. −704.2 kJ mol^{-1}

37. -75.1 kJ mol^{-1}
38. (b) -56 kJ mol^{-1}
39. 910°C
41. (a) 1.2 kJ (b) 500 J (c) 1.7 kJ
42. 21 J mol^{-1}
43. 3.2 kJ
44. -330 kJ mol^{-1}
45. 16 kJ mol^{-1}
46. 16 kJ mol^{-1}
47. 159 kJ mol^{-1}, endothermic
48. -927 kJ mol^{-1}
49. -806 kJ mol^{-1}
50. -5817 kJ mol^{-1}
51. 1130 kJ mol^{-1}
52. -361 kJ mol^{-1}
53. (b) 70 J (c) the internal energy becomes 170 J
54. (a) 16.2 dm^3 (b) 21.2 dm^3
56. (a) 587 kJ (b) 387 J
57. 2.27 kJ
58. (a) 263 K (b) 2.6 kJ
59. (a) 507 J (b) 100 K (c) 25 m
60. 22 dm^3
61. 1.5 atm
62. 1.7 atm
63. 113 dm^3
64. -97.6 J K^{-1}
65. 126.9 J K^{-1} mol^{-1}
66. (a) 11.1 J K^{-1} mol^{-1} (b) -9.97 kJ
69. -6.7 J K^{-1}
70. 340 kPa
71. 360 K
72. 880 mmHg
73. 295 K
74. (b) (i) increased (ii) decreased (iii) decreased (iv) decreased (v) decreased
75. -702.6 kJ

76. 109 K
77. −808 kJ
78. 30.8 kJ mol^{-1}
80. −1.1 kJ
81. 1.9 kJ
82. 73.7 dm^{3}
83. 3 atm
84. 4.2 kJ
85. 205 K
86. 1.52 mol
87. (a) 181 kJ (b) −17.0 kJ
88. −80.9 J K^{-1}
89. 7.5 J K^{-1}
90. 4.1 J K^{-1}
92. 1110 K
93. (b) (i) 26.1% (ii) 19.3% (iii) 33.1% (iv) 25.4%
94. (a) 250 J (b) 2250 J (c) 90%
95. (a) 600 J (b) 910 J

10
Chapter
Electrochemistry

Electricity can be generated by means of chemical reactions, while electricity can be used to bring about the decomposition of chemical substances. The branch of chemistry dealing with the relationships between electricity and chemical reactions is called electrochemistry.

10.1 ELECTROCHEMICAL CELLS

When a metal plate is inserted in an aqueous solution of its ions, an equilibrium is set up between the plate and its ions. The metal ions (cations) in solution can take up electrons from the plate and become deposited on its surface as neutral atoms (solid metal) as follows:

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

This equilibrium leaves the solution negatively charged due to an excess of electrons (negative charges), while the surface of the metal becomes positively charged due to an excess of positive charges. An example of this type of equilibrium is that between copper and its ions in solution:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu\ (s)$$

As we discussed earlier, this process is called reduction.

On the other hand, atoms of the metal can lose electrons and move into the solution as positively charged ions. This makes the surface of the metal to become negatively charged due to an excess of electrons (negative charges), while the solution becomes positively charged as follows:

$$M(s) \rightarrow M^{n+}(aq) + ne^-$$

An example of this type of equilibrium is that between zinc and its ions in solution:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

As we noted earlier, this process is called oxidation.

The oxidized and the reduced species in each of the systems described above are called a redox couple. A redox couple is denoted as follows:

Oxidized specie/reduced specie

The slash (/) denotes the junction between the two species. A comma (,) is used if no junction exist between the two species, i.e., when both are present in the electrolyte. Thus the redox couples described above are written as $\mathrm{Cu}^{2+}(aq)/\mathrm{Cu}(s)$ and $\mathrm{Zn}^{2+}(aq)/\mathrm{Zn}(s)$.

Each of the system or set-up described above is called a half-cell or metal ion/metal system (or equilibrium). Although the metallic plate fitted into the electrolyte is termed an electrode, it is also a common practice to refer to the entire set-up or half-cell as electrode. The convention for specifying an electrode is the reverse of that of a redox couple:

Reduced specie|oxidized specie

The vertical line denotes the junction between the two species. Thus the above systems are called copper|copper ion half-cell, $\mathrm{Cu}(s)|\mathrm{Cu}^{2+}$, and zinc|zinc ion half-cell, $\mathrm{Zn}(s)|\mathrm{Zn}^{2+}(aq)$ respectively. Some other examples are $\mathrm{Ag}(s)|\mathrm{Ag}^{+}(aq)$, $\mathrm{Pt}|\mathrm{Cl}_2(aq)|\mathrm{Cl}(aq)$, $\mathrm{Pt}|\mathrm{H}_2(g)|\mathrm{H}^{+}(aq)$, $\mathrm{Pt}|\mathrm{Fe}^{2+}(aq),\mathrm{Fe}^{3+}(aq)$, etc.

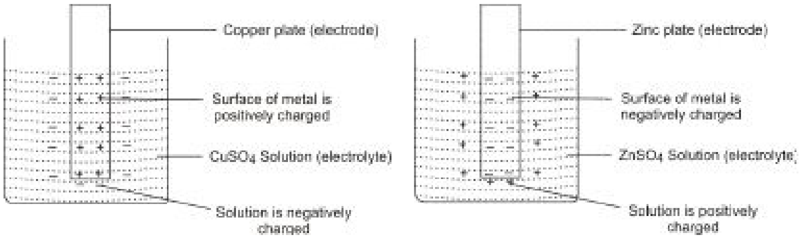

Figure 10.1 (a) $\mathrm{Cu(s)}|\mathrm{Cu}^{2+}(aq)$ Half-cell (b) $\mathrm{Zn(s)}|\mathrm{Zn}^{2+}(aq)$ Half-cell.

The potential difference that is set up between a couple is called electrode potential E. The electrode potential of a half-cell (electrode) is measured by comparing its electrode potential to that of the standard hydrogen electrode (SHE), which is assigned an arbitrary value of zero at all temperatures. The standard hydrogen electrode consists of hydrogen gas bubbling over inert platinum that is in contact with a solution containing 1 mole of hydrogen ions at 25°C and 1 atm. It is specified as [1]$\mathrm{Pt}|\mathrm{H}_2(g)|\mathrm{H}^{+}(aq)$. The standard electrode potential $E°$ of a half-cell is the electrode potential of that cell when the electrode is in contact with one-molar solution of its ions at 25°C. The unit of electrode potential is the volt (V).

By convention, electrode potential is assigned a positive (+) sign if the electrode is reduced, i.e., if electrons flow to the electrode from the hydrogen electrode; and negative (−) if the electrode is oxidized, i.e., electrons flow from the electrode to the hydrogen electrode. For example, when the copper electrode is connected to the standard hydrogen electrode, a potential difference of 0.34 V is recorded by a voltmeter connected to the system. The needle of the voltmeter is deflected to the left signifying that electrons flow from the hydrogen electrode to the copper electrode. Thus the copper electrode is reduced, and its standard electrode (reduction) potential is given as +0.34 V. The oxidation potential is opposite to the reduction potential. For example, the oxidation potential of the copper electrode is −0.34 V. The standard electrode potentials listed in tables are reduction potentials.

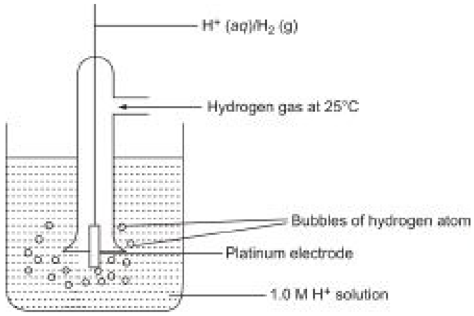

Figure 10.2 The standard hydrogen electrode.

Table 10.1 is a list of standard reduction potentials in the increasing order of magnitude (a longer list is given in Appendix 5). This is termed the electrochemical series. The electrodes with the negative potentials occupy the top. These are the substances with high reducing abilities. As we move down the table the electrode potentials increase, turn to zero at the hydrogen electrode, and then become positive at the lower end of the table. These are the substances with high oxidizing ability.

Table 10.1 The electrochemical series

Couple	*Reduction half-reaction*	*E °*
Li^+/Li	$Li^+ + e^- \rightarrow Li$	−3.04
K^+/K	$K^+ + e^- \rightarrow K$	−2.93

[1] We have to include platinum in the specification of an electrode that does not involve a metal to provide electrical contract with the couple.

Ca^{2+}/Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.87
Na^+/Na	$Na^+ + e^- \rightarrow Na$	−2.71
Mg^{2+}/Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
Al^{3+}/Al	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
Zn^{2+}/Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
Fe^{2+}/Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
Sn^{2+}/Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
Pb^{2+}/Pb	$Pb^{2+} + 2e \rightarrow Pb$	−0.13
Fe^{3+}/Fe	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.04
$H^+/H_2/Pt$	$2H^+ + 2e^- \rightarrow H$	0.00 (reference electrode)
Cu^{2+}/Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$O_2/4OH^-/Pt$	$O_2 + 2H_2O \rightarrow 4OH^-$	+0.40
$I_2/2I^-/Pt$	$I_2 + 2e^- \rightarrow 2I^-$	+0.53
Fe^{3+}/Fe^{2+}	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.80
Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag$	+0.77
$Br_2/2Br^-/Pt$	$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09
$Cl_2/2Cl^-/Pt$	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
Au^+/Au	$Au^+ + e^- \rightarrow Au$	+1.69

$F_2/2F^-/Pt$	$F_2 + 2e^- \rightarrow 2F^-$	+2.87

An electrochemical cell, also called a voltaic or galvanic cell, is a device in which chemical energy is converted into electrical energy. An electrochemical cell consists of two half-cells whose electrolytes, though prevented from mixing, are in ionic contact. The difference in potential between the two electrodes makes electrons to flow from one half-cell to the other. The exchange of ions is necessary to maintain electrical neutrality of the electrolytes and to complete the circuit. One way of achieving this is by means of a porous partition if the two half-cells occupy the same compartment. Another way is to link the half-cells by means of a salt-bridge if they occupy different compartments (Fig. 11.3).

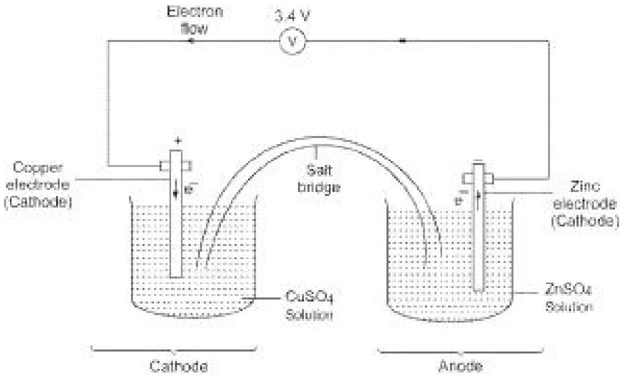

Figure 10.3 An electrochemical cell. The electrolyte of the half-cell on the left is $ZnSO_4$, while that of the right is $CuSO_4$. This cell is called Daniell cell.

It is also possible for the two electrodes in an electrochemical cell to share the same electrolytes. This is the case in the lead-acid cell or accumulator. In this case no porous partition or salt-bridge is required.

The electrode from which the electrons flow is the anode (marked −), while the electrode to which the electrons flow is the cathode (marked +). Oxidation occurs at the anode and reduction at the cathode. The reaction occurring at the anode is the oxidation half-reaction, while that at the cathode is the reduction half-reaction. The cathode is usually the more electronegative of the two electrodes. Thus the electrode which serves as the anode occupies the upper part of the electrochemical series, while the cathode occupies the lower part.

Electrochemical cells cannot supply electricity indefinitely. Their potentials reduce with time due largely to the problems of polarization and local action. Thus some cells have to be discarded once they are depleted. These are called primary cells. A example is the Leclanché or dry cell (with e.m.f. of 1.5 V), which is the common cell used to power small appliances. Other examples include Daniell cell, alkaline cell (whose electrolyte could be sodium or potassium hydroxide), mercury cell, etc.

Some cells can be recharged after being depleted. These are called secondary cells. An example is the lead-acid accumulator (with e.m.f. of 12 V), which is the common car battery. It consists of lead (anode) and lead(IV) oxide (cathode) electrodes in contact with dilute sulphuric acid. Another example is the nickel-cadmium cell.

A connection of two are more cells is called battery.

10.1.1 Cell Diagram

A cell diagram is the notation for a particular cell. By convention, the anodic (oxidation) half-reaction is written first in the notation of an electrochemical cell, as follows:

$$\text{anodic half-reaction} \,|\,|\, \text{cathodic half-reaction}$$

where the double vertical lines represents a salt-bridge or porous partition.

For example, the two reactions in the Daniell cell are:

Anodic half-reaction $\mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+}(aq) + 2\mathrm{e}^-$

Cathodic half-reaction $\mathrm{Cu}^{2+}(aq) + 2\mathrm{e}^- \rightarrow \mathrm{Cu}(s)$

Thus the cell diagram for the Daniell cell is

$$\mathrm{Zn}(s)|\mathrm{Zn}^{2+}(aq)|\,|\mathrm{Cu}^{2+}(aq)|\mathrm{Cu}(s)$$

The cell diagram shows that oxidation occurs at the zinc cathode, and reduction at the copper cathode.

10.1.2 Cell Potential

Cell potential *E*, also called electromotive force (e.m.f.) or voltage, is a measure of the power of a cell to drive electrons through an external circuit. This flow of electrons is called electric current. Cell potential is the algebraic difference between the electrode potentials of the cathode (right-hand side electrode) and the anode (left-hand side electrode), i.e.

$$E = E_1 - E_2$$

where E_1 = Electrode potential of the cathode.

E_2 = Electrode potential of the anode.

The standard cell potential E° of a cell is the cell potential when each electrode (half-cell) is in its standard state, i.e., each electrode is in contact with one-molar solution of its ion at 1 atm. Thus

$E^o = E^o_1 - E^o_2$

where E^o_1 = Standard electrode potential of the cathode.

E^o_2 = Standard electrode potential of the anode.

The above relation shows that cell potential depends on the choice of electrodes. A cell with a large potential is obtained by choosing two electrodes that are very far apart in the electrochemical series.

Example 1 Calculate the e.m.f. of the cell $Zn(s)|Zn^{2+}(aq)|\,|Cu^{2+}(aq)|Cu(s)$

$(E^o[Zn^{2+}(aq)/Zn(s)] = -0.76\text{ V}, E^o[Cu^{2+}(aq)/Cu(s)] = 0.34\text{ V})$

Solution This is a direct application of the relation

$$E^o = E^o_1 - E^o_2$$

Copper is the cathode. Thus

$E^o_1 = 0.34\text{ V}$

$E^o_2 = -0.76\text{ V}$

$E^o = ?$

Substituting we obtain

$E^o = 0.34\text{ V} - (-0.76\text{ V})$

$= 0.34\text{ V} + 0.76\text{ V}$

$= 1.10\text{ V}$

Example 2 Calculate the e.m.f. of the cell $Zn(s)|Zn^{2+}(aq)|\,|Ag^{+}(aq)|Ag(s)$

$(E^o[Zn^{2+}(aq)/Zn(s)] = -0.76\text{ V}, E^o[Ag^{+}(aq)/Ag(s)] = 0.80\text{ V})$

Solution We have to apply the relation

$E^o = E^o_1 - E^o_2$

$E^o_1 = 0.80\text{ V}$

$E^o_2 = -0.76\text{ V}$

$E^o = ?$

Substituting we have

$E^o = 0.80\text{ V} - (-0.762\text{ V})$

$= 0.80\text{ V} + 0.76\text{ V}$

$= 1.56\text{ V}$

Practice Problems

1. Calculate the e.m.f. of the cell $Mg(s)|Mg^{2+}(aq)|\,|Pb^{2+}(aq)|Pb(s)$

   ($E^o[Mg^{2+}(aq)/Mg(s)] = -2.37$ V, $E^o[Pb(aq)/Pb(s)] = -0.13$ V) [*Answer:* 2.24 V]

2. $Ca(s)|Ca^{2+}(aq)|\,|Fe^{3+}(aq)|Fe(s)$

   ($E^o[Ca^{2+}(aq)/Ca(s)] = -2.87$ V, $E^o[Fe^{3+}(aq)/Fe(s)] = 0.77$ V) [*Answer:* 3.64 V]

10.1.3 Cell Potential and Free Energy

The relation between the potential of a cell and its free energy change is given by the relation

$\Delta G = -nFE$

where ΔG = The free energy change of the cell.

n = The number of moles of electrons transferred.

E = The electrode potential of the cell.

F = Faraday's constant = 96,500 C mol^{-1} (or 96,490 C mol^{-1} to be more precise).

The standard free energy change DG^o of a cell is calculated from its standard electrode potential:

$$\Delta G^o = -nFE^o$$

Example 1 Calculate the ΔG^o for the half-cell $Zn^{2+}(aq)|Zn(s)$.

$$(F = 96500 \text{ C mol}^{-1},\ E^o = -0.76 \text{ V})$$

Solution We have to apply the relation

$$DG^o = -nFE^o$$

The number of moles of electrons transferred during the reaction is obtained by writing the balanced equation for the reduction of zinc:

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$$

Thus $n = 2$ mol

$F = 96500$ C mol^{-1}

$E^o = -0.76$ V

$\Delta G^o = ?$

Substituting we have

$$\Delta G^o = -2\ \cancel{\text{mol}} \times \frac{96500\ \text{C}}{1\ \cancel{\text{mol}}} \times (-0.76\ \text{V})$$

$= 146.7$ kJ

Note that 1 C × 1 V = 1 J.

The positive value of DG^o shows that the reaction in the half-cell is not spontaneous, i.e., not feasible. However, reversing the reaction in the half-cell will give a negative value of DG^o, i.e. −146.7 kJ mol^{-1}. A negative value of DG^o shows that the reaction in the half-cell is feasible. This is obtained by using the standard (oxidation) potential of the reversed half-cell:

$$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2\text{e}^- \quad E^o = 0.76\ \text{V}$$

$$\text{So}\ \ \Delta G^o = -2\ \cancel{\text{mol}} \times \frac{96500\ \text{C}}{1\ \cancel{\text{mol}}} \times 0.76\ \text{V}$$

$= -146.7$ kJ

Example 2 Calculate the electrode (reduction) potential of the half-cell, $\text{Cu}^{2+}(aq)|\text{Cu}(s)$ when its free energy change is −60.58 kJ.

(F = 96.5 kC mol^{-1})

Solution This problem does not refer to standard conditions. Thus

$$\Delta G = -nFE$$

$$\therefore\ E = -\frac{\Delta G}{nF}$$

The half-cell (reduction) reaction is

$$\text{Cu}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cu}(s)$$

Thus n = 2 mol

F = 96.5 kC mol^{-1}

ΔG = −60.58 kJ = −60.58 kC V

We can now substitute to obtain

$$E = -\frac{60.58\ \cancel{\text{kC}}\ \text{V} \times 1\ \cancel{\text{mol}}}{2\ \cancel{\text{mol}} \times 96.5\ \cancel{\text{kC}}}$$

$= 0.30$ V

Example 3 Calculate the ΔG^o of the Daniell cell, $Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$.

($E^o[Zn^{2+}(aq)/Zn(s)] = -0.76V$, $E^o[Cu^{2+}(aq)/Cu(s)] = 0.36V$, $F = 96500\ \text{C mol}^{-1}$)

Solution We have to apply the relation

$$\Delta G^o = -nFE^o$$

The half-equations are:

Anodic half-reaction $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^o = 0.76$ V (Oxidation)
Cathodic half-reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^o = 0.36$ V (Reduction)

Note that the E^o for $Zn^{2+}(aq)/Zn(s)$ is positive in the above half-equation because we are now considering the oxidation potential of the half-cell. It must always be remembered that the values given in tables are reduction potentials. We have already obtained E^o to be 1.10 V in Section 8.1.2.

$n = 2$ mol
$F = 96500\ \text{C mol}^{-1}$

We now substitute to obtain

$G^o = ?$

$$\Delta G^o = -2\ \cancel{\text{mol}} \times \frac{96500\ \text{C}}{1\ \cancel{\text{mol}}} \times 1.10\ \text{V}$$

$$= -212\ \text{kJ}$$

Example 4 The standard electrode potentials of $Sn^{2+}(aq)/Sn(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$ are −0.14 V and 0.77 V, respectively. Calculate the reduction in the e.m.f. of the cell $Sn(s)|Sn^{2+}(aq)||Fe^{2+}(aq),Fe^{3+}(aq)|Pt$ when the DG^o of the cell is reduced to −120.6 kJ.

($F = 96500\ \text{C mol}^{-1}$)

Solution We start by working out the standard cell potential or e.m.f.:

$E^o = E^o_1 - E^o_2$
$E^o_1 = 0.80$ V
$E^o_2 = -0.76$ V
$E^o = ?$

So $E^o = 0.77\ \text{V} - (-0.14\ \text{V})$
$= 0.77\ \text{V} + 0.14\ \text{V} = 0.92\ \text{V}$

This corresponds to when DG = DG^o.

We must now calculate the e.m.f. of the cell when D$G = -120.6\ \text{kJ mol}^{-1}$, using the equation

$\Delta G = -nFE$

$\therefore\ E = -\frac{\Delta G}{nF}$

The half-cell reactions are:

Anodic half-reaction Sn(s) " $Sn^{2+}(aq) + 2e$ $E^o = 0.14$ V (Oxidation)

Cathodic half-reaction $Fe^{3+}(aq) + e^-$ " $Fe^{2+}(aq)$ $E^o = 0.77$ V (Reduction)

We have to balance the number of moles of electrons in the two half-cells by multiplying the cathodic half-reaction by 2 to obtain

$$2Fe^{3+}(aq) + 2e^- \text{ " } 2Fe^{2+}(aq)$$

Thus $n = 2$ mol

$\Delta G = -120.6$ kJ $= -120600$ C V

$F = 96500$ C mol^{-1}

We now substitute to obtain

$$E = \frac{[-120600]\,\cancel{C}\,V \times 1\,\cancel{mol}}{-2\,\cancel{mol} \times 96500\,\cancel{C}}$$

$= 0.600$ V

Finally, we can now work out the reduction in the e.m.f. of the cell by subtracting its potential when $\Delta G = -120.6$ kJ from the potential when $\Delta G = \Delta G^o$:

$$\Delta E = 0.92 \text{ V} - 0.600 = 0.30 \text{ V}$$

Practice Problems

1. Calculate the ΔG^o of the half-cell $Mn^{2+}(aq)$, $H_2O(l)|MnO_4^-(aq)$, $H^+(aq)$, give that its standard electrode potential is 1.52 V. What would be the percentag reduction in the e.m.f. of the cell when its ΔG^o is reduced to 600 kJ mol^{-1}?

[*Answer:* −733 kJ mol^{-1}, 33%

2. Calculate the ΔG^o of the cell $K(s)|K^+(aq)||MnO_4^-(aq)$, $H^+(aq)|Mn^{2+}(aq)$, $H_2O($

($E^o[MnO_4^-(aq)$, $H^+(aq)/Mn^{2+}(aq)$

$H_2O(l)] = 1.52$ V, $E^o[K^+(aq)/K(s)] = -2.92$ V, $F = 96500$ C mo $^{-1}$)

[*Answer:* 2.14 MJ mol^{-1}]

10.1.4 The Equilibrium Constant of a Cell

Standard free energy is related to equilibrium constant (Chapter 11) by the equation

$\Delta G^o = RT \ln K_c$ (10.1)

We also know that ΔG^o is related to E^o by the equation

$\Delta G^o = -nFE^o$ (10.2)

Equating Equations (10.1) and (10.2) we have

$-nFE^o = -RT \ln K_c$

Thus $\ln K_c = \frac{nFE^o}{RT}$ (10.3)

In terms of common logarithm we have

$$\log K_c = \frac{nFE^o}{2.303\,RT}$$

where R = Universal gas constant = 8.314 J $\text{K}^{-1}\,\text{mol}^{-1}$
n = The number of moles of electrons transferred.
E^o = Standard cell potential.
F = Faraday’s constant = 96490 C mol^{-1}
T = The absolute temperature = 298 K at standard conditions.

Note that ln x = log 2.303 x.

The numerical value of the term RT/F is obtained by substituting the above data:

$$\frac{RT}{F} = \frac{8.314\,\cancel{C}\,\text{V}\,\cancel{\text{mol}^{-1}} \times 298\,\cancel{\text{K}}}{96490\,\cancel{C}\,\cancel{\text{mol}^{-1}} \times 1\,\cancel{\text{K}}}$$

= 0.02569 V

We can now substitute the reciprocal of this value into Equation (10.3) to obtain

$\ln K_c = \frac{nE^o}{0.02569\text{ V}}$ (10.4)

In terms of common logarithm we have

$$\log K_c = \frac{nE^\circ}{0.0592\ \text{V}}$$

The equilibrium constant of a cell is calculated from any of these two relations.

Example 1 Calculate the K_c for the electrode (half-cell) Cu(*s*)|Cu^{2+}(*aq*) at 25°C if its standard reduction potential is 0.34 V.

Solution We start from the half-cell reaction:

$$\text{Cu}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cu}(s)$$

The equation shows that 2 mol of electrons are transferred. As we will see in Chapter 11, the equilibrium constant of this half-cell is expressed as

$$K_c = \frac{1}{[\text{Cu}^{2+}]}$$

However, we do not have enough information to use this expression since we are not given the concentration of copper(II) ions. Thus we have to apply the relation

$\log K_c = \frac{nE^\circ}{0.0592\ \text{V}}$

$n = 2$
$E^o = 0.34$ V
$K_c = ?$

We now substitute to obtain

$$\log K_c = \frac{2 \times 0.34\ \cancel{\text{V}}}{0.0592\ \cancel{\text{V}}} = 11.5$$

Finally, we now take the common antilogarithms of both sides to obtain

$$K_c = 10^{11.5} = 3.2 \times 10^{11}$$

The large value of K_c shows that the reaction is spontaneous.

Example 2 Calculate the equilibrium constant for the cell Fe(*s*)|Fe^{2+}(*aq*)| |Ag^+

(aq)|Ag(s).

(E^o[Fe^{2+}(aq)/Fe(s)] = −0.44 V, E^o[(Ag^+(aq)/Ag(s)] = 0.80 V)

Solution We have to apply the equation

$$\ln K_c = \frac{nE^\circ}{0.02569\ \text{V}}$$

The half-equations are:

Anodic half-reaction Fe(s) → Fe^{2+}(aq) + $2e^-$ (Oxidation) $E^o = 0.44$ V

Cathodic half-reaction Ag^+(aq) + e^- → Ag(s) (Reduction) $E^o = 0.80$ V

We have to multiply the cathodic-half reaction by 2 in order to balance the equations, i.e.

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$

This shows that 2 mol of electrons are transferred.
The e.m.f. of the cell is obtained from the relation

$E^o = E^o_1 - E^o_2$

$E^o_1 = 0.80$ V

$E^o_2 = -0.44$ V

$E^o = ?$

So $E^o = 0.80\ \text{V} - (-0.44\ \text{V})$

$= 0.80\ \text{V} + 0.44\ \text{V} = 1.20\ \text{V}$

$K_c = ?$

Substituting we have

$$\ln K_c = \frac{2 \times 1.20\ \cancel{\text{V}}}{0.02569\ \cancel{\text{V}}} = 40.5$$

Finally, we now take the natural antilogarithms of both sides to obtain

$$K_c = 10^{40.5} = 3.2 \times 10^{40}$$

Example 3 Calculate the solubility product (equilibrium constant) for the reaction $PbSO_4$(s) ⇔ Pb^{2+}(aq) + SO_4^{2-}(aq).

(E^o[Pb^{2+}(aq)/Pb(s)] = −0.13 V, E^o[SO_4^{2-}(aq)/$PbSO_4$(s)/Pb(s)] = −0.36 V)

Solution From our previous work on solubility product, we know that the solubility product for the above dissociation is given as

$$K_{sp} = [Pb^{2+}]\,[SO_4^{2-}]$$

We can easily calculate K_{sp} if $[Pb^{2+}]$ and $[SO_4^{2-}]$ are known. These data, however, are not known, making it is impossible to calculate the equilibrium constant from the concentrations of the two ions. Nevertheless, we can calculate K_{sp} of the cell in two ways:

- Directly from the potential of the cell whose net reaction corresponds to $PbSO_4(s) \Leftrightarrow Pb^{2+}(aq) + SO_4^{2-}(aq)$.
- Indirectly from the cell potential of the cell whose net reaction corresponds to $Pb^{2+}(aq) + SO_4^{2-}(aq) \Leftrightarrow PbSO_4(aq)$, i.e. the reversed cell. The equilibrium constant of the stated cell is obtained as the reciprocal of that of this cell.

We will now use the second method, knowing that the cell which satisfies our requirement, i.e. the cell whose net reaction corresponds to $Pb^{2+}(aq) + SO_4^{2-}(aq) \Leftrightarrow PbSO_4(aq)$ is

$$Pb(s)|PbSO_4(s)|SO_4^{2-}(aq)|\,|Pb^{2+}(aq)|Pb(s)$$

We can verify this by writing the half-equations and combining them:

Anodic half-reaction $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$ $E^o = 0.36$ V (Oxidation)

Cathodic-half reaction $Pb^{2+}(aq) + 2e^-(aq) \rightarrow Pb(s)$ $E^o = -0.13$ V (Reduction)

2 mol of electrons are transferred. A combination of the two half-equations gives the net reaction

$$\cancel{Pb(s)} + SO_4^{2-}(aq) + Pb^{2+}(aq) + \cancel{2e} \Leftrightarrow PbSO_4(s) + \cancel{Pb(s)}$$

So $SO_4^{2-}(aq) + Pb^{2+}(aq) \Leftrightarrow PbSO_4(s)$

This shows that the net reaction of the cell is opposite to that of dissociation of $PbSO_4$; meaning that we are correct in our choice of cell. As usual, the K_c of the cell is calculated using the relation

$$\log K_c = \frac{nE^o}{0.0592\ \text{V}}$$

$E^o = E^o_1 - E^o_2$

$E^o_1 = -0.13$ V

$E^o_2 = -0.36$ V

$E^o = ?$

So $E^o = -0.13\ \text{V} - (-0.36\ \text{V})$

= – 0.13 V + 0.36 V = 0.23 V

K_c = ?

Substituting we have

$$\log K_{sp} = \frac{2 \times 0.23 \cancel{V}}{0.0592 \cancel{V}} = 7.77$$

We now take the common antilogarithms of both sides to obtain

$$K_c = 10^{7.77} = 6.3 \times 10^{7}$$

Finally, since we have been dealing with the cell whose net reaction is the reverse of the dissociation of $PbSO_4$, then we have to find the reciprocal of the above value in order to obtain the K_{sp} for the dissociation of $PbSO_4$:

$$K_{sp}(PbSO_4) = \frac{1}{K_c\{Pb^{2+}(aq) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s)\}} = \frac{1}{6.3 \times 10^{7}}$$

$= 1.6 \times 10^{-8}$ M^2

This value is the same with that in data book. Note that the unit of M^2 is obtained from the expression for the solubility product of the compound. It should be remembered that we can always work out the K_{sp} of a compound using the cell whose net reaction corresponds to the dissociation of the compound. This is illustrated in the next example.

Example 4 Calculate the equilibrium constant for the reaction AgBr(*s*) ⇔ Ag^+(*aq*) + Br^-(*aq*).

(E^o[Ag^+(*aq*)/Ag(*s*)] = 0.80 V, E^o[(Br^-(*aq*)/AgBr(*s*)/Ag(*s*)] = 0.070 V)

Solution The equilibrium constant (solubility product) for the reaction is the same as the equilibrium constant of the cell whose net reaction is AgBr(*s*) ⇔ Ag^+(*aq*) + Br^-(*aq*). The cell satisfying this requirement is

$$Ag(s)|Ag^+(aq)|\,|Br^-(aq)|AgBr(s)|Ag(s)$$

This can be shown as follows:

Anodic half-reaction Ag(*s*) → Ag^+(*aq*) + e^- E^o = −0.80 V (Oxidation)

Cathodic half-reaction AgBr(*s*) + e^- ⇔ Ag(*s*) + Br^-(*aq*) E^o = 0.07 V (Reduction)

Combining the half-equations we have

$$\cancel{Ag(s)} + AgBr(s) + \cancel{e^-} \Leftrightarrow \cancel{Ag(s)} + Br^-(aq) + Ag^+(aq) + \cancel{e^-}$$

So $AgBr(s) \Leftrightarrow Ag^+(aq) + Br^-(aq)$

Thus $K_{sp} = [Ag^+][Br^-]$

We can see from the net reaction that we are right in our choice of cell. The rest of the workings is easy as we only need to apply the relation

$$\log K_c = \frac{nE^o}{0.0592\ V}$$

$E^o = E^o_1 - E^o_1$

$E^o_1 = 0.070\ V$

$E^o_1 = 0.80\ V$

$E^o = ?$

So $E^o = 0.07\ V - 0.80\ V = -0.73\ V$

$n = 1$

We now substitute to obtain

$$\log K_{sp} = \frac{1 \times (-0.73\cancel{V})}{0.592\cancel{V}} = -12.3$$

Finally, we now take the common antilogarithms of both sides to obtain

$$K_c = 10^{-12.3} = 5.0 \times 10^{-13}\ M^2$$

Practice Problems

1. Calculate the equilibrium constant for the cell represented by the reaction $Zn(s) + Cu^{2+}(aq) \Leftrightarrow Zn^{2+}(aq) + Cu(s)$.

   $(E^o[(Zn^{2+}(aq)/Zn(s)) = -0.76\ V,\ E^o[(Cu^{2+}(aq)/\ Cu(s)] = 0.34\ V)$

   [*Answer:* 1.6×10^{37}]
2. Calculate the solubility product for the dissociation of AgCl from the data given below.

   $(E^o[Ag^+(aq)/Ag(s) = 0.80\ V,\ E^o[Cl^-(aq)/AgCl(s)/Ag(s)] = 0.22\ V)$

   [*Answer:* $1.6 \times 10^{-10}\ M^2$)

10.1.5 Cell Potential and Concentration

Cell potential is a function of the concentration of the electrolyte(s). The dependence of cell potential on concentration is given by Nernst equation, named in honour of the German chemist, Walther Nernst:

$$E = E^o - \frac{0.02569\ \text{V}}{n}$$

In terms of common logarithm we have

$$E = E^o - \frac{0.0592\ \text{V}}{n}$$

where E = The cell potential at a particular concentration of the electrolyte(s).
E^o = The standard cell potential.
n = The number of moles of electrons transferred.
Q = The reaction quotient.

Figure 10.4 Walther Hermann Nernst, German chemist and physicist (1864–1941). He won the Nobel Prize for Chemistry in 1920.

Example 1 Derive the Nernst equation.

Solution We begin from the relationship between free energy change and concentration, i.e.

$$\Delta G = -RT\,\text{In}\,\frac{K}{Q} \quad (10.5)$$

So $\Delta G = -RT \ln K + RT \ln Q$ (10.6)

Now, we know that D$G^o = -RT \ln K$. Substituting into Equation (10.6) we obtain

$$\Delta G = \Delta G^o + RT \ln Q \quad (10.7)$$

Next, we have to write ΔG and ΔG^o in terms of cell potential, using the relations

$$\Delta G = -nFE \quad (10.8)$$

$$\Delta G^o = -nFE^o \quad (10.9)$$

We now substitute Equations (10.8) and (10.9) into Equation (10.7) to obtain

$$-nFE = -nFE^o + RT \ln Q \quad (10.10)$$

We now divide Equation (10.10) through $-nF$ to obtain

$$E = E^o - \frac{RT}{nF} \ln Q \quad (10.11)$$

We have earlier obtained the value of RT/F to be 0.02569 V. Thus Equation (10.11) now becomes

$$E = E^o - \frac{0.02569\ \text{V}}{n} \ln Q \quad (10.12)$$

In terms of common logarithm we have

$$E = E^o - \frac{0.0592\ \text{V}}{n} \log Q \quad (10.13)$$

Example 2 Calculate the electrode potential of the cell $\text{Fe}(s)|\text{Fe}^{3+}(aq)$ when the concentration of Fe^{3+} is 0.15 M.

($E^o = -0.44$ V)

Solution We have to apply the Nernst equation

$$E = E^o - \frac{0.0592\ \text{V}}{n} \log Q$$

We have to write the equation of reaction in order to know the number of moles of electrons transferred and the expression for the reaction quotient Q. The equation of reaction is

$$\text{Fe}^{3+}(aq) + 3\text{e}^- \rightarrow \text{Fe}(s) \quad E^o = -0.44\ \text{V}$$

So $Q = \frac{1}{[\text{Fe}^{3+}]}$

$[\text{Fe}^{3+}] = 0.15$ M

$\therefore\ Q = \frac{1}{0.15} = 6.7$

$n = 3$
$E = ?$

Note that we have denoted [Fe(s)] by 1 in the expression for Q because the concentration of a solid is constant. Finally, we now substitute into the Nernst equation to obtain

$$E = -0.44\text{ V} - \frac{0.0592\text{ V}}{3}\log 6.7$$

$$= -0.44\text{ V} - (0.0197\text{ V} \times 0.83)$$
$$= -0.46\text{ V}$$

Example 3 Calculate the e.m.f. of the Daniell cell when the concentration of Zn^{2+} is thirty times that of Cu^{2+}.

($E^o[Zn^{2+}(aq)/Zn(s)] = -0.76$ V, $E^o[Cu^{2+}(aq)/Cu(s)] = 0.34$ V)

Solution We have to apply the equation

$$E = E^o - \frac{0.0592\text{ V}}{n}\log Q$$

The half-equations and the net equation are

Anodic-half reaction $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^o = 0.76$ V (Oxidation)
Cathodic half-reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^o = 0.34$ V (Reduction)

We now combine the above equations to obtain

$$Zn(s) + Cu^{2+}(aq) + \cancel{2e^-} \Leftrightarrow Zn^{2+}(aq) + \cancel{2e^-} + Cu(s)$$

So $Zn(s) + Cu^{2+}(aq) \Leftrightarrow Zn^{2+}(aq) + Cu(s)$

We can now see from the net equation that

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

where $[Zn^{2+}] = 30 \times [Cu^{2+}]$

Thus $Q = \frac{30 \times \cancel{[Cu^{2+}]}}{\cancel{[Cu^{2+}]}} = 30$

We have already obtained E^o to be 1.10 V.

n = 2
E = ?

Substituting into the equation we have

$$E = 1.10\text{ V} - \frac{0.0592\text{ V}}{2}\log 30$$

$= 1.10\text{ V} - (0.0592\text{ V} \times 1.48)$
$= 1.01\text{ V}$

Example 4 Calculate the potential of the cell $Mg(s)|Mg^{2+}(aq)||MnO_4^-\,(aq)$, $H^+\,(aq)|Mn^{2+}$
(aq), $H_2O(l)$ when the concentrations of Mg^{2+}, MnO_4^- and H^+ are 0.15 M, 0.15 M and 1.20 M respectively.

($E^o[Mg^{2+}(aq)/Mg(s) = -2.36\text{ V}$, $E^o[(aq), H^+(aq)|Mn^{2+}(aq), H_2O(l)] = 1.51\text{ V}]$)

Solution We are applying the equation

$$E = E^o - \frac{0.02569\text{ V}}{n}\ln Q$$

The half-equations and the net equation are as follows:

Anodic half-reaction $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ $E^o = 2.36\text{ V}$ (Oxidation)

Cathodic half-reaction $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ $E^o = 1.51\text{ V}$ (Reduction)

The net equation is obtained by adding 2 times the anodic half-reaction to 5 times the cathodic half-reaction:

$5Mg(s) + 2MnO_4^-(aq) + 16H^+(aq) + \cancel{10e^-} \Leftrightarrow 5Mg^{2+}(aq) + \cancel{10e^-} + 2Mn^{2+}(aq) + 8H_2O(l)$

So $5Mg(s) + 2MnO_4^-(aq) + 16H^+(aq) \Leftrightarrow 5Mg^{2+}(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$

Then $Q = \dfrac{[Mg^{2+}]^5[Mn^{2+}]^2}{[MnO_4^-]^2[H^+]^{16}}$

$[Mg^{2+}] = 0.15\text{ M}$
$[Mn^{2+}] = 0.10\text{ M}$
$[MnO_4^-] = 0.15\text{ M}$
$[H^+] = 1.20\text{ M}$

Substituting we have

$$Q = \frac{(0.15)^6 \times (0.10)^2}{(0.15)^2 \times (1.20)^{16}} = 1.8 \times 10^{-6}$$

The standard e.m.f. of the cell is obtained from the relation

$E^o = E^o_1 - E^o_2$

$E^o_1 = 1.51$ V

$E^o_2 = -2.36$ V

$E^o = ?$

$E^o = 1.51$ V – (−2.36 V)

= 1.51 V + 2.36 V = 3.87 V

$n = 10$

$E = ?$

We now substitute to obtain

$$E = 3.87\ \text{V} - \frac{0.02569\ \text{V}}{10}$$

Thus $E = 3.87$ V – [0.002569 V × (−13.23 V)]

= 3.87 V + 0.034 V

= 3.90 V

Practice Problems

1. Calculate the potential Sn(*s*)|Sn^{2+}(*aq*) when the concentration of Sn^{2+} is 5 M.
   ($E^o = -0.14$ V) [*Answer:* −0.53 V]
2. Calculate potential of the couple Fe^{3+}(*aq*)/Fe^{2+}(*aq*) when the concentration of Fe^{3+} is twice that of Fe^{2+}.
   ($E^o = 0.77$ V) [*Answer:* 0.79 V]
3. Calculate the potential of the cell Cr(*s*)|Cr^{3+}(*aq*)| |Fe^{3+}(*aq*)/Fe(*s*) when the concentrations of Cr^{3+} and Fe^{3+} are 0.01 M and 0.0001 M respectively.
   (E^o[Cr(*aq*)$^{3+}$/Cr(*s*)] = −0.74 V, E^o[Fe $^{3+}$(*aq*)/Fe(*s*)] = −0.40 V) [*Answer:* 0.66 V]
4. The net reaction in the Daniell cell is given by the equation Zn(*s*) + Cu^{2+}(*aq*) ⇔ Zn^{2+}(*aq*) + Cu(*s*). What concentration of Zn^{2+} must be coupled with 0.55 M of Cu^{2+} to get a cell potential of 1.5 V?
   ($E^o = 1.10$ V) [*Answer:* 1.8×10^{-14} M]

10.2 ELECTROLYSIS

Electrolysis is the use of electric current to bring about the decomposition of chemical substances consisting of free or mobile ions. As we said in Section 7.5, the ions are the carriers of electric charges in solution. Also, a substance can only contain mobile ions if it is molten or in aqueous solution. A chemical substance which can be dissociated into its ions in solution or when molten is called an electrolyte. In other words, an electrolyte is a chemical substance that can conduct electricity when in solution or molten.

An electrolytic cell is the compartment in which electrolysis occurs. This consists of two electrodes fixed into an electolyte. Unlike the electrochemical cell, the positive electrode is called anode, while the negative electrode is called cathode. Oxidation occurs at the anode, while reduction occurs at the cathode.

Ions move randomly in an electrolyte before the application of electric current. After the electrodes are connected to voltage supply, the anions (negatively charge ions) migrate to the anode, where they get oxidized by losing electrons and are then discharged from the solution as their element. At the same time the cations (positively charged ions) migrate to the cathode, where they get reduced by gaining electrons and are then discharged from the solution as their element.

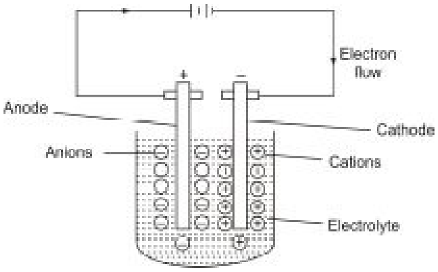

Figure 10.5 An electrolytic cell showing the mechanism of electrolysis.

For example, in the electrolysis of acidified water, the hydrogen ions (cations) migrate to the cathode where each hydrogen ion gains an electron to become reduced to the neutral hydrogen atom. Two hydrogen atoms then combine to form hydrogen gas or molecule. A summary of these reactions, called cathodic half-reaction, is given below:

$H^+(aq) + e^- \rightarrow H$

$H + H \rightarrow H_2(g)$

Thus $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Each hydroxide ion (anion) loses an electron at the anode to become the neutral hydroxyl group, −OH. Two of this group then combine to form a molecule of water and oxygen atom. The oxygen atoms produced from each pair of this reaction now combine to form oxygen gas. A summary of these reactions, called anodic half-reaction, is given below:

$OH^{-}(aq) \rightarrow OH + e^{-}$

$OH + OH \rightarrow H_2O(l) + O$

$O + O \rightarrow O_2(g)$

So $4OH^{-}(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^{-}$

The net or overall reaction is obtained by summing the two half-reactions. We must always remember to ensure that the number of moles electrons involved in the two half-equations are equal. Thus we have to multiplty the cathodic half-equation by 2, which now leads to the net or overall reaction

$$4H^{+}(aq) + \cancel{4e} + 4OH^{-}(aq) \rightarrow 2H_2(g) + 2H_2O(l) + O_2(g) + \cancel{4e}$$

Thus $4H^{+}(aq) + 4OH^{-}(aq) \rightarrow 2H_2(g) + 2H_2O(l) + O_2(g)$

We can now see that the products of the electrolysis of acidified water are two molecules of hydrogen at the cathode and one molecule of oxygen at the anode. The solution becomes more acidic due to the removal of water from the solution.

Most times, two different ions are present at an electrode during electrolysis. These ions are produced by the solvent (water) and the solute (electrolyte). For example, a solution of copper sulphate, $CuSO_4$, contains two cations: H^{+} (from water) and Cu^{2+} (from the solute). It also contains two anions: OH^{-} (from water) and SO_4^{2-} (from the solute). It then follows that two different ions will be present at each electrode during electrolysis, of which one will be discharged while the other remains in solution. Whether an ion would be preferentially discharged from solution depends on three factors—the relative position of the ions in the electrochemical series, relative concenration of the ions, and the nature of the electrodes used.

In the electrolysis of the compound described above, copper(II) ions are discharged at the cathode in preference to hydrogen ions because Cu^{2+} is lower than H^{+} in the electrochemical series. At the anode, OH^{-} is discharged in preference to SO_4^{2-} because it (OH^{-}) is lower in the series.

When two ions are very close in the electrochemical series, then an ion that will not normally be discharged by virtue of its position in the series will be preferentially discharged if its concentration is raised above that of the competing ion. For example, in the electrolysis of sodium chloride, NaCl, increasing the concentration of the chloride ions by dissolving more of the salt in the solution will make the chloride ions to be discharged in preference to hydroxide ions because Cl^{-} and OH^{-} are very close in the series. On the other hand, SO_4^{2-} is never discharged at the anode during the electrolysis of copper sulphate, no matter its concentration, because it is very far apart from OH^- in the series.

Using an electrode that has a high affinity for an ion will promote its discharge from solution. For example, in the electrolysis of sodium chloride, NaCl, the use of a platinum cathode will make H^+ to be discharged in preference to Na^+ because H^+ occupies a lower position in the series. Changing the cathode to mercury, however, will effect the preferential discharge of Na^+ because mercury has the tendency to bind with sodium to form sodium amalgam. An electrode with an affinity for an ion called a reactive electrode. An electrode with no affinity for any of the ions in solution is called an inert electrode.

Another example of the effect of the choice of electrodes in the preferential discharge of ions is the electrolysis of copper(II) sulphate. Copper(II) ions will be discharged at the anode in preference to hydrogen ions if copper cathode and carbon (or platinum) anode are used, with the colour of the solution (blue) gradually fading away as copper (II) ions are discharged from the solution. However, no ion will be discharged if the anode is changed to copper. Instead copper atoms from the anode ionize by going into solution as ions; to the effect that the anode becomes gradually thinner. At the same time, the copper(II) ions get discharged at the copper cathode, to the effect that the cathode becomes thicker with time. The composition of the electrolyte remains constant during electrolysis.

Unlike the reactions in electrochemical cells, electrolysis is not a spontaneous process. It requires a certain amount of electrical energy to drive it. Thus the electrodes must be connected to a voltage (potential difference) supply. The theoretical minimum voltage required to drive electrolysis is the potential of the electrolytic cell if it were being used as an electrochemical cell. However, we must supply a higher voltage than the minimum value for any significant product formation to occur. The extra voltage supplied to the electrolyte is called overpotential.

Electrolysis has important applications. It is used in the electroplating of metals, where the metal to be electroplated is made the cathode. The electrolyte is the solution of the salt of the metal to be used for electroplating. Another application of electrolysis is the production of certain elements and compounds. For example, sodium is produced by the electrolysis of molten sodium chloride by the Downs process. Moreover, hydrogen, chlorine and sodium hydroxide are produced by the electrolysis of brine in the Kellner-Solvay cell, and aluminium is produced by the electrolysis of fused bauxite.

Besides, electrolysis is used for purifying certain metals like copper and silver, where the impure metal is made the anode and the pure metal the cathode. The electrolyte is a solution of the salt of the metal. The metallic atoms on the surface of the anode lose electrons and go into the solution as the metallic ions. These ions migrate to the cathode, gain electrons and get deposited as the pure metal on the surface of the cathode. The result is that the anode gets thinner, while the cathode becomes thicker.

10.2.1 Faraday’s First Law

Faraday’s first law of electrolysis states that the mass m of an element deposited during electrolysis is directly proportional to the quantity of electricity Q passed through its electrolyte, i.e.

$$m \ \mu \ Q$$

where $Q = It$.

Substituting into the above variation we have

$$m \ \mu \ It$$

We now introduce the constant of proportionality to obtain

$$m = EIt$$

where m = Mass in gram (g).
Q = The quantity of electricity in coulombs (C).
I = Current in amperes (A).
t = Time in seconds (s).
E = The electrochemical equivalent of the substance.

The electrochemical equivalent of a substance is defined as its mass deposited by the passage of 1 C of electricity through its electrolyte. The unit is gram per coulomb (g C^{-1}).

From the above relation, we can restate Faraday’s first law by saying that the mass of a substance deposited or liberated during electrolysis is directly proportional to the current passing through its electrolyte and the time of current flow.

The faraday or Faraday’s constant F is the quantity of electricity required to deposit 1 mol of a univalent ion, or 1 mole of electrons. It is approximately equal to 96500 C mol^{-1}. Similarly, it would require 2 faradays ($2F$) of electrolysis to liberate 1 mole of a divalent ion.

Figure 10.6 Michael Faraday, British physicist and chemist (1781–1867). The father of electricity. He was one of the greatest experimental scientists of the 18th century.

Example 1 What mass of copper would be deposited when 2 A of electric current is passed through a solution of copper(II) sulphate, $CuSO_4$, for 30 s.

$$(\text{Cu} = 63.5,\ F = 96500\ \text{C mol}^{-1})$$

Solution The first step is to write the equation of reaction, i.e., cathodic half-equation:

$$\text{Cu}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cu}(s)$$

Each Cu^{2+} takes up 2 electrons to become deposited as 1 mol of metallic copper. This implies that 2 F of electricity are needed to deposit 1 mol or 63.5 g of copper. The quantity of electricity used during the electrolysis is obtained from the relation

$Q = I \times t$
$I = 2\ \text{A}$
$t = 30 \times 60\ \text{s} = 1800\ \text{s}$
$Q = ?$

Substituting we have

$$Q = 2\ \text{A} \times 1800\ \text{s} = 3600\ \text{C}$$

Note that 1 A × 1 s = 1 C.

Finally, we can now work out the quantity of copper that would be deposited by this quantity of electricity, as follows:

2 F (2 × 96500 C) of electricity deposits 63.5 g (1 mol) of copper, then 3600 C of electricity would deposit x, i.e.

$2 \times 96500\ \text{C} = 63.5\ \text{g}$
$3600\ \text{C} = x$

Thus $x \times 193000\ \text{C} = 228600\ \text{g C}$

Then $x = \dfrac{228600\ \text{g}\cancel{\text{C}}}{193000\ \cancel{\text{C}}}$

$= 1.20\ \text{g}$

Example 2 Calculate amount (in mol) of silver would be deposited when 5 A of electric current is passed through a solution of silver chloride for 1 hour.

(Ag = 108, F = 96500 C mol^{-1})

Solution The equation of reaction is

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$

It is obvious from the equation that 1 F of electricity is needed to liberate 1 mol or 108 g of silver. As usual, the quantity of electricity used is obtained from the relation

$Q = I \times t$

$I = 5\ \text{A}$

$t = 1 \times 60 \times 60\ \text{s} = 3600\ \text{s}$

$Q = ?$

Substituting we have

$$Q = 5\ \text{A} \times 3600\ \text{s} = 18000\ \text{C}$$

Since 1 F (96500 C) of electricity deposits 1 mol of silver, then 18000 C will deposit x, i.e.

96500 C = 1 mol

18000 C = x

Thus $x \times 96500\ \text{C} = 18000\ \text{C} \times 1\ \text{mol}$

So $x = \frac{18000\ \cancel{\text{C}} \times 1\text{mol}}{96500\ \cancel{\text{C}}}$

$= 0.20\ \text{mol}$

The mass equivalent of this amount of silver, if required, can be obtained from the relation

$n = \frac{m}{M}$

$\therefore\ m = M \times n$

$M = 108\ \text{g mol}^{-1}$

$m = ?$

Thus $m = \frac{108\ \text{g} \times 0.20\ \cancel{\text{mol}}}{1\ \cancel{\text{mol}}}$

$= 22\ \text{g}$

Example 3 15.8 g of aluminium was deposited in 2 hours 45 minutes during the electrolysis of aluminium sulphate. Calculate the amount of the current used.

(Al = 27, F = 96500 C mol^{-1})

Solution The very first step is to write the equation of reaction

$$Al^{3+}(aq) + 3e^{-} \rightarrow Al(s)$$

The equation shows that 3 F of electricity are needed to deposit 1 mol or 27 g of aluminium. Since 3 F (3 × 96500 C) of electricity liberate 27 g of aluminium, then Q would liberate 15.8 g, i.e.

$289500\ \text{C} = 27\ \text{g}$

$Q = 15.8\ \text{g}$

Thus $Q \times 27\ \text{g} = 289500\ \text{C} \times 15.8\ \text{g}$

$$\text{Then } Q = \frac{289500\ \text{C} \times 15.8\ \cancel{\text{g}}}{27\ \cancel{\text{g}}}$$

$= 169411\ \text{C}$

We can now obtain the current used from the relation

$Q = I \times \text{t}$

$$\therefore\ I = \frac{Q}{t}$$

$t = (45 \times 60\ \text{s}) + (2 \times 60 \times 60\ \text{s}) = 2700\ \text{s} + 7200\ \text{s} = 9900\ \text{s}$

$I = ?$

Finally, we can now substitute to obtain

$$I = \frac{169411\ \text{A}\ \cancel{\text{s}}}{9900\ \cancel{\text{s}}}$$

$= 17\ \text{A}$

Example 4 What volume of hydrogen is liberated at 25°C and 800 mmHg when 2.5 A of electric current is passed through acidified water for 5.3 minutes at STP?

(Molar volume of gases at STP = 22.4 dm^{3} mol^{-1}, 1 F = 96500 C mol^{-1})

Solution The equation of reaction is

$$2H^{+}(aq) + 2e^{-} \rightarrow H_2(g)$$

The equation shows that 2 F of electricity would liberate 22.4 dm^{3} of the hydrogen gas at STP, i.e. 273 K and 760 mmHg. The quantity of electricity used is obtained from the relation

$Q = I \times t$

$I = 2.5$ A

$t = 5.3 \times 60$ s = 318 s

$Q = ?$

Substituting we have

$$Q = 2.5 \text{ A} \times 318 \text{ s} = 795 \text{ C}$$

Since 2 F (2 × 96500 C) of electricity produces 22.4 dm^3 of hydrogen at STP, then 795 C would produce x , i.e.

193000 C = 22.4 dm^3

795 C = x

Then $x \times 193000 \text{ C} = 22.4 \text{ dm}^3 \times 795 \text{ C}$

Thus $x = \frac{22.4 \text{ dm}^3 \times 795 \cancel{\text{C}}}{193000 \cancel{\text{C}}}$

$= 0.0923 \text{ dm}^3$

This is the volume of hydrogen liberated at STP We must now convert this to the volume at 25°C and 800 mmHg by using the relation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore \; V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

P_1 = 760 mmHg

V_1 = 0.0923 dm^3

T_1 = 273 K

P_2 = 800 mmHg

T_2 = 25 + 273 K = 298 K

V_2 = ?

Finally, we now substitute to obtain

$V_2 = \frac{760\ \cancel{\text{mmHg}} \times 0.0923\ \text{dm}^3 \times 298\ \cancel{\text{K}}}{800\ \cancel{\text{mmHg}} \times 273\ \cancel{\text{K}}}$

$= 0.1\ \text{dm}^3$

Example 5 2.5 A of electric current was passed through acidified water for 10 minutes. What is the amount of oxygen liberated at STP?

(Molar volume of a gas at STP = 22.4 $\text{dm}^3\ \text{mol}^{-1}$, F = 96,500 C mol^{-1})

Solution This is similar to the previous problem. The equation of reaction is

$$4\text{OH}^-(aq) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) + 4\text{e}^-$$

The equation shows that 4 F of electricity would produce 1 mol (22.4 dm^3) of oxygen gas at STP As usual, the quantity of electricity used is obtained from the relation

$Q = I \times t$

I = 2.5 A

t = 10 × 60 s = 600 s

Q = ?

Substituting we have

$$Q = 2.5\ \text{A} \times 600\ \text{s} = 1500\ \text{C}$$

Since 4 F (4 × 96500 C) of electricity produce 1 mol of oxygen at STP, then 1500 C would produce x, i.e.

386000 C = 1 mol

1500 C = x

Then $x \times 386000\ \text{C} = 1\ \text{mol} \times 1500\ \text{C}$

Thus $x = \frac{1\ \text{mol} \times 1500\ \cancel{\text{C}}}{386000\ \cancel{\text{C}}}$

$= 0.0039$ mol

Alteratively, we can say that 4 × 96500 C of electricity produces 22.4 dm^3 of oxygen at STP, then 1500 C would produce x, i.e.

386000 C = 22.4 dm^3

1500 C = x

Then $x \times 386000\ \text{C} = 22.4\ \text{dm}^3 \times 1500\ \text{C}$

Thus $x = \frac{22.4\ \text{dm}^3 \times 1500\ \cancel{\text{C}}}{386000\ \cancel{\text{C}}}$

$= 0.087\ \text{dm}^3$

We now obtain the corresponding number of moles of this volume of oxygen at STP, by using the relation

$n = \frac{V}{22.4\ \text{dm}^3\ \text{mol}^{-1}}$

$n = ?$

Substituting we have

$n = \frac{0.087\ \cancel{\text{dm}^3} \times 1\ \text{mol}}{22.4\ \cancel{\text{dm}^3}}$

$= 0.0039$ mol

Example 6 What quantity of aluminium would be deposited by the same quantity of electricity that is required to deposit 35 g of iron from a solution of iron(III) sulphate?

(Al = 27, Fe = 56, $F = 96500\ \text{C mol}^{-1}$)

Solution As usual, we start with the equation of reaction:

$$\text{Fe}^{3+}(aq) + 3\text{e}^{-} \rightarrow \text{Fe}(s)$$

The equation shows that 3 F of electricity would be needed to liberate 1 mol or 55.8 g of iron from Fe^{3+}. Since 3 F (3 × 96000 C) of electricity would liberate 55.8 g of iron, then Q would liberate 35 g, i.e.

289500 C $= 55.8$ g

$Q = 35$ g

Thus $289500\ \text{C} \times 35\ \text{g} = Q \times 55.8\ \text{g}$

So $Q = \frac{289500\ \text{C} \times 35\ \cancel{\text{g}}}{56\ \cancel{\text{g}}}$

$= 180937.5$ C

We must now find the mass of aluminium that would be deposited by the same quantity of electricity. The equation of reaction is

$$\mathrm{A1^{3+}}(aq) + 3\mathrm{e^-} \rightarrow \mathrm{Al}(s)$$

The equation shows that 3 F of electricity is required to deposit 1 mol or 27 g of aluminium. Since 3 F (3 × 96500 C) of electricity deposit 27 g of aluminuim, then 180937.5 C would deposit x, i.e.

289500 C = 27 g

180937.5 C = x

Then $x \times 289500\ \mathrm{C} = 27\ \mathrm{g} \times 80937.5\ \mathrm{C}$

So $x = \dfrac{27\ \mathrm{g} \times 180937.5\ \cancel{\mathrm{C}}}{289500\ \cancel{\mathrm{C}}}$

$= 17\ \mathrm{g}$

This problem can also be solved by applying Faraday’s second law, which we will see this shortly.

Example 7 A quantity of electricity was passed through two electrolytic cells connected in series containing concentrated solutions of copper(II) chloride and a chloride of cobalt. 0.68 g of copper and 0.63 g of cobalt were liberated in the first and second cells respectively. Calculate the oxidation state of cobalt in the chloride, hence give the IUPAC name of the chloride.

(Co = 59, Cu = 63.5, F = 96500 C)

Solution The very first step is to calculate the quantity of electricity used. This is easily obtained from the mass or amount of copper deposited. To do this we must first write the equation of reaction:

$$\mathrm{Cu}(aq) + 2\mathrm{e^-} \rightarrow \mathrm{Cu}(s)$$

The equation shows that 2 F (2 × 96500 C) of electricity would liberate 1 mol of copper. Since 2 F (2 × 96500 C) of electricity liberate 63.5 g, then Q would liberate 0.68 g, i.e.

19300 C = 63.5 g

Q = 0.68 g

So $Q \times 63.5\ \mathrm{g} = 193000\ \mathrm{C} \times 0.68\ \mathrm{g}$

Thus $Q = \dfrac{193000\ \mathrm{C} \times 0.68\ \cancel{\mathrm{g}}}{63.5\ \cancel{\mathrm{g}}}$

$= 2066.8\ \mathrm{C}$

The same quantity of electricity was passed through the two cells. Thus this is the same quantity of electricity that would liberate 0.63 g of cobalt. If the charge or oxidation number of cobalt in the chloride is x, then the equation of reaction is

$$\mathrm{Co}^{x+}(aq) + x\mathrm{e}^{-} \rightarrow \mathrm{Co}(s)$$

The equation shows that $x\ F$ of electricity are required to liberate 1 mol of cobalt. Since 2066.8 C of electricity liberates 0.63 g of cobalt, then $x\ F$ ($x \times$ 965000 C) would liberate 59 g, i.e.

$x \times 96500\ \mathrm{C} = 59\ \mathrm{g}$

$2066.8\ \mathrm{C} = 0.63\ \mathrm{g}$

Then $x \times 60795\ \mathrm{g\ C} = 2066.8\ \mathrm{C} \times 59\ \mathrm{g}$

Thus $x = \dfrac{2066.8\,\cancel{\mathrm{C}} \times 59\,\cancel{\mathrm{g}}}{60795\,\cancel{\mathrm{g}}\,\cancel{\mathrm{C}}}$

$= 2$

The IUPAC name of the compound is cobalt(II) chloride.

Practice Problems

1. What mass of silver is deposited when 2.5 A of electric current is passed th
   for 45 minutes?

   (Ag = 108,
   C)

   [*Answer:* 7.6 g]
2. What quantity of electricity is required to deposit 20.0 g of aluminium from
   the electrolysis if it costs £1.00 × 10^{-3} per coulomb?

   (Al = 27,
   C)

   [*Answers:* 214000 C, £214]
3. For how long must 3.0 A of electricity be passed through a solution of gold c

   (Au = 197,
   C)

   [*Answer:* 54 min.]
4. What volume of chlorine would be liberated at 790 mmHg and 27°C when
   through sodium chloride solution for 10 minutes at STP?

   (F = 96500 C mol^{-1}, molar volume of gases at STP = 22.4

10.2.2 Faraday’s Second Law

Faraday’s second law of electrolysis states that when the same quantity of electricity is passed through different electrolytes, the relative numbers of moles of the elements discharged are inversely proportional to the charges on their ions. For two electrolytes we have

$$\frac{n_A}{n_B} = \frac{x_B}{x_A}$$

where n_A = The amount of element A deposited.

n_B = The amount of element B deposited.

x_A = The charge on the ion of element A.

x_B = The charge on the ion of element B.

Example 1 What mass of aluminium would be deposited by the same quantity of electricity that is required to deposit 35 g of iron from a solution of iron(III) sulphate.

(Al = 27, Fe = 56)

Solution We have earlier solved this problem using Faraday’s first law. Applying Faraday’s second law we have

$$\frac{n_A}{n_B} = \frac{x_B}{x_A}$$

The cathodic half-reactions in the two cells are:

$$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$$

$$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$$

The amount of iron liberated is obtained from the relation

$$n = \frac{m}{M}$$

m = 35 g

M = 56g mol^{-1}

n_A = ?

Thus $n_A = \frac{35\,\cancel{g} \times 1\,mol}{56\,\cancel{g}} = 0.63$ mol

$x_A = 3$
$x_B = 3$
$n_B = ?$

We now substitute to obtain

$$\frac{0.63 \text{ mol}}{n_B} = \frac{3}{3}$$

Thus $0.63 \text{ mol} \times 3 = n_B \times 3$

$$\therefore\ n_B = \frac{0.63 \text{ mol} \times \cancel{3}}{\cancel{3}}$$

= 0.63 mol of aluminium

It then follows that the same quantity of electricity would liberate equal amounts of different substances from their electrolytes provided the charges on their ions are equal. Finally, we can now determine the mass of aluminium from the relation

$m = n \times M$
$M = 27 \text{ g mol}^{-1}$
$m = ?$

Substituting we have

$$m = \frac{0.63\,\cancel{\text{mol}} \times 27 \text{ g}}{1\,\cancel{\text{mol}}}$$

= 17 g

This is consistent with the result we got earlier (Example 6 of Section 12.2.1).

Example 2 A quantity of electricity was passed through three electrolytic cells connected in series. The cells contain solutions of copper(II) sulphate, aluminium nitrate and iron (II) sulphate. If 0.25 mol of copper was deposited in the first cell, calculate

(a) the mass of aluminium deposited in the second cell;
(b) the mass of iron deposited in the third cell.

(Al = 27, Fe = 56, Cu = 63.5)

Solutions

(a) The fact that the cells are connected in series means that the same quantity of electricity will pass through each electrolyte. The mass of aluminium deposited in the second cell can be obtained from the relation

$$\frac{n_A}{n_B} = \frac{x_B}{x_A}$$

The cathodic half-reactions in the first and second cells are:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$

Thus $n_A = 0.25$ mol

$x_A = 2$

$x_B = 3$

$n_B = ?$

We now substitute to obtain

$$\frac{0.25\ \text{mol}}{n_B} = \frac{3}{2}$$

Cross-multiplying we obtain

$n_B \times 3 = 0.25\ \text{mol} \times 2$

$\therefore\ n_B = \frac{0.25\ \text{mol} \times 2}{3}$

$= 0.167$ mol

We can now calculate the mass of aluminium from the relation

$m = n \times M$

$M = 27\ \text{g mol}^{-1}$

$m = ?$

Substituting we have

$m = \frac{0.167\ \cancel{\text{mol}} \times 27\ \text{g}}{1\ \cancel{\text{mol}}}$

$= 4.5$ g

(b) The cathodic half-reactions in the first and third cells are:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

$$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$$

Since the ions of copper and iron elements possess the same charge, then 0.25 mol of iron would also be deposited in the third cell. Alternatively, we can work with the second and third cells, and use the relation

$$\frac{n_A}{n_B} = \frac{x_B}{x_A}$$

The cathodic half-reactions in the cells are:

$$Al^{3+}(aq) + 2e^{-} \rightarrow Al(s)$$

$$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$$

$n_A = 0.167$ mol

$x_A = 3$

$x_B = 2$

$n_B = ?$

Substituting we obtain

$$\frac{0.167\ \text{mol}}{n_B} = \frac{2}{3}$$

Cross-multiplying we have

$0.167\ \text{mol} \times 3 = n_B \times 2$

$\therefore\ n_B = \frac{0.167\ \text{mol} \times 3}{2}$

$= 0.25$ mol

Finally, we can now calculate the mass of iron deposited from the relation

$m = n \times M$

$M = 56\ \text{g mol}^{-1}$

$m = ?$

Substituting we have

$m = \frac{0.25\ \cancel{\text{mol}} \times 56\ \text{g}}{1\ \cancel{\text{mol}}}$

$= 14$ g

Example 3 A quantity of electricity was passed through acidified water and silver chloride solution at STP. Calculate the volume of oxygen liberated in the second cell at 30°C and 940 mmHg, given that 12.5 g of silver was deposited in the second cell.

(Ag = 108, molar volume of a gases at STP = 22.4 $\text{dm}^3\,\text{mol}^{-1}$)

Solution We must first determine the amount of oxygen liberated at STP, using the relation

$$\frac{n_A}{n_B} = \frac{x_B}{x_A}$$

The amount of silver deposited is obtained from the relation

$$n = \frac{m}{M}$$

m = 12.5 g

M = 108 g mol^{-1}

n_A = ?

Substituting we have

$$n_A = \frac{12.5\,\cancel{\text{g}} \times 1\,\text{mol}}{108\,\cancel{\text{g}}}$$

= 0.116 mol

The oxidation half-reaction in the first cell is:

$$4\text{OH}^-(aq) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) + 4\text{e}^-$$

The reduction half-reaction in the second cell is

$$\text{Ag}^+(aq) + 2\text{e}^- \rightarrow \text{Ag}(s)$$

$x_A = 1$

$x_B = 4$

$n_B = ?$

Substituting we obtain

$$\frac{0.116\,\text{mol}}{n_B} = \frac{4}{1}$$

Cross-multiplying we have

$0.116\,\text{mol} = n_B \times 4$

$\therefore \quad n_B = \frac{0.116 \text{ mol}}{4}$

= 0.0290 mol of O_2 at STP

We can now convert this to the volume at STP by using the relation

$V = n \times 22.4 \text{ dm}^3 \text{mol}^{-1}$

So $V = \frac{0.0290 \cancel{\text{mol}} \times 22.4 \text{ dm}^3}{1 \cancel{\text{mol}}}$

= 0.650 dm^3

Finally, we must now convert this to the volume at 30°C and 840 mmHg:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore \; V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

P_1 = 760 mmHg

V_1 = 0.650 dm^3

T_1 = 273 K

P_2 = 840 mmHg

T_2 = 273 + 30°C= 303 K

V_2 = ?

We now substitute to obtain

$$V_2 = \frac{760 \cancel{\text{mmHg}} \times 0.650 \text{ dm}^3 \times 303 \cancel{\text{K}}}{940 \cancel{\text{mmHg}} \times 273 \cancel{\text{K}}}$$

= 0.58 dm^3

Example 4 A quantity of electricity was passed through solutions of copper(II) chloride and a chloride of cobalt. Calculate the oxidation state of cobalt in the chloride and give its IUPAC name, given that 0.68 g of copper and 0.63 g of cobalt were deposited in the first and second cells respectively.

(Co = 59, Cu = 63.5, 1 *F* = 96500 C)

Solution We have solved this problem in Example 7 of Section 12.2.1. We will now apply Faraday’s second law, i.e.

$$\frac{n_A}{n_B} = \frac{x_B}{x_A}$$

The reduction half-reactions in the two cells are:

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$
$$Co^{x+}(aq) + 2e^{-} \rightarrow Co(s)$$

The amount of each element deposited is obtained from the relation

$$n = \frac{m}{M}$$

For copper we have

m = 0.68 g
M = 63.5 g mol^{-1}
n_A = ?

So $n_A = \frac{0.68\,\cancel{g} \times 1\,mol}{63.5\,\cancel{g}}$

= 0.011 mol

For cobalt we have

m = 0.63 g
M = 59 g mol^{-1}
n_B = ?

So $n_B = \frac{0.63\,\cancel{g} \times 1\,mol}{59\,\cancel{g}}$

= 0.011 mol

Since equal amounts of copper and cobalt were liberated, then their ions must carry the same charge, i.e., the oxidation state of cobalt in the chloride is +2. Thus the IUPAC name of the chloride is cobalt (II) chloride.

Example 5 A quantity of electricity was passed through dilute hydrochloric acid and silver bromide solutions. 15.5 dm^3 of hydrogen and 110.5 g of bromine were liberated at STP in the first and second cells respectively. Calculate

(a) the mass of hydrogen liberated in the first cell;
(b) the molar mass of bromine.

(H = 1.0, molar volume of gases at STP = 22.4 dm^3 mol^{-1})

Solutions

(a) The very first step is to obtain the amount of hydrogen liberated at STP

$$n = \frac{V}{22.4\ \text{dm}^3\ \text{mol}^{-1}}$$

V = 15.5 dm^3

n = ?

Substituting we have

$$n = \frac{15.5\ \cancel{\text{dm}^3} \times 1\ \text{mol}}{22.4\ \cancel{\text{dm}^3}}$$

= 0.692 mol

We can now obtain the mass of hydrogen:

$m = n \times M$

$M = (2 \times 1.0)\ \text{g mol}^{-1} = 2.0\ \text{g mol}^{-1}$

m = ?

Substituting we have

$$m = \frac{0.692\ \cancel{\text{mol}} \times 2.0\ \text{g}}{1\ \cancel{\text{mol}}}$$

= 1.4 g

(b) We have to apply the relation

$$\frac{n_A}{n_B} = \frac{x_B}{x_A}$$

The reduction half-reaction in the first cell is:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

The oxidation half-reaction in the second cell is:

$$2Br^-(aq) \rightarrow Br_2(g) + 2e^-$$

Each of hydrogen and bromine was liberated from ions possessing a total charge of 2. Thus the amount of bromine liberated must also be 0.692 mol. Finally, we can now calculate the molar mass of bromine from the relation

$n = \frac{m}{M}$

$\therefore\ M = \frac{m}{n}$

$m = 110.5\ \text{g}$

$M = ?$

Substituting we have

$M = \frac{110.5\ \text{g}}{0.692\ \text{mol}}$

$= 160\ \text{g mol}^{-1}$

Practice Problems

1. What amount of copper would be deposited from a solution of copper(II) sulphate by the same quantity of electricity required to deposit 10.7 g of aluminium?

   (Al = 27, Cu = 63.5) [*Answer:* 0.27 mol]

2. A quantity of electricity was passed through solutions of iron(III) chloride and silver nitrate. If 0.75 mol of iron was deposited, then determine

(a) the mass of silver deposited;
(b) the volume of chlorine liberated at 2.05×10^4 Pa and 20°C.

(Cl = 35.5, Fe = 56, Ag = 108, F = 96500 C mol^{-1}, molar volume of gases at STP = 22.4 $\text{dm}^3\ \text{mol}^{-1}$) [*Answers:* (a) 243 g (b) 5.49 dm^3]

3. A quantity of electricity was passed through the solutions of a salt of iron and sodium hydroxide. What the oxidation number of iron in the salt, given that 8.5 g and 0.45 g of iron and hydrogen were respectively were liberated? [*Answer:* 3]

SUMMARY

- A half-cell consists of an electrode fixed into an electrolyte.
- A couple consists of the oxidized and reduced species in a half-cell.
- An electrochemical cell is a device that converts chemical energy into

electrical energy.

- Electrode potential is the potential difference between an electrode and an electrolyte.
- Cell potential is the algebraic difference between electrode potential of the cathode and that of the anode.
- The potential of a cell is related to its free energy change by the relation

$$\mathrm{D}G = -nFE \text{ or } \mathrm{D}G^\circ = -nFE^o \text{ (at standard conditions)}$$

- The equilibrium constant of a cell is related to its potential by the relation

$$\ln K_c = \frac{nE^\circ}{0.02569\ \mathrm{V}} \text{ or } \log K_c = \frac{nE^\circ}{0.0592\ \mathrm{V}}$$

- The potential of a cell is related to concentration by the Nernst equation

$$E = E^o - \frac{0.02569\ \mathrm{V}}{n} \text{ or } E = E^o - \frac{0.0592\ \mathrm{V}}{n}$$

- Electrolysis is the use of electric current to bring about the decomposition of molten or liquid chemicals substances.
- Faraday's first law of electrolysis states that the mass of a substance liberated during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte.
- The quantity of electricity used during electrolysis is the product of current and time in seconds, i.e.

$$Q = It$$

- 1 Faraday of electricity is the quantity of electricity required to discharge 1 mol of a univalent ion, or electrons. It is approximately equal to 96500 C mol^{-1}.
- Faraday's second law of electrolysis states that if the same quantity of electricity is passed through a solution of different electrolytes, then the relative numbers of moles of the elements discharged are inversely proportional to the charges on their ions. For two elements, we have

$$\frac{n_A}{n_B} = \frac{x_B}{x_A}$$

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. What is the e.m.f. of the cell represented by Zn(s)|Zn^{2+}| |$2Br^-$(aq)|Br_2(l)?

$$(E^o[\mathrm{Zn}^{2+}(aq)/\mathrm{Zn}(s) = -0.76\ \mathrm{V},\ E^o[2\mathrm{Br}_2(aq)/\mathrm{Br}_2(l)] = 1.06\ \mathrm{V})$$

A. −1.80 V B. −0.30 V

C. 0.30 V D. 1.02 V

E. 1.82 V

2. The e.m.f. of the cell K(s)|K$^+$(aq)| |Pb^{2+}(aq)|Pb(s) is 2.70 V. What is the standard electrode potential of the couple K$^+$(aq)/K(s) if the standard electrode potential of the couple is Pb^{2+}(aq)/Pb(s) is −0.13 V?

A. –2.93 V B. −1.92 V

C. 1.90 V D. 1.92 V

E. 2.92 V

Use the cell diagram below to answer Questions 3-4.

$$\mathrm{Zn}(s)|\mathrm{Zn}^{2+}(aq)|\ |\mathrm{Cu}^{2+}(aq)|\mathrm{Cu}(s)$$

3. What does the double line represent?

A. Anode B. Salt bridge

C. Half-cell D. Electrode

E. Electrolyte

4. The anode in the cell is

A. Zn^{2+}(aq) B. Cu^{2+}(aq)

C. Cu(s) D. Zn(s)

E. Zn(s)/Cu^{2+}(aq)

5. What is the numerical value of 1 F?

A. 96500 C B. 96510 C

C. 193000 C D. 217500 C

E. 896500 C

6. What is the DG^o for the reaction La^{3+}(aq) + 3e$^-$ → La(s)?

$$(F = 96500\ \mathrm{C\ mol^{-1}},\ E^o = -2.52\ \mathrm{V})$$

A. −730 kJ B. −80.5 kJ

C. 72.9 kJ D. 80.5 kJ

E. 730 kJ

7. What is the E^o of a couple whose reaction is the reduction of a divalent ion?

$$(F = 96500\ \mathrm{C\ mol^{-1}},\ \mathrm{D}G^o = -65.62\ \mathrm{kJ\ mol^{-1}})$$

A. −0.77 V B. −0.74 V

C. −0.34 V D. 0.34 V

E. 0.77 V

8. What is the equilibrium constant of the reaction $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$?

(E^o = 0.77 V)

A. 1.8×10^8 M^{-1} B. 1.0×10^{13} M^{-1}

C. 1.5×10^{13} M^{-1} D. 1.5×10^{14} M^{-1}

E. 2.4×10^{14} M^{-1}

9. The reaction taken place in a particular couple is the reduction of an ion to its metal. What is the charge on the ion if the K_c for the reaction is 6.6×10^{11} M^{-1}?

(E^o = 0.70 V)

A. −1 B. −2

C. +1 D. +2

E. +3

10. How many faradays of electricity are needed to liberate 1 mol of iron from a solution of iron (III) chloride?

A. 1.0 B. 2.0

C. 2.5 D. 3.0

E. 5.0

11. 2.0 A of electric current was passed through an electrolyte for 2.5 hours. Calculate the quantity of electricity used.

A. 300 C B. 5000 C

C. 14400 C D. 18000 C

E. 18460 C

12. For how long must a current of 1.5 A be passed through an electrolyte to consume 183400 C of electricity?

A. 24 hrs B. 29 hrs

C. 30 hrs D. 32 hrs

E. 34 hrs

13. What mass of aluminium would be deposited if 2.5 A of electric current is passed through a solution of aluminium nitrate for 40 minutes?

(A1 = 27, 1 F = 96500 C mol^{-1})

A. 0.41 g B. 0.52 g

C. 0.56 g D. 0.90 g

E. 1.50 g

14. A quantity of electricity was passed through solutions of iron(III) sulphate and copper(II) sulphate. What is the mass of iron deposited if 20.0 g of copper was deposited?

(Fe = 56, Cu = 63.5)

A. 10 g B. 11 g
C. 12 g D. 13 g
E. 15 g

ESSAY TYPE QUESTIONS

Electrochemical cells

15. (a) What is electrode potential?
    (b) Differentiate between a couple and half-cell.
    (c) What is an electrochemical cell?
    (d) What do you understand by cell potential?

16. Calculate the e.m.f. of each of the following cells:
    (a) Sn|Sn^{2+}(aq)| |Ag^{+}(aq)|Ag(s)
    (E^{o}[Sn^{2+}(aq)/Sn(s) = −0.14 V, E^{o}[Ag^{+}(aq)/Ag(s)] = 0.80 V)
    (b) Al(s)|Al^{3+}(aq)| |2Cl^{-}(aq)|Cl$_2$(g)
    (E^{o}[Al^{3+}(aq)/Al(s) = −1.66 V, E^{o}[2Cl^{-}(aq)/Cl$_2$(g)] = 1.36 V)
    (c) Ca(s)|Ca^{2+}(aq)| |Cu^{2+}(aq)|Cu(s)
    (E^{o}[Ca^{2+}(aq)/Cu(s)] = −2.87 V, E^{o}[Ca^{2+}(aq)/Cu(s)] = 0.34 V)
    (d) Fe(s)/Fe^{2+}(aq)| |2I^{-} (aq)|I$_2$(g)
    (E^{o}[Fe^{2+}(aq)/Fe(s) = 0.44 V, E^{o}[2I^{-}(aq)/I$_2$(g)] = 0.54 V)
    (e) Na(s)/Na^{+}(aq)//2F^{-}(aq)/F$_2$(g)
    (E^{o}[Na^{+}(aq)/Na(s)] = −2.71V, E^{o}[2F^{-}(aq)/F$_2$(g)] = 2.87 V)
    (f) K(s)|K^{+}(aq)| |Pt^{2+}(aq)|Pt(s).
    (E^{o}[K^{+}(aq)/K(s)] = −2.93 V, E^{o}[Pt^{2+}(aq)/Pt(s)] = 1.20 V)××

17. Calculate the DG^{o} of the following cells:
    (a) Ca^{2+}(aq) + 2e^{-} → Ca(s) E^{o} = −2.87 V
    (b) Au^{3+}(aq) + 3e^{-} → Au(s) E^{o} = 1.40 V
    (c) Fe(s) → Fe^{2+}(aq) + 2e^{-} E^{o} = 0.44 V
    (d) Cu(s)|Cu^{+}(aq)| |Cl$_2$(g)|2Cl^{-}(aq)|Pt
    (E^{o}[Cu^{+}(aq)/Cu(s)] = 0.52 V, E^{o}[Cl$_2$(g)/2Cl^{-}(aq)] = 1.36 V)

(e) $Zn(s)/Zn^{2+}(aq)//Fe^{2+}(aq)/Fe(s)$

($E^o[Zn^{2+}(aq)/ Zn(s)] = -0.76$ V, $E^o[Fe^{2+}(aq)/Fe(s)] = -0.44$ V, 1 F = 96500 C mol^{-1})

18. Calculate the K_c for each of the following reactions:

(a) $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $E^o = -0.14$ V

(b) $Fe(s) + 3Ag^+(aq) \rightarrow Fe^{3+}(aq) + 3Ag(s)$

($E^o[Fe(s)/Fe^{3+}(aq) =$ 0.04 V, $E^o[Ag^+(aq)/Ag(s)] = 0.80$ V

(c) $Cd(OH)_2(s) \rightarrow Cd^{2+}(aq) + 2OH^-(aq)$

($E^o[Cd^{2+}(aq)/Cd(s)] = -0.40$ V, $E^o[OH^-(aq)/Cd(OH)_2(s)/Cd(s)] = -0.81$ V)

(d) $AgI(s) \rightarrow Ag^+(aq) + I^-(aq)$

($E^o[I^-(aq)/AgI(s)/Ag(s] = -0.15$ V, $E^o[Ag^+(aq)/Ag(s)] = 0.80$ V)

(e) $Zn(s)|Zn^{2+}(aq)|\,|Sn^{2+}(aq)|Sn(s)$

($E^o[Zn^{2+}(aq)/Zn(s)] = -0.76$ V, $E^o[Sn^{2+}(aq)/Sn(s)] = -0.14$ V)

19. Derive the Nernst equation

$$E = E^o - \frac{0.0592\text{ V}}{n}\log Q$$

where E = Cell potential.

E^o = Standard cell potential.

Q = Reaction quotient.

20. What is the potential (reduction) of the couple $F_2(g) + 2e^- \rightarrow 2F^-(aq)$ (E^o = 2.87 V) when the concentrations of F^- and F_2 are 0.25 M and 1.0 M?

21. What is the potential (oxidation) of the couple whose reaction is $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$ ($E^o = -0.77$ V) when the concentration of Fe^{2+} is 100 times that of Fe^{3+}?

22. Consider the cell represented by $Sn(s)|Sn^{2+}(aq)|\,|Al^{3+}(aq)|Al(s)$. What concentration of Sn^{2+} must be coupled with 0.52 M of Al^{3+} to produce a cell whose e.m.f. is 1.8 V?

($E^o[Al^{3+}(aq)/Al(s)] = -1.66$ V, $E^o[Sn^{2+}(aq)/Sn(s)] = -0.14$ V)

23. Explain the electrochemical series. What information that can be obtained from the series?

Electrolysis

24. (a) What is electrolysis?

(b) State Faraday's first law of electrolysis.

(c) State Faraday's second law of electrolysis.

(d) What is the faraday?

(e) How many faradays of electricity would liberate 2 mol of aluminium from an electrolyte?

25. 2.5 A of electric current was passed through a solution of copper(II) chloride for 2.5 hours. Calculate

(a) the mass of copper deposited;

(b) the volume chlorine liberated at 0.95×10^5 Pa^2 and 27°C.

(Cl = 35.5, Cu = 63.5, molar volume of gases at STP = 22.4 $dm^3 mol^{-1}$, 1 F = 96500 C mol^{-1})

26. 2.8 g of hydrogen was discharged at the cathode during the electrolysis of dilute
hydrochloric acid. Calculate the quantity of electricity used.

(H = 1, F = 96500 C mol^{-1})

27. 5.0 A of electric current was passed through molten sodium chloride until 3.5 g of sodium was deposited at the cathode. How long did it take for this mass of sodium to be deposited?

(Na = 23, F = 96500 C mol^{-1})

28. An amount of electric current was passed through the solution of dilute copper(II) sulphate for 3.5 minutes. Calculate the amount of the current if 2.5 g of copper was deposited at the cathode.

(Cu = 63.5, F = 96500 C mol^{-1})

29. The production of 100 g of sodium by the electrolysis of brine costs £20 in electricity consumption. How much would be spent on electricity if the same mass of calcium is to be obtained?

(Na = 23, Ca = 40, F = 96500 C mol^{-1})

30. What mass of aluminium will be deposited by the same quantity of electricity that is required to deposit 30.5 g of copper from a solution of copper (II) sulphate?

(Al = 27, Cu = 63.5, F = 96500 C mol^{-1})

31. A quantity of electricity was passed through solutions of copper (II) chloride, silver nitrate and calcium chloride. If 0.75 g of copper was deposited in the first cell, calculate

(a) the mass of calcium deposited in the third cell;

(b) the mass of silver deposited in the second cell;

(c) the volume of chlorine liberated at 800 mmHg and 20°C.

(Cl = 35.5, Ca = 40, Ag = 108, molar volume of gases = 22.4 $dm^3\ mol^{-1}$, F = 96500 C mol^{-1})

32. A quantity of electricity was passed through solutions of copper (II) chloride and a salt of iron for the same duration. Calculate the charge carried by the ion of iron, given that
0.222 g and 0.200 g of copper and iron were respectively deposited in the first and second cells.

(Fe = 56, Cu = 63.5)

33. A quantity of electricity was passed through concentrated sodium chloride solution and acidified water. If 17.5 dm^3 and 1.56 g of oxygen and chlorine were respectively liberated, calculate

(a) the mass of oxygen liberated at STP;

(b) the relative atomic mass of chlorine;

(c) the molar mass of chlorine.

(O = 16, molar volume of gases at STP = 22.4 $dm^3 mol^{-1}$)

34. State and explain the factors influencing the discharge of ions during electrolysis.

35. Why do you think highly electropositive elements like sodium and potassium are never discharged from their electrolytes, regardless of concentrations?

36. State and explain the different applications of electrolysis.

Answers

1. E 2. A 3. B 4. D 5. A

6. E 7. D 8. B 9. C 10. D

11. D 12. E 13. C 14. C

16. (a) 0.94 V (b) 3.02 V(c) 3.21 V (d) 0.10 V (e) 5.58 V (d) 4.13 V

17. (a) 554 kJ (b) −405 kJ (c) −85 kJ (d) −160 kJ (e) −62 kJ

18. (a) 1.9×10^{-5} M^{-1} (b) 3.2×10^{38} M^{-2} (c) 1.4×10^{-14} M^3
(d) 8.9×10^{-17} M^2 (e) 8.9×10^{20}

20. 2.91 V

21. −0.65 V

22. 5.9 M

25. (a) 7.4 g (b) 3 dm^3
26. 270 K_c
27. 18 min.
28. 36 A
29. £23.00
30. 8.6 g
31. (a) 0.5 g (b) 2.5 g (c) 0.25 dm^3
32. +2
33. 25 g

11

Chapter Chemical Equilibria

A reversible reaction is that which proceeds in two directions. In other words, a reversible reaction is a reaction in which the products also react or decompose, under suitable conditions, to form the reactants. As we stated in Chapter 2, a reversible reaction is denoted with double arrows:

$$A + B \Leftrightarrow C + D$$

The reaction between A and B to form C and D is termed the forward reaction, indicated by the arrow pointing to the right. On the other hand, the decomposition of C and D to from A and B is termed the backward reaction, indicated by the arrow pointing to the left. A good example of a reversible reaction is the formation of ammonia through the Haber process:

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$$

Another example is the formation of hydrogen iodide:

$$H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$$

Some other examples include the formation of hydrogen chloride, decomposition of bromine chloride, atomization of chlorine, etc.

Chemical equilibrium is an example of dynamic equilibrium in which both the forward and backward reactions proceed at the same rate, such that there is no net formation of the products. In other words, upon the attainment of equilibrium, the products decompose or react to form the reactants immediately they are formed. A good knowledge of chemical equilibria is of great importance as it helps to know the best conditions under which to effect reactions in order to obtain the maximum yield of a desired product.

11.1 LE CHATELIER'S PRINCIPLE AND THE POSITION OF EQUILIBRIUM

Equilibrium position refers to which of the reactants or products are being favoured to be formed under a given conditions. In other words, it shows which of the forward or backward reactions is proceeding at a faster rate. When the position of equilibrium shifts to the right, then the formation of the products is favoured, and vice versa.

Equilibrium position will always change when the equilibrium conditions are altered. This is summed up in Le Chatelier's principle which states that a system in dynamic equilibrium will always act, i.e., change direction, so as to nullify or oppose any change in the equilibrium conditions. This could be a change in pressure, temperature, or concentration. The concentration of a reaction can be altered either by adding more of the reactants, or removing the products as they are formed. The effects of these factors on the direction of equilibrium depend on the nature of the reaction under consideration.

Figure 11.1 Henry Louis Le Chatelier, French chemist and engineer (1850–1936).

11.1.1 Effect of Change in Temperature

The response of an equilibrium system to a change in temperature depends on whether the reaction is endothermic or exothermic. An increase in temperature shifts the position of equilibrium to the direction of endothermic reaction, while a reduction in temperature shifts the position of equilibrium to the direction of exothermic change.

An important example is the production of ammonia by the Haber process. The formation of ammonia is an exothermic process:

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g) \quad \Delta H^{o}_{f} = -46.1 \text{ kJ mol}^{-1}$$

Raising the temperature of the system will promote the decomposition of ammonia, reducing its yield or composition in the equilibrium mixture. At the same time, the compositions of the reactants in the equilibrium mixture increase (as the rate of decomposition of ammonia now increases). In other words, an increase in temperature favours the backward reaction, which is endothermic.

11.1.2 Effect of Change in Concentration

The formation of the products, or forward reaction is favoured by reducing the concentration of a product (by removing it from the equilibrium mixture), or by introducing more of a reactant into the system. For example, if we removed ammonia from the above system, or we added more nitrogen or hydrogen, then the response of the system to the 'disturbance' would be a shift in the position of equilibrium to the right, yielding more of ammonia.

Conversely, an increase in the concentration of a product, or decrease in the concentration of a reactant will favour the formation of the reactants from the products.

11.1.3 Effect of Pressure

A change in pressure would only distorts the direction of equilibrium of a gas-phase reactions in which there is a difference in the total number of moles of the reactants and products. The position of equilibrium in reactions involving reactants and products in the solid and liquid phases, heterogeneous systems and gas-phase reactions in which there is no difference in the total number of moles of the reactants and products are not responsive to pressure change. For example, the direction of equilibrium in the reaction $H_2(g) + Cl_2(g) \Leftrightarrow 2HCl(g)$ is not amenable to change of pressure.

The response of an equilibrium system to pressure change is based on the fact that volume is inversely proportional to pressure. Thus when the pressure of a homogeneous gaseous system is increased, the position of equilibrium shifts to the direction involving a reduction in the total number of moles or volume. On the other hand, reducing the pressure of such a system would shift the equilibrium position to the direction involving an increase in the total number of moles or volume. For example, an increase in pressure increases the yield of ammonia, as the forward direction involves a reduction in volume from 4 to 2 cm^3; while the formation of the reactants is reduced as the reverse direction involves an increase in volume from 2 to 4 cm^3. Consequently, the synthesis of the compound is carried out at a very high pressure of 150 to 600 atm.

11.2 EQUILIBRIUM CONSTANT AND REACTION QUOTIENT

Equilibrium constant K is a temperature dependent factor that refers to a system in equilibrium. The expression for equilibrium constant is determined from

Guldberg and Waage's law of mass action, which states that the rate of a chemical reaction is proportional to the active masses of the reactants. The active mass of a substance is taken as its concentration (or partial pressure in case of gase-phase reactions) raised to its stoichiometric coefficient in the equation.

Consider the following reaction:

$$mA + nB\ pC + qD$$

where r_1 = The rate of the forward reaction.

r_2 = The rate of the reverse reaction.

From the law of mass action we have

$$r_1\,\mu\,[A]^m \times [B]^n$$

We now introduce a constant of proportionality k_1 to obtain

$r_1 = k_1[A]^m \times [B]^n$

where k_1 = The Velocity constant of the forward reaction at the prevailing temperature.

r_1

r_2

$[A]^m$ = The concentration of A.

$[B]^n$ = The concentration of B.

A similar expression can also be obtained for r_2:

$r_2 = k_2[C]^p \times [D]^q$

where k_2 = Velocity constant of the backward reaction at the prevailing temperature.

$[C]$ = The concentration of C.

$[D]$ = The concentration of B.

Now we know that at equilibrium the rates of the forward and backward reactions are equal, i.e.

$$k_1[A]^m \times [B]^n = k_2[C]^p \times [D]^q$$

Dividing both sides by k_2, and making k_1/k_2 the subject of the formula we have

$$\frac{k_1}{k_2} = \frac{[C]^p[D]^q}{[A]^m[B]^n}\ K_c$$

The ratio k_1/k_2 is called the equilibrium constant K_c of the reaction. As the expression shows, it is measured in terms of the equilibrium concentrations of the reactants and products, with the concentration of each substance raised to its stoichiometric coefficient. It is interesting to see that the products appear in the numerator, while the reactants appear in the denominator.

The equilibrium constants of gas-phase reactions are measured in terms of the equilibrium partial pressures of the reactants and products. This type of equilibrium constant is termed K_P, which is expressed in much the same way as K_c, but with the equilibrium concentrations replaced with equilibrium partial pressures:

$$K_P = \frac{(P_C)^c\,(P_D)^d}{[P_A)^a\,(P_B]^b}$$

The value of the equilibrium constant K_c shows the extent to which the reaction occurs. If $K_c > 1$, then the formation of the products is favoured. A very high value of K_c shows that the reactants are completely converted to the products at the prevailing temperature, i.e., the reaction goes to completion before equilibrium is established., On the other hand, if $K_c < l$, then the formation of the reactants is favoured at the prevailing temperature, i.e., equilibrium is established before the reaction goes to completion.

The reaction quotient Q is expressed in exactly the same way as the equilibrium constant, but the concentrations or partial pressures are not necessarily those measured at equilibrium (as in the case of K). Thus

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$Q_P = \frac{(P_C)^c\,(P_D)^d}{[P_A)^a\,(P_B]^b}$$

The extent to which a reaction would occur is determined by comparing Q_c to K_c, as follows:

If $Q_c = K_c$, the reaction is at equilibrium.

If $Q_c < K_c$, the formation of the products is favoured.

If $Q_c > K_c$, the formation of the reactants is favoured.

Example 1 Write the expression for the equilibrium constant for the reaction

$3H_2(g) + N_2(g) \Leftrightarrow 2NH_3(g)$.

Solution All we have to do is substitute each reactant and product into the expression we have derived earlier:

$$K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]}$$

In terms of the equilibrium partial pressure of each specie we have

$$K_P = \frac{(P_{NH_3})^2}{(P_{H_2})^3 \times P_{N_2}}$$

Example 2 Write an expression for the equilibrium constant for the reaction $3Fe(s) + 4H_2O(g) \Leftrightarrow Fe_3O_4(s) + 4H_2(g)$.

Solution As usual,

$$K_c = \frac{[Fe_3O_4][H_2]^4}{[Fe]^3[H_2O]^4}$$

However, since the concentrations of solids and water are usually fairly constant (taken to be unity), we now substitute 1 into expression to obtain

$$K_c = [H_2]^4$$

Example 3 Nitrogen and oxygen were mixed in a 2.0 dm^3 vessel. At equilibrium, the number of moles of nitrogen, oxygen and nitrogen monoxide were found to be 0.25 mol, 0.42 mol and 0.70 mol respectively. Calculate the equilibrium constant at the prevailing temperature.

Solution We have to begin by writing the equation of reaction:

$$N_2(g) + O_2(g) \Leftrightarrow 2NO(g)$$

So $K_c = \frac{[NO]^2}{[N_2][O_2]}$

The molar concentration (molarity) of each component is obtained from relation

$$C = \frac{n}{V}$$

We know that a gas will occupy the entire volume of the vessel in which it is confined. Thus the volume of each component is 2.0 dm^3.

For nitrogen we have

n = 0.25 mol

$[N_2]$ = ?

Substituting we have

$$[N_2] = \frac{0.25\ \text{mol}}{2.0\ \text{dm}^3}$$

= 0.13 M

For oxygen we have

n = 0.42 mol

$[O_2]$ = ?

Substituting we have

$$[O_2] = \frac{0.42\ \text{mol}}{2.0\ \text{dm}^3}$$

= 0.21 M

For nitrogen monoxide we have

n = 0.70 mol

[NO] = ?

Substituting we obtain

$$[\text{NO}] = \frac{0.70\ \text{mol}}{2.0\ \text{dm}^3}$$

= 0.35 M

K_c = ?

Finally, we now substitute into the expression for the equilibrium constant to obtain

$$K_c = \frac{(0.35\ \text{M})^2}{0.13\ \text{M} \times 0.21\ \text{M}}$$

Thus $K_c = \frac{0.12\,\cancel{M^2}}{0.027\,\cancel{M^2}}$

= 4.4

Since $K_c > 1$, then the formation of the product is favoured. This will be at the expense of the reversed reaction whose equilibrium constant is given as the reciprocal of the forward reaction:

$K_c = \frac{1}{4.4}$

= 0.22

The fact that $K_c < 1$ indicates that the backward reaction is not favoured.

Example 4 Sulphur dioxide was sparked with oxygen to produce sulphur trioxide at 427°C. Calculate the equilibrium constant if the equilibrium partial pressures of sulphur dioxide, oxygen and sulphur trioxide are 0.11 atm, 0.013 atm and 2.2 atm respectively.

Solution The very first step is to write the equation of reaction:

$$2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$$

Thus $K_P = \frac{(P_{SO_3})^2}{(P_{SO_2})^2 \times P_{O_2}}$

P_{SO3} = 2.2 atm

P_{SO2} = 0.11 atm

P_{O2} = 0.013 atm

K_P = ?

Substituting we have

$K_P = \frac{[2.2\text{ atm}]^2}{[0.11\text{ atm}]^2 \times 0.013\text{ atm}}$

Then $K_P = \frac{4.9\text{ atm}^2}{0.00016\text{ atm}^3}$

$= 3.0 \times 10^{-4}\text{ atm}^{-1}$

Example 5 Hydrogen and bromine were sparked together to form hydrogen bromide. The equation of reaction is:

$$H_2(g) + Br_2(g) \Leftrightarrow 2HBr(g)$$

At a particular temperature, the concentrations of hydrogen, bromine and hydrogen bromide were measured to be 1.1 M, 1.2 M and 2.5 M respectively. Predict if the reaction would produce more hydrogen bromide at the prevailing temperature.

$$(K_c = 1.3 \times 10^4)$$

Solution All we have to do is to calculate the reaction quotient and compare this to the given equilibrium constant. We can use the information provided above to predict if there is the tendency for more of the product to be formed. The reaction quotient is expressed as

$$Q_c = \frac{[HBr]^2}{[H_2][Br_2]}$$

$[HBr] = 2.5$ M

$[H_2] = 1.1$ M

$[Br_2] = 1.2$ M

$Q_c = ?$

Substituting we have

$$Q_c = \frac{(2.5\,M]^2}{1.1\,M \times 1.2\,M}$$

So $$Q_c = \frac{6.3\,\cancel{M^2}}{1.3\,\cancel{M^2}}$$

$= 4.8$

Since the $Q_c < K_c$ (1.3×10^4), then there is no tendency for more of the product to be formed. On the other hand, there is the tendency for the product to dissociate into the reactants.

Example 6 The pressure of hydrogen iodide changes by 0.233 atm at a temperature of 730.8 K. Calculate the equilibrium constant for the dissociation of the compound, given that equilibrium is reached at this temperature and that the initial pressure of the compound is 1.00 atm.

Solution The dissociation of hydrogen peroxide is given as

$$2HI(g) \Leftrightarrow H_2(g) + I_2(g)$$

Then $K_p = \frac{P_{H_2} \times P_{I_2}}{(P_{HI})^2}$

That initial partial pressure of HI is 1.00 atm. The equilibrium partial pressure is obtained by subtracting the change in pressure (0.223 atm) from the initial pressure. The initial pressures of hydrogen and iodine are both zero at the beginning of the reaction. The equilibrium partial pressures of both substances can be obtained from stoichiometry to be 0.0112 atm. This is summarized in the following table:

	2HI	H_2	I_2
Initial pressure (atm)	1.00	0	0
Change in pressure (atm)	−0.223	+0.112	+0.112
Equilibrium pressure (atm)	0.777	0.112	0.112

Note that the plus and minus signs indicate that the concentration of the reactants and products are increasing and decreasing with time respectively. We now substitute the equilibrium partial pressure of each component into the equation to obtain

$$K_p = \frac{0.112 \text{ atm} \times 0.112 \text{ atm}}{(0.777 \text{ atm})^2}$$

So $K_p = \frac{0.0125 \cancel{\text{atm}^2}}{0.604 \cancel{\text{atm}^2}}$

$= 0.0207$

Example 7 Nitrogen and oxygen were mixed at a certain temperature. At equilibrium, the number of moles of nitrogen, oxygen and nitrogen dioxide were found to be 0.55 mol, 0.75 mol, and 0.25 mol respectively. Calculate the equilibrium constant at this temperature if the total pressure at equilibrium is 0.224 atm.

Solution We begin by specifying the equation of reaction:

$$N_2(g) + O_2(g) \Leftrightarrow 2NO(g)$$

Thus $K_p = \frac{(P_{NO})^2}{P_{N_2} \times P_{O_2}}$

The partial pressure of each component is obtained from its mole fraction and total pressure as follows:

$$P = x_i \times P_t = \frac{n_i}{n_t} \times P_t$$

The total number of moles n_t is given as

$n_t = n_{NO2} + n_{N2} + n_{O2}$

$n_{NO2} = 0.25$ mol

$n_{N2} = 0.55$ mol

$n_{O2} = 0.75$ mol

$n_t = ?$

Substituting we have

$n_t = 0.55$ mol + 0.25 mol + 0.75 mol = 1.33 mol

$P_t = 0.224$ atm

$P_{NO2} = ?$

$P_{N2} = ?$

$P_{O2} = ?$

We can now substitute into the above relation to obtain

$P_{NO2} = \frac{0.25 \text{ mol}}{1.33 \text{ mol}} \times 0.224$ atm

= 0.0042 atm

$P_{N2} = \frac{0.55 \text{ mol}}{1.33 \text{ mol}} \times 0.224$ atm

= 0.093 atm

$P_{O2} = \frac{0.75 \text{ mol}}{1.33 \text{ mol}} \times 0.224$ atm

= 0.13 atm

K_p = ?

Finally, we can now substitute into the original equation to obtain

$$K_p = \frac{(0.0042\ \text{atm})^2}{0.93\ \text{atm} \times 0.13\ \text{atm}}$$

Then $K_p = \dfrac{1.8 \times 10^{-5}\ \cancel{\text{atm}^2}}{0.12\ \cancel{\text{atm}^2}}$

$= 1.5 \times 10^{-4}$

Example 8 Ammonia was found to be 83.4% dissociated at a certain temperature when equilibrium has been reached. Determine the equilibrium constant in terms of concentration for the decomposition of ammonia at this temperature.

Solution The equation of reaction is

$$2NH_3(g) \Leftrightarrow 3H_2(g) + N_2(g)$$

So $K_c = \dfrac{[H_2]^3[N_2]}{[H_2]^2}$

No explicit concentration is given. However, we can easily obtain the equilibrium concentration of each component by working with an arbitrary initial number of moles of the reactant, i.e., we choose a basis for the calculation.

If we assume that the reaction is effected in a 1.00 dm^3 vessel, and we choose a basis of 1.0 mol of ammonia, then the initial concentration becomes 1.00 M. Since 83.4% of NH_3 is dissociated at the reference temperature, then the change in concentration, or conversion of 1.00 M of the compound will be 0.834 M. The change in the concentration of the other components can easily be obtained from stoichiometry as summarized in the following table:

	$2NH_3$	$3H_2$	N_2
Initial concentration (M)	1.00	0	0
Change in concentration (M)	−0.834	+1.25	+0.417

Equilibrium concentration (M) 0.166 1.25 0.417

We now substitute the equilibrium concentrations into the expression for the equilibrium constant to obtain

$$K_c = \frac{[1.25\ \mathrm{M}]^3 \times 0.417\ \mathrm{M}}{(0.166\ \mathrm{M})^2}$$

So $K_c = \frac{0.814\ \mathrm{M}^4}{0.0276\ \mathrm{M}^2}$

$= 29.5\ \mathrm{M}^2$

Example 9 The K_c for the reaction between hydrogen and carbon dioxide is 1.59 at 986°C. What would be the equilibrium concentrations of all the components if 0.20 M of hydrogen was mixed with 0.30 M of carbon dioxide at this temperature? The equation of reaction is $H_2(g) + CO_2(g) \Leftrightarrow H_2O(g) + CO(g)$.

Solution The first step is to write the expression for the equilibrium constant:

$$K_c = \frac{[H_2O][CO]}{[H_2][CO_2]} = 1.59$$

The initial concentrations of H_2 and CO_2 are 0.20 M and 0.30 M respectively. The concentrations of H_2O and CO are both zero at the beginning of the reaction. During the reaction, each component undergoes a change in concentration. If we denote the conversion of hydrogen with x, then the equilibrium concentration of each component can be obtained from stoichiometry as laid out in the following table:

	H_2	CO_2	H_2O	CO
Initial concentration (M)	0.20	0.30	0	0
Changes in concentration (M)	$-x$	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$0.20 - x$	$0.30 - x$	x	x

Omitting the units and substituting we have

$$\frac{x \times x}{[0.20 - x][0.30 - x]} = 1.59$$

Thus $\frac{x^2}{x^2 - 0.50x + 0.060} = 1.59$

We now rearrange this equation to obtain:

$$-0.59x^2 + 0.80x - 0.095 = 0$$

This equation is easily solved by using the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$a = -0.59$, $b = 0.80$, $c = -0.095$

Substituting we have

$$x = \frac{-0.80 \pm \sqrt{(0.80)^2 - 4(-0.59)(-0.095)}}{2(-0.59)}$$

So $x = \frac{-0.80 \pm 0.64}{-1.18}$

Thus $x = 0.14$ M or 1.2 M

There are two values of x, each of which is mathematically correct. However, the correct value with regard to this problem is 0.14 M. We have to disregard 1.2 M because none of the reactants can undergo a conversion that is greater than its initial concentration.

To obtain the actual value of the equilibrium concentration of each component, we have to substitute 0.14 M for x in the expression for its equilibrium concentration in the table above: table, i.e.

$[H_2]$ = 0.20 M − 0.14 M = 0.060 M

$[CO_2]$ = 0.30 M – 0.14 M = 0.16 M

$[H_2O]$ = [CO] = 0.14 M

Example 10 Phosphorus pentachloride dissociates as follows:

$$PCl_5(g) \Leftrightarrow PCl_3(g) + Cl_2(g)$$

The K_c for the dissociation is 0.0015 at 300 K. Find the equilibrium composition of the system after 0.125 M of PCl_5 is allowed to reach equilibrium at this temperature.

Solution We start with the expression for the equilibrium constant:

$$K_c = \frac{[PCl_5][Cl_2]}{[PCl_5]} = 0.0015$$

The initial concentration of PCl_5 is 0.125 M. Since the conversion is not known, then we can denote this with x and draw up a table as follows:

	PCl_5	PCl_3	Cl_2
Initial concentration (M)	0.125	0	0
Conversion (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$0.125 - x$	x	x

Omitting the units and substituting we have

$$\frac{x \times x}{0.125 - x} = 0.0015$$

So $\frac{x^2}{0.125 - x} = 0.0015$

Like the previous problem, this would give a quadratic equation which can easily be solved using the quadratic formula. However, we can simply iterate by using reasonable guesses based on the value of the equilibrium constant. We will have to check how good each guess is by comparing it with the original guess. We will be correct if subsequent guesses do not vary significantly from the original one. Since the K_c is very small, then it is safe to conclude that the conversion x would be very small compared to 0.125 M. In other words, only a very small part of the reactant would be converted to the products at equilibrium. Thus we can assume that $0.125 - x$ 0.125, such that the above equation now becomes

$$\frac{x^2}{0.125} = 0.0015$$

Thus $x^2 = 1.9 \times 10^{-4}$

Taking the square roots of both sides we have

So $x = \sqrt{1.9 \times 10^{-4}}$

$= 0.014$ M

Note that the negative value as been disregarded since conversion cannot be negative. We will now check to see how good this approximation is by substituting into the original equation:

$$\frac{x^2}{0.1250 - 0.14} = 0.0015$$

Thus $x^2 = 1.7 \times 10^{-4}$

So $x = \sqrt{1.7 \times 10^{-4}}$

$= 0.013$ M

This is not consistent with the previous result of 0.14 M. We iterate again by substituting 0.013 into the original equation to obtain

$$\frac{x^2}{0.125 - 0.13} = 0.0015$$

Thus $x^2 = 1.7 \times 10^{-4}$

So $x = \sqrt{1.7 \times 10^{-4}}$

$= 0.013$

Since this is consistent with the previous guess, then our final answer is 0.013 M.

It would not have made any difference if we had applied the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

The original equation gives the quadratic equation of the form

$$x^2 + 1.5 \times 10^{-3}x - 1.9 \times 10^{-4} = 0$$

$a = 1$, $b = 1.5 \times 10^{-3}$, $c = -1.9 \times 10^{-4}$

Substituting we obtain

Thus $x = \dfrac{-1.5 \times 10^{3}\sqrt{(1.5 \times 10^{-3})^2 - 4(-1.9 \times 10^{-4})}}{2}$

Then $x = \dfrac{\pm 1.5 \times 10^{-3} \pm 0.027}{2}$

So $x = 0.013$ or -0.015

We ignore the negative value to obtain

$$x = 0.013\ \text{M}$$

This is consistence with the previous result.

Finally, we must now substitute 0.013 M into equilibrium concentrations in the above table to obtain:

$[\text{PCI}_5] = 0.125\ \text{M} - 0.013\ \text{M} = 0.112\ \text{M}$

$[\text{PCI}_3] = [\text{CI}_2] = 0.013\ \text{M}$

Example 11 The oxidation of sulphur dioxide to sulphur trioxide has $K_c = 1.5 \times 10^{-4}\ \text{M}^{-1}$ at a certain temperature. Calculate the equilibrium concentrations of all the components if 0.20 mol of sulphur dioxide and 0.50 mol of oxygen are combined and brought to equilibrium in a 2.0 dm^3 vessel. The equation of reaction is $2\text{SO}_2(g) + \text{O}_2(g) \Leftrightarrow 2\text{SO}_3(g)$.

Solution We begin with the expression for K_c:

$$\frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = 1.5 \times 10^{-4}$$

The initial concentrations of the reactants are calculated from the relation

$C = \frac{n}{V}$

$V = 2.0\ \text{dm}^3$

For SO_3 we have

$n = 0.20$ mol

$[\text{SO}_3] = ?$

Substituting we have

$[\text{SO}_2] = \frac{0.20\ \text{mol}}{2.0\ \text{dm}^3}$

$= 0.10\ \text{M}$

For O_2 we have

$n = 0.50$ mol

$[\text{O}_2] = ?$

Substituting we have

$$[O_2] = \frac{0.50\ \text{mol}}{2.0\ \text{dm}^3}$$

$$= 0.25\ \text{M}$$

We now denote the conversion of oxygen with x, and set up the table of concentrations as follows:

	$2SO_2$	O_2	$2SO_3$
Initial concentration (M)	0.10	0.25	0
Conversion (M)	$-2x$	$-x$	$+2x$
Equilibrium concentration (M)	$0.10 - 2x$	$0.25 - x$	$2x$

Substituting the equilibrium concentrations into the expression for the equilibrium constant we have

$$\frac{(2x)^2}{(0.10 - 2x)^2 \times (0.25 - x)} = 1.5 \times 10^{-4}$$

The rearrangement of this equation gives a cubic equation, i.e., a polynomial of the third degree. This sort of equation can only be solved with a graphical calculator or by using numerical methods, such as Newton-Raphson's. Nevertheless, we can solve the equation by making a reasonable approximation. Since K_c is very small, then we know that x would be very small at equilibrium compared to 0.25 M. Hence we substitute zero for x in the denominator to obtain

$$\frac{4x^2}{(0.10)^2 \times 0.25} = 1.5 \times 10^{-4}$$

Thus $4x^2 = 3.8 \times 10^{-7}$

So $x^2 = \frac{3.8 \times 10^{-7}}{4} = 9.5 \times 10^{-7}$

Taking the square roots of both sides we have

$$x = \sqrt{9.5 \times 10^{-7}}$$

$$= 3.1 \times 10^{-4}\ \text{M}$$

Our approximation is very good since $x << 0.25$ M, i.e. $x << 5\%$ of the original concentration of oxygen.

Finally, the equilibrium compositions are obtained by substituting x into the equilibrium concentrations in the table:

$[SO_2]$ = 0.10 M – (2 × 3.1 × 10^{-4} M) = 0.10 M

$[O_2]$ = 0.25 M – 3.1 × 10^{-4} M = 0.25 M

$[SO_3]$ = 2 × 3.1 × 10^{-4} M = 6.2 × 10^{-4} M

Example 12 Hydrogen reacts with carbon dioxide as follows:

$$H_2(g) + CO_2(g) \Leftrightarrow H_2O(g) + CO(g)$$

The K_c for the reaction is 1.59 at 986°C. The equilibrium compositions of hydrogen, carbon dioxide, steam and carbon monoxide are 0.10 M, 0.050 M, 0.45 M and 0.35 M respectively. Calculate the new equilibrium compositions when 0.50 M of carbon monoxide was added to the vessel at the same temperature.

Solution This is a bit different from the problems we have encountered so far. However, all we need do is to be mindful of certain fundamental principles. From our knowledge of chemical equilibria we know that K_c is independent of concentration. Thus K_c remains constant at 1.59. In addition, the introduction of a product would shift the equilibrium position to the left, favouring the formation of the reactants, i.e., hydrogen and carbon dioxide. Thus we anticipate that the concentrations of the products would decrease, while those of the reactants would increase.

Moreover, we have to take the equilibrium compositions of the components as the initial concentrations. Since CO is being introduced into the system, then its initial concentration must be its equilibrium concentration plus the concentration introduced. With this we can now solve the problem by first writing the expression for K_c:

$$K_c = \frac{[H_2O][CO]}{[H_2][CO_2]} = 1.59$$

We now draw up the table of concentrations:

	H_2	CO_2	H_2O	CO
Initial concentration (M)	0.10	0.050	0.45	0.35 + 0.50
Conversion (M)	$+x$	$+x$	$-x$	$-x$
Equilibrium concentration (M)	$0.10 + x$	$0.050 + x$	$0.45 - x$	$0.85 - x$

Substituting the equilibrium concentrations we have

$$\frac{[0.45 - x][0.85 - x]}{[0.10 + x][0.50 + x]} = 1.59$$

So $\frac{x^2 - 1.3x + 0.3}{x^2 + 0.15x + 0.005} = 1.59$

Rearranging this equation we now obtain

$$-0.59x^2 - 1.54x + 0.37 = 0$$

We can easily solve this equation with the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$a = -0.59$, $b = -1.54$, $c = 0.37$

Substituting we obtain

$$x = \frac{-(-1.54] \pm \sqrt{(-1.54]^2 - 4(-0.59)(0.37)}}{2(-0.59]}$$

So $x = \frac{1.54 \pm 1.24}{-1.18}$

Thus $x = -2.83$ or 0.22

As usual, we ignore the negative term and choose 0.22 M as our solution.

Finally, we can now substitute 0.22 M into the equilibrium compositions in the table:

$[H_2]$ = 0.10 M + 0.22 M = 0.32 M

$[CO_2]$ = 0.050 M + 0.22 M = 0. 27 M

$[H_2O]$ = 0.45 M − 0.22 M = 0.23 M

$[CO]$ = 0.85 M – 0.22 M = 0.63 M

Example 13 Phosphorus pentachloride dissociates as follows:

$$PCl_5(g) \Leftrightarrow PCl_3(g) + Cl_2(g)$$

The K_p for the reaction is 4.5 atm at 3090 K. Calculate the equilibrium partial pressures of all the components if the reaction started with 0.57 mol of PCl_5 and 2.5 mol of Cl_2, and are brought to equilibrium at the same temperature and the total pressure of 1.0 atm.

Solution We have to express the equilibrium constant in terms of the equilibrium partial pressures of the components:

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = 4.5 \text{ atm}$$

The equilibrium partial pressure of each component is obtained from the realation

$$P = x_i P_t = \frac{n_i}{n_t}$$

where n_i and n_t are the equilibrium number of moles of each component and total equilibrium number of moles of all the components respectively.

$$P_t = 1.0 \text{ atm}$$

With this we can now draw up the table of partial pressure:

	PCl_5	PCl_3	Cl_2
Initial number of moles (mol)	0.57	0	2.5
Conversion (mol)	$-x$	$+x$	$+x$
Equilibrium number of moles (mol)	$0.57 - x$	x	$2.5 + x$
Equilibrium partial pressure (atm)	$\left(\frac{0.57 - x}{3.1 + x}\right)$	$\left(\frac{x}{3.1 + x}\right)$	$\left(\frac{2.5 + x}{3.1 + x}\right)$

Note that the total equilibrium number of moles $n_t = (0.57 - x) + x + (2.5 + x) = 3.1 + x$

We can now substitute the equilibrium partial pressures to obtain

$$\frac{\left(\frac{x}{3.1 + x}\right)\left(\frac{2.5 + x}{3.1 + x}\right)}{\left(\frac{0.57 - x}{3.1 + x}\right)} = 4.5$$

Simplifying we obtain

$$\frac{x^2 + 2.5x}{-x^2 + 2.5x + 1.8} = 4.5$$

This finally leads to the equation

$$5.5x^2 + 13.8x - 8.1 = 0$$

We can now solve the equation by using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$a = 5.5$, $b = 13.8$, $c = -8.1$

Substituting we have

$$x = \frac{-13.8 \pm \sqrt{(13.8)^2 - 4(5.5)(-8.1)}}{2(5.5)}$$

So $x = \frac{-13.8 \pm 19.19}{11}$

Thus $x = 0.49$ or -3.0

Hence the solution is 0.49 atm.

To obtain the exact value of the equilibrium partial pressure of each component we now substitute into the equilibrium partial pressures in the table to obtain

$$P_{PCI5} = \left(\frac{0.57 - 0.49}{3.1 + 0.49}\right) \text{ atm} = \left(\frac{0.080}{3.5}\right) \text{ atm}$$

$$= 0.023 \text{ atm}$$

$$P_{PCI3} = \left(\frac{0.49}{3.1 + 0.49}\right) \text{ atm} = \left(\frac{0.49}{3.59}\right) \text{ atm}$$

$$= 0.14 \text{ atm}$$

$$P_{CI2} = \left(\frac{2.5 + 0.49}{3.1 + 0.49}\right) = \left(\frac{2.99}{3.49}\right) \text{atm}$$

$$= 0.83 \text{ atm}$$

The partial pressures should add up to the total pressure of 1 atm:

$$P_t = 0.022 \text{ atm} + 0.14 \text{ atm} + 0.83 \text{ atm} = 0.99 \text{ atm}$$

The slight difference is due to rounding.

Practice Problems

1. Write the expression for the K_p of the reaction $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$.

[*Answer:* $K_p = \frac{(P_{SO_3})^2}{(P_{SO_2})^2 \times P_{O_2}}$]

2. Write the expression for the K_c of the reaction $CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$.

[*Answer:* $K_c = [CO_2]$]

3. Write the expression for the K_c of the reaction $CH_3COOH(aq) + NaOH(aq) \Leftrightarrow CH_3COONa(aq) + H_2O(l)$.

[*Answer:* $K_c = \frac{[CH_3COONa]}{[CH_3COOH][NaOH]}$]

4. The preparation of ammonia by the Haber process is given by the equation $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$. At a certain temperature, the equilibrium partial pressures of nitrogen, hydrogen and ammonia are 0.12 atm, 0.15 atm and 0.25 atm respectively. Evaluate the K_p for the reaction at this temperature. [*Answer:* 150 atm^{-2}]
5. Nitrogen monoxide dissociates according to the reaction $2NO(g) \Leftrightarrow N_2(g) + O_2(g)$. Equilibrium was established at a certain temperature at which the number of moles of NO, N_2 and O_2 are 0.50 mol, 2.5 mol and 2.0 mol respectively. Calculate the K_c for the reaction if the reaction was effected in a 2.0 dm^3 vessel. [*Answer:* 2.0×10^3]
6. Predict if more nitrogen would be formed in the above reaction at a temperature at which the concentrations of NO, N_2 and O_2 were measured to be 0.12 M, 0.11 M and 0.18 M respectively.

($K_c = 12.2$) [*Answer*: No]

7. Sulphur trioxide dissociates according to the equation $2SO_3(g) \Leftrightarrow 2SO_2(g) +$

$O_2(g)$. Calculate the equilibrium compositions of all the components at a temperature at which the K_c of the reaction is 2.5×10^{-4} M, given that the initial concentrations of sulphur trioxide and sulphur dioxide are 0.55 M and 0.20 M respectively.

[*Answer:* $[SO_3] = 0.55$ M,$[SO_2] = 0.20$ M, $[O_2] = 3.8$ mM]

8. Chlorine reacts with methane according to the equation $CH_4(g) + Cl_2(g) \Leftrightarrow CH_3Cl(g) + HCl(g)$. Determine the Equilibrium partial pressures of all the components if 2.5 mol each of CH_4 and Cl_2 were combined and brought to equilibrium at the same temperature and a pressure of 1.0 atm. The equilibrium constant at the prevailing temperature is 1.2×10^5.

[*Answer:* $P_{CH4} = P_{Cl2} = 0$, $P_{CH3Cl} = P_{HCl} = 0.50$ atm]

11.2.1 Relationship between K_c and K_P

Consider the reaction:

$$aA(g) + bB(g) \Leftrightarrow cC(g) + dD(g)$$

The K_P of the reaction is expressed as

$$K_P = \frac{[P_C)^c (P_D)^d}{[P_A)^a (P_B]^b} \quad (11.1)$$

We can use the fact that partial pressure is proportional to concentration to obtain a relationship between K_c and K_P. We know that the ideal gas equation is given by

$$PV = nRT$$

So $P = \frac{n}{V}$

So $P_X = [X]\,RT$ (11.2)

Substituting Equation (11.2) into (11.1) we have

$$K_P = \frac{[[C]RT]^c ([D]RT)^d}{[[A]RT)^a [[B]RT]^b} \quad (11.3)$$

We now expand Equation (11.3) to obtain

$$K_P = \frac{[C]^c[D]^d \times (RT)^c (RT)^d}{[A]^a[B]^b \times (RT)^a (RT)^b}$$

So $K_p = \dfrac{[\mathrm{C}]^c[\mathrm{D}]^d \times (RT)^{c+d}}{[\mathrm{A}]^a[\mathrm{B}]^b \times (RT)^{a+b}}$ (11.4)

Then $K_p = \dfrac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} \times (RT)^{(c+d)-(a+b)}$ (11.5)

Finally, Equation (11.5) now becomes

$K_p = K_c(RT)^{\Delta n}$ (11.6)

where R = Universal gas constant = 0.082 $\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}$

T = Absolute temperature.

Δn = The difference in the sum of the number of moles of gaseous products and reactants.

It is easy to see from the above equation that $K_p = K_c$ when there is no change in the total number of moles of reactants and products.

Example 1 The K_c of the reaction $\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \Leftrightarrow 2\mathrm{HCl}(g)$ is 4.0×10^{18} at 227°C. Calculate the K_p for the reaction at the same temperature.

Solution We have to apply the relation

$K_p = K_c(RT)^{\Delta n}$

$K_c = 4.0 \times 10^{18}$

$\Delta n = 2 - 2 = 0$

$K_p = ?$

Since the reactants and products are equimolar, then K_p will be equal to K_c, regardless of the value of T, i.e.

$K_p = 4.0 \times 10^{18} \times (RT)^0$

Thus $K_p = 4.0 \times 10^{18} \times 1 = 4.0 \times 10^{18}$

Example 2 The K_c for formation of ammonia is 0.060 $\mathrm{M^{-2}}$ at a 500°C. What is the K_p at the same temperature?

(R = 0.082 $\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}$)

Solution As usual, we have to apply the relation

$$K_p = \mathrm{K_c}(RT)^{\Delta n}$$

The equation for the reaction is

$$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \Leftrightarrow 2\mathrm{NH_3}(g)$$

$K_c = 0.060\ \mathrm{M^{-2}} = 0.060\ \mathrm{mol^{-2}\,dm^6}$

$T = 500°\text{C} + 273\ \text{K} = 773\ \text{K}$

$R = 0.082\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}$

$\Delta n = 2 - 4 = -2$

$K_P = ?$

Substituting we have

$$K_P = \frac{0.060\ \text{dm}^6}{1\ \text{mol}^2} \times \left(\frac{0.082\ \text{dm}^3\ \text{atm}}{1\ \cancel{\text{K}} \times 1\ \text{mol}} \times 773\ \cancel{\text{K}}\right)^{-2}$$

So $K_P = \frac{0.060\ \text{dm}^6}{1\ \text{mol}^2} \times \left(\frac{63.386\ \text{dm}^3\ \text{atm}}{1\ \text{mol}}\right)^{-2}$

Then $K_P = \frac{0.060\ \cancel{\text{dm}^6}}{1\ \cancel{\text{mol}^2}} \times \frac{2.49 \times 10^{-4} \times 1\ \cancel{\text{mol}^2}}{1\ \cancel{\text{dm}^6} \times 1\ \text{atm}^2}$

$= 1.5 \times 10^{-5}\ \text{atm}^{-2}$

Example 3 The reaction $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$ has $K_P = 4.0 = 4.0 \times 10^{24}\ \text{atm}^{-1}$ at 298 K. What is the K_c for the reaction at the same temperature?

($R = 0.082\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}$)

Solution We have to apply the relation

$K_P = K_c\,(RT)^{Dn}$

$\therefore\ K_c = \frac{K_p}{(RT)^{\Delta n}}$

$K_P = 4.0 \times 10^{24}\ \text{atm}^{-1}$

$R = 0.082\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}$

$T = 298\ \text{K}$

$Dn = 2 - 3 = -1$

$K_c = ?$

Substituting we have

$$K_c = \frac{4.0 \times 10^{24}}{\left(\frac{0.082\ \text{dm}^3\ \text{atm mol}^{-1}}{1\ \cancel{\text{K}}} \times 298\ \cancel{\text{K}}\right)^{-1} \times 1\ \text{atm}}$$

So $K_c = \frac{4.0\ 10^{24}}{(24.436\ \text{dm}^3\ \text{atm mol}^{-1})^{-1} \times 1\ \text{atm}}$

Thus $K_c = \frac{4.0 \times 10^{24} \times 1\ \text{dm}^3 \times 1\ \cancel{\text{atm}}}{4.09 \times 10^{-2}\ \text{mol}^{-1} \times 1\ \cancel{\text{atm}}}$

$= 9.8 \times 10^{25}\ \text{M}^{-1}\ (\text{dm}^3\ \text{mol}^{-1})$

Practice Problems

1. The K_p of the reaction $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$ is $3.5 \times 10^{-5}\ \text{atm}^{-2}$ at 500 K. Calculate the K_c of the reaction at the same temperature.

   ($R = 0.082\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}$)

   [*Answer:* $0.059\ \text{M}^{-1}$]

2. At a certain temperature, the K_c and K_p of the reaction $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$ were measured to be 1700 atm and 0.082 M respectively. Calculate the temperature.

   ($R = 0.082\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}$)

   [*Answer:* 500 K]

11.2.2 Equilibrium Constant and Free Energy Change

The standard free energy of a reaction is related to its equilibrium constant by the equation

$$\Delta G^o = -RT \ln K$$

In terms of common logarithms we have

$\Delta G^o = -2.30RT \log K$

where R = Gas constant.

T = Absolute temperature.

ΔG^o = The standard free energy change of reaction.

K is the K_p for gas-phase reactions. For reactions taking place in an aqueous medium, K is the K_c and other types of equilibrium constants like K_{sp}, K_b and K_a.

Example 1 The standard free energy change of the reaction $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$ is −32.4 kJ mol^{-1} at 25°C. Calculate the equilibrium constant of the reaction at this temperature.

$$(R = 8.314 \text{ J K}^{-1}\text{mol}^{-1})$$

Solution Since a gas-phase reaction is involved, then we have to apply the relation

$$\Delta G^o = -RT \ln K_P$$

$$\therefore \ln K_P = \frac{-\Delta G^o}{RT}$$

$\Delta G^o = -32.4 \text{ kJ mol}^{-1} = -32400 \text{ J mol}^{-1}$

$R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}$

$T = 273 \text{ K} + 25°\text{C} = 298 \text{ K}$

$K_P = ?$

Substituting we have

$$\ln K_P = \frac{-(-32400\,\cancel{J}\,\cancel{mol}^{-1})\times 1\,\cancel{K}}{8.314\,\cancel{J}\,\cancel{mol}^{-1}\times 298\,\cancel{K}}$$

$$\text{Thus } \ln K_P = \frac{32400}{2480}$$

$$= 13.1$$

We must now take the natural antilogarithm of both sides to obtain

$$K_P = e^{13.1} = 4.9 \times 10^5$$

The only way we can obtain the correct unit is to specify the expression for the equilibrium constant:

$$K_P = \frac{(P_{NH_3})^2}{(P_{H_2})^2 \times P_{N_2}}$$

This expression shows that the unit of K_P must be atm^{-2}. We now insert the unit to obtain

$$K_P = 4.9 \times 10^5 \text{ atm}^{-2}$$

Example 2 Calculate the equilibrium constant for the reaction $2AgCl(s) + Br(l)$

⇔ 2AgBr(*s*) + Cl_2(*g*) at 298 K.

(R = 8.314 J K^{-1} mol^{-1}, DG^o=25.8 kJ mol^{-1})

Solution The expression for the equilibrium constant in terms of pressure is

$$K_P = PCl_2$$

Since only the gas appears in the expression for the equilibrium constant, then

$\Delta G^o = -RT \ln K_P$

$\therefore \ \ln K_P = \frac{-\Delta G^o}{RT}$

ΔG^o = 25.8 kJ mol^{-1} = 25800 kJ mol^{-1}

T = 298 K

R = 8.314 J mol^{-1} K^{-1}

K_P = ?

Substituting into the above relation we have

$$\ln K_P = \frac{-25800 \cancel{J} \cancel{mol^{-1}} \times 1 \cancel{K}}{8.314 \cancel{J} \cancel{mol^{-1}} \times 298 \cancel{K}}$$

$= -10.4$

Taking the natural antilogarithms of both sides we obtain

$$K_P = e^{-10.4} = 3.0 \times 10^{-5}$$

The expression for the equilibrium constant suggests that its unit should be atm. Thus

$$K_P = 3.0 \times 10^{-5} \text{ atm}$$

Example 3 The solubility product of copper (I) chloride is 1.0×10^{-6} M^2 at 298 K. Calculate the standard free energy of the dissolution of the compound.

(R = 8.314 J K^{-1} mol^{-1})

Solution We have to apply the relation

$\Delta G^o = -RT \ln K_{sp}$

R = 8.314 J K^{-1} mol^{-1}

T = 298 K

$K_{sp} = 1.0 \times 10^{-6}$

$\Delta G^o = ?$

Substituting we have

$$\Delta G^o = \frac{-8.314 \text{ J mol}^{-1}}{1 \cancel{\text{K}}} \times 298 \cancel{\text{K}} \times \ln 1.0 \times 10^{-6}$$

So $\Delta G^o = -8.314 \text{ J mol}^{-1} \times 298 \times (-13.8)$

$= 34.2 \text{ kJ mol}^{-1}$

Thus the compound would not dissolve in water at 25°C.

Example 4 Calculate the vapour pressure of water at 25°C, given that the standard Gibb's free energy of formation water and water vapour are −237.13 kJ mol^{-1} and −228.57 kJ mol^{-1} respectively.

(R = 8.314 J K^{-1} mol^{-1})

Solution We have to apply relation

$$\Delta G^o = -RT \ln K_P$$

The equation for the process is

$H_2O(l) \Leftrightarrow H_2O(g) \quad K_P = P_{H2O(g)}$

ΔG^o is obtained from the relation

$\Delta G^o = \sum n\Delta G^o_f \text{ (products)} - \sum n\Delta G^o_f \text{ (reactants)}$

$\sum n\Delta G^o_f \text{ (products)} = 1 \times \Delta G^o_f[H_2O(g)]$

Thus $\sum n\Delta G^o_f \text{ (products)} = -228.57 \text{ kJ mol}^{-1}$

$\sum n\Delta G^o_f \text{ (reactants)} = 1 \times \Delta G^o_f[H_2O(l)]$

Thus $\sum n\Delta G^o_f \text{ (reactants)} = -237.13 \text{ kJ mol}^{-1}$

$\Delta G^o = ?$

Substituting we have

$\Delta G^o = -228.57 \text{ kJ mol}^{-1} - (-237.13 \text{ kJ mol}^{-1})$

So $DG^o = -228.57 \text{ kJ mol}^{-1} + 237.13 \text{ kJ mol}^{-1} = 8.56 \text{ kJ mol}^{-1} = 8560 \text{ J mol}^{-1}$

$T = 273 \text{ K} + 25°\text{C} = 298 \text{ K}$

$K_P = ?$

Substituting we obtain

$$8560 \text{ J mol}^{-1} = \frac{-8.314 \text{ J mol}^{-1}}{1 \cancel{\text{K}}} \times 298 \cancel{\text{K}} \times \ln K_P$$

Thus $8560 \text{ J mol}^{-1} = -2477.6 \text{ J mol}^{-1} \times \ln K_P$

So $\ln K_P = \dfrac{8560 \cancel{\text{J}} \cancel{\text{mol}^{-1}}}{2477.6 \cancel{\text{J}} \cancel{\text{mol}^{-1}}} = -3.45$

Taking the natural antilogarithms of both sides we obtain

$$K_P = e^{-3.45} = 0.032$$

Since $K_P = P_{H2O(g)}$, then $P_{H2O(g)} = 0.032$ atm.

Example 5 Calculate the vapour pressure of ethane at 55°C, given that the melting point and heat of fusion of the gas are 5.7°C and 9.9 kJ mol^{-1} respectively.

$$(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$

Solution As usual, we have to apply the relation

$$\Delta G = -RT \ln K_P$$

The equation for the phase change is

$$\text{C}_6\text{H}_6(l) \Leftrightarrow \text{C}_6\text{H}_6(g) \; K_P = \text{K}_{\text{C6H6(g)}}$$

The ΔG for the process at 55°C can be obtained from the value at 5.7°C (melting point of benzene), using the Gibbs–Helmholtz equation

$$\frac{\Delta G_2}{T_2} = \frac{\Delta G_1}{T_1} \; \Delta H_f \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Since solid benzene is at equilibrium with its liquid at its melting point, then DG_1 = 0. Other data are

T_1 = 273 K + 5.7°C = 278.7 K

T_2 = 273 K + 55°C = 328 K

ΔH_f = 9900 J mol^{-1}

ΔG_2 = ?

Substituting we have

$$\frac{\Delta G_2}{328 \text{ K}} = 9900 \text{ J mol}^{-1} \times \left(\frac{1}{328 \text{ K}} - \frac{1}{278.7 \text{ K}}\right)$$

Then $\frac{\Delta G_2}{328\ \text{K}} = 9900\ \text{J mol}^{-1} \times \left(-\frac{5.39 \times 10^{-4}}{1\ \text{K}}\right)$

So $\frac{\Delta G_2}{328\ \text{K}} = -\frac{5.34}{1\ \text{K}}$

Cross-multiplying we have

$\Delta G_2 = 328\cancel{\text{K}} \times \left(-\frac{5.34}{1\cancel{\text{K}}}\right)$

$\Delta G_2 = -1750\ \text{J mol}^{-1}$
$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$
$T = 328\ \text{K}$
$K_P = ?$

Substituting into the original equation we have

$-1750\ \text{J mol}^{-1} = \frac{-8.314\ \text{J mol}^{-1}}{1\cancel{\text{K}}} \times 328\ \cancel{\text{K}} \times \ln K_P$

Thus $-1750\ \text{J mol}^{-1} = -2727\ \text{J mol}^{-1} \times \ln K_P$

So $\ln K_P = \frac{-1750\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}}{-2727\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}} = 0.642$

Taking the natural antilogarithms of both sides we obtain

$$K_P = e^{0.642} = 1.90$$

Since $K_P = K_{C6H6(g)}$ then $P_{C6H6(g)} = 1.90$ atm.

Practice Problems

1. Calculate the equilibrium constant of the reaction $H^+(aq) + OH^-(aq) \Leftrightarrow H_2O(l)$ at 25°C, given that the standard free energy of the reaction is −79.9 kJ mol^{-1}.
   ($R = 8.314\ \text{J mol}^{-1}\text{K}^{-1}$) [*Answer:* $K_c = 9.6 \times 10^{13}\ \text{M}^{-2}$]
2. The reaction $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g) + O_2(g)$ has $K_p = 4.0 \times 10^{24}$ at 298

K. Calculate the standard free energy of the reaction.

(R = 8.314 J mol^{-1} K^{-1}) [*Answer:* −140 kJ mol^{-1}]

3. Estimate the vapour pressure of water at 50°C. The melting point and heat of fusion of water are 0°C and 6.01 kJ mol^{-1} respectively.

   (R = 8.314 J K^{-1} mol^{-1}) [*Answer:* 1.5 atm]

4. Calculate the vapour pressure of ethanol at 28°C, given that the standard free energy change of formation of ethanol and its vapour are −174.78 kJ mol^{-1} and −168.49 kJ mol^{-1} respectively.

   (R = 8.314 J K^{-1} mol^{-1}) [*Answer:* 0.081 atm]

11.2.3 Equilibrium Constant and Temperature

As we said earlier, equilibrium constant changes with temperature. Equilibrium constant is related to temperature by the van't Hoff equation

$$\ln \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where ΔH^o = The standard heat of the reaction.

R = Universal gas constant.

K_1 = Equilibrium constant at absolute temperature T_1.

K_2 = Equilibrium constant at temperature T_2.

The van't Hoff equation is used for calculating the equilibrium constant of a reaction at any temperature provided the value at some other temperature is known. We can as well write the equation in terms of common logarithm:

$$\log \frac{K_1}{K_2} = \frac{\Delta H^\circ}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Figure 11.2 Jacobus Henricus van't Hoff, Dutch chemist (1852–

1911). He won the Nobel Prize for Chemistry in 1901.

Example 1 Derive the van't Hoff equation.

Solution We begin from the relation

$$\ln K = \frac{\Delta G^{\circ}}{RT} \quad (11.7)$$

At a temperature T_1 Equation (11.7) becomes

$$\ln K_1 = \frac{\Delta G_1^{\circ}}{RT_1} \quad (11.8)$$

At a temperature T_2 we have

$$\ln K_2 = \frac{\Delta G_2^{\circ}}{RT_2} \quad (11.9)$$

Substracting Equation (11.9) from (11.8) we have

$$\ln K_1 - \ln K_2 = \frac{\Delta G_1^{\circ}}{RT_1} + \frac{\Delta G_2^{\circ}}{RT_2} \quad (11.10)$$

We now multiply Equation (11.10) through by −1 and rearrange to obtain

$$\ln K_2 - \ln K_1 = \frac{\Delta G_1^{\circ}}{RT_1} - \frac{\Delta G_2^{\circ}}{RT_2} \quad (11.11)$$

Now we know that

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

Using this in Equation (11.11) we have

$$\ln K_2 - \ln K_1 = \left(\frac{\Delta H_1^{\circ} - T_1\Delta S_1^{\circ}}{RT_1}\right) - \left(\frac{\Delta H_2^{\circ} - T_2\Delta S_2^{\circ}}{RT_2}\right) \quad (11.12)$$

ΔH^{o} and ΔS^{o} are approximately independent of temperature, i.e. $\Delta H^{o}_1 = \Delta H^{o}_2$ and $\Delta H^{o}_1 =$ ΔH^{o}_2; Equation (11.12) then becomes

$$\ln K_2 - \ln K_1 = \left(\frac{\Delta H^\circ - T_1\Delta S^\circ}{RT_1}\right) - \left(\frac{\Delta H^\circ - T_2\Delta S^\circ}{RT_2}\right) \quad (11.13)$$

Then $$\ln K_2 - \ln K_1 = \frac{1}{R}\left(\frac{T_2\Delta H^\circ - T_1T_2\Delta S^\circ - T_1\Delta H^\circ + T_1T_2\Delta S^\circ}{T_1T_2}\right) \quad (11.14)$$

which now simplifies to

$$\ln K_2 - \ln K_1 = \frac{\Delta H^\circ}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right) \quad (11.15)$$

Equation (11.15) can be further simplified to obtain

$$\text{In}\,\frac{K_1}{K_2} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (11.16)$$

Example 2 The equilibrium constant for the reaction $3H_2(g) + N_2(g) \Leftrightarrow 3NH_3(g)$ is 6.8×10^5 atm^{-2} at 25°C. Calculate the equilibrium constant at 55°C, given that the enthalpy change of the reaction is −92 kJ mol^{-1}.

($R = 8.314$ J K^{-1}mol^{-1})

Solution We have to apply the van’t Hoff equation:

$$\text{In}\,\frac{K_1}{K_2} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$K_1 = 6.8 \times 10^5$ atm^{-2}
$T_1 = 25°\text{C} + 273\text{ K} = 298\text{ K}$
$T_2 = 55°\text{C} + 273\text{ K} = 328\text{ K}$
$R = 8.314$ J K^{-1} mol^{-1}
$\Delta H^o = -92$ kJ mol^{-1} = -92000 J mol^{-1}
$K_2 = ?$

Substituting we have

$$\ln \frac{K_2}{6.8 \times 10^6\ \text{atm}^{-2}} = \frac{-92000\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}} \times 1\text{ K}}{8.314\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}} \times \left(\frac{1}{298\text{ K}} - \frac{1}{328\text{ K}}\right)$$

Thus $\ln \frac{K_2}{6.8 \times 10^5 \text{ atm}^{-2}} = -11065.7 \cancel{\text{K}} \times \frac{3.1 \times 10^{-4}}{1 \cancel{\text{K}}}$

Then $\ln \frac{K_2}{6.8 \times 10^5 \text{ atm}^{-2}} = -3.4$

We now take the natural antilogarithms of both sides to obtain

$$\frac{K_2}{6.8 \times 10^5 \text{ atm}^{-2}} = e^{-3.4} = 0.033$$

Cross-multiplying we have

$K_2 = 0.033 \times 6.8 \times 10^5 \text{ atm}^{-2}$

$= 2.2 \times 10^4 \text{ atm}^{-2}$

Example 3 The K_c for the reaction $H_2(g) + CO_2(g) \Leftrightarrow H_2O(g) + CO(g)$ is 1.59 at 986°C. Calculate the temperature at which its K_c would be 1.25.

($\Delta H^o_f[H_2O(g)] = -241.8$ kJ mol^{-1}, $\Delta H^o_f[CO(g)] = -110.5$ kJ mol^{-1}, $\Delta H^o_f[CO_2(g)] = -340.8$ kJ mol^{-1}, $R = 8.314$ J K^{-1} mol^{-1})

Solution As usual, we have to apply the equation

$$\text{In} \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The ΔH^o of the reaction is obtained from the relation

$\Delta H^o = \sum n\Delta H^\circ_f \text{(products]} - \sum n\Delta H^\circ_f \text{[reactants]}$

$\sum n\Delta H^\circ_f \text{(products]} = \Delta H^o_f[H_2O(g)] + \Delta H^o_f[CO(g)]$

$\Delta H^o_f[H_2O(g)] = -241.8 \text{ kJ mol}^{-1}$

$\Delta H^o_f[CO(g)] = -110.5 \text{ kJ mol}^{-1}$

So $\sum n\Delta H^\circ_f \text{(products]} = -241.8 \text{ kJ mol}^{-1} + (-110.5 \text{ kJ mol}^{-1}) = -352.3 \text{ kJ mol}^{-1}$

$\sum n\Delta H^\circ_f \text{(reactants]} = \Delta H^o_f[CO_2(g)] + \Delta H^o_f[H_2(g)]$

$\Delta H^o_f[CO_2(g)] = -340.8 \text{ kJ mol}^{-1}$

$\Delta H^o_f[H_2(g)] = 0$

So $\sum n\Delta H_f^\circ(\text{reactants})$ = −340.8 kJ mol^{-1} = −340.8 kJ mol^{-1}

$\Delta H^o = ?$

Substituting we have

$\Delta H^o = -352.3 \text{ kJ mol}^{-1} - (-340.8 \text{ kJ mol}^{-1})$

Then $\Delta H^o = -352.3 \text{ kJ mol}^{-1} + 340.8 \text{ kJ mol}^{-1} = -11.5 \text{ kJ mol}^{-1} = -11530 \text{ J mol}^{-1}$

Other data are:

$K_1 = 1.59$

$K_2 = 1.25$

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$T_1 = 986\ °\text{C} + 273 \text{ K} = 1259 \text{ K}$

$T_2 = ?$

We now substitute to obtain

$$\text{In}\,\frac{1.25}{1.59} = \frac{-11530\,\cancel{\text{J}}\,\cancel{\text{mol}^{-1}} \times 1\text{ K}}{8.314\,\cancel{\text{J}}\,\cancel{\text{mol}^{-1}}} \times \left(\frac{1}{1259\text{ K}} - \frac{1}{T_2}\right)$$

$$\text{So } -0.24 = \frac{-1386.8\,\cancel{\text{K}}}{1259\,\cancel{\text{K}}} + \frac{1386.8\text{ K}}{T_2}$$

$$\text{Thus, } -0.24 = -1.10 + \frac{1386.8\text{ K}}{T_2}$$

We now collect like terms to obtain

$$\frac{1386.8\text{ K}}{T_2} = -0.24 + 1.10 = 0.86$$

Cross-multiplying we obtain

$T_2 \times 0.86 = 1386.8 \text{ K}$

$$\therefore\ T_2 = \frac{1386.8\text{ K}}{0.86}$$

$= 1600 \text{ K}$

Example 4 The conversion of sulphur dioxide to sulphur trioxide has $K_p = 4.0 \times 10^{24}$ atm^{-1} and 2.2×10^{15} atm^{-1} at 298 K and 400 K respectively. Calculate the standard enthalpy change of the reaction.

(R = 8.314 J K^{-1} mol^{-1})

Solution We have to apply the equation

$$\text{In}\ \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

K_1 = 4.0 × 10^{24} atm^{-1}
K_2 = 2.2 × 10^{15} atm^{-1}
T_1 = 298 K
T_2 = 400 K
R = 8.314 J K^{-1} mol^{-1}
ΔH^o = ?

Substituting we have

$$\text{In}\ \frac{2.2 \times 10^{15}\ \cancel{atm^{-1}}}{4.0 \times 10^{24}\ \cancel{atm^{-1}}} = \frac{\Delta H^\circ \times 1\ K}{8.314\ J\ mol^{-1}} \times \left(\frac{1}{298\ K} - \frac{1}{400\ K}\right)$$

So $-21.3 = \frac{\Delta H^\circ \times 1\ \cancel{K}}{8.314\ J\ mol^{-1}} \times \frac{8.6 \times 10^{-4}}{1\ \cancel{K}}$

Thus $\frac{\Delta H^\circ \times 1.03 \times 10^{-4}}{1\ J\ mol^{-1}} = -21.3$

We now cross-multiply to obtain
$\Delta H^o \times 1.03 \times 10^{-4} = -21.3$ J mol^{-1}

Thus $\Delta H^o = \frac{-21.3\ J\ mol^{-1}}{1.03 \times 10^{-4}}$

= 208 kJ mol^{-1}

Example 5 Hydrogen iodide decomposes according to the reaction $2HI(g) \Leftrightarrow H_2(g) + I_2(g)$. By what factor would the K_c of the reaction at 298 K be greater than that at 400 K, given that the ΔH^o of the reaction is 51.9 kJ mol^{-1}?

(R = 8.314 J K^{-1} mol^{-1})

Solution We have to apply the equation

$$\text{In}\ \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

All we have to do is to find the value of K_1/K_2. Thus we need not know the values of the two equilibrium constants at the specified temperatures.

T_1 = 298 K

T_2 = 400 K

R = 8.314 J K^{-1} mol^{-1}

ΔH^o = −51.9 kJ mol^{-1} = −51900 J mol^{-1}

Substituting we have

$$\text{In}\ \frac{K_2}{K_1} = \frac{-51900\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}} \times 1\ \text{K}}{8.314\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}} \times \left(\frac{1}{298\ \text{K}} - \frac{1}{400\ \text{K}}\right)$$

$$\text{So}\ \frac{K_2}{K_1} = -6242.5\ \cancel{\text{K}} \times \frac{8.6 \times 10^{-4}}{1\ \cancel{\text{K}}} = -5.4$$

Taking the natural antilogarithms of both sides, we have

$$\frac{K_2}{K_1} = e^{-5.4} = 4.5 \times 10^{-3}$$

Practice Problems

1. The K_c of the reaction $H_2(g) + Cl_2(g) \Leftrightarrow 2HCl(g)$ is 4.0×10^{31} at 27°C. Calculate the K_c at 50°C.

   (ΔH^o_f [HCl(g)] = −92.3 kJ mol^{-1}) [*Answer:* 2.1×10^{29}]

2. The K_P of the reaction $N_2O_4(g) \Leftrightarrow 2NO_2(g)$ is 1700 atm at 500.0 K. At what temperature would the K_P be 1200 atm?

   ($\Delta H^o_f[N_2O_4(g)]$ = 9.16 kJ mol^{-1}, $\Delta H^o_f[NO_2(g)]$ = 33.18 kJ mol^{-1}) [*Answer:* 510 K]

SUMMARY

- A reversible reaction is that which proceeds in both directions.
- Le Chatelier’s principle states that a system in dynamic equilibrium will

always act in such a way as to nullify or oppose any change in the equilibrium conditions.

- An increase in temperature shifts the position of equilibrium to the direction of endothermic reaction, while a reduction in temperature shifts the position of equilibrium to the direction of exothermic change.
- A decrease in the concentration of specie in an equilibrium mixture would shift the equilibrium position to the side containing that specie, and vice versa.
- For gas-phase reactions, an increase in pressure would shift the position of equilibrium to the direction involving a reduction in the total number of moles of reactants and products, and vice versa.
- In terms of concentration, the equilibrium constant of the reaction $a\mathrm{A}(g) + b\mathrm{B}(g) \Leftrightarrow c\mathrm{C}(g) + d\mathrm{D}(g)$ is given as

$$K_c = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

- In terms of partial pressure, the equilibrium constant of the reaction $a\mathrm{A}(g) + b\mathrm{B}(g) \Leftrightarrow c\mathrm{C}(g) + d\mathrm{D}(g)$ is given a

$$K_P = \frac{[P_\mathrm{C})^c(P_\mathrm{D})^d}{[P_\mathrm{A})^a(P_\mathrm{B}]^b}$$

- Reaction quotient is expressed in the same way as equilibrium constant, but the concentrations or partial pressures are not necessarily those measured at equilibrium.
- K_p and K_c are related by the equation

$$K_P = \mathrm{K}_c(RT)^{Dn}$$

- The free energy of a reaction is related to its equilibrium constant by the equation

$$\Delta G^o = -RT \ln K$$

- The temperature dependence of equilibrium constant is given by the van’t Hoff equation

$$\frac{K_1}{K_2} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \text{ or } \log\frac{K_1}{K_2} = \frac{\Delta H^\circ}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. Which of the following has **NO** effect on the position of equilibrium?

A. Catalyst B. Concentration

C. Temperature D. Pressure

E. None of the above

2. Which of the following varies with temperature?

A. Reaction quotient B. Equilibrium constant

C. Position of equilibrium D. Rate of reaction

E. All of the above

3. In which of the following reactions would the position of equilibrium change when the pressure is altered?

A. $2HI(g) \Leftrightarrow H_2(g) + I_2(g)$

B. $H_2(g) + Cl_2(g) \Leftrightarrow 2HCl(g)$

C. $HCl(aq) + NaOH(aq) \Leftrightarrow NaCl(aq) + H_2O(l)$

D. $N_2O_2(g) \Leftrightarrow 2NO_2(g)$

E. $CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$

4. What effect would the decrease in temperature have on the following reaction?

$$2NH_3(g) \Leftrightarrow N_2(g) + 3H_2(g) \quad \Delta H^{o} = 92.2 \text{ kJ}$$

A. The rate of decomposition of ammonia would increase.

B. The concentrations of nitrogen and hydrogen in the equilibrium mixture would increase.

C. The concentrations of nitrogen and hydrogen in the equilibrium mixture would decrease.

D. The position of equilibrium would shift to the left.

E. The position of equilibrium would be unaltered.

5. What is the effect of pressure increase on the reaction $NH_4Cl(s) \Leftrightarrow HCl(g) + NH_3(g)$?

A. The rate of decomposition of ammonium chloride increases.

B. The rate of formation of the products reduces.

C. The position of equilibrium would shift to the right.
D. Both the forward and reverse reactions would occur faster.
E. None

6. In which of the following reactions is $K_P = K_c$?

i. $PCl_5(g) \Leftrightarrow PCl_3(g) + Cl_2(g)$
ii. $H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$
iii. $2O_3(g) \Leftrightarrow 3O_2(g)$
iv. $2NO(g) \Leftrightarrow N_2(g) + O_2(g)$

A. i only B. ii only
C. i and ii D. ii and iv
E. iii and iv

7. Which of the following is/are true?

i. Free energy has no effect on equilibrium constant.
ii. Free energy is proportional to the logarithm of equilibrium constant.
iii. Equilibrium constant can be obtained from free energy.
iv. Only K_P can be obtained from free energy.

A. i and iv B. ii and iii
C. i and ii D. iii and iv
E. iii only

8. The response of an equilibrium system to an external factor can be explained in terms of

A. The law of mass action
B. The law of reciprocal proportions
C. Le Chatelier’s principle
D. van’t Hoff equation
E. Dynamic equilibrium

9. Calculate the equilibrium constant of a gas-phase reaction at 298 K, given that the standard free energy of the reaction is −30.2 kJ mol^{-1}.

A. 5.0×10^{-6} B. 5.3×10^{-5}
C. 2.0×10^{5} D. 2.2×10^{5}
E. 2.5×10^{6}

($R = 8.314$ J K^{-1} mol^{-1})

10. Calculate the K_P of the reaction $CO(g) + Cl_2(g) \Leftrightarrow COCl_2(g)$ if the K_c is 2.1×10^{-4} M^{-1} at 27°C.

A. 4.5×10^{-7} atm^{-1} B. 9.0×10^{-6} atm^{-1}
C. 8.0×10^{-6} atm^{-1} D. 5.5×10^{-3} atm^{-1}
E. 5.2×10^{-3} atm^{-1}

($R = 0.082$ dm^3 atm K^{-1} mol^{-1})

ESSAY TYPE QUESTIONS

Le Chatelier's principle and the position of equilibrium

11. (a) State Le Chatelier's principle.

(b) Explain the difference between reaction quotient and equilibrium constant. What picture does reaction quotient give concerning a reaction?

12. Explain the effect of each of the following factors on a reaction at equilibrium:

(a) Temperature (b) Concentration (c) Pressure

Equilibrium constant and reaction quotient

13. (a) What do you understand by equilibrium constant? What picture does it give concerning a reaction?

(b) State an equation that relates equilibrium constant to the free energy change of a reaction.

14. Write the expression for the equilibrium constant (K_c) of each of the following reactions:

(a) $CO(g) + Cl_2(g) \Leftrightarrow COCl_2(g)$

(b) $Hg(g) + Cl_2(g) \Leftrightarrow HgCl_2(s)$

(c) $2O_3(g) \Leftrightarrow 3O_2(g)$

(d) $Cu^{2+}(aq) + NH_3(aq) \Leftrightarrow [Cu(NH_3)]^{2+}(aq)$

(e) $CH_3COOH(aq) + C_2H_5OH(aq) \Leftrightarrow CH_3COOC_2H_5(aq) + H_2O(l)$

15. Write the expression for the equilibrium constant (K_P) of each of the following reactions:

(a) $2NH_3(g) \Leftrightarrow 3H_2(g) + N_2(g)$

(b) $N_2O_4(g) \Leftrightarrow 2NO_2(g)$

(c) $H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$

(d) $Cl_2(g) \Leftrightarrow 2Cl(g)$

(e) $I_2(g) \Leftrightarrow 2I(g)$

16. Carbon monoxide and chlorine were confined in a 2.5 dm^3 vessel at a certain temperature. The amounts of CO, Cl_2 and $COCl_2$ present at equilibrium were 0.15 mol, 0.17 mol and 0.22 mol respectively. Determine the K_c for the reaction at the prevailing temperature. The equation of reaction is $CO(g) + Cl_2(g) \Leftrightarrow COCl_2(g)$.

17. Nitrogen monoxide and oxygen are sparked at a certain temperature to produce nitrogen dioxide according to the following reaction $2NO(g) + O_2(g) \Leftrightarrow 2NO_2(g)$. The amounts of NO, O_2 and NO_2 present at equilibrium are 0.25 mol, 0.30 mol and 0.15 mol respectively. Calculate the equilibrium partial pressures of all components if the total equilibrium pressure is 2.4 atm. Hence determine the K_P of the reaction at the prevailing temperature.

18. Bromine chloride, BrCl, is 68% dissociated at 300 K. Calculate the K_c and K_P of the reaction at this temperature.

($R = 0.082$ dm^3 atm K^{-1} mol^{-1})

19. The equation for the oxidation of iron by steam is $3Fe(s) + 4H_2O(g) \Leftrightarrow Fe_3O_4(s) + 4H_2(g)$. Calculate the K_c of the reaction at the temperature at which the equilibrium concentrations of steam and hydrogen are 0.30 M and 0.10 M respectively.

20. The K_c for the reaction $2BrCl(g) \Leftrightarrow Br_2(g) + Cl_2(g)$ is 32 at 500 K. Calculate the equilibrium composition of the system if the initial concentration of BrCl is 2.50 M.

21. The reaction $H_2(g) + I_2(g) \Leftrightarrow 2HI$ has $K_c = 794$ at 25°C. Calculate the equilibrium composition of the system if the initial amounts of H_2 and I_2 were 1.0 mol and 1.5 mol respectively, assuming that the reaction was effected in a 1.0-dm^3 vessel.

22. The K_c for the reaction $PCl_5(g) \Leftrightarrow PCl_3(g) + Cl_2(g)$ is 0.80 M at 613 K. Calculate

(a) The equilibrium compositions of the components if the initial concentrations of PCl_5, PCl_3 and Cl_2 are 0.20 M, 0.15 M and 0.17 M respectively;

(b) The K_P of the reaction at the same temperature;

($R = 0.082$ dm^3 atm K^{-1} mol^{-1})

23. The reaction $N_2(g) + O_2(g) \Leftrightarrow 2NO(g)$ has $K_c = 1.0 \times 10^{-5}$ at 1500 K. Calculate the K_P for the reaction at the same temperature. Hence determine

the equilibrium partial pressures of all the components if the initial numbers of moles of N_2, O_2 and NO are 0.45 mol, 0.75 mol and 0 respectively. Assume that the reaction was brought to equilibrium at a total pressure of 1.0 atm.

24. At high temperature, sulphur trioxide decomposes according to the equation $2SO_3(g) \Leftrightarrow 2SO_2(g) + O_2(g)$. Assuming the initial concentration of SO_3 is 0.50 M, calculate the equilibrium compositions of all the components at a temperature at which the K_c is 1.7×10^{-5}.

25. Prove that the K_c and K_p of a reaction are related by the equation $K_p = K_c (RT)^{\Delta n}$.

26. Calculate the K_p for the reaction $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$ at 298 K.

($\Delta G^o_f [SO_2(g)] = -300.2$ kJ mol^{-1}, $\Delta G^o_f [SO_3(g)] = -371.1$ kJ mol^{-1}, $R = 8.314$ J K^{-1} mol^{-1})

27. The oxidation of nitrogen monoxide is given by the equation $2NO(g) + 2O_2(g) \Leftrightarrow 2NO_2(g)$. What is the equilibrium constant at 298 K?

($\Delta G^o_f [NO(g)] = 86.55$ kJ mol^{-1}, $\Delta G^o_f [NO_2(g)] = 51.31$ kJ mol^{-1}, $R = 8.314$ J K^{-1} mol^{-1})

28. A reaction has $K_p = 794$ at 25°C. Calculate the ΔG^o of the reaction at this temperature.

($R = 8.314$ J K^{-1} mol^{-1})

29. Estimate the vapour pressure of water at 130°C, given that the boiling point and heat of vaporisation of water are 100°C and 44 kJ mol^{-1} respectively.

($R = 8.314$ J K^{-1} mol^{-1})

30. Calculate the vapour pressure of methanol at 25°C, given that the standard free energy of formation of methanol and its vapour are −166.27 kJ mol^{-1} and −161.96 kJ mol^{-1} respectively.

($R = 8.314$ J K^{-1} mol^{-1})

31. The vapour pressure of ethanol at 25°C is 0.0775 atm. What is the standard free energy associated with the conversion of the liquid to its vapour at this temperature.

($R = 8.314$ J K^{-1} mol^{-1})

32. Show that the equilibrium constants of a reaction at two different temperatures are related by the equation

$$\frac{K_1}{K_2} = \frac{H^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

where K_1 = The equilibrium constant at absolute temperature T_1.

K_2 = The equilibrium constant at absolute temperature T_2.

ΔH° = The standard enthalpy change of the reaction.

R = Universal gas constant.

33. The oxidation of nitrogen is given by the equation $N_2(g) + O_2(g) \Leftrightarrow 2NO(g)$. Calculate the K_p at 298 K if the K_p is 1.0×10^{-5} at 1500 K.

(ΔH°_f [NO] = 90.25 kJ mol^{-1}, R = 8.314 J K^{-1} mol^{-1})

34. The K_c for the reaction $CH_4(g) + H_2O(g) \Leftrightarrow CO(g) + 3H_2(g)$ is 0.260 M^2 at 1200 K. Calculate the temperature at which K_c would be 1.20×10^{-3} M^2.

(ΔH°_f [$CH_4(g)$] = −74.8 kJ mol^{-1}, ΔH°_f [$H_2O(g)$] = −241.8 kJ mol^{-1}, ΔH°_f [$CO(g)$] = −110.5 kJ mol^{-1}, R = 8.314 J K^{-1} mol^{-1})

Answers

1. A 2. E 3. D 4. A 5. E
6. D 7. B 8. C 9. C 10. B

14. (a) $\frac{[CoCl_2]}{[Co][Cl_2]}$ (b) $\frac{1}{[Hg][Cl_2]}$

(c) $\frac{[O_2]^3}{[O_3]^2}$ (d) $\frac{[\{Cu(NH_3)\}^{2+}]}{[Cu^{2+}][NH_3]}$

(e) $\frac{[CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]}$

15. (a) $\frac{(P_{H_2})^3 \times P_{N_2}}{(P_{NH_3})^2}$ (b) $\frac{(P_{NO_2})^2}{P_{N_2O_4}}$

(c) $\frac{(P_{HI})^2}{P_{H_2} \times P_{I_2}}$ (d) $\frac{(P_{Cl})^2}{P_{Cl_2}}$

(e) $\frac{(P_I)^2}{P_{I_2}}$

16. 22 M^{-1}
17. NO : 0.86 atm, O_2: 1.0 atm, NO_2: 0.51 atm, $K_p = 0.35$ atm^{-1}
18. $K_c = K_p = 1.1$
19. $K_c = 0.012$
20. [BrCl] = 0.20 M, $[Br_2] = [Cl_2] = 1.15$ M
21. $[H_2] = 0.010$ M, $[I_2] = 1.5$ M, [HI] = 2.0 M
22. (a) $[PCl_5] = 0.09$ M, $[PCl_3] = 0.26$ M, $[Cl_2] = 0.28$ M (b) 40 atm
23. $K_P = 1.0 \times 10^{-5}$, N_2: 0.37 atm, O_2: 0.62 atm, NO: 0.0015 atm
24. $[SO_3] = 0.48$ M, $[SO_2] = 0.020$ M, $[O_2] = 0.010$ M
26. 7.2×10^{24} atm^{-1}
27. 2.3×10^{12} atm^{-1}
28. −16.5 kJ
29. 2.9 atm
30. 0.18 atm
31. 6.34 kJ mol^{-1}
33. 2.3×10^{20}
34. 1620 K

12

Chapter Acid-Base Equilibria

Figure 12.1 Svante August Arrhenius, Swedish chemist (1859–1927). He won the Nobel Prize for Chemistry in 1903.

Acids and bases can be defined based on the following theories:

Arrhenius theory: Swedish chemist Svente Arrhenius defined an acid as a compound that dissociates or ionizes in water to produce hydrogen ions or protons (H^+) as the only positive ion. Substances that behave in this way are called Arrhenius acids. An example is hydrochloric acid which dissociates to produce hydrogen and chloride ions:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

As we said ealier, hydrogen ions combine with water molecule in an aqueous medium to produce hydronium ions, H_3O^+:

$$H^+(aq) + H_2O(aq) \rightarrow H_3O^+(aq)$$

Other examples of Arrhenius acids include nitric acid, HNO_3; sulphuric acid, H_2SO_4; acetic acid, CH_3COOH; etc.

A base is defined as a compound that ionizes in water to produce hydroxide ions, OH^- as the only negative ion. Substances which behave in this way are called Arrhenius bases. An example is sodium hydroxide, NaOH, which dissociates to produce sodium and hydroxide ions:

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

Some other examples of Arrhenius bases include potassium hydroxide, KOH, calcium hydroxide, $Ca(OH)_2$; etc. A soluble base is called an alkali. Common examples are sodium hydroxide and potassium hydroxide.

Bronsted-Lowry theory: A major shortfall of the Arrhenius theory is that it only applies to reactions in aqueous medium. Danish chemist Johannes Bronsted and English chemist Thomas Lowry extended the definitions of acids and bases beyond reactions occurring in aqueous medium. According to the Bronsted-Lowry theory, an acid is defined as a substance that donates a proton, while a base is defined as a proton acceptor. Substances that behave in this way are called Bronsted-Lowry acids and bases.

Thus any substance that donates a proton is called an acid, while a substance which accepts the proton is a base, e.g.

$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$

acid base

$CH_3COOH(aq) + OH^-(aq) \Leftrightarrow CH_3COO^-(aq) + H_2O(l)$

acid base base acid

$HCl(g) + NH_3(g) \rightarrow NH_4^+(s) + Cl^-(s)$

acid base acid base

$NH_3(aq) + H_2O(g) \rightarrow NH_4^+ (aq) + OH^+(aq)$

base acid acid base

An acid-base combination such as $NH_3(aq)$ and $NH_4^+(aq)$ in which one is related to the other by a gain or loss of proton is called a conjugate acid-base pair. Thus a conjugate acid is a substance formed when a Bronsted Lowry base accepts a proton, while a conjugate base is a substance formed when a Bronsted-Lowry acid loses a proton.

Figure 12.2 Johannes Nicloaus Bronsted, Danish chemist (1879–1947).

Lewis Theory: Gilbert Lewis expanded the Bronsted-Lowry theory to include reactions that do not involve proton transfer. According to Lewis theory, an acid is as an electron-pair acceptor, while a base is an electron-pair donor. Substances that behave in this way are called Lewis acids and bases.

The reaction between a Lewis acid and a Lewis base results in the formation of a complex, e.g.

$Ag^+(aq) + 6H_2O(l) \rightarrow [Ag(OH_2)_6]^+$

acid base

$Ni + 4CO \rightarrow Ni(CO)_4$

acid base

Figure 12.4 Gilbert Newton Lewis, American chemist (1875–1946).

12.1 ACID AND BASE IONIZATION CONSTANTS

Nitric acid, HNO_3, and sodium hydroxide, NaOH, undergo complete dissociation or ionization in solution:

$HNO_3(aq) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

$NaOH(aq) \rightarrow Na^+ (aq) + OH^-(aq)$

Acids and bases, such as nitric acid and sodium hydroxide, that undergo complete dissociation in solution are called strong acids and bases. In other words, a solution of a strong acid or base contains its ions with almost no undissociated acid or base. Other examples include hydrochloric acid, HCl, sulphuric acid, H_2SO_4, potassium hydroxide, KOH, etc. We must be careful not to confuse a strong acid for a concentrated acid. A concentrated acid means an acid solution that contains a large amount of the pure acid in a small amount of the solvent, usually water.

Weak acids and bases undergo incomplete dissociation in solution. In other words, they can exist in equilibrium with their ions in solution. Examples are calcium hydroxide, $Ca(OH)_2$ and acetic acid, CH_3COOH:

$Ca(OH)_2(s) \Leftrightarrow Ca^{2+}(aq) + OH^-(aq)$

$CH_3COOH(aq) + H_2O(l) \Leftrightarrow CH_3CO_2^-(aq) + H_3O^+(aq)$

Other examples of weak acids and bases include methanoic acid, carbonic acid, phenol, ammonia, urea, methylamine, etc.

The strength or degree of dissociation of a weak acid or base is determined from the equilibrium constant for its dissociation at a specific temperature. The standard temperature is 25°C. The equilibrium constant for the dissociation of an acid is called the acid dissociation constant K_a, while that for a base is called the base dissociation constant K_b. The smaller the value of K_a or K_b, the weaker is the acid or base. It is interesting to note that for a conjugate acid-base pair, the product of K_a and K_b equals K_w (Section 14.2):

$$K_a \times K_b = 1.00 \times 10^{-14}\ \mathrm{M}^2$$

The degree of ionization of an acid is measured in terms of the index of the acid ionization constant pK_a, which is defined as the negative logarithm of the acid dissociation constant:

$pK_a = -\log K_a$

Similarly, $pK_b = -\log K_b$

The larger the value of pK_a or pK_b, the weaker is the acid or base. For a conjugate acid-base pair, the product of pK_a and pK_b equals pK_w (Section 14.2):

$$pK_a \times pK_b = pK_w = 14.00$$

Example 1 Write the expression for the acid dissociation constant of acetic acid, CH_3COOH.

Solution We must first specify the equation of reaction:

$$CH_3COOH(aq) + H_2O(l) \Leftrightarrow CH_3CO_2^-(aq) + H_3O^+(aq)$$

Thus $K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3COOH]}$

Example 2 Write the expression for the acid dissociation constant of carbonic acid, H_2CO_3.

Solution H_2CO_3 is a polytropic acid, i.e. it is capable of donating more than one proton or hydrogen ion. The overall equation for the dissociation of the acid is given as

$$H_2CO_3(aq) + 2H_2O(l) \Leftrightarrow CO_3^{2-}(aq) + 2H_3O^+(aq)$$

Thus $K_a = \frac{[CO_3^{2-}][H_3O^+]}{[H_2CO_3]}$

The above ionization occurs in two stages, each with its own ionization constant:

$$H_2CO_3(aq) + H_2O(l) \Leftrightarrow HCO_3^-(aq) + H_3O^+(aq)$$

Thus $K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]}$

The second stage is the dissociation of HCO_3^-, the conjugate base of H_2CO_3:

$$HCO_3^-(aq) + H_2O(l) \Leftrightarrow CO_3^{2-}(aq) + H_3O^+(aq)$$

Thus $K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]}$

The overall ionization constant can be obtained by multiplying K_{a1} and K_{a2}:

$K_a = K_{a1} \times K_{a2}$

Thus $K_a = \frac{\cancel{[HCO_3^-]}[H_3O^+]}{[H_2CO_3]} \times \frac{[CO_3^{2-}][H_3O^+]^2}{[H_2CO_3]}$

So $K_a = \frac{[CO_3^{2-}][H_3O^+]^2}{[H_2CO_3]}$

Example 3 Write the expression for the base dissociation constant of zinc hydroxide, $Zn(OH)_2$.

Solution The equation of ionization is given as

$$Zn(OH)_2(s) \Leftrightarrow Zn^{2+}(aq) + 2OH^-(aq)$$

Thus $K_b = [Zn^{2+}] [OH^-]^2$

Note that we have not included the concentration of the base because the concentration of a solid is usually fairly constant.

Example 4 Calcium hydroxide is dissolved in water at a particular temperature until the solution becomes saturated. Calculate the dissociation constant and the index of the base dissociation constant at this temperature, given that the concentration of calcium and hydroxide ions in the solution are 0.10 M and 0.20 M respectively.

Solution The very first step is to write the equation for the dissociation of the base:

$$Ca(OH)_2(s) \Leftrightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

So $K_b = [Ca^{2+}]\,[Ca^{2+}]$

$[Ca^{2+}] = 0.10$ M

$[OH^-] = 0.20$ M

$K_b = ?$

Substituting we have

$K_b = 0.10 \text{ M} \times (0.20 \text{ M})^2$

So $K_b = 0.10 \text{ M} \times 0.040 \text{ M}^2$

$= 4.0 \times 10^{-3} \text{ M}^3$

The fact that $K_b << 1$ indicates that the base is a weak base that is poorly ionized at the prevailing temperature.

The pK_b is obtained from the relation

$pK_b = -\log K_b$

$pK_b = ?$

Substituting we have

$pK_b = -\log 4.0 \times 10^{-3}$

So $pK_b = -(-2.4) = 2.4$

The large value of pK_b also indicates a weak base.

Example 5 Pure acetic acid was dissolved in water at a 25°C. The concentrations of the acid, ethanoate and hydrogen ions were measured to be 5.6 M, 0.010 M and 0.010 M respectively. Calculate the acid ionization constant and index of the acid ionization constant of the acid if equilibrium was established at this temperature.

Solution The equation for the dissociation of the acid is

Then $K_a = CH_3COOH(aq) + H_2O(l) \Leftrightarrow CH_3CO_2^-(aq) + H_3O^+(aq)$

Thus $K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3COOH]}$

$[CH_3CO_2]$ = $[H_3O^+]$ = 0.010 M

$[CH_3COOH]$ = 5.6 M

K_a = ?

Substituting we have

$$K_a = \frac{0.010\,\text{M} \times 0.01\,\cancel{\text{M}}}{5.6\,\cancel{\text{M}}}$$

$= 1.8 \times 10^{-5}$ M

The K_a is very small, showing that the compound is a very weak acid.
The pK_a is obtained from the relation

pK_a = −log K_a

pK_a = ?

Substituting we have
pK_a = −log 1.8×10^{-5}

So pK_a = − (−4.7) = 4.7

The large value of pK_a is an indication of a weak acid.

Example 6 The base ionization constant of silver hydroxide, AgOH, is 1.1×10^{-4} M^2 at 25°C. What are the maximum concentrations of silver and hydroxide ions in solution at this temperature?

Solution The equation for the dissociation is:

$$AgOH(s) \Leftrightarrow Ag^+(aq) + OH^-(aq)$$

Then $K_b = [Ag^+]\,[OH^-]$

Let the concentration of Ag^+ be x. Since Ag^+ and OH^- are equimolar, then

$[Ag^+]$ = $[OH^-]$ = x

K_b = $1.1 \times 10^{-4}\,M^2$

Substituting we have

$$1.1 \times 10^{-4}\ M^2 = x \times x$$

So $x^2 = 1.1 \times 10^{-4}\ M^2$

Taking the square roots of both sides we have

$$x = \pm\sqrt{1.1 \times 10^{-4}\,M^2}$$

= + 0.010 or −0.010

We have to disregard the negative value to obtain

$$[Ag^+] = [OH^-] = 0.010\ M$$

Example 7 The initial concentration of ammonia in a solution is 4.0 M. Calculate the base ionization constant; given the base is 5% ionized at the prevailing temperature.

Solution The equation for the dissociation of the base is

$$NH_3(aq) + H_2O(l)\ (aq) \Leftrightarrow NH_4^+(aq) + OH^-(aq)$$

Thus $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$

Since the base is 5% ionized, then the concentration of the base dissociated is

$C = \frac{5}{100} \times 4.0\ M$

= 0.20 M

The equilibrium concentration of each specie is obtained as follows:

	NH_3	NH_4^+	OH^-
Initial concentration (M)	4.0	0	0
Change in concentration (M)	−0.20	+0.20	+0.20
Equilibrium concentration (M)	3.8	0.20	0.20

We now substitute into the above expression to obtain

$K_b = \frac{0.20\ M \times 0.20\ \cancel{M}}{3.8\ \cancel{M}}$

$= 1.1 \times 10^{-2}\ M$

Practice Problems

1. The initial concentration of ammonia in pure water is 0.20 M at 25°C. Determine the K_b and pK_b of the base, given that the base is 0.94% dissociated at this temperature.

[*Answers:* $K_b = 1.8 \times 10^{-5}$ M, p$K_b = 4.7$]

2. Acetic acid was dissolved in water at a certain temperature. Calculate the K_a and pK_a of the acid at this temperature, given that the equilibrium concentrations of the acid, ethanoate ions and hydronium ions were measured to be 0.15 M, 7.3 mM and 7.3 mM respectively. [*Answers:* $K_a = 3.6 \times 10^{-4}$ M, p$K_a = 3.4$]
3. The pK_b is 2.43 for the dissociation of calcium hydroxide is 25°C. Calculate the concentrations of calcium and hydroxide ions at this temperature.

[*Answers:* $[Ca^{2+}] = 0.098$ M, $[OH^-] = 0.20$ M]

12.2 WATER AUTOIONIZATION CONSTANT AND HYDROGEN ION CONCENTRATION

Autoionization is the process by which a substance acts both as a Bronsted acid and Bronsted base by donating a proton to itself to undergo ionization. Substances which behave in this way are said to be amphiprotic. A water molecule, for example, donates a proton to another water molecule to undergo autoionization:

$$H_2O(l) + H_2O(l) \rightarrow OH^-(aq) + H_3O^+(aq)$$

Thus $K_c = [OH^-][H_3O^+]$

Other examples of amphiprotic substances are ethanoic acid and ammonia.

The autoionization of water yields 1.00×10^{-7} M each of hydrogen and hydroxide ions at 25°C. Thus at this temperature, the equilibrium constant for the dissociation of water, called ionic product of water (or water autoionization constant) K_w is given as

$$K_w = 1.00 \times 10^{-7}\ \text{M} \times 1.00 \times 10^{-7}\ \text{M} = 1.00 \times 10^{-14}\ \text{M}^2$$

The acidity or alkalinity of a solution depends on the concentrations of hydrogen (or hydronium) and hydroxide ions. Pure water is neutral, i.e., it is neither acidic nor basic. This is because pure water contains equal concentrations of hydrogen ions (which determine acidity) and hydroxide ions (which determine alkalinity). When a base, which produces hydroxide ions, is added to a neutral solution, the concentration of the hydroxide ions in the solution increases, while that of the hydrogen ions decreases. This makes the solution to be alkaline. On the other hand, if an acid is added, the concentration of hydrogen ions increases, while that of the hydroxide ions decreases, making the solution acidic. Consequently, the value of K_w will always remain constant at 1.00×10^{-14} M^2.

As we have implied above, we can easily judge whether a solution is acidic, basic, or neutral from the concentration of hydronium ions. When the concentration is above 1.00×10^{-7} M, then the solution is acidic. Conversely, when the concentration is below 1.0×10^{-7} M, then the solution is basic. The hydronium ions concentratiion of 1.0×10^{-7} M indicates a neutral solution. It is more convenient to avoid the use of negative exponents in reporting hydrogen ion concentrations. This is achieved by using a term called the hydrogen ion index pH. The pH of a solution is defined as the negative logarithm of the hydrogen (or hydronium) ion concentration to base 10:

$$\text{pH} = -\log [\text{H}^-] = -\log [\text{H}_3\text{O}^+]$$

For example, the hydrogen ion concentration of 1.00×10^{-7} M corresponds to a neutral pH of 7, i.e.

$$\text{pH} = -\log 1.00 \times 10^{-7} = 7.00$$

The full range of pH is given by the pH scale, which consists of numbers 0 to 14. A pH below 7 indicates acidity, while that above 7 indicates alkalinity. It then follows that the lower the pH of a substance, the higher the acidity. On the other hand, the higher the pH of a substance, the higher its alkalinity. The solution with a pH of 2, for example, is more acidic than that with a pH of 3. Conversely, a substance with the pH of 9 is more alkaline than that with a pH of 8.

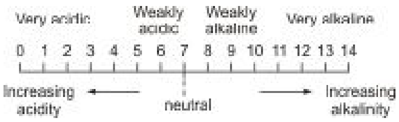

Figure 12.5 The pH scale.

Similarly, the hydroxide ion index pOH is expressed as

$$\text{pOH} = -\log [\text{OH}^-]$$

However, we do not have to know the concentration of hydroxide ions in a solution to determine its pOH. Since the K_w of a solution always remains constant at 1.0×10^{-14}, then the sum of pH and pOH of a solution should always be 14, i.e.

$$\text{pH} + \text{pOH} = 14.00$$

Thus once we know the pH of a solution, then its pOH can be easily determined, and vice versa.

Example 1 The concentration of hydronium ions in a solution is 4.00×10^{-4} M. Determine the pH and pOH of the solution.

Solution We have to apply the relation

$\text{pH} = -\log [H_3O^+]$

$[H_3O^+] = 4.00 \times 10^{-4}$ M

$\text{pH} = ?$

Substituting we have

$\text{pH} = -\log (4.00 \times 10^{-4})$

So $\text{pH} = -(-3.40) = 3.40$

Since the pH is less than 7, then the solution is acidic. The low pH of 3.40 indicates that the solution is very acidic.

The pOH is determined from the relation

$\text{pH} + \text{pOH} = 14.00$

$\therefore\ \text{pOH} = 14.00 - \text{pH}$

$\text{pOH} = ?$

Substituting we have

$\text{pOH} = 14.00 - 3.40$

$= 10.60$

Example 2 Calculate the pH of 1.00×10^{-3}-M solution of hydrochloric acid.

Solution Hydrochloric acid is a strong acid which undergoes complete ionization as follows:

$$HCl(aq) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

Since 1 mol of HCl produces 1 mol of H_3O^+, then

$$[HCI] = [H_3O^+] = 1.00 \times 10^{-3}\ M$$

We can now determine the pH from the relation

$\text{pH} = -\log [H_3O^+]$

$\text{pH} = ?$

Substituting we have

$\text{pH} = -\log 1.00 \times 10^{-3}$

So $\text{pH} = -(-3.00) = 3.00$

Example 3 Calculate the hydronium ion concentration of a 0.15-M sodium hydroxide solution.

Solution We have to apply the relation

$[H_3O^+] \times [OH^-] = 1.00 \times 10^{-14}\ M^2$

$\therefore\ [H_3O^+] = \frac{1.00 \times 10^{-14}\ M^2}{[OH^-]}$

Sodium hydroxide dissociates completely into sodium and hydroxide ions as follows:

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

Since 1 mol of NaOH produces 1 mol of OH^-, then

$[NaOH] = [OH^-] = 0.15\ M$

$[H_3O^+] = ?$

Substituting we obtain

$[H_3O^+] = \frac{1.00 \times 10^{-14}\ M^2}{0.15\ M}$

$= 6.67 \times 10^{-14}\ M$

We may as well determine the pH from the relation

$pH = -\log [H_3O^+]$

$pH = ?$

So $pH = -\log 6.67 \times 10^{-14}$

Thus $pH = -(-13.18) = 13.18$

The very high pH indicates that the solution is highly basic.

Example 4 What is the hydronium ions concentration of the solution with a pH of 2.4?

Solution We have to apply the relation

$pH = -\log [H_3O^+]$

$pH = 2.4$

$[H_3O^+] = ?$

Substituting we have

$$2.4 = -\log [H_3O^+]$$

Taking the common antilogarithms of both sides we have

$$[H_3O^+] = 10^{-2.4} = 3.9 \times 10^{-3}\ M$$

Example 5 Calculate the pH of 0.10-M solution of sodium hydroxide.

Solution Sodium hydroxide is a strong base which dissociates as follows:

$$\mathrm{NaOH}(aq) \rightarrow \mathrm{Na}^{+}(aq) + \mathrm{OH}^{-}(aq)$$

This equation shows that 0.10-M solution of NaOH produces 0.10 M of hydroxide ions, OH^-. Thus the hydroxide ion index is

$$\mathrm{pOH} = -\log 0.10 = 1.0$$

But we know that

$$\mathrm{pH} + \mathrm{pOH} = 14.00$$

So $\mathrm{pH} = 14.00 - 1.0$

$= 13.0$

Example 6 Calculate the pH of a 0.15-M ammonia solution, given that its ionization constant is 1.8×10^{-5} M.

Solution Ammonia is a weak base which dissolves in water as follows:

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \Leftrightarrow \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq)$$

Since only a very small fraction of the aqueous ammonia dissociates, it would be entirely wrong to assume that the concentration of OH^- should be 0.15 M. Thus the concentration of OH^- has to be found from equilibrium calculation by setting up a table of concentrations:

	NH_3	NH_4^+	OH^-
Initial concentration (M)	0.15	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$0.15 - x$	x	x

From the above equation we have

$$K_b = \frac{[\mathrm{NH_4^+}][\mathrm{OH^-}]}{[\mathrm{NH_3}]}$$

$$K_b = 1.8 \times 10^{-5}\ \mathrm{M}$$

Substituting K_b and the equilibrium concentrations we have

$$1.8 \times 10^{-5}\ \mathrm{M} = \frac{x^2}{(0.15 - x)\ M}$$

Since only a very small fraction of the base dissociates, then x would be very small (< 5%) compared to 0.15 M. The denominator can then be approximated to 0.15 M, such that the equation now becomes

$$1.8 \times 10^{-5}\ \text{M} = \frac{x^2}{0.15\ \text{M}}$$

Cross-multiplying we have

$$x^2 = 2.7 \times 10^{-6}\ \text{M}^2$$

Taking the square roots of both sides we obtain

$x = \sqrt{2.7 \times 10^{-6}\ \text{M}^2}$

$= -1.64 \times 10^{-3}\ \text{M}$

$x = [\text{OH}^-] = 1.64 \times 10^{-3}\ \text{M}$

This is about 1% of the original concentration of the base. Thus we are correct in the above assumption. It would have made no difference if we had solved for x from the quadratic equation

$x^2 + 1.8 \times 10^{-5}x - 2.7 \times 10^{-6} = 0$

$\text{pOH} = -\log [\text{OH}^-]$

Thus $\text{pOH} = -\log 1.64 \times 10^{-3} = 2.79$

Now $\text{pOH} + \text{pH} = 14.00$

So $2.79 + \text{pH} = 14.00$

Then $\text{pH} = 14.00 - 2.79$

$= 11.21$

Example 7 Calculate the pH of 0.25-M solution of ammonium chloride, given that the base ionization constant of ammonia is 1.8×10^{-5} M.

Solution Ammonium chloride is a salt of a weak base (NH_3) and strong acid (HCl). It undergoes complete dissociation in water as follows:

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

The NH_4^+ also reacts with water molecules as follows:

$$NH_4^+(aq) + H_2O(l) \Leftrightarrow NH_3(aq) + H_3O^+(aq)$$

It is obvious from this equation that NH_4^+ and NH_3 are conjugate acid and base. The acid ionization constant K_a of the conjugate acid (NH_4^+) is expressed as

$$K_a = \frac{[\mathrm{NH_3}][\mathrm{H_3O^+}]}{[\mathrm{NH_4^+}]}$$

As we know the equilibrium concentrations are determined by setting up a table of concentrations:

	NH_4^+	NH_3	H_3O^+
Initial concentration (M)	0.25	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$0.25 - x$	x	x

The acid ionization constant is obtained from the relation

$K_a \times K_b = K_w$

$K_w = 1.0 \times 10^{-14}\,\mathrm{M}^2$

$K_b = 1.8 \times 10^{-5}\,\mathrm{M}$

$K_a = ?$

Substituting we have

$K_a \times 1.8 \times 10^{-5}\,\mathrm{M} = 1.0 \times 10^{-14}\,\mathrm{M}^2$

Thus $K_a = \dfrac{1.0 \times 10^{-14}\,\mathrm{M}^2}{1.8 \times 10^{-5}\,\mathrm{M}}$

$= 5.6 \times 10^{-10}\,\mathrm{M}$

Substituting this and the equilibrium concentrations into the expression for the acid ionization constant we have

$$5.6 \times 10^{-10}\,\mathrm{M} = \frac{x^2}{(0.25 - x)\,\mathrm{M}}$$

Since the acid ionization constant is very small, we expect that x would be very small compared to 0.25 M. Thus the equation now reduces to

$$5.6 \times 10^{-10}\,\mathrm{M} = \frac{x^2}{0.25\,\mathrm{M}}$$

Cross-multiplying we have

$$x^2 = 1.4 \times 10^{-10}\,\mathrm{M}^2$$

Taking the square roots of both sides we have

$x = \sqrt{1.4 \times 10^{-10}\,\mathrm{M}^2}$

$= -1.2 \times 10^{-5}$ M

Thus the concentration of H^+ or H_3O^+ in the solution is 1.2×10^{-5} M, which is 0.0048% of the initial concentration of the salt. Thus our approximation is justified.

Now pH $= -\log [H_3O^+]$

So pH $= -\log 1.2 \times 10^{-5} = 4.9$

Example 8 Calculate the pH of a 0.010-M sulphuric acid solution. The second ionization constant of the acid is 0.012 M.

Solution As with all polyprotic acids, H_2SO_4 undergoes a step-wise dissociation. Since the acid is a diprotic, i.e., capable of donating two hydrogen ions (protons), then its ionization is in two stages, each involving the donation of a proton. The total H_3O^+ concentration in the solution is the sum of the concentrations of the H_3O^+ obtained from the two stages of dissociation. The first stage is the complete ionization of the acid into H_3O^+ and its conjugate base, HSO_4^{2-}:

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^{2-}(aq)$$

Since this stage involves the complete ionization of the acid, then we can be sure from the equation that the H_3O^+ concentration produced at this stage is equal to the initial concentration of the acid, i.e. 0.010 M.

The second stage involves the ionization of HSO_4^{2-}:

$$HSO_4^{2-}(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + SO_4^{2-}(aq) \quad K_{a2} = 0.012 \text{ M}$$

Although H_2SO_4 is a strong acid, it would be wrong to assume that the H_3O^+ concentration at this stage is equal to 0.010 M. HSO_4^{2-}, the conjugate base of H_2SO_4, is a weak base as the value of the acid dissociation constant of the second stage shows. However, the value of the dissociation constant is large enough to show that significant ionization of HSO_4^{2-} occurs to form H_3O^+ whose concentration must be determined from equilibrium calculation. As usual, we have to set up a table of concentrations:

	HSO_4^{2-}	SO_4^{2-}	H_3O^+
Initial concentration (M)	0.010	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$0.010 - x$	x	x

The acid dissociation constant is given by

$$K_{a2} = \frac{[H_3O^+][SO_4^{2-}]}{[H_2SO_4^{2-}]}$$

K_{a2} = 0.012 M

Substituting K_{a2} and the equilibrium concentrations into the expression we have

$$0.012\ \text{M} = \frac{x^2}{(0.010 - x)\ \text{M}}$$

We cannot approximate (0.010 – x) M to 0.010 M because the K_a value of 0.012 M shows that there is a significant ionization of HSO_4^{2-}. Thus we have to cross-multiply and rearrange the above equation to obtain

$$x^2 + 0.012x + 1.2 \times 10^{-4} = 0$$

We now solve for x using the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

a = 1, b = 0.012, c = 1.2 × 10^{-4}

Substituting we have

$$x = \frac{-0.012 + \sqrt{[(-0.012)^2\ 4\ (1)(-1.2 \times 10^{-4}]}}{2(1)}$$

So $x = \frac{-0.012 \pm 0.025}{2}$

Thus x = 0.0065 or x = −0.019

Since it is inadmissible that concentration should be negative, then the required solution is 0.065 M. Consequently, the total H_3O^+ concentration in the solution is

$[H_3O^+]$ = 0.010 M + 0.0065 M = 0.017 M

Now pH = −log $[H_3O^+]$

So pH = −log 0.017 = 1.8

Example 9 Calculate the pH of 0.050-M solution of carbonic acid.

(pK_a = 6.37, pK_{a2} = 10.25)

Solution Carbonic acid, H_2CO_3, is a weak diprotic acid which undergoes two stages of ionization. The first stage is

$$H_2CO_3(aq) + H_2O(l) \Leftrightarrow HCO_3^-(aq) + H_3O^+(aq) \quad pK_a = 6.37$$

It would be wrong to assume that the concentration of H_3O^+ is equal to the initial concentration of the acid. The large pK_a value of 6.37 shows that H_2CO_3 is a weak acid with a small degree of ionization. Thus we have to obtain the concentration of H_3O^+ from equilibrium calculation, as follows:

	H_2CO_3	HCO_3^-	H_3O^+
Initial concentration (M)	0.050	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$0.50 - x$	x	x

The expression for the acid ionization constant is

$$K_{a1} = \frac{[HCO_3^-][H3O^+]}{[H_2CO_3]}$$

Now we know that

$pK_a = -\log K_a$

$pK_{a1} = 6.37$

$K_{a1} = ?$

Substituting we have

$6.37 = -\log K_{a1}$

Thus $\log K_{a1} = -6.37$

Taking the common antilogarithms of both sides we have

$$K_{a1} = 4.3 \times 10^{-7}\ \text{M}$$

Note that the unit of K_{a1} is obtained from the expression for the ionization constant. We now substitute the equilibrium concentrations and the acid ionization constant into the expression for the acid ionization constant to obtain

$$4.3 \times 10^{-7}\ \text{M} = \frac{x^2}{(0.50 - x)}$$

Since the ionization constant is very small, then we expect that x would be very small compared to 0.050 M; the equation now reduces to

$4.3 \times 10^{-7}\ \text{M} = \frac{x^2}{0.50\ \text{M}}$

So $x^2 = 2.2 \times 10^{-8}\ \text{M}^2$

Taking the square roots of both sides we obtain

$x = \sqrt{2.2 \times 10^{-8}\ \text{M}^2}$

$= 1.5 \times 10^{-4}\ \text{M}$

Thus the concentration of H_3O^+ produced by the first step of the dissociation is 1.5×10^{-4} M, which is 0.3% of the original concentration of H_2CO_3.

The second stage of the ionization is

$HCO_3^-(aq) + 2H_2O(l) \Leftrightarrow CO_3^{2-}(aq) + 2H_3O^+(aq)\quad pK_a = 10.25$

The pK_a value of this step is so big (the ionization constant is so small) that its contribution to the H_3O^+ concentration could be deemed negligible. Thus the total H_3O^+ concentration in the solution is that of the first step, i.e.

$$[H_3O^+] = 1.5 \times 10^{-4}\,\text{M}$$

Finally, we can now obtain the pH of the solution:

$\text{pH} = -\log\,[H_3O^+]$

So $\text{pH} = -\log 1.5 \times 10^{-5} = 4.8$

Example 10 Calculate the pH of the solution obtained by mixing 20.0 dm^3 of a 0.15-M solution of sodium hydroxide with 8.5 dm^3 of a 0.10-M solution of hydrochloric acid.

Solution The very step is to calculate the number of moles of NaOH and HCl from their respective solutions:

$$n = C \times V$$

For NaOH we have

$C = 0.15\ \text{mol dm}^{-3}$

$V = 20.0\ \text{dm}^3$

$n = ?$

Substituting we have

$n = \frac{0.15\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 20.0\ \cancel{\text{dm}^3}$

= 3.0 mol

For HCl we have

C = 0.10 mol dm^{-3}
V = 8.5 dm^3
n = ?

Substituting we have

$$C = \frac{0.10\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 8.5\ \cancel{\text{dm}^3}$$

= 0.85 mol

The equation of reaction is:

$$H_3O^+(aq) + OH^-(aq) \rightarrow NaCl(aq)$$

The equations show that 1 mol of H_3O^+ would react with 1 mol OH^- in solution. Thus 0.85 mol of OH^- would react with 0.85 mol of H_3O^+. Consequently, the excess OH^- in the resulting solution would be

$$OH^- = 3.0\ \text{mol} - 0.85\ \text{mol} = 2.2\ \text{mol}$$

Next, we have to calculate the concentration of HO^- in the resulting solution:

$$C = \frac{n}{V}$$

Since the two volumes are additive, then the volume of the resulting mixture is

V = 20.0 dm^3 + 8.5 dm^3 = 28.5 dm^3
C = ?

Substituting we have

$$C = \frac{2.2\ \text{mol}}{28.5\ \text{dm}^3}$$

= 0.077 M

We can now calculate the pOH of the solution:

pOH = $-\log [OH^-]$

So pOH $= -\log 0.077 = 1.1$

Finally, we can now obtain the pH of the solution from the relation

$$\text{pH} + \text{pOH} = 14.0$$

Thus $\text{pH} + 1.1 = 14.0$

Then $\text{pH} = 14.0 - 1.1$

$= 12.9$

Example 11 A student added an extra volume of 5.0 cm^3 of 0.15-M solution of sulphuric acid after reaching the equivalence point of the titration of 25.0 cm^3 of a 0.10 M-solution of potassium hydroxide with the acid. What is the pH of the resulting mixture?

Solution The key to solving this problem is to obtain the concentration of hydrogen ions in the resulting solution, using the relation

$$C = \frac{n}{V}$$

This is the titration of a strong acid against a strong base of which the pH at the equivalence point is 7. Thus the concentration of H_3O^+ in the solution is due to the addition of the extra 5.0 cm^3 of the acid. The equivalent number of moles of this volume of the acid is obtained with the relation

$n = C \times V$

$V = 5.0\ \text{cm}^3 = 5.0 \times 10^{-3}\ \text{dm}^3$

$C = 0.15\ \text{mol dm}^{-3}$

$n = ?$

Substituting we have

$$n = \frac{0.15\ \text{mol}}{1\ \text{dm}^3} \times 5.0 \times 10^{-3}\ \text{dm}^3$$

$= 7.5 \times 10^{-4}$ mol

The volume of the resulting solution is the sum of the volume of the base, volume of the acid added to reach the equivalence point and the extra volume of the acid added. The only unknown of these volumes is the volume of the acid added to reach the equivalence point, which can be determined from the famous relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_a}{n_b}$$

The equation of reaction is

$$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$$

$C_A = 0.15$ M

$C_B = 0.10$ M

$V_B = 25.0\ \text{cm}^3$

$n_a = 1$

$n_b = 2$

$V_A = ?$

Substituting we have

$$\frac{0.15\ \text{M} \times V_A}{0.10\ \text{M} \times 25.0\ \text{cm}^3} = \frac{1}{2}$$

Cross-multiplying we obtain

$0.30\ \text{M} \times V_A = 0.10\ \text{M} \times 25.0\ \text{cm}^3$

Thus $V_A = \frac{0.10\ \cancel{\text{M}} \times 25.0\ \text{cm}^3}{0.30\ \cancel{\text{M}}}$

$= 8.3\ \text{cm}^3$

Thus the total volume of the mixture is

$V = 25.0\ \text{cm}^3 + 8.3\ \text{cm}^3 + 5.0\ \text{cm}^3 = 38.3\ \text{cm}^3$

$= 0.038\ \text{dm}^3$

$C = [H_3O^+] = ?$

We now substitute into the original equation to obtain

$[H_3O^+] = \frac{7.5 \times 10^{-4}\ \text{mol}}{0.038\ \text{dm}^3}$

$= 0.020$ M

Finally, we now calculate the pH of the solution from the relation

$\text{pH} = -\log [H_3O^+]$

So $\text{pH} = -\log 0.020 = 1.7$

Example 12 A student is titrating 25.00 cm^3 of 0.20-M solution of acetic acid against a 0.15-M solution of sodium hydroxide. Calculate the pH of the solution obtained when only 10.00 cm^3 of the base has been added to the acid.

$$(K_a = 1.80 \times 10^{-5}\,M)$$

Solution This is an example of the titration of a weak acid against a strong base. As the base is being added to the acid, its pH rises. In fact, the pH at the equivalence point of this type of titration is always basic. This example involves the calculation of the pH before the equivalence point is reached. We have to apply the Henderson-Hasselbalch equation (Section 14.3):

$$\text{pH} = \text{pKa} - \log \frac{[\text{Acid}]}{[\text{Base}]}$$

The acid and base are the conjugate acid-base pair of CH_3COOH and $CH_3CO_2^-$ respectively. The conjugate base is obtained from the ionization of CH_3COOH, i.e.

$$CH_3COOH(aq) + H_2O(l) \Leftrightarrow CH_3CO_2^-(aq) + H_3O^+(aq)$$

The concentration of the acid is its concentration remaining when 10.0 cm^3 of the base has been added, while the concentration of its conjugate base ($CH_3CO_2^-$) is its concentration produced by the addition of the same volume of the base. To calculate these we must determine the amount of the acid and base:

$$n = C \times V$$

For the acid we have

C = 0.20 mol dm^{-3}

V = 25 cm^3 = 0.025 dm^3

n = ?

So $n = \dfrac{0.20\text{ mol}}{1\,\cancel{dm^3}} \times 0.025\,\cancel{dm^3}$

$= 5.0 \times 10^{-3}$ mol

For the added base we have

C = 0.15 mol dm^{-3}

V = 10.0 cm^3 = 0.10 dm^3

n = ?

So $n = \frac{0.15\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 0.01\ \cancel{\text{dm}^3}$

$= 1.5 \times 10^{-3}$ mol

The base reacts with the acid as follows:

$$NaOH(aq) + CH_3COOH(aq) \rightarrow CH_3COONa(aq) + H_2O(aq)$$

The equation shows that the 1 mol of the acid is consumed for every mol of the base added. Thus the addition of the base would reduce the initial amount of the acid to

$$n = 5.0 \times 10^{-3}\ \text{mol} - 1.5 \times 10^{-3}\ \text{mol} = 3.5 \times 10^{-3}\ \text{mol}$$

1 mol of the the salt (CH_3COONa) is also produced for every mol of the base added. The salt dissociates in solution to produce 1 mol of the conjugate base:

$$CH_3COONa(aq) \rightarrow CH_3CO_2^-(aq) + Na^+(aq)$$

Thus the addition of 1.5×10^{-3} mol of the base to the acid would increase the amount of the conjugate base to 1.5×10^{-3} mol. We can now determine the concentration of the acid and its conjugate base from the relation

$$n = \frac{C}{V}$$

The total volume of the solution is sum of the initial volume of the acid and the volume of the base added:

$V = 25.00\ \text{cm}^3 + 10.00\ \text{cm}^3 = 30.00\ \text{cm}^3$

$= 0.030\ \text{dm}^3$

For the acid we have

$C = \frac{3.5 \times 10^{-3}\ \text{mol}}{0.030\ \text{dm}^3}$

$= 0.12$ M

Since the acid and its conjugate base are present in the same solution, then the concentration of the conjugate base is

$C = \frac{1.5 \times 10^{-3}\ \text{mol}}{0.030\ \text{dm}^3}$

$= 0.050$ M

The pK_a is obtained from the relation

$pK_a = -\log K_a$

$K_a = 1.80 \times 10^{-5}$ M

Thus $pK_a = -\log 1.80 \times 10^{-5}$ M = 4.70

pH = ?

Finally, we now substitute to obtain

$$\text{pH} = 4.70 - \log \frac{0.12\,\cancel{\text{M}}}{0.050\,\cancel{\text{M}}}$$

So pH = 4.70 – 0.38

= 4.32

Alternatively, since the acid and its conjugate base pair are present in the same solution, we can substitute the number of moles directly into the equation to obtain

$$\text{pH} = 4.70 - \log \frac{3.5 \times 10^{-3}\,\cancel{\text{mol}}}{1.5 \times 10^{-3}\,\cancel{\text{mol}}}$$

So pH = 4.70 – 0.37

= 4.33

The slight difference is due to rounding.

Example 13 Calculate the pH at the equivalence point of a titration of 20.00 cm^3 of 0.10-M solution of acetic acid against a 0.15-M solution of potassium hydroxide.

($K_a = 1.8 \times 10^{-5}$ M)

Solution This example illustrates the calculation of the pH at the equivalence point of the titration of weak acid with a strong base. Since the equivalence point is the point at which just the required amount of the base has reacted with the acid, then all the initial amount of the acid present would have reacted with the base, with no excess base introduced into the mixture. The equation of reaction is

$$CH_3COOH(aq) + KOH(aq) \rightarrow CH_3COOK(aq) + H_2O(l)$$

At the same time, the salt produced dissociates into $CH_3CO_2^-$ and K^+:

$$CH_3COOK(aq) \rightarrow CH_3CO_2^-(aq) + K^+(aq)$$

The $CH_3CO_2^-$ reacts with water to set up the equilibrium

$$CH_3CO_2^-(aq) + H_2O(l) \Leftrightarrow CH_3COOH(aq) + OH^-(aq)$$

The pH of the solution must be determined from the OH^- concentration in this equilibrium. This can be obtained from the expression for base ionization constant:

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3CO_2^-]}$$

The concentration of $CH_3CO_2^-$ is determined from the relation

$$C = \frac{n}{V}$$

From the above equation, 1 mol of the acid produces 1 mol of the salt, which in turn dissociates to produce 1 mol of $CH_3CO_2^-$. Thus the number of moles of $CH_3CO_2^-$ present at the equivalence point is equal to the initial number of moles of the acid present. This is obtained from the relation

$n = C \times V$

$V = 20.00\ cm^3 = 0.020\ dm^3$

$C = 0.10\ mol\ dm^{-3}$

$n = ?$

So $n = \frac{0.10\ mol}{dm^3} \times 0.020\ dm^3$

$= 2.0 \times 10^{-3}\ mol$

The volume of the solution at the equivalence point is the initial volume of the acid plus the volume of the base added to the reach the equivalence point. The required volume of the base is obtained from the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_a}{n_b}$$

$C_A = 0.10\ M$

$V_A = 25.00\ cm^3$

$C_B = 0.15\ M$

$n_a = 1$

$n_b = 1$

$V_B = ?$

Substituting we have

$$\frac{0.10\,\cancel{M} \times 25.00\ \text{cm}^3}{0.15\,\cancel{M} \times V_B} = \frac{1}{1}$$

Cross-multiplying we have

$0.15 \times V_B = 2.0\ \text{cm}^3$

Thus $V_B = \frac{2.00\ \text{cm}^3}{0.15}$

$= 13.33\ \text{cm}^3$

Adding this to the initial volume of the acid gives

$V = 20.00\ \text{cm}^3 + 13.33\ \text{cm}^3 = 33.33\ \text{cm}^3 = 0.033\ \text{dm}^3$

$n = ?$

Substituting we have

$C = \frac{2.0 \times 10^{-3}\ \text{mol}}{0.033\ \text{dm}^3}$

$= 0.060\ \text{M}$

The concentration of CH_3COOH and OH^- must be obtained from equilibrium calculation, as follows:

	$CH_3CO_2^-$	CH_3COOH	OH^-
Initial concentration (M)	0.060	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$0.060 - x$	x	x

The ionization constant of $CH_3CO_2^-$, the conjugate base of CH_3COOH, is obtained from the relation

$K_a \times K_b = 1.0 \times 10^{-14}\ \text{M}^2$

$K_a = 1.8 \times 10^{-5}\ \text{M}$

$K_b = ?$

So $K_b = \frac{1.0 \times 10^{-14}\ \text{M}^2}{1.8 \times 10^{-5}\ \text{M}}$

$= 5.6 \times 10^{-10}\ \text{M}$

We now substitute this and the equilibrium concentrations into the expression for the base ionization constant to obtain

$$5.6 \times 10^{-10}\,\text{M} = \frac{x^2}{(0.060 - x)\,\text{M}}$$

The very low value of K_b suggests that the dissociation of the conjugate base is very small. Thus x would be very small compared to 0.060 M. So

$$5.6 \times 10^{-10}\,\text{M} = \frac{x^2}{0.060\,\text{M}}$$

Cross-multiplying we have

$$x^2 = 3.4 \times 10^{-11}\,\text{M}^{2]}$$

Taking the square roots of both sides we have

$$x = \sqrt{3.4 \times 10^{-11}\,\text{M}^2}$$

$$= 5.8 \times 10^{-6}\,\text{M}$$

Thus the concentration of OH^- at equivalence point is 5.8×10^{-6} M.

Now pOH $= -\log [OH^-]$

Thus pOH $= -\log 5.8 \times 10^{-6} = 5.2$

Finally, we can now determine the pH of the solution from the relation

$$\text{pH} + \text{pOH} = 14.00$$

So $\text{pH} + 5.2 = 14.00$

Then $\text{pH} = 14.00 - 5.2$

$= 8.8$

This shows that the pH at the equivalence point of the titration of a weak acid with a strong base is 7. Once the equivalence point is passed, the pH is determined from the concentration of the excess OH^- added to the mixture.

Example 14 Calculate the pH at the equivalence point of the titration of 20.00 cm^3 of 0.10-M solution of ammonia with 0.10-M solution of hydrochloric acid.

$$(K_b = 1.8 \times 10^{-5}\,\text{M})$$

Solution This example illustrates how to obtain the pH at the equivalence point of the titration of a weak base with a strong acid. As we said in Chapter 10, the pH at the equivalence point of this type of titration is always less than 7 due to the presence of more hydrogen ions than hydroxide ions in solution. The base reacts with the acid according to the reaction

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$

At the same time, NH_4Cl dissociates completely to produce NH_4^+ and Cl^-. NH_4^+ in turn reacts with water to set up the following equilibrium:

$$NH_4^+(aq) + H_2O(l) \Leftrightarrow NH_3(aq) + H_3O^+(aq)$$

The pH of the solution is determined from the concentration of H_3O^+ in this equilibrium. The expression for the acid ionization constant of NH_4^+, the conjugate acid of NH_3 is

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

The concentration of NH_4^+ at the equivalence point is obtained from the relation

$$C = \frac{n}{V}$$

We know from the above equations that 1 mol of NH_3 reacts with 1 mol of HCl to produce 1 mol of NH_4Cl; which dissociates completely to produce 1 mol of NH_4^+. Thus the amount of NH_4^+ is equal to the initial amount of NH_3, which is calculated with the relation

$n = C \times V$

$C = 0.25\ \text{mol dm}^{-3}$

$V = 20.00\ \text{cm}^3 = 0.020\ \text{dm}^3$

$n = ?$

Thus $n = \frac{0.25\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 0.020\ \cancel{\text{dm}^3}$

$= 5.0 \times 10^{-3}$ mol

The volume at the equivalence point is the sum of the initial volume of the base ($20.00\ \text{cm}^3$) and the volume of the acid added to reach the equivalence point. This volume of the acid is obtained from the relation

$$\frac{C_A V_A}{C_B V_B} = \frac{n_a}{n_b}$$

$C_A = 0.10$ M

$C_B = 0.10$ M

$V_B = 20.00$ cm^3

$n_a = 1$

$n_b = 1$

$V_A = ?$

Substituting we have

$$\frac{0.10\cancel{M} \times V_A}{0.10\cancel{M} \times 20.00 \text{ cm}^3} = \frac{1}{1}$$

We now cross-multiply to obtain

$0.10 \times V_A = 2.0$ cm^3

So $V_A = \frac{2.0 \text{ cm}^3}{0.10}$

$= 20.00$ cm^3

Thus the total volume of the solution at the equivalence point is

$V = 20.00$ cm^3 + 20.00 cm^3 = 40.00 cm^3 = 0.040 dm^3

$C = ?$

We now substitute to obtain

$C = \frac{5.0 \times 10^{-3} \text{ mol}}{0.040 \text{ dm}^3}$

$= 0.13$ M

The concentrations of NH_3 and H_3O^+ are determined from equilibrium calculation:

	NH_4^+	NH_3	H_3O^+
Initial concentration (M)	0.13	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$0.13 - x$	x	x

The acid ionization constant of NH_4^+ is obtained from the relation

$K_a \times K_b = 1.0 \times 10^{-4}$ M^2

$K_b = 1.8 \times 10^{-5}$ M

$K_a = ?$

Then $K_a = \frac{1.0 \times 10^{-14}\,\mathrm{M}^2}{1.8 \times 10^{-5}\,\mathrm{M}}$

$= 5.6 \times 10^{-10}\,\mathrm{M}$

Substituting into the expression for the acid ionization constant we have

$$5.6 \times 10^{-10}\,\mathrm{M} = \frac{x^2}{(0.13 - x)\,\mathrm{M}}$$

Since K_a is very small, then the equation becomes

$$5.6 \times 10^{-10}\,\mathrm{M} = \frac{x^2}{0.13\,\mathrm{M}}$$

Cross-multiplying we have

$$x^2 = 7.3 \times 10^{-11}\,\mathrm{M}^2$$

Taking the square roots of both sides we obtain

$x = \sqrt{7.3 \times 10^{-11}\,\mathrm{M}^2}$

$= 8.5 \times 10^{-6}\,\mathrm{M}$

Thus the H_3O^+ concentration at the equivalence point is 8.5×10^{-6} M. Finally, we can now calculate the pH from the equation

$\mathrm{pH} = -\log [H_3O^+]$

So $\mathrm{pH} = -\log 8.5 \times 10^{-6} = 5.1$

This agrees with the assertion that the pH at the equivalence point of the titration of weak base against a strong acid is always less than 7.

Practice Problems

1. Determine the pH of the following:

(a) A solution with a hydronium ions concentration of 1.5×10^{-3} M;

(b) A solution with a pOH of 2.70. [*Answers*: (a) 2.82 (b) 11.30]

2. Calculate the hydronium ion concentration of the solution with a pH of 10.22.

[*Answer*: 6.03×10^{-11} M]

3. What is the hydroxide ion concentration of a 1.50×10^{-3}-M nitric acid solution?

[*Answer:* 6.67 × 10^{-12} M]

4. Calculate the pH of 0.15-M solution of acetic acid, CH_3COOH.

   ($pK_a = 4.75$) [*Answer:* 2.8]

5. Calculate the pH of 0.050-M solution of sodium hydrogen carbonate, $NaHCO_3$.

   ($K_a = 4.3 \times 10^{-7}$) [*Answer:* 9.5]

6. Calculate the pH of 0.15-M solution of H_2S.

   ($pK_{a1} = 6.88$, $pK_{a2} = 14.15$) [*Answer:* 3.9]

7. Calculate the pH of a solution obtained by adding 2.50 cm^3 of 0.15-M solution of hydrochloric acid after the equivalence point has been reached in the titration of 20.00 cm^3 of 0.20-M potassium hydroxide solution with the acid.

12.3 BUFFER SOLUTIONS

Buffer solutions are solutions that resist changes in pH on the addition of small amounts of acids or alkalis. A buffer consists of a weak acid or base and its salt, e.g., acetic acid and sodium acetate, carbonic acid and sodium hydrogen carbonate, ammonia and ammonium chloride, etc. A buffer could also consist of the acidic and normal salts of a polyprotic acid, or two

of a polyprotic acid in which one contain more protons than the other. Examples include $KHSO_4$ and Na_2SO_4, NaH_2PO_4 and Na_2HPO_4, etc. Buffers are very important in biological systems as the cells can only function or survive at a fairly constant pH.

The action of buffers is based on the common-ion effect. This refers to the situation in which the same ion is produced by two different compounds in solution. The concentrations of such ion are additive. This can be illustrated with acetic acid and sodium acetate. As noted earlier, acetic acid is a weak acid that undergoes partial dissociation in solution:

$$CH_3COOH(g) + H_2O(l) \Leftrightarrow H_3O^+(aq) + CH_3CO_2^-(aq)$$

On the other hand, sodium acetate is ionic. It undergoes complete ionization in solution:

$$CH_3COONa(s) \rightarrow Na^+(aq) + CH_3CO_2^-\ (aq)$$

Both compounds produce acetate ions, $CH_3CO_2^-$, which react with the H_3O^+ produced by the acid to produce acetic acid. According to Le Chatelier's principle, this shifts the equilibrium position to the right and reduces the number of H_3O^+ in the solution. Thus the presence of CH_3COONa ‘mops’ up the excess H_3O^+ and keeps the pH fairly constant.

There is a limit to which every buffer solution can function. This limit, called buffer capacity, is defined as the maximum amount of an acid or base that can be added to the solution before it loses its buffering function or capacity.

We will now derive an equation for calculating the pH of a buffer solution. Consider a weak acid, HA in solution:

$$HA(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + A^-(aq)$$

Thus $K_a = \frac{[H_3O^+][A^-]}{[HA]}$ (12.1)

Cross-multiplying we have

$[H_3O^+] = [A–] = K_a[HA]$

So $[H_3O^+] = \frac{K_a[HA]}{[A^-]}$ (12.2)

where [HA] = The equilibrium molar concentration of the acid.

However, since the acid is poorly ionized, [HA] can be assumed to be equal to the initial concentration of the acid, i.e.,

$[HA] = [HA]_{in.}$ (12.3a)

$[A^-]$ = The total equilibrium concentration of the anion. Since the salt is completely dissociate, then $[A^-]$ can be taken as the initial concentration of the salt, i.e.

$[A^-] = [salt]_{in.}$ (12.3b)

Substituting Equations (12.3a) and (12.3b) into (12.2) we have

$[H_3O^+] = \frac{K_a[acid]_{in.}}{[salt]_{in.}}$ (12.4)

We now take the common logarithms of both sides to obtain

$\text{Log } [H_3O^+] = \log \frac{K_a[acid]_{in.}}{[salt]_{in.}}$

So $\log [H_3O^+] = \log K_a + \log \frac{[acid]_{in.}}{[salt]_{in.}}$ (12.5)

Multiply Equation (12.5) by –1 we have

$$-\log [H_3O^+] = -\log K_a - \log \frac{[\text{acid}]_{\text{in.}}}{[\text{salt}]_{\text{in.}}} \quad (12.6)$$

Now we know that

$$\text{pH} = -\log [H_3O^+]$$

$$\text{p}K_a = -\log K_a$$

Substituting this into Equation (12.6) we have

$$\text{pH} = \text{p}K_a - \log \frac{[\text{acid}]_{\text{in.}}}{[\text{salt}]_{\text{in.}}} \quad (12.7)$$

$$\text{or} \quad \text{pH} = \text{p}K_a + \log \frac{[\text{salt}]_{\text{in.}}}{[\text{acid}]_{\text{in.}}} \quad (12.8)$$

Equation (12.7) or (12.8) is called the Henderson-Hasselbalch equation. It must be well noted that this equation is only applied to a process involving the donation of only one proton. The analogous equation for the pOH of a buffer consisting of a weak base and its salt is

$$\text{pOH} = \text{p}K_b - \log \frac{[\text{base}]_{\text{in.}}}{[\text{salt}]_{\text{in.}}} \quad (12.9)$$

$$\text{or} \quad \text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]_{\text{in.}}}{[\text{base}]_{\text{in.}}} \quad (12.10)$$

Example 1 Calculate the pH of a buffer solution containing 0.20 M acetic acid and 0.15 M sodium acetate at 25°C.

$$(K_a = 1.8 \times 10^{-5}\ \text{M})$$

Solution We will first calculate the pH using the common-ion effect, after which we will apply the Henderson-Hasselbalch equation. The two compounds dissociate as follows:

$$CH_3COOH(g) + H_2O(l) \Leftrightarrow H_3O^+(aq) + CH_3CO_2^-(aq)$$

$$CH_3COONa(s) \rightarrow Na^+(aq) + CH_3CO_2^-(aq)$$

If the equilibrium concentration of H_3O^+ is x, then, according to the equation, the concentration of $CH_3CO_2^-$ produced by the dissociation of the acid would also be x. Since the salt undergoes complete dissociation in solution, then the concentration of $CH_3CO_2^-$ produced by the salt would be 0.15 M. From the common-ion effect, the total equilibrium concentration of $CH_3CO_2^-$ is the sum of the concentrations of the ion produced by the acid and salt. The total equilibrium concentrations of all the species are laid out as follows:

	CH_3COONa	CH_3COOH	H_3O^+	$CH_3CO_2^-$
Initial concentration (M)	0.15	0.20	0	0
Change in concentration (M)	−0.15	$-x$	x	$0.15 + x$
Equilibrium concentration (M)	0	$0.20 - x$	x	$0.15 + x$

From the dissociation of the acid we have

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3COOH]}$$

$K_a = 1.8 \times 10^{-5}$ M

$x = ?$

Omitting the units and substituting K_a and the equilibrium concentrations into the above expression we have

$$\frac{x \times (0.15 + x)}{0.20 - x} = 1.8 \times 10^{-5}$$

Since K_a is very small, then we can make approximation to obtain

$$\frac{0.15x}{0.20} = 1.8 \times 10^{-5}$$

Cross-multiplying we have

$0.15x = 3.6 \times 10^{-6}$

Then $x = \frac{3.6 \times 10^{-6}}{0.15}$

$= 2.4 \times 10^{-5}$ M

We can now obtain the pH from the relation

$\text{pH} = -\log [H_3O^+]$

Thus $\text{pH} = -\log 2.4 \times 10^{-5}$

So $\text{pH} = -(-4.62) = 4.62$

The same result would be obtained with the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a - \log \frac{[\text{acid}]_{\text{in.}}}{[\text{salt}]_{\text{in.}}}$$

pK_a is obtained from the relation

$pK_a = -\log K_a$
$K_a = 1.8 \times 10^{-5}$ M
$pK_a = ?$

Substituting we have

$pK_a = -\log 1.8 \times 10^{-5}$
So $pK_a = -(-4.74) = 4.74$
$[\text{acid}]_{\text{in.}} = 0.20$ M
$[\text{salt}]_{\text{in.}} = 0.15$ M
pH = ?

Substituting we have

$$\text{pH} = 4.74 - \log \frac{0.20\ \text{M}}{0.15\ \text{M}}$$

So pH = 4.74 – log 1.33

Thus pH = 4.74 – 0.12
= 4.62

This agrees perfectly with the previous result.

Example 2 Calculate the pH of a solution containing 0.25 M of ammonia and 0.15 M NH_4Cl at 25°C.

($K_b = 1.8 \times 10^{-5}$ M)

Solution We will simply apply equation

$$\text{pOH} = pK_b + \log \frac{[\text{salt}]_{\text{in.}}}{[\text{base}]_{\text{in.}}}$$

$pK_b = -\log K_b$
$K_b = 1.8 \times 10^{-5}$ M
$pK_b = ?$
Thus $pK_b = -\log 1.8 \times 10^{-5}$
So $pK_b = -(-4.74) = 4.74$
$[\text{base}]_{\text{in.}} = 0.25$ M

$[\text{salt}]_{\text{in.}} = 0.15\ \text{M}$

pOH = ?

Substituting we have

$$\text{pOH} = 4.74 + \log \frac{0.15\ \text{M}}{0.25\ \text{M}}$$

Then pOH = 4.74 + log 0.60

So pOH = 4.74 – 0.22 = 4.52

But pH + pOH = 14.00

$\therefore$ pH = 14.00 − pOH

pH = ?

Substituting we have

pH = 14.00 − 4.52

= 9.48

Example 3 Calculate the number of moles of ammonia that is required to produce a 250.0-cm^3 buffer solution containing 0.10 M ammonium chloride, and whose pH is 8.50.

($K_b = 1.8 \times 10^{-5}$ M)

Solution We have to apply the relation

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]_{\text{in.}}}{[\text{base}]_{\text{in.}}}$$

$\text{p}K_b = -\log K_b$

$K_b = 1.8 \times 10^{-5}$ M

$\text{p}K_b$ = ?

Thus $\text{p}K_b = -\log 1.8 \times 10^{-5}$

So $\text{p}K_b = -(-4.74) = 4.74$

But pH + pOH = 14.00

$\therefore$ pOH = 14.00 − pH

pH = 8.50

pOH = ?

Then pOH = 14.00 – 8.50 = 5.50

$[\text{salt}]_{\text{in.}} = 0.10\ \text{M}$

$[\text{base}]_{\text{in.}} = ?$

Substituting we have

$$5.50 = 4.74 + \log \frac{0.10\ \text{M}}{[\text{base}]_{\text{in.}}}$$

$$\text{So } \log \frac{0.10\ \text{M}}{[\text{base}]_{\text{in.}}} = 5.50 - 4.74$$

$$\text{Thus } \log \frac{0.10\ \text{M}}{[\text{base}]_{\text{in.}}} = 0.76$$

Taking the common antilogarithms of both sides we have

$$\frac{0.10\ \text{M}}{[\text{base}]_{\text{in.}}} = 10^{0.76} = 5.75$$

We now cross-multiply to obtain

$[\text{base}]_{\text{in.}} \times 5.75 = 0.10\ \text{M}$

So $[\text{base}]_{\text{in.}} = 0.017\ \text{M}$

We can now obtain the amount of the base from the relation

$n = C \times V$

$V = 250.0\ \text{cm}^3 = 0.25\ \text{dm}^3$

$n = ?$

Finally, we now substitute to obtain

$$n = \frac{0.017\ \text{mol}}{\cancel{\text{dm}^3}} \times 0.25\ \cancel{\text{dm}^3}$$

$= 4.3 \times 10^{-3}$ mol

Example 4 Calculate the mass of $NaHCO_3$ that is required to prepare a 500.0-cm^3 buffer solution containing 0.15 M H_2CO_3, and whose pH is 6.00.

(H = 1.0, C = 12.0, O = 16.0, $\text{p}K_{a1} = 3.68$)

Solution We have to apply the relation

$$\text{pH} = \text{p}K_a - \log \frac{[\text{acid}]_{\text{in.}}}{[\text{salt}]_{\text{in.}}}$$

The formation of HCO_3^- from H_2CO_3 corresponds to the first step of dissociation of the acid. Thus

$\mathrm{p}K_a = \mathrm{p}K_{a1} = 3.68$
pH = 6.00
$[\text{acid}]_{\text{in.}} = 0.15$ M
$[\text{salt}]_{\text{in.}} = ?$

Substituting we have

$$6.00 = 4.68 - \log \frac{0.15\ \text{M}}{[\text{salt}]_{\text{in.}}}$$

So $$-\log \frac{0.15\ \text{M}}{[\text{salt}]_{\text{in.}}} = 6.00 - 3.68 = 2.32$$

Thus $$\log \frac{0.15\ \text{M}}{[\text{salt}]_{\text{in.}}} = -2.32$$

Taking the common antilogarithms of both sides we have

$$\frac{0.15\ \text{M}}{[\text{salt}]_{\text{in.}}} = 10^{-2.32} = 4.79 \times 10^{-3}$$

Cross-multiplying we have

$$[\text{salt}]_{\text{in}}. \times 4.79 \times 10^{-3} = 0.15\ \text{M}$$

So $$[\text{salt}]_{\text{in.}} = \frac{0.15\ \text{M}}{4.79 \times 10^{-3}} = 0.31\ \text{M}$$

We can now calculate the number of moles of the salt from the relation

$n = C \times V$
$V = 500.0\ \text{cm}^3 = 0.50\ \text{dm}^3$
$n = ?$

So $$n = \frac{0.31\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 0.50\ \cancel{\text{dm}^3}$$

$= 0.16$ mol

Finally, we can now obtain the mass of the salt from the relation

$$n = \frac{m}{M}$$

$m = n \times M$

$\therefore\ M = [(2 \times 1) + 12 + (16 \times 3)]\ \text{g mol}^{-1} = 62\ \text{g mol}^{-1}$

$m = ?$

Substituting we have

$$m = 0.16\,\cancel{\text{mol}} \times \frac{62\ \text{g}}{1\,\cancel{\text{mol}}}$$

$= 9.9$ g

Example 5 Calcuate the pH of a buffer solution prepared by mixing 250.0 cm^3 of 0.15-M CH_3COOH solution and 100.0 cm^3 of 0.25-M CH_3COONa solution.

$$(\text{p}K_a = 4.75)$$

Solution The applicable relation is

$$\text{pH} = \text{p}K_a - \log \frac{[\text{acid}]_{\text{in.}}}{[\text{salt}]_{\text{in.}}}$$

Since volume is additive, then the concentrations of the substances in the resulting buffer solution would be different from their concentrations in their original solutions. Thus we have to calculate the concentrations of the salt and acid in the 400.0 cm^3 solution, which is their total volume. In the meanwhile we must first calculate the number of moles of the acid and salt in their respective solutions:

$$n = C \times V$$

For the acid we have

$C = 0.15\ \text{mol dm}^{-3}$

$V = 250.0\ \text{cm}^3 = 0.25\ \text{dm}^3$

$n = ?$

Substituting we have

$$n = \frac{0.15\ \text{mol}}{1\,\cancel{\text{dm}^3}} \times 0.25\,\cancel{\text{dm}^3}$$

$= 0.038$ mol

For the salt we have

$C = 0.25\ \text{mol dm}^{-3}$

$V = 100.0\ \text{cm}^3 = 0.10\ \text{dm}^3$

$n = ?$

Substituting we have

$$n = \frac{0.25\ \text{mol}}{1\ \cancel{\text{dm}^3}} \times 0.10\ \cancel{\text{dm}^3}$$

$= 0.025$ mol

Since the amount of each substance is constant, then we can easily determine the concentrations of the two substances in the final solution as follows:

$$C = \frac{n}{V}$$

For the acid we have

$V = 400.0\ \text{cm}^3 = 0.40\ \text{dm}^3$

$C = ?$

Substituting we have

$$C = \frac{0.038\ \text{mol}}{0.40\ \text{dm}^3}$$

$= 0.095$ M

For the salt we have

$V = 400.0\ \text{cm}^3 = 0.40\ \text{dm}^3$

$C = ?$

Substituting we have

$$C = \frac{0.025\ \text{mol}}{0.40\ \text{dm}^3}$$

$= 0.063$ M

$\text{p}K_a = 4.75$

$\text{pH} = ?$

Finally, we now substitute to obtain

$$\text{pH} = 4.75 - \log \frac{0.095\ \cancel{M}}{0.063\ \cancel{M}}$$

So $\text{pH} = 4.75 - \log 1.5$

Thus $\text{pH} = 4.75 - 0.18$

$= 4.57$

Example 6 What is the pH of a buffer solution containing 0.12 M of $NaHSO_4$ and 0.30 M of K_2SO_4?

$$(\mathrm{p}K_{a2} = 6.91)$$

Solution As usual, we have to apply the relation

$$\mathrm{pH} = \mathrm{p}K_a - \log \frac{[\text{acid}]_{\text{in.}}}{[\text{salt}]_{\text{in.}}}$$

The acid is the anion is of the acidic salt, i.e. HSO_4^-. The dissociation of the acid to SO_4^{2-} corresponds to the second and final stage of the dissociation of H_2SO_4. Thus $\mathrm{p}K_a = \mathrm{p}K_{a2} = 6.91$

$[\text{acid}]_{\text{in.}} = 0.12$ M

$[\text{salt}]_{\text{in.}} = 0.30$ M

pH = ?

Substituting we have

$$\mathrm{pH} = 6.91 - \log \frac{0.12\ \mathrm{M}}{0.30\ \mathrm{M}}$$

So pH = 6.91 – log 0.40

Thus pH = 6.91 + 0.40

= 7.31

Practice Problems

1. Calculate the pH of a buffer solution containing 0.15-M H_2CO_3 and 0.35-M $NaHCO_3$.

   ($K_{a1} = 2.1 \times 10^{-4}$ M) [*Answer:* 4.05]

2. Calculate the concentration of NaH_2PO_4 that must be added to give a buffer solution containing 0.15-M H_3PO_4, and whose pH is 5.00.

   ($K_{a1} = 7.6 \times 10^{-3}$ M) [*Answer:* 1.3×10^{-3} M]

3. What is the pH of a buffer solution prepared by mixing 750.0 cm^3 of 0.15-M NH_3 solution and 250.0 cm^3 of 0.47-M NH_4Cl solution?

   ($K_a = 1.8 \times 10^{-5}$ M) [*Answer:* 4.79]

12.4 SALTS

A salt is a substance formed when the hydrogen or hydroxide ions in an acid or base are partially or completely replaced by metallic or ammonium ions. One way of producing salts is by neutralization reaction, which is the reaction between an acid and base to produce salt and water, e.g.

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

$$Na_2O(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$$

Other ways of preparing salts include:

Displacement reaction between a metal and dilute acid: The metal must be more electropositive than hydrogen for this reaction to be feasible. An example is the reaction between zinc and hydrochloric acid to produce zinc chloride:

$$Zn(s) + HCl(aq) \rightarrow ZnCl_2(s) + H_2(g)$$

The salt can be recovered from solution by evaporating the solution to dryness.

Combination reaction: This involves the direct reaction between constituent elements. This method is used in the preparation of insoluble salts like iron (III) chloride, $FeCl_2$:

$$Fe(s) + Cl_2(s) \rightarrow FeCl_3(s)$$

Precipitation reaction: This involves the reaction between two soluble salts to produce two other salts, one of which is insoluble, e.g.

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

Reaction between carbonates and dilute acid: This reaction produces a soluble salt in addition to carbon dioxide and water, e.g.

$$Na_2CO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(aq)$$

12.4.1 TYPES OF SALTS

Salts can be grouped as follows:

Normal salts: A normal salt is formed when all the hydrogen ions in an acid have been replaced by metallic or ammonium ions. Examples are sodium chloride, NaCl; potassium choride, KCl; sodium carbonanate, Na_2CO_3; potassium sulphate, K_2SO_4; ammonium chloride, NH_4Cl; etc.

Acidic salts: An acidic salt is formed when there is an insufficient amount of a base to neutralize an acid, or when a strong acid reacts with a weak base. Examples include sodium hydrogensulphate, $NaHSO_4$; sodium hydrogencarbonate, $NaHCO_3$; potassium dihydrogen- phosphate, KH_2PO_4; etc.

Basic salts: A basic salt is formed when there is an insufficient amount of an acid to neutralize a base, or when a strong base reacts with a weak acid. Examples include zinc chloride hydroxide, $Zn(OH)Cl$; magnesium hydroxide nitrate, $Mg(OH)NO_3$; etc.

Double salts: These salts contain three different types of ions, usually two cations and an anion. Examples include ammonium iron (II) sulphate-6-water, $(NH_4)_2Fe(SO_4)_2.6H_2O$; aluminium potassium sulphate-12-water, $KAl(SO_4)_2.12H_2O$; etc.

Complex salts: A complex salt contains a complex ion, e.g., tetraamminecopper(II) sulphate, $Cu[(NH_3)_4SO_4]$; sodium tetrahydrozozincate (II), $Na_2[Zn(OH)_4]$; potassium hexacynoferate (II), $K_4[Fe(CN)_6]$; etc.

The pH of a salt solution depends on the strengths of the parent acid and base. The solution of the salt of a strong acid and strong base is always neutral. That of a strong acid and weak base is always acidic, while that of a strong base and weak acid is always basic. The pH of the solution of the salt of a weak base and weak acid depends on which of the acid and base is stronger.

12.4.2 Hydrated Salts

Hydrated salts are salts that contain water of crystallization, which is the molecule of water that is loosely associated with a salt. Examples of such salts include cobalt(II) chloride-6-water, $CoCl_2.6H_2O$; copper(II) sulphate-10-water, $CuSO_4.10H_2O$; iron(II) sulphate-7-water, $FeSO_4.7H_2O$; etc. Salts with no water of crystallization are called anhydrous salts, e.g., sodium chloride, NaCl; potassium permanganate, KMnO4; calcium chloride, $CaCl_2$, etc.

The water of crystallization of hydrated salts can be completely or partially removed by heating. The water of crystallization of a hydrated salt can be completely expelled by heating the salt to a constant mass. The molar mass or mass of a hydrated salt can be obtained from the mass of its water of crystallization, or vice versa, by applying the relation

$$\frac{(18n)\,g\,mol^{-1}}{M} = \frac{m_1}{m_2}$$

where n = The number of molecules of water of crystallization driven off.
M = The molar mass of the hydrated salt.
m_1 = The mass of water driven off.
m_2 = The mass of the hydrated salt sample.

This relation is based on the fact that the mass composition of water of crystallization in any quantity of the hydrated salt is always constant.

Example 1 10.0 g of iron(II) sulphate-6-water, $FeSO_4.7H_2O$, was heated to a mass of 8.2 g. Calculate the number of molecules of water of crystallization driven off, hence write the molecular formula of the resulting salt sample.

(H = 1.0, O = 16.0, S = 32.1, Fe = 55.8)

Solution We have to apply the relation

$$\frac{(18n)\,\text{g mol}^{-1}}{M} = \frac{m_1}{m_2}$$

M = [55.8 + 32.1 + (16.0 × 4) + 7(18)] g mol^{-1} = 277.9 g mol^{-1}
m_1 = 10.0 g − 8.2 = 1.8 g
m_2 = 10.0 g
n = ?

Substituting we have

$$\frac{18n\,\cancel{\text{g}}\,\cancel{\text{mol}^{-1}}}{277.8\,\cancel{\text{g}}\,\cancel{\text{mol}^{-1}}} = \frac{1.8\,\cancel{\text{g}}}{10.0\,\cancel{\text{g}}}$$

Cross-multiplying we have

$n \times 180 = 500$

So $n = \frac{500}{180}$

$= 3$

Thus, 3 molecules of water of crystallization were driven off. The remaining number of molecules of water of crystallization is 7 – 3 = 4, hence the molecular formula of the resulting salt sample is $FeSO_4.4H_2O$.

Example 2 13.8 g of hydrated sodium carbonate, $Na_2CO_3.nH_2O$, was heated and weighed several times until its mass remained constant at 5.2 g. Calculate the number of molecules of water of crystallization in the salt, and write its chemical formula.

(O = 16, C = 12, Na = 23)

Solution Here, all the molecules of water of crystallization have been driven off. This must correspond to the number of molecules of water of crystallization in the salt. To obtain this we have to apply the relation

$$\frac{(18n)\text{ g mol}^{-1}}{M} = \frac{m_1}{m_2}$$

$M = [(23 \times 2) + 12 + (16 \times 3) + n(18)]\text{ g mol}^{-1} = (106 + 18n)\text{ g mol}^{-1}$

$m_1 = 13.8\text{ g} - 5.2\text{ g} = 8.6\text{ g}$

$m_2 = 13.8\text{ g}$

$n = ?$

Substituting we have

$$\frac{18n\,\cancel{\text{g}}\,\cancel{\text{mol}^{-1}}}{(106+18n)\,\cancel{\text{g}}\,\cancel{\text{mol}^{-1}}} = \frac{8.6\,\cancel{\text{g}}}{13.8\,\cancel{\text{g}}}$$

Cross-multiplying we have

$910 + 154.8n = 248.4n$

So $248.4n - 154.8n = 911.6$

Thus $93.6n = 911.6$

Then $n = \frac{911.6}{93.6}$

$= 10$

The salt contains 10 molecules of water of crystallization, hence the formula of the salt is $Na_2CO_3.nH_2O$.

Practice Problems

1. 8.3 g of $CuSO_4.10H_2O$ was heated to a mass of 6.5 g. Calculate the number of molecules of water of crystallization driven off.

(H = 1.0, O = 16, S = 32, Cu = 63.5) [*Answer:* 4]

2. 7.2 g of hydrated cobalt(II) chloride, $CoCl_2.nH_2O$, was heated and weighed several times, until its mass became constant at 3.9 g. Calculate the number of molecules of water of crystallization in the hydrated salt, hence write the molecular formula of the salt.

   (H = 1.0, O = 16, Cl = 35.5, Co = 58.9) [*Answers:* 6, $CoCl_2.6H_2O$]

SUMMARY

- An Arrhenius acid is a compound that ionizes in water to produce hydrogen ion (proton) as the only positive ion. An Arrhenius base is a compound that ionizes in water to produce hydroxide ion as the only negative ion.
- A Bronsted-Lowry acid is a proton donor, while a Bronsted-Lowry base is a proton acceptor.
- An acid-base combination in which one is related to the other by a gain or loss of proton is called a conjugate acid-base pair.
- A Lewis acid is as an electron-pair acceptor, while a Lewis base is an electron-pair donor.
- Autoionization is the process by which a substance acts both as a Bronsted acid and Bronsted base by donating a proton to itself to undergo ionization.
- The hydronium ion index pH is the negative logarithm of the hydronium ion concentration of a solution to base 10:

$$pH = -\log [H_3O^+]$$

- The equilibrium constant for the dissociation or ionization of an acid is called the acid dissociation or ionization constant K_a.
- The acid dissociation or ionization constant index pK_a negative logarithm of acid dissociation or ionization constant to base 10;

$$pK_a = -\log K_a$$

- The equilibrium constant for the dissociation or ionization of a base is called the base dissociation or ionization constant K_b.
- The base dissociation or ionization constant index pK_b is the negative logarithm of the base dissociation or ionization constant to base 10:

$$pK_b = -\log K_b$$

- A buffer solution is a solution that resists changes in pH on dilution or addition of small amounts of acids or base.

- The common-ion effect refers to the situation in which the same ion is produced by two different compounds in solution.
- The pH of a buffer solution is calculated using the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_a - \log \frac{[\mathrm{acid}]_{\mathrm{in.}}}{[\mathrm{salt}]_{\mathrm{in.}}} \text{ or } \mathrm{pOH} = \mathrm{p}K_b - \log \frac{[\mathrm{base}]_{\mathrm{in.}}}{[\mathrm{salt}]_{\mathrm{in.}}}$$

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. The K_a for an acid is 0.30 at 25°C. What is the pK_a of the acid?

   A. −5.20 B. −0.52
   C. 0.30 D. 0.52
   E. 5.20

2. What is the K_b for a base if its pK_b is 5.8 at 25°C?

   A. 1.6×10^{-7} B. 1.5×10^{-6}
   C. 1.6×10^{-6} D. 1.8×10^{-5}
   E. 4.5×10^{-5}

3. Which of the following is the pK_w of water?

   A. 2.40 B. 4.00
   C. 6.00 D. 7.00
   E. 14.00

4. Which of the following salts will dissolve in water to produce a solution whose pH is greater than 7?

   A. NaCl B. K_2SO_4
   C. Na_2CO_3 D. KCl
   E. NH_4Cl

5. Which of the following is the conjugate base of H_2SO_4?

   A. SO_4^{2-} B. H_2CO_3
   C. HSO_4^- D. HSO_3^-
   E. NH_3

6. Which of the following is **NOT** an Arrhenius base?

A. $Ca(OH)_2$ B. NaOH
C. $Ba(OH)_2$ D. KOH
E. CO

7. Which of the following statements is/are correct?

i. All Arrhenius acids are Brønsted-Lowry acids.
ii. All Brønsted-Lowry bases are Arrhenius bases.
iii. A Lewis acid is an electron pair acceptor.
iv. The pH of a solution of the salt of a weak acid and a strong base is usually less than 7.

A. i only B. ii and iv
C. iv only D. i and iii
E. ii and iii

8. Which of the following is **NOT** true of an acid with a pK_a of 1.3×10^{-5}?

A. It is a weak acid.
B. It has a K_a of 1.0.
C. It undergoes complete ionization.
D. It is a strong acid.
E. It undergoes neutralization reaction.

9. Which of the following statements is/are correct?

i. All bases are alkalis.
ii. All alkalis are bases.
iii. The sum of the pK_a and pK_b of a conjugate acid-base pair is 1.00×10^{-14} M.
iv. Salts can only be produced by neutralization reaction.

A. i and ii B. i only
C. ii and iv D. ii and iii
E. iii and i.

10. The pH of a solution whose hydrogen ion concentration is 1.80×10^{-5} M is

A. 4.74 B. 7.25
C. 8.75 D. 9.00
E. 9.25

11. Which of the following pH values indicates neutrality?

A. 3.0 B. 7.0

C. 10.0 D. 11.0

E. 14.0

Use the table to answer Questions 12 and 13.

Solution	i	ii	iii	iv
pH	7.2	4.2	8.6	1.0

12. Which of the following options indicates the arrangement of the solutions in the decreasing order of acidity?

A. i, ii, iv, iii B. i, ii, iii, iv

C. iii, ii, i, iv D. iii, i, ii, iv

E. iv, ii, i, iii

13. Which of the solutions would turn red litmus paper blue?

A. i and iii only B. ii only

C. iv and iii only D. iii only

E. i , ii, iii and iv

14. Which of the following correctly denotes pH of a solution?

A. log [H_3O^+] B. log [H^+][OH^-]

C. −log [OH] D. log log [H_3O^+]

E. −log [H]

ESSAY TYPE QUESTIONS

Theories of acids and bases

15. Define the following:

i. Arrhenius acid and base ii. Bronted-Lowry acid and base iii. Lewis acid and base

16. (a) What do you understand by autoionization? Name two substances that undergo autoionization.

(b) What do you understand by a conjugate acid-base pair?

17. (a) What is a conjugate acid?

(b) What is a conjugate base?

Acid and base ionization constants

18. (a) What do you understand by acid and base ionization constants?

(b) Write out the expression for the K_a or K_b of the following:

(i) HCOOH (ii) C_6H_5OH (iii) HNO_2 (iv) CH_3NH_2 (v) $C_6H_5NH_2$

19. 2.4 mM of oxochlorous acid, HClO, was dissolved in water at 25°C. Calculate the K_a and pK_a of the acid if the acid was 0.35% dissociated at this temperature.

20. 0.100 M of aniline, $C_6H_5NH_2$ was found to be 0.0066% dissociated at 25°C. Determine its K_b and pK_b at this temperature.

21. Hypobromous acid, HBrO, dissociates in solution as follows:

$$HBrO(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + BrO^-(aq)$$

Calculate the equilibrium concentrations of H_3O^+ and BrO^- at 25°C, given that the initial concentration of the acid is 0.20 M. Hence calculate the percentage ionization of the acid at the specified temperature.

$$(K_a = 2.0 \times 10^{-9}\ M)$$

Water autoionization constant and hydrogen ion concentration

22. (a) What do you understand by the pH of a solution?

(b) Calculate the pH of a solution whose hydronium ion concentration is 2.41×10^{-5} M.

(c) Calculate the pOH of a solution whose hydronium ion concentration is 1.70×10^{-6} M.

(d) The pH of a solution is 1.70. What is the hydrogen ion concentration of the solution?

23. Calculate the pH of 0.25-M solution of hydrochloric acid.

24. Calculate the pH of 0.0050-M solution of carbonic acid.

$$(pK_{a1} = 6.37,\ pK_{a2} = 10.25)$$

25. Calculate the pH of a phosphoric acid solution when its concentration is 1.22 M.

$$(pK_{a1} = 2.12,\ pK_{a2} = 7.21,\ pK_{a3} = 12.67)$$

26. Calculate the pH of a nitrous acid solution when its concentration is 0.025 M.

$$(K_a = 4.3 \times 10^{-4} M)$$

27. What is the pH of 0.10-M solution of hydroxylamine, NH_2OH?

$$(pK_b = 7.97)$$

28. What is the pH of 0.015-M solution of ammonia?

$(K_b = 1.8 \times 10^{-5}\,\text{M})$

29. Calculate the pH of 0.15-M solution of methylamine, CH_3NH_2.

$(K_b = 4.2 \times 10^{-4}\,\text{M})$

30. Calculate the pH of 0.050-M solution of ethylamine, $C_2H_5NH_2$.

$(K_b = 6.5 \times 10^{-4}\,\text{M})$

31. Aniline is a very weak base formed when an amino group ($-NH_2$) substitutes one of the hydrogen atoms of benzene. Determine the pH of a 0.57-M solution of the base.

$(pK_b = 9.37)$

32. What is the pH of a 0.012-M solution of ammonium sulphate?

$(pK_b = 4.74)$

33. Calculate the pH of a 0.11-M solution of potassium acetate.

$(K_a = 1.8 \times 10^{-5}\,\text{M})$

34. Calculate the pH of 0.050-M solution of sodium hydrogencarbonate.

$(K_a = 4.3 \times 10^{-7}\,\text{M})$

35. Calculate the pH of a 0.050-M solution of calcium dihydrogenphosphate, $Ca(H_2PO_4)_2$.

$(K_a = 7.6 \times 10^{-3}\,\text{M})$

36. Calculate the pH of the solution obtained when 25.00 cm^3 of 0.150-M hydrochloric acid solution is titrated with 8.00 cm^3 of 0.100-M solution of sodium hydroxide.

37. Calculate the pH of the solution obtained when 10.00 cm^3 of 0.015-M solution of nitric acid is added to 21.10 cm^3 of 0.15-M solution of sodium hydroxide.

38. What is the pH of the solution obtained when 10.00 cm^3 of 0.15 M of hydrochloric acid is added to0the solution obtained at the equivalence point of the titration of 20.00 cm^3 of 0.10 M of potassium hydroxide solution with the acid.

39. A student reported his average titre value to be 22.20 cm^3 in the titration of 25.00 cm^3 of 0.20-M solution of sodium hydroxide with 0.25-M solution of nitric acid. Determine the pH of the resulting solution.

40. Calculate the pH of the solution obtained by adding 7.50 cm^3 of a 0.20-M solution of sodium hydroxide to 20.00 cm^3 of 0.50-M solution of acetic acid.

$$(K_a = 1.8 \times 10^{-5}\ \text{M})$$

41. A student was asked to determine the equivalence point of the titration of 20.00 cm^3 of 0.25-M solution of methanoic acid with 0.20-M solution of potassium hydroxide. Calculate the pH of the solution after the addition of just 3.60 cm^3 of the base.

$$(K_a = 1.8 \times 10^{-4}\ \text{M})$$

42. What volume of 0.150-M solution of sodium hydroxide must be added to 25.00 cm^3 of 0.200-M solution of acetic acid to reach the equivalence point? Hence determine the pH of the solution at the equivalence point.

$$(K_a = 1.8 \times 10^{-5}\ \text{M})$$

43. A student titrated 20.00 cm^3 of 0.22-M solution of methanoic acid against 0.15-M solution of sodium hydroxide. Calculate the pH of the solution at the equivalence point.

$$(K_a = 1.8 \times 10^{-4}\ \text{M})$$

44. Calculate the pH of the solution obtained at the equivalence point of the titration of 20.00 cm^3 of 0.20-M ammonia solution with 0.15-M solution of nitric acid.

$$(K_b = 1.8 \times 10^{-5}\text{M})$$

45. A student titrated 25.00 cm^3 of 0.10-M solution of ammonia with 0.15-M solution of sulphuric acid. Calculated the pH of the solution obtained at the equivalence point.

Buffer solutions

46. (a) What is a buffer solution?
    (b) Explain the industrial and biological importance of buffers.
    (c) What do you understand by the common-ion effect?

47. Calculate the pH of a buffer solution containing 0.20-M HF and 0.30-M NaF at 25°C.

$$(K_a = 3.5 \times 10^{-4}\ \text{M})$$

48. Calculate the pH of a buffer solution containing 0.100-M H_2PO_3 and 0.15-M $NaHPO_4$ at 25°C.

$$(\text{p}K_{a1} = 2.12)$$

49. Calculate the pH of a solution containing 0.15-M NH_3 and 0.20-M NH_4Cl at 25°C.

($K_b = 1.8 \times 10^{-5}$ M)

50. Calculate the amount of H_2SO_3 that must be added to a 200.0 cm^3 solution containing 0.45-M $NaHSO_3$ to produce the solution with a pH of 2.30.

($K_{a1} = 1.6 \times 10^{-2}$ M)

51. What mass of NH_4Cl is required to prepare 500.0 cm^3 of a buffer solution containing 0.15-M NH_3, and whose pH is 9.50?

(H = 1.0, N = 14.0, Cl = 35.5, $K_b = 1.8 \times 10^{-5}$ M)

52. What is the pH of a solution prepared by mixing 500.0 cm^3 of 0.20-M HF solution and 300.0 cm^3 0.15-M NaF solution?

($K_a = 3.5 \times 10^{-4}$ M)

53. What is the pH of a buffer solution prepared by mixing 150.0 cm^3 of 0.18-M NaH_2PO_4 solution and 250.0 cm^3 of 0.30-M Na_2HPO_4 solution?

(pK_{a2} = 7.61)

54. Show that the pH of a buffer solution can given by the equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]_{\text{in.}}}{[\text{acid}]_{\text{in.}}}$$

where $[\text{acid}]_{\text{in.}}$ = The initial concentration of acid.

$[\text{salt}]_{\text{in.}}$ = The initial concentration of salt.

Answers

1. D 2. C 3. E 4. C
5. C 6. E 7. D 8. A
9. D 10. A 11. B 12. E
13. A 14. E

18. (b) (i) $K_a = \frac{[HCO_2^-][H_3O^+]}{[HCOOH]}$ (ii) $K_a = [C_6H_5O^-][H_3O^+]$

(iii) $K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]}$ (iv) $K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NO_2]}$

(v) $K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$

19. $K_a = 3.0 \times 10^{-8}$ M, p$K_a = 7.53$

20. $K_a = 4.4 \times 10^{-10}$ M, p$K_a = 9.36$

21. $[H_3O^+] = [BrO^-]$ = 0.020 mM, 0.01%

22. (b) 4.62 (c) 8.23 (d) 0.020 M

23. 0.60 M 24. 4.3 25. 1.0 26. 2.5

27. 9.51 28. 10.7 29. 11.9 30. 11.8

31. 9.2 32. 5.4 33. 8.9 34. 9.5

35. 7.4 36. 1.05 37. 13 38. 1.5

39. 1.9 40. 4.7 41. 3 42. 33.3 cm^3, 8.8

43. 8.3 44. 5.2 45. 5.2 47. 3.64

48. 2.30 49. 9.14 50. 0.028 mol

51. 2.3 g 52. 3.11 53. 8.05

13

Chapter Chemical Kinetics

Chemical kinetics is the study of the rates of chemical reactions. Chemical reaction occurs when the particles of reactants collide with enough energy to break their bonds. This results in the formation of new species as new bonds are formed. The assumption that chemical reaction occurs as a result of the collision of reactant particles is called collision theory. The collisions resulting in the formation of products are called effective collisions.

The minimum energy with which the reactants particles must collide in order for chemical reaction to occur is called activation energy or energy barrier E_a. Activation energy is constant for any particular reaction.

13.1 RATES OF REACTIONS

The rate r of a chemical reaction is the speed at which the reactants disappear (are used up) or the speed at which the products are being formed. The rate of chemical reaction can be measured as follows:

∑ ***From concentration:*** The measurement of reaction rates is often based on concentration, i.e.

$$r = \frac{\Delta[X]}{\Delta t}$$

where $\Delta[X]$ = The change in the concentration of a reactant or product X.

Δt = The time taken for the change.

The unit of rate of reaction depends on the units of concentration and time. For example, when concentration is in M (mol dm^{-3}), and time in seconds (s), then the unit of rate of reaction will be mol dm^{-3} s^{-1}.

∑ ***From mass:*** The rate of reaction is given as

$$r = \frac{\Delta m}{\Delta t}$$

where Δm = Change in the mass of a reactant or product.

Δt = The time taken for the change.

The unit of rate of reaction depends on the units of mass and time. For example, when mass is in g, and time in s, then the unit of rate of reaction will be g s^{-1}.

∑ ***From volume:*** On the basis of volume we have

$$r = \frac{\Delta V}{\Delta t}$$

where ΔV = The change in the volume of reactant or product.

Δt = The time taken for the change.

The unit of rate of reaction depends on the units of volume and time. For example, when volume is in cm^3, and time in s, then the unit of rate of reaction is cm^3 s^{-1}.

Reaction rate is not constant over the course of a reaction. The rate of reaction is fastest at the beginning of a reaction, and gradually reduces as the reactants are being used up. The rate of reaction becomes zero after the reactants are depleted.

The graph showing how reaction rate varies with time is called a rate curve. The average rate of reaction is determined from the total change in mass, volume or concentration of the reactants over the course of the reaction and the time taken for such a change. The rate of reaction at any particular instant can be obtained by drawing a tangent to the rate curve and measuring its gradient. Such a reaction rate is called the instantaneous rate of reaction.

The rate of chemical reaction depends on the following factors:

1. Temperature: Particles of reactants gain more kinetic energy at higher temperature, increasing the speed and frequency of collisions. Thus the number of effective collisions increases, resulting in an increase in the rate of chemical reaction. The dependence of rate of reaction on temperature is given by the Arrhenius equation, which will be treated shortly.

2. Concentration: Increasing the concentration of reactants increases the rate of chemical reaction because the speed and frequency of collisions increase when the particles are more crowdly packed together.

3. Nature of reactants: Some substances react very slowly, while others react very fast. This is due to the activation energy of the individual reactants. Reactants with low activation energies have a high rate of reaction, while those with high activation energies would react slowly. Some systems will not react at all because of their very high energy contents. An example is the action of gold on dilute hydrochloric acid.

4. Catalyst: A catalyst is a substance which increases the rate of chemical reaction without being consumed in the process. A catalyst works by providing an alternative pathway with a lower activation energy for a reaction. An example of a catalyst is manganese(IV) oxide, MnO_4, which is used in the production of oxygen by the thermal decomposition of potassium chlorate, $KClO_3$.

The practice of using catalysts in chemical reactions is called catalysis. A catalyst could be in the same or different phase with the reactants. A homogeneous catalyst is a catalyst which is in the same phase with the reactants, and the practice of using such catalysts is called homogeneous catalysis. A heterogeneous catalyst is one which is of a different phase from the reactants, and the practice of using such a catalyst is called heterogeneous catalysis.

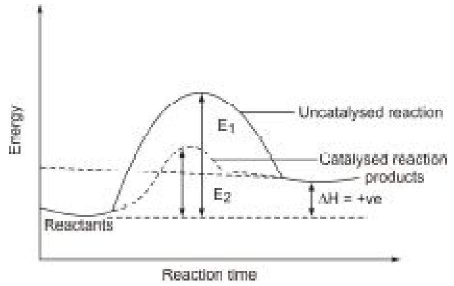

Figure 13.1 Energy profile diagram showing the effect of a catalyst on the rate of reaction.

5. Light: Certain reactions cannot occur in the absence of light. Reactions that are catalysed by light are called photochemical reactions. Examples include photosynthesis, decomposition of hydrogen peroxide, substitution reaction between methane and chlorine, etc.

6. Surface area of reactants: Increasing the surface area of reactants increases the rate of chemical reaction by increasing the area with which the particles collide. The reaction between zinc and hydrochloric acid, for example, would take place at a much faster rate if zinc granules are used instead of lumps of zinc.

7. Pressure: The molecules of a gas would occupy a smaller volume if its pressure is increased. This leads to faster collision of particles. Thus an increase in the pressure of a gas-phase reaction increases its rate of reaction.

Example 1 The concentration of hydrogen peroxide changed by 0.075 M in 50.0 s during the decomposition of the compound. Calculate:

(a) the rate of reaction decomposition of hydrogen peroxide;
(b) the rate of formation of oxygen.

Solution

(a) Since the decomposition is based on the measurement of concentration, then we have to apply the relation

$$r = \frac{\Delta[H_2O_2]}{\Delta t}$$

$\Delta[H_2O_2] = 0.075 \text{ mol dm}^{-3}$

$\Delta t = 50 \text{ s}$

$r = ?$

Substituting we have

$$r = \frac{0.075 \text{ mol dm}^{-3}}{50.0 \text{ s}}$$

$$= 1.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$$

(b) The change in concentration of oxygen is not known. Nevertheless, we can obtain its rate of formation from the rate of decomposition of hydrogen peroxide. The equation of reaction is

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

From the equation, the rate of formation of oxygen is expressed as

$$r = \frac{1}{2}\frac{\Delta[H_2O_2]}{t}$$

$$\therefore r = \frac{1.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}}{2}$$

$$= 7.5 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

Example 2 1.0 g of zinc was left after 20.0 s of adding 5 g of zinc granules to dilute hydrochloric acid. What was the rate of reaction of zinc?

Solution We should calculate the rate of reaction on the basis of disappearance of the mass of zinc. Thus

$$r = \frac{\Delta m}{\Delta t}$$

Δm = The initial mass of zinc – Final mass of zinc = 5.0 g – 1.0 g = 4 g

Δt = 20.0 s

r = ?

Substituting we have

$$r = \frac{4.0\ \text{g}}{20.0\ \text{g}}$$

$= 0.2\ \text{g s}^{-1}$

Example 3 50.0 cm^3 of ammonia was produced in 10.0 min. when hydrogen and nitrogen were mixed. What is the rate of formation of ammonia in cm^3 hr^{-1}?

Solution We have to apply the relation

$$r = \frac{\Delta V}{\Delta t}$$

Since the initial volume of ammonia is zero, then

$$\Delta V = 50.0\ \text{cm}^3$$

Since the rate is required in cm^3 hr^{-1}, then we must convert the time to hour:

Δt = 10.0 min. = 0.20 hr

r = ?

We now substitute to obtain

$$r = \frac{50.0\ \text{cm}^3}{0.20\ \text{hr}}$$

$= 250\ \text{cm}^3\ \text{hr}^{-1}$

Example 4 75 cm^3 of oxygen was liberated during the decomposition of hydrogen peroxide in the laboratory. How long did it take for this volume of oxygen to be produced if the rate of reaction was obtained to be 2.5 cm^3 min^{-1}?

Solution We have to apply the relation

$$r = \frac{\Delta V}{\Delta t}$$

$$\therefore \ \Delta t = \frac{\Delta V}{r}$$

$\Delta V = 75 \text{ cm}^3$
$r = 2.5 \text{ cm}^3 \text{ min.}^{-1}$
$\Delta t = ?$

We now substitute to obtain

$$\Delta t = \frac{75 \cancel{\text{cm}^3} \times 1 \text{ min}}{2.5 \cancel{\text{cm}^3}}$$

$= 30 \text{ min.}$

Practice Problems

1. A dilute solution of sulphuric acid was added to a 0.150-M solution of sodium carbonate. Determine the rate of reaction, given that the concentration of sodium carbonate reduced to 0.125 M after 2.0 minutes?

[*Answer:* 0.013 mol dm^{-3} min.$^{-1}$]

2. The following data were obtained during the laboratory experiment on the rate of formation of hydrogen form zinc and hydrochloric acid:

t (s)	0	10	20	30	40	50	60	70
V (c m^3)	0	5	10	15	20	22	22	22

Calculate:

(a) The rate of reaction when the time was 10 s;
(b) The rate of reaction between 15 s and 22 s;
(c) The average rate of reaction for the whole process.

[*Answers:* (a) 2 cm^3 s^{-1} (b) 3 cm^3 s^{-1} (c) 0.3 cm^3 s^{-1}]

13.2 RATE LAW

A rate law is an equation expressing the rate of reaction in terms of the concentration of the substances involved in a chemical reaction. An example of rate law is

$r = k[\mathrm{A}]^a$

where k = The rate or velocity constant.

$[\mathrm{A}]$ = The concentration of a reactant A.

a = The order of reaction.

The value of rate constant is characteristic of a particular reaction. It increases with temperature, but independent of pressure and concentration.

The order of reaction is the power to which the concentration of a reactant is raised in a rate law. A reaction is said to be first-order when the concentration of a reactant is raised to unity. Doubling the concentration of the reactant increases the rate of reaction by a factor of 2. An example is the decomposition of dinitrogen pentoxide.

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g) \quad r = k[N_2O_5]$

A reaction is said to be second-order when the concentration of a reactant is squared or raised to 2 in its rate law. Doubling the concentration of the reactant increases the rate of reaction by a factor of 4. A example is the decomposition of hygrogen iodide:

$2HI(g) \xrightarrow{\Delta, W} I_2(g) + H_2(g) \quad r = k[HI]^2$

A zero-order reaction is a reaction whose rate is independent of concentration. Thus the rates of zero-order reactions are the same as their repective rate constants. An example is the decomposition of ammonia:

$2NH_3(g) \xrightarrow{W} N_2(g) + 3H_2(g) \quad r = k[NH_3]^0 = k^1$

Unlike the rate laws described so far, some rate laws are expressed in terms of the concentrations of more than one substance, i.e.

$$r = k[\mathrm{A}]^a[\mathrm{B}]^b[\mathrm{C}]^c \ldots$$

The reaction is said to be *a*-order in A, *b*-order in B, and *c*-order in C, etc. The overall order of a reaction is the sum of the powers to which the concentrations of the substances appearing in its rate law are raised. Thus the overall order is given as $a + b + c + \ldots + n$. An example of such reactions is the formation of hydrogen iodide:

$H_2(g) + I_2(g) \rightarrow 2HI(g) \quad r = k[H_2][I_2]$

The reaction is said to be first-order in H_2 and I_2, while it is second-order overall. Doubling the concentration of any of the reactants increases the rate of reaction by a factor of 2. Doubling the concentrations of both reactants increases the rate of reaction by a factor of 4. When the initial concentrations of both reactants are equal, then the rate law can be expressed in terms of the concentrations of any of the reactants:

$H_2(g) + I_2(g) \rightarrow 2HI(g) \quad r = k[H_2]^2$ or $r = k[I_2]^2$

In this case, a reaction that is second-order overall can be treated like a second-order reaction.

It must be clearly noted that rate laws cannot be determined from chemical equations, but only through experimental data.

An integrated rate law is an equation connecting the initial concentration of a substance and its concentration at any instant over the course of a reaction. It is obtained by integrating the differential form of a rate law. For a zero-order reaction, the integrated rate law is given as

$$kt = [A]_0 - [A]_t$$

For a first-order reaction we have

$$kt = \frac{[A]_0}{[A]_t} \text{ or } \ln [A]_t = \ln [A]_0 - kt$$

For a second-order reaction we have

$$kt = \frac{1}{[A]_t} - \frac{1}{[A]_0} \text{ or } \frac{1}{[A]_t} = \frac{1}{[A]_0}$$

where $[A]_0$ = The initial concentration of the reactant.

$[A]_0$ = The concentration of the reactant at any time t.

k = The rate or velocity constant.

A comparison of the integrated rate law for a first-order reaction with the equation of a straight line, i.e. $y = mx + c$ shows that a plot of ln $[A]_t$ against t would produce a straight-line graph of slope $-k$ and intercept $[A]_0$ on the y-axis. For a reaction of the second-order, a plot of $1/[A]_t$ against t must produce a straight line of slope k and intercept $1/[A]_0$ on the y-axis.

Example 1 Show that the integrated rate law for a zero-order reaction is given by the equation

$$kt = [A]_0 - [A]_t$$

Solution We begin by considering the zero-order reaction:

$A \rightarrow B + C \quad r = k \quad (13.1)$

The differential form of the rate law is written as

$$r = -\frac{d[A]}{dt} \quad (13.2)$$

The differential rate law shows the rate of change of concentration with time or the instantaneous change of concentration. The minus sign indicates that the concentration of A decreases with time t. We now equate Equations (13.1) and (13.2) to obtain

$$k = -\frac{d[A]}{dt}$$

Cross-multiplying we have

$$k\,dt = -d[A] \quad (13.3)$$

We can now integrate Equation (13.3) within the limits $[A] = [A]_0$ at $t = 0$ and $[A] = [A]_t$ at $t = t$:

$$k\int_0^t dt = -\int_{[A]_0}^{[A]_t} d[A]$$

Note that the rate constant k has been brought out of the integral sign because it is a constant.

So $kt = -([A]_t - [A]_0) \quad (13.4)$

Finally, we now rearrange Equation (13.4) to obtain

$$kt = [A]_0 - [A]_t \quad (13.5)$$

Example 2 Show that the integrated rate law for a first-order reaction is given by the equation

$$kt = \ln\frac{[A]_0}{[A]_t}$$

Solution We begin by considering a first-order reaction:

$A \rightarrow B + C \quad r = k[A] \; (13.6)$

In the differential form we have

$r = -\frac{d[A]}{dt}$ (13.7)

We now equate Equations (13.6) and (13.7) to obtain

$k[A] = -\frac{d[A]}{dt}$ (13.8)

We now divide Equation (13.8) by [A], and multiply the result by dt to obtain

$k\mathrm{d}t = -\frac{d[A]}{[A]}$ (13.9)

We can now integrate Equation (13.9) within the limits $[A] = [A]_0$ at $t = 0$ and $[A] = [A]_t$ at $t = t$:

$$k\int_0^t dt = -\int_{[A]_0}^{[A]_t} \frac{1}{[A]} d[A]$$

Thus $kt = -[\ln[A]]_{[A]_0}^{[A]_t}$

So $kt = -(\ln [A]t - \ln [A]_0)$ (13.10)

Finally, we now apply the law of logarithm to Equation (13.10) to obtain

$$kt = -\ln \frac{[A]_t}{[A]_0}$$

Thus $kt = \frac{[A]_0}{[A]_t}$ (13.11)

We can as well take the natural antilogarithms of both sides to obtain

$\frac{[A]_0}{[A]_t} = e^{kt}$ (13.12)

Example 3 1.50 M of a substance A was subjected to decomposition. If it was found after the experiment that its rate of decomposition is independent of concentration. Calculate:

(a) the rate constant, given that 0.58 M of A was left after 5 minutes;
(b) the concentration of A left after 7 minutes;
(c) the time taken for A to decompose to 9% of its initial concentration.

Solution

(a) Since the rate of reaction (decomposition) is independent of concentration, then the reaction is zero-order. Thus we have to apply the relation

$kt = [A]_0 - [A]_t$

$\therefore\ k = \frac{[\text{A}]_0 - [\text{A}]_t}{t}$

$[\text{A}]_0 = 1.50 \text{ mol dm}^{-3}$

$[\text{A}]_t = 0.58 \text{ mol dm}^{-3}$

$t = 5 \times 60 \text{ s} = 300 \text{ s}$

$k = ?$

Substituting we have

$$k = \frac{1.50 \text{ mol dm}^{-3} - 0.58 \text{ mol dm}^{-3}}{300\, s}$$

$$\text{Thus } k = \frac{0.92 \text{ mol dm}^{-3}}{300\, s}$$

$$= 3.1 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$$

(b) We have to apply the relation

$kt = [\text{A}]_0 - [\text{A}]_t$

$\therefore\ [\text{A}]_t = [\text{A}]_0 - kt$

$[\text{A}]_0 = 1.50 \text{ mol dm}^{-3}$

$t = 7 \times 60 \text{ s} = 420 \text{ s}$

$k = 3.1 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$

$[\text{A}]_t = ?$

Substituting we have

$$[\text{A}]_t = 1.50 \text{ mol dm}^{-3} - \left(\frac{3.1 \times 10^{-3} \text{ mol dm}^{-3}}{1\, \cancel{s}} \times 420\, \cancel{s}\right)$$

So $[\text{A}]_t = 1.50 \text{ mol dm}^{-3} - 1.302 \text{ mol dm}^{-3}$

$= 0.20 \text{ M}$

(c) As usual, we have to apply the equation

$kt = [\text{A}]_0 - [\text{A}]_t$

$\therefore\ t = \frac{[\text{A}]_0 - [\text{A}]_t}{k}$

---

[1] When the differential of a denominator equal the numerator, then the integral of the fraction equals the natural logarithm of the denominator, i.e. $\int \frac{1}{x}\, dx = \ln x$.

$[A]_t = \frac{90}{100} \times 1.50 \text{ mol dm}^{-3} = 1.35 \text{ mol dm}^{-3}$

$k = 3.1 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$

$[A]_0 = 1.50 \text{ mol dm}^{-3}$

$t = ?$

Substituting we have

$$t = \frac{1.50 \text{ mol dm}^{-3} - 1.35 \text{ mol dm}^{-3} \times 1 \text{ s}}{3.1 \times 10^{-3} \text{ mol dm}^{-3}}$$

$$\text{So } t = \frac{0.15 \cancel{\text{mol}} \text{ dm}^{-3} \times 1 \text{ s}}{3.1 \times 10^{-3} \cancel{\text{mol}} \cancel{\text{dm}^{-3}}}$$

$= 48 \text{ s}$

Example 4 The following data were obtained during an experiment to determine the rate of decomposition of dinitrogen pentoxide, N_2O_5, at 25 °C:

t (min.)	0	5	10	15	20	25	30
[N_2O_5] (M)	1.0	0.989	0.978	0.967	0.957	0.946	0.936

(a) Confirm that the decomposition of N_2O_5 is first-order and calculate its rate constant.

(b) What is the concentration of N_2O_5 18 min. after the beginning of the experiment?

Solution

(a) The integrated rate law for a first-order reaction is given by the equation

$$kt = \ln \frac{[A]_0}{[A]_t} \text{ or } \ln [A]_t = [A]_t -$$

Comparing this with the equation of a straight line, $y = mx + c$, shows that a plot of ln $[A]_t$ against time t would produce a straight-line graph of slope (gradient) k, and intercept ln $[A]_0$ Thus we can be sure that the decomposition is first-order if a plot of ln [N_2O_5] against time yields a straight-line graph. To do this we must first obtain ln [N_2O_5] for each value of [N_2O_5]:

t (min.)	0	5	10	15	20	25	30
$[N_2O_5]$ (M)	1.000	0.989	0.978	0.967	0.957	0.946	0.936
In $[N_2O_5]$	0.00	−0.011	−0.022	−0.034	−0.044	−0.056	−0.066

The plot of ln $[N_2O_5]$ against *t* is shown below. Note that we can also plot a graph of log $[N_2O_5]$ against *t* provided we use the equation

$$\log [A]_t = \log[A]_0 - \frac{k}{2.303}$$

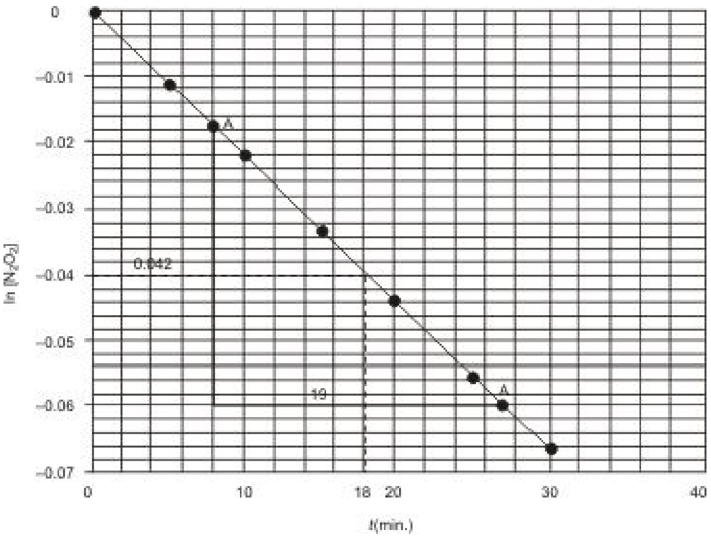

Figure 13.2 Graph of $[N_2O_5]$ against t.

Since the graph is a straight line, then we can conclude that the decomposition is first-order. As we said earlier, the slope of the graph is the rate constant *k*. The slope of the graph is

$$k = \frac{(\ln[N_2O_5])_B - (\ln[N_2O_5])_A}{t_B - t_A}$$

So $k = \frac{-0.042}{19 \text{ min.}}$

$= -2.2 \times 10^{-3}$ min.$^{-1}$ $= -3.7 \times 10^{-5}$ s^{-1}

Alternatively, we can obtain a quick result for *k* by choosing any two values of $\ln[N_2O_5]$from the table. It should be noted that the farther the values are from one another, the more accurate is our result. Choosing 0 and −0.056 we have

$$k = \frac{-0.056 - 0}{25\ \text{min.}}$$

$$= -2.2 \times 10^{-3}\ \text{min.}^{-1}$$

Note that the minus sign indicates that the concentration of N_2O_5 decreases with time.

(b) We can obtain the concentration of N_2O_5 after 18 min. by tracing the point t = 18 min. to the line, and then to the y-axis. From this we obtain

$$\ln [N_2O_5] = -0.040$$

Taking the natural antilogarithms of both sides we have

$$[N_2O_5] = e^{-0.040} = 0.96\ \text{M}$$

Alternatively, we can apply the relation

$\ln [A]_t = \ln [A]_0 - kt$

$k = 2.2 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{min.}^{-1}$

$[A]_0 = 1.000$

$t = 18$ min.

$[A]_t = ?$

Substituting we have

$$\ln [A]_t = 1.000\ \text{mol dm}^{-3} - \left(\frac{2.2 \times 10^{-3}\ \text{mol dm}^{-3}}{1\ \cancel{\text{min.}}} \times 18\ \cancel{\text{min.}}\right)$$

So $\ln [A]_t = 0 - 0.040 = -0.040$

Finally, taking the natural antilogarithm we have

$$\ln [A]_t = e^{-0.040} = 0.96\ \text{M}$$

Example 5 Calculate the time required for 2.50 M of nitrogen dioxide to decompose to 15% of its initial concentration at the temperature at which the rate constant is 0.54 $\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, given that the decomposition is second-order.

Solution The integrated rate law for the second-order decomposition is given by the equation

$kt = \frac{1}{[A]_t} - \frac{1}{[A]_0}$

$\therefore\ t = \frac{1}{k}\left(\frac{1}{[A]_t} + \frac{1}{[A]_0}\right)$

$k = 0.54\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$
$[A]_0 = 2.50\ \mathrm{mol\ dm^{-3}}$

$[A]_t = \frac{15}{100} \times 2.50\ \mathrm{mol\ dm^{-3}} = 0.375\ \mathrm{mol\ dm^{-3}}$

$t = ?$

We now substitute to obtain

$$t = \frac{1 s \times 1\ \mathrm{mol}}{0.54\ \mathrm{dm^3}}\left(\frac{1\ \mathrm{dm^3}}{0.375\ \mathrm{mol}} - \frac{1\ \mathrm{dm^3}}{2.50\ \mathrm{mol}}\right)$$

Thus $t = \frac{1 s \times 1\ \cancel{\mathrm{mol}}}{0.54\ \cancel{\mathrm{dm^3}}}\left(\frac{2.27\ \cancel{\mathrm{dm^3}}}{1\ \cancel{\mathrm{mol}}}\right)$

$= 4.2$ s

Example 6 The following data were obtained during the measurement of the rate of formation of hydrogen iodide:

$[H_2]$ (M)	*$[I_2]$ (M)*	*r (mol dm^{-3} s^{-1})*
0.15	0.25	0.098
0.20	0.25	0.130
0.20	0.30	0.156

Determine:

(a) the order of reaction with respect to each reactant, rate law and the overall order of reaction;

(b) the rate constant at the temperature at which the experiment was performed;

(c) the rate of reaction when the concentrations of hydrogen and iodine are both 0.35 M.

Solution

(a) Since two reactants are involved, the effect of the concentration of each reactant on the rate of reaction can only be obtained by keeping the concentration of one reactant constant, and varying that of the other reactant as shown above.

As we said earlier, a reaction is zero-order in a reactant if a change in the concentration of that reactant has no effect on the reaction rate. A reaction is first-order in a particular reactant if that rate of reaction increases by the same factor in which the concentration of that reactant is increased, while it is second-order in a reactant if the factor in which the reaction rate is increased doubles that in which its concentration is increased. Assuming a reaction is of order *a* in a particular reactant if the rate of reaction increases by a factor *x* when its concentration is increased by a factor *f*, then the value of *a* is determined from the relation

$$x^a = f$$

When the concentration of hydrogen is increased from 0.15 M to 0.20 M, its concentration increases by the factor

$$x = \frac{0.20}{0.15} = 1.33$$

This increases the rate of reaction by the factor

$$f = \frac{0.130}{0.098} = 1.33$$

Since the reaction rate increases by the same factor in which the concentration is increased, then the reaction is first-order in hydrogen. We may as well substitute into the above equation to obtain

$1.33^a = 1.33$

$\therefore\ a = 1$

When the concentration of iodine is increased from 0.25 M to 0.30 M, its concentration increases by the factor

$$x = \frac{0.30}{0.25} = 1.20$$

This increases the rate of reaction by the factor

$$f = \frac{0.156}{0.130} = 1.2$$

Thus the reaction is also first-order in iodine. Consequently, the rate law is given as

$$r = k\,[H_2][I_2]$$

The overall order of reaction is obtained by summing up the order in each reactant, i.e., the power of each reactant. So the reaction is second-order overall.

(b) The rate constant can be obtained by using the rate law

$r = k\,[H_2][I_2]$

$\therefore\ k = \frac{r}{[H_2][I_2]}$

We can use the data from any of the three rows. Using the middle row, we have

$r = 0.130 \text{ mol dm}^{-3} \text{ s}^{-1}$

$[H_2] = 0.20 \text{ mol dm}^{-3}$

$[I_2] = 0.25 \text{ mol dm}^{-3}$

$k = ?$

Substituting we have

$$k = \frac{0.130 \text{ mol dm}^{-3} s^{-1}}{0.20 \text{ mol dm}^{-3} \times 0.25 \text{ mol dm}^{-3}}$$

Thus $k = \frac{0.130 \text{ mol dm}^{-3} s^{-1}}{0.050 \text{ mol}^2 \text{ dm}^{-6}}$

$= 2.6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

(c) We have to apply the rate law

$r = k\,[H_2][I_2]$

$[H_2] = [I_2]0.35 \text{ mol dm}^{-3}$

r = ?

Substituting we have

$$r = \frac{2.6\ \text{dm}^3}{1\ \text{mol} \times 1\ \text{s}} \times \left(\frac{0.35\ \text{mol}}{\text{dm}^3}\right)^2$$

$$r = \frac{2.6\ \text{dm}^3}{1\ \text{mol} \times 1\ \text{s}} \times \frac{0.123\ \text{mol}^2}{\text{dm}^6}$$

$$= 0.32\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

Example 7 The following data was obtained for the reaction A + 5B + 6C → 3D + 3E at a certain temperature:

[A](M)	*[B](M)*	*[C](M)*	*r (mol dm^{-3} s^{-1})*
0.12	0.10	0.25	0.54
0.22	0.10	0.25	1.82
0.22	0.15	0.25	2.73
0.22	0.15	0.30	3.27

Use the above data to determine the rate law of the reaction.

Solution Let the rate law be expressed as follows.

$$r = [\text{A}]^a\ [\text{B}]^b\ [\text{C}]^c$$

We must now determine the powers *a*, *b* and *c*, i.e. the order of reaction in each reactant. We will proceed as we did in the previous example, but we have to be careful to use two rows in which the concentrations of the two other reactants are constant when dealing with each reactant. Starting with A, the first two rows satisfy this requirement. When its concentration is increased from 0.12 M to 0.22 M, the concentration changed by the factor

$$x = \frac{0.22}{0.12} = 1.8$$

This increases the reaction rate by the factor

$$f = \frac{1.82}{0.54} = 3.4$$

We can now determine the order a from the equation

$x^a = f$

Thus $1.8^a = 3.4$

A very easy way of solving this equation is to introduce logarithm to both sides of the equation:

$\log 1.8^a = \log 3.4$

Thus $a \log 1.8 = \log 3.4$

So $a = \frac{\log 3.4}{\log 1.8}$

Then $a = \frac{0.53}{0.26} = 2.$

Thus the reaction is second-order in A.

Next, we determine b, the reaction order in B. The second and third rows satisfy our requirement. When the concentration of B is increased from 0.10 M to 0.15 M, its concentration increases by the factor

$$x = \frac{0.15}{0.10} = 1.5$$

This increases the reaction rate by the factor

$$f = \frac{2.73}{1.82} = 1.5$$

Since the concentration of the reactant and the reaction rate increase by the same factor, then the reaction is first-order in B.

Finally, we now determine c, i.e. the order in C. The last two rows satisfy our requirement. When the concentration of the reactant is increased from 0.25 M to 0.30 M, its concentration increases by the factor

$$x = \frac{0.30}{0.25} = 1.20$$

This increases the reaction rate by the factor

$$f = \frac{3.27}{2.73} = 1.20$$

Since the concentration of the reactant and the reaction rate increased by the same factor, then the reaction is also first-order in C. We can now substitute the order of reaction in each reactant into the above rate law to obtain

$$r = k[\mathrm{A}]^2[\mathrm{B}][\mathrm{C}]$$

Thus the reaction is of the fourth-order overall.

Example 8 The following data were obtained during the decomposition of ozone, i.e.

$$2\mathrm{O}_3(g) \rightarrow 3\mathrm{O}_2(g)$$

$[O_3]$ (M)	$[O_2]$ (M)	r (mol dm^{-3} s^{-1})
0.20	0.15	0.013
0.40	0.15	0.053
0.40	0.25	0.032

Use this information to obtain the rate law for the decomposition of ozone.

Solution Since the data show that the decomposition depends on the concentrations of ozone and oxygen, then we should write the rate law as follows:

$$r = k[\mathrm{O}_3]^a[\mathrm{O}_2]^b$$

We now have to determine a and b, i.e., the order of reaction in each substance. When the concentration of ozone increases from 0.30 M to 0.40 M, its concentration increases by the factor

$$x = \frac{0.40}{0.20} = 2.0$$

This increases the reaction rate by the factor

$$f = \frac{0.053}{0.013} = 4.1$$

The order of reaction *a* in ozone can now be obtained from the relation

$x^a = f$

$2.0^a = 4.1$

Thus $\log 2.0^a = \log 4.1$

Then $a \log 2.0 = \log 4.1$

So $a = \frac{\log 4.1}{\log 2.0}$

$\therefore\ a = \frac{0.61}{0.30} = 2$

Thus the decomposition is second-order in ozone.

Similarly, when the concentration of oxygen increases from 0.15 M to 0.25 M, its concentration increases by the factor

$$x = \frac{0.25}{0.15} = 1.7$$

This increases the reaction rate by the factor

$$f = \frac{0.032}{0.053} = 0.60$$

We can now determine the order of reaction *b* in oxygen from the relation

$x^a = f$

So $1.7^a = 0.60$

Thus $\log 1.7^a = \log 0.60$

So $a \log 1.7^a = \log 0.60$

Then $a = \frac{\log 0.60}{\log 1.7}$

$\therefore\ a = \frac{0.22}{0.23} = -1.$

Thus the decomposition is of the order of −1 in oxygen. Finally, we now substitute the reaction orders into the above rate law to obtain

$$r = k\,[O_3]^2[O_2]^{-1} \text{ or } r = k\,\frac{[O_3]^2}{[O_2]}$$

The rate law shows that the rate of decomposition of ozone decreases as the concentration of oxygen increases.

Practice Problems

1. The rate law for a second-order reaction is given by the equation $r = k\,[A]^2$. Show that the time-dependent rate law for reaction is given by the equation

$$kt = \frac{1}{[A]_t} - \frac{1}{[A]_0}$$

2. The decomposition of dinitrogen monoxide, N_2O, is governed by the rate law $r = k\,[N_2O]$. What percentage of 40.40 M of N_2O would remain after 5.0 s at a temperature at which the rate constant is 0.165 s^{-1}? [*Answer:* 45%]

3. The following data were obtained during an experiment on the decomposition of dinitrogen monoxide at a certain temperature:

t (min.)	0	1	2	3	5	6
$[N_2O]$ (M)	5.7	3.7	2.7	2.0	1.1	0.80

(a) Show that the reaction is first-order.
(b) Calculate the equilibrium constant at the prevailing temperature.
(c) At what time would the concentration of the oxide reduce to two-thirds of its initial concentration?

[*Answers:* (a) The decomposition is first-order because the plot of $\ln[N_2O]$ against time t gives a straight-line graph (b) 0.31 $min.^{-1}$ (c) 1.4 min.]

4. The following data were obtained during an experiment to determine the rate of reaction of a strong acid with a strong base at 25 °C:

$[H^+] \times 10^{-6}$(M)	*$[OH^-] \times 10^{-5}$ (M)*	*r (mol dm^{-3} s^{-1})*
1.5	2.5	5.6
1.7	2.5	6.3
1.7	3.8	9.5

From the above data determine:

(a) the rate law for the reaction;

(b) the rate constant at 25 °C;

(c) the rate of reaction when the concentrations of hydrogen and hydroxide ions are 1.5×10^{-6} M and 1.9×10^{-4} M respectively.

[*Answers:* (a) $r = k$[H+][OH–] (b) 1.5×10^{11} dm^3 mol^{-1} s^{-1} (c) 43 mol dm^{-3} s^{-1}]

5. The following data were obtained during an experiment on the rate of the reaction between nitrogen dioxide and carbon monoxide, i.e. $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$:

$[N_2O]$ (M)	*[CO] (M)*	*r (dm^3 mol^{-1} s^{-1})*
0.10	0.20	0.065
0.20	0.20	0.260
0.20	0.30	0.260

Determine the rate law for the reaction from the above data.

[*Answer:* $r = [NO_2]^2$]

13.2.1 Half-life

The half-life $t_{1/2}$ of a reactant is the time taken for its concentration to fall to half its initial value. The half-life of a first-order reaction is given by the equation

$$t_{1/2} = \frac{0.693}{k}$$

Consequently, the half-life of a first-order reaction is constant.

The half-life of a second-order reaction is inversely proportional to the initial concentration of the reactant. It is given by the equation

$$t_{1/2} = \frac{1}{k[\mathrm{A}]_0}$$

Unlike first-order half-life, the half-life of a second-order reaction is not constant. In fact, the half-life of a second-order reaction increases by a factor of 2 after each half-life. This is the same for the half-life of radioactive decay (Chapter 14).

Example 1 Derive the expression for the half-life of a first-order reaction.

Solution We start from the integrated rate law for a first-order reaction:

$\ln [\mathrm{A}]_t = \ln[\mathrm{A}]_0 - kt$ (13.13)

At half-life we have

$$[\mathrm{A}]_t = \tfrac{1}{2}[\mathrm{A}]_0$$

Substituting into Equation (13.13) we have

$\ln \tfrac{1}{2}[\mathrm{A}]_0 = [\mathrm{A}]_0 - kt_{1/2}$ (13.14)

Thus $\ln [\mathrm{A}]_0 - \ln \tfrac{1}{2}[\mathrm{A}]_0 = kt_{1/2}$ (13.15)

So $t_{1/2} = \ln \frac{[\mathrm{A}]_0}{\frac{1}{2}[\mathrm{A}]_0}$

Then $t_{1/2} = \frac{\ln 2}{k}$ (13.16)

Finally, Equation (13.16) now becomes

$t_{1/2} = \frac{0.693}{k}$ (13.17)

Example 2 Calculate the half-life for the decomposition of dinitrogen monoxide,

N_2O, at a temperature at which the rate constant is 0.76 s^{-1}, given that the reaction is first-order.

Solution Since the reaction is first-order, then we have to apply the equation

$$t_{1/2} = \frac{0.693}{k}$$

$k = 0.76\ s^{-1}$

$t_{1/2} = ?$

Substituting we have

$$t_{1/2} = \frac{0.963 \times 1s}{0.76}$$

$= 0.91$ s

Example 3 The decomposition of ethane is first-order. Calculate the rate of constant at 700°C if it takes 63 hours for 1.50 M of ethane to reduce to one-eighth of its initial value.

Solution Since the reaction is first-order, then

$$t_{1/2} = \frac{0.693}{k}$$

$$\therefore\ k = \frac{0.693}{t_{1/2}}$$

We must resist the temptation of using 63 hrs as the half-life because it is only the time taken for the initial concentration of the compound to reduce to one-eighth of its initial value. Since if takes 3 half-lives for the concentration of the reactant to fall to one-eighth of its initial value, then we have to obtain the half-life by dividing 63 hrs by 3:

$$t_{1/2} = \frac{63\ hrs}{3} = 21\ hrs$$

$k = ?$

We can now substitute to obtain

$$k = \frac{0.693}{21\ hrs}$$

$= 0.033\ \text{hr}^{-1} = 5.5 \times 10^{-4}\ \text{s}^{-1}$

Example 4 How long would it take 1.0 M of nitrogen dioxide, NO_2, to decompose to 0.25 M at a temperature at which the rate constant is 0.54 $\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, given that the reaction is second-order?

Solution We must first obtain the half-life of the original concentration of the compound. We can then calculate the total time required for the compound to decompose to 0.25 M from this value. We have to apply the equation

$$t_{1/2} = \frac{1}{k[\text{A}]_0}$$

$k = 0.54\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$

$[\text{A}]_t = 1.0\ \text{mol dm}^{-1}$

$t_{1/2} = ?$

Substituting we obtain

$$t_{1/2} = \frac{1 \times 1\ \cancel{\text{mol}} \times 1\ \text{s} \times 1\ \cancel{\text{dm}^3}}{0.54\ \cancel{\text{dm}^3} \times 1.0\ \cancel{\text{mol}}}$$

$= 1.9\ \text{s}$

During the next half-life, 0.50 M of the compound would decompose to 0.25 M. This should double the first half-life:

$t_{1/2} = 2 \times 1.9\ \text{s}$

$= 3.8\ \text{s}$

Alternatively, we can substitute into the above equation to obtain

$$t_{1/2} = \frac{1 \times 1\ \cancel{\text{mol}} \times 1\ \text{s} \times 1\ \cancel{\text{dm}^3}}{0.54\ \cancel{\text{dm}^3} \times 0.50\ \cancel{\text{mol}}}$$

$= 3.7\ \text{s}$

Note that the slight difference is due to rounding.

We can now obtain the total time required for the decomposition of the compound by adding the two half-lives:

$t = 1.9\ \text{s} + 3.7\ \text{s}$

$= 5.6\ \text{s}$

Practice Problems

1. The half-life of the first-order decomposition of a compound at a certain temperature is 0.46 s. What is the rate constant? [*Answer:* 0.15 s^{-1}]
2. Derive the equation for the half-life of a second-order reaction.
3. Calculate the time required for the second-order decomposition of 2.50 M of a compound to 0.3125 M, at a temperature at which the rate constant is 0.50 $dm^3\ mol^{-1}\ s^{-1}$.

[*Answer:* 12 s]

13.2.2 Temperature and Rate Constant

The relationship between temperature and rate constant is given by the Arrhenius equation

$$\ln k = \ln A - \frac{E_a}{RT} \text{ or } k = Ae^{-Ea/RT}$$

where k = The rate constant.

A = Frequency or preexponential factor.

E_a = Activation energy in J mol^{-1}.

T = The absolute temperature.

R = The universal gas constant in J mol^{-1} K^{-1}.

This equation leads to another equation which relates the rate constants at two different temperatures:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{RT}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{ or } \log \frac{k_1}{k_2} = \frac{E_a}{2.303\,RT}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where k_1 and k_2 are the rate constants at temperatures T_1 and T_2 respectively.

Example 1 Calculate the rate constant for the first-order decomposition of N_2O_5 at 30°C.

(R = 8.314 J K^{-1} mol^{-1}, E_a = 88 kJ mol^{-1}, $A = 6.3 \times 10^{14}$ s^{-1})

Solution We have to apply the equation

$k = Ae^{-Ea/RT}$

$A = 6.3 \times 10^{14}$ s^{-1}

T = 30°C + 273 K = 303 K

$R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}$

$E_a = 88 \times 1000 \text{ J mol}^{-1} = 88000 \text{ J mol}^{-1}$

$k = ?$

Thus $\frac{E_a}{RT} = \frac{88000 \cancel{\text{J}} \cancel{\text{mol}^{-1}} \times 1 \cancel{\text{K}}}{8.314 \cancel{\text{J}} \cancel{\text{mol}^{-1}} \times 303 \cancel{\text{K}}} = 34.9$

Substituting we have

$k = 6.3 \times 10^{14} \text{ s}^{-1} \times e^{-34.9}$

Thus $k = 6.3 \times 10^{14} \text{ s}^{-1} \times 7.0 \times 10^{-16}$

$= 0.44 \text{ s}^{-1}$

Example 2 The rate constant for the first-order decomposition of N_2O at 800 K is $3.8 \times 10^{-5} \text{ s}^{-1}$. What is the activation energy of the reaction?

($R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}$, $A = 8.0 \times 10^{11} \text{ s}^{-1}$)

Solution We know that

$\ln k = \ln A - \frac{E_a}{RT}$

$\therefore E_a = RT(\ln A - \ln k)$

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$A = 8.0 \times 10^{11} \text{ s}^{-1}$

$k = 3.8 \times 10^{-5} \text{ s}^{-1}$

$T = 800 \text{ K}$

$E_a = ?$

Substituting we have

$E_a = \frac{8.314 \text{ J mol}^{-1}}{1 \cancel{\text{K}}} \times 800 \cancel{\text{K}} (\ln 8.0 \times 10^{11}\text{s}^{-1} - \ln 3.8 \times 10^{-5}\text{s}^{-1})$

So $E_a = 6651.2 \text{ J mol}^{-1} \times [(27.4 - (-10.2)]$

Thus $E_a = 6651.2 \text{ J mol}^{-1} \times 37.6$

$= 250 \text{ kJ mol}^{-1}$

Example 3 The following data were obtained during an experiment on the rate of the reaction $2N_2O_5(g) \rightarrow 2NO(g) + O_2(g)$:

Temperature (°C)	298	350	400	450	460
k (s^{-1})	0.24	46.37	2031.93	38435.66	64006.57

Use these data to obtain the activation energy and preexponential factor of the reaction.

(R = 8.314 J K^{-1} mol^{-1})

Solution A comparison of the Arrhenius equation ln k = ln A– $\frac{E_a}{RT}$ equation of a straight line, i.e.
$y = mx + c$ shows that a plot of ln k against $1/T$ would produce a straight-line graph of slope $-E_a/R$, and intercept ln A on the y-axis. Thus we can determine the activation energy of the reaction by equating the slope of the graph obtained from the above data to $-E_a/R$; and the preexponential factor by measuring the intercept on the y-axis.

The very first step is to draw up the table of data as follows:

Temperature (K)	*k* (s^{-1})	$1/T \times 10^{-3}$	*ln k*
298	0.24	3.36	−1.43
350	46.37	2.86	3.84
400	2031.93	2.50	7.62
450	38435.66	2.22	10.56
460	64006.57	2.17	11.07

The plot of ln k against $1/T$ is shown below.

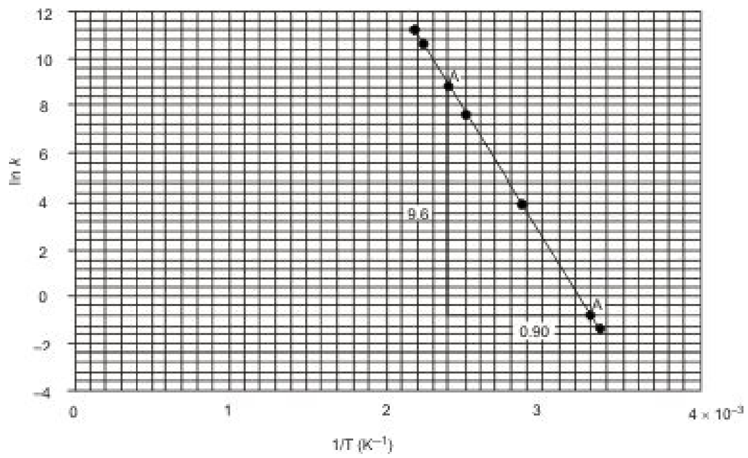

Figure 13.3 Graph of ln *k* against 1/*T*.

The slope of the graph is calculated from the coordinates of points A and B:

$$s = \frac{(\ln k)_B - (\ln k)_A}{(1/T)_B - (1/T)_B}$$

So $s = \frac{-9.6 \times 1\ \mathrm{K}}{0.90 \times 10^{-3}} = 10666.7\ \mathrm{K}$

We now equate the slope to $-E_a/R$ to obtain

$$-\frac{E_a}{R} = -10666.7\ \mathrm{K}$$

So $E_a = -R \times (-10666.7\ \mathrm{K})$

$R = 8.314\ \mathrm{J\ K^{-1}\,mol^{-1}}$

Substituting we obtain

$$E_a = -\frac{8.314\ \mathrm{J\ mol^{-1}}}{1\ \cancel{\mathrm{K}}} \times (-\ 10666.7\cancel{\mathrm{K}})$$

$= 88.7\ \mathrm{kJ\ mol^{-1}}$

Example 4 Show that the rate constants at two different temperatures are related by the equation

$$\ln\frac{k_1}{k_2} = \frac{E_a}{RT}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Solution We have to start from the Arrhenius equation

$$\ln k = \ln A - \frac{E_a}{RT} \quad (13.18)$$

where E_a, A and R are constants.

At temperature T_1 the rate constant is k_1. Substituting into Equation (13.18) we have

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad (13.19)$$

Similarly, at temperatute T_2 the rate constant is k_2. Substituting into Equation (13.19) we have

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad (13.20)$$

Subtracting Equation (13.20) from (13.19) we obtain

$$\ln k_1 - \ln k_2 = \left(\ln A - \frac{E_a}{RT_1}\right) - \left(\ln A - \frac{E_a}{RT_2}\right) \quad (13.21)$$

So $\ln k_1 - \ln k_2 = \ln A - \frac{E_a}{RT_1} - \ln A + \frac{E_a}{RT_2}$

Thus $\ln k_1 - \ln k_2 = -\frac{E_a}{RT_1} + \frac{E_a}{RT_2} \quad (13.22)$

Finally, Equation (13.22) now simplifies to

$$\ln \frac{k_1}{k_2} = \frac{E_a}{RT}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{ or } \ln \frac{k_2}{k_1} = \frac{E_a}{RT}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Example 5 Calculate the rate constant for the decomposition of N_2O at 550°C if its rate constant is $0.76\ s^{-1}$ at 727°C.

$(E_a = 250\ \text{kJ mol}^{-1},\ R = 8.314\ \text{J K}^{-1}\text{mol}^{-1})$

Solution We have to apply the above equation

$\ln \frac{k_1}{k_2} = \frac{E_a}{RT}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$T_1 = 727°\text{C} + 273\ \text{K} = 1000\ \text{K}$

$T_2 = 550°\text{C} + 273 = 823\ \text{K}$

$k_1 = 0.76\ \text{s}^{-1}$

$R = 8.314\ \text{J K}^{-1}\text{mol}^{-1}$

$E_a = 250000\ \text{J mol}^{-1}$

$k_2 = ?$

Substituting we have

$\ln \frac{0.76\ ^{-1}}{k_2} = \frac{250000\ \text{J mol}^{-1} \times 1\ \text{K}}{8.314\ \text{J mol}^{-1}}\left(\frac{1}{823\ \text{K}} - \frac{1}{1000\ \text{K}}\right)$

So $\ln \frac{0.76\ s^{-1}}{k_2} = \frac{250000\ \cancel{J}\ \cancel{\text{mol}^{-1}} \times 1\ \cancel{K}}{8.314\ \cancel{J}\ \cancel{\text{mol}^{-1}}} \times \frac{2.15 \times 10^{-4}}{1\ \cancel{K}}$

Thus $\ln \frac{0.76\ s^{-1}}{k_2} = 6.46$

Taking the natural antilogarithms of both sides we have

$$\frac{0.76\ s^{-1}}{k_2} = e^{6.46} = 639$$

Cross-multiplying we obtain

$k_2 \times 639 = 0.76\ \text{s}^{-1}$

$\therefore\ k_2 = \frac{0.76\ s^{-1}}{639}$

$= 1.2 \times 10^{-3}\ \text{s}^{-1}$

Example 6 Calculate the temperature at which the rate constant of the acid hydrolysis of starch will be one-third its value at 40°C?

($E_a = 108$ kJ mol^{-1}, $R = 8.314$ J K^{-1}mol^{-1})

Solution We have to apply the equation

$$\ln \frac{k_1}{k_2} = \frac{E_a}{RT}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Let the rate constant at 40°C be *k*. Then

$k_1 = k$

$k_2 = k/3$

$T_1 = 40°C + 273\ K = 313\ K$

$R = 8.314\ J\ K^{-1} mol^{-1}$

$E_a = 108000\ J\ mol^{-1}$

$T_2 = ?$

Substituting we obtain

$$\ln \frac{k}{k/3} = \frac{108000\ \cancel{J}\ \cancel{mol^{-1}} \times 1\ K}{8.314\ \cancel{J}\ \cancel{mol^{-1}}}\left(\frac{1}{T_2} - \frac{1}{313\ K}\right)$$

Then $\ln \frac{3\cancel{k}}{\cancel{k}} = \frac{12990.14\ K}{T_2} - \frac{12990.14\ \cancel{K}}{313\ \cancel{K}}$

Thus $1.099 = \frac{12990.14\ K}{T_2} - 41.5$

So $\frac{12990.14\ K}{T_2} = 1.099 + 41.5 = 42.6$

Cross-multiplying we have

$12990.14\ K = T_2 \times 42.6$

$\therefore\ T_2 = \frac{12990.14\ K}{42.6}$

$= 305\ K$

Example 7 The rate constants of a reaction are $6.9 \times 10^{-7}\ s^{-1}$ and 1.1×10^{-4} at 723 K and 823 K respectively. Calculate the activation energy of the reaction.

(R = 8.314 J K^{-1} mol^{-1})

Solution We have to apply the equation

$$\ln \frac{k_1}{k_2} = \frac{E_a}{RT}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

k_1 = 6.9 × 10^{-7} s^{-1}
k_2 = 1.1 × 10^{-4} s^{-1}
T_1 = 723 K
T_2 = 823 K
R = 8.314 J K^{-1} mol^{-1}
E_a = ?

Substituting we obtain

$$\ln \frac{6.9\times10^{-7}\ \cancel{s^{-1}}}{1.1\times10^{-4}\ \cancel{s^{-1}}} = \frac{E_a\times1\ \text{K}}{8.314\ \text{J mol}^{-1}}\left(\frac{1}{823\ \text{K}} - \frac{1}{723\ \text{K}}\right)$$

Thus $-5.07 = \dfrac{E_a\times1\ \cancel{\text{K}}}{8.314\ \text{J mol}^{-1}}\times\left(-\dfrac{1.68\times10^{-4}}{1\ \cancel{\text{K}}}\right)$

Then $-5.07 = -\dfrac{1.68\times10^{-4}\times E_a}{8.314\ \text{J mol}^{-1}}$

Cross-multiplying we have

$-1.68\times10^{-4}\times E_a = -5.07\times8.314$ J mol^{-1} = -42.15 J mol^{-1}

$\therefore\ E_a = \dfrac{-42.15\ \text{J mol}^{-1}}{-1.68\times10^{-4}}$

= 250 kJ mol^{-1}

Example 8 The use of a catalyst reduces the activation energy of a reaction from 384 kJ mol^{-1} to 184 kJ mol^{-1}. By what factor would the reaction rate increase at 637°C?

(R = 8.314 J mol^{-1} K^{-1})

Solution Since the reaction rate is directly proportional to the rate constant, we know that the reaction rate would also increase by the same factor by which the rate constant increases. The factor by which the rate constant is increased is obtained by dividing the rate constant when the catalyst is added by that in the absence of the catalyst, at the same temperature. The rate constant in each case has to be obtained from the equation

$$k = Ae^{-Ea/RT}$$

We have no idea of the value of the prexponential factor. However, this need not constitute any problem since it is a constant which will eventually cancel out. We begin from when the reaction is not catalysed:

E_a = 384000 J mol^{-1}
T = 637°C + 273 K = 910 K
k_1 = ?

Thus $\frac{E_a}{RT} = \frac{384000\ \cancel{J}\ \cancel{mol^{-1}} \times 1\ \cancel{K}}{8.314\ \cancel{J}\ \cancel{mol^{-1}} \times 910\ \cancel{K}} = 50.8$

Substituting into the above equation we have

$k_1 = Ae^{-50.8}$
Thus $k_1 = A \times 8.7 \times 10^{-23}$ (13.23)

We now calculate the rate constant for the catalysed reaction at the same temperature:

E_a = 184000 J mol^{-1}
T = 910 K
k_2 = ?

Thus $\frac{Ea}{RT} = \frac{184000\ \cancel{J}\ \cancel{mol^{-1}} \times 1\ \cancel{K}}{8.314\ \cancel{J}\ \cancel{mol^{-1}} \times 910\ \cancel{K}} = 24.3$

Substituting into the above equation we have

$k_2 = Ae^{-24.3}$
Thus $k_2 = A \times 2.8 \times 10^{-11}$ (13.24)

We now divide Equation (13.24) by (13.23) to obtain

$$\frac{k_2}{k_1} = \frac{\cancel{A} \times 2.8 \times 10^{-11}}{\cancel{A} \times 8.7 \times 10^{-23}}$$

$$= 3.2 \times 10^{11}$$

Thus the catalyst increases the reaction rate by 3.2×10^{11} times.

Practice Problems

1. Calculate the rate constant of the first-order decomposition of N_2O at 350°C.

   (E_a = 250 kJ mol^{-1}, $A = 8.0 \times 10^{11}$ dm^3 mol^{-1} s^{-1}, R = 8.314 J K^{-1} mol^{-1})

   [*Answer:* 8.7×10^{-10}]

2. The following table shows the variation of the rate constant of the second-order acid hydrolysis of sucrose.

Temperature (°C)	20	30	40	50	60
$k \times 10^{-5}$ *(*dm^3 mol^{-1} s^{-1}*)*	8.3	36	140	510	1700

Determine the activation energy of the reaction.

[*Answer:* 108 kJ mol^{-1}]

3. What is the rate constant for the decomposition of N_2O_5 at 35 °C if the rate constant is 3.7×10^{-5} s^{-1} at 25 °C?

   (E_a = 88 kJ mol^{-1}, R = 8.314 J K^{-1} mol^{-1}) [*Answer:* 1.2×10^{-4} s^{-1}]

4. The rate constants for the reaction $H_2(g) + I_2(g) \xrightarrow{\Delta, Pt}$ HI (g) are 4.4×10^{-4} dm^3 mol^{-1} s^{-1} and 2.4×10^{-3} dm^3 mol^{-1} s^{-1} at 600 K and 700 K respectively. What is the activation energy of the reaction?

   (R = 8.314 J mol^{-1} K^{-1}) [*Answer:* 59 kJ mol^{-1}]

SUMMARY

- The rate of chemical reaction is the speed at which the products are being formed, or the speed at which the reactants disappear.
- Factors which influence the rate of chemical reaction include temperature, concentration, nature of reactants, catalysts, light, suface area of reactants

and pressure.

- The collision theory assumes that there must be collisions between the particles of reactants before chemical reaction can occur. The collisions that result in the formation of products are called effective collisions.
- A rate law is an equation expressing the rate of reaction in terms of the concentration(s) of the substance(s) involved in the reaction.
- The order of reaction is the power to which the concentration of a reactant is raised in a rate law.
- The order of reaction in a substance is the power to which its concentration is raised in a rate law when it is not the only substance appearing in the rate law.
- The order of a reaction with respect to a particular reactant is obtained from the equation

$$x^a = f$$

- The overall order of reaction is the sum of the powers or exponents of the substances appearing in a rate law.
- The differential form of a rate law shows the variation of concentrations of substances with time.
- An integrated rate law is obtained by integrating the differential form of a rate law.
- The integrated rate law for a zero-order reaction is

$$kt = [\mathrm{A}]_0 - [\mathrm{A}]_t$$

- The integrated rate law for a first-order reaction is

$$kt = \ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}$$

- The integrated rate law for a second-order reaction is

$$kt = \frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0}$$

- The half-life $t_{1/2}$ of a reaction is the time taken for the concentration of a reactant to fall to half its initial value.
- The half-life of a first-order reaction is given as

$$t_{1/2} = \frac{0.693}{k}$$

- The half-life of a second-order reaction is given as

$$t_{1/2} = \frac{1}{k[\mathrm{A}]_0}$$

- The temperature dependence of reaction rate is given by the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \text{ or } k = Ae^{-E_a/RT}$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{RT}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{ or } \log \frac{k_1}{k_2} = \frac{E_a}{2.303\,RT}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. Which of these is a correct unit of rate of chemical reaction?
   A. g cm^{-3} B. g $cm^{-3}\,s^{-1}$
   C. $cm^3\,s^{-1}$ D. $cm^3\,s^{-2}$
   E. $cm^3\,mm^{-2}$
2. 0.075 M of a product was formed in 30.0 s during a reaction. What is the rate of reaction?
   A. 0.0025 mol $dm^{-3}\,s^{-1}$ B. 0.035 mol $dm^{-3}\,s^{-1}$
   C. 0.25 mol $dm^{-3}\,s^{-1}$ D. 0.75 mol $dm^{-3}\,s^{-1}$
   E. 0.082 mol $dm^{-3}\,s^{-1}$
3. How long would it take 10.0 g of a product to be formed if the reaction rate is 0.40 g $min.^{-1}$?
   A. 10 min. B. 18 min.
   C. 25 min. D. 30 min
   E. 40 min.
4. Dinitrogen pentoxide, N_2O_5, decomposes according to the equation $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. What is the rate of formation NO_2 when the rate of decomposition of N_2O_5 is 0.045 mol $dm^{-1}\,s^{-1}$?
   A. 0.022 mol $dm^{-1}\,s^{-1}$ B. 0.023 mol $dm^{-1}\,s^{-1}$
   C. 0.045 mol $dm^{-1}\,s^{-1}$ D. 0.090 mol $dm^{-1}\,s^{-1}$
   E. 0.180 mol $dm^{-1}\,s^{-1}$
5. Consider the reaction:

$$C_2H_5Br(aq) + OH^-(aq) \rightarrow C_2H_5OH(aq) + Br^-(aq)$$

The rate of the reaction can be increased by all the following methods except

A. using a catalyst.
B. raising the temperature.
C. increasing the concentrations of the reactants.
D. increasing the pressure.
E. none of the above.

6. What is the overall-order of the reaction represented by the rate law $r = \frac{[SO_2]}{[SO_3]^{1/2}}$?

A. –3/2 B. –1/2
C. 1/2 D. 1/2
E. 3/2

7. A reaction is represented by the rate law $r = \frac{[O_3]^2}{[O_2]^x}$.

Of what order is the reaction in O_2 if the reaction is of the first-order overall?

A. –3/2 B. −1
C. 1 D. 2
E. 3

8. How long would it take 0.500 M of a substance to decompose to 0.125 M if the decomposition is first-order?

$(k = 1.0 \times 10^{-3}\ s^{-1})$

A. 177 s B. 693 s
C. 800 s D. 840 s
E. 1390 s

9. Which of these is/are **NOT** true of a zero-order reaction?

A. The rate constant is the same as the rate of reaction.
B. The power to which the concentration of the reactant is raised in its rate law is zero.
C. The rate constant has the unit of s^{-1}.
D. The rate constant has the unit of mol $dm^{-3}\ s^{-1}$.
E. C and D

10. Which of these is the correct unit for the rate constant of a second-order

reaction?

A. s^{-1} B. mol dm^{-3}

C. dm^3 mol^{-1} s^{-1} D. $mol^{-1} s^{-1}$

E. $dm^3 s^{-1}$

11. What is the third half-life of the second-order decomposition of a compound, given that its first half-life is 20 s?

A. 20 s B. 40 s

C. 80 s D. 84 s

E. 120 s

12. A catalyst increases the rate of chemical reaction by

A. speeding up the rate at which the particles collide.

B. raising the activation energy.

C. reducing the frequency factor.

D. providing alternative pathway for reaction.

E. increasing the surface area of the reactants.

ESSAY TYPE QUESTIONS

Rates of reaction

13. (a) What is reaction rate?

(b) The concentration of hydrochloric acid decreased by 0.25 M in 7.0 min. during the reaction between sodium hydroxide and the acid. What is the rate of reaction?

(c) 5.0 g of zinc chloride was formed in 5 min. when zinc granules were added to a concentrated acid solution. Calculate the rate of reaction.

14. Explain how each the following affects the rate of chemical reaction:

(a) Temperature (b) Addition of a catalyst (c) Surface area of reactants (d) Pressure (e) Nature of reactants (f) Light.

15. Explain the following:

i. Activation energy ii. Frequency of collision iii. Collision theory iv. Effective collision

16. The following data were obtained during the decomposition of hydrogen peroxide:

t (s)	0	10	20	30	40	50	60	70	80	90
V (cm ^{3}*)*	0	5	10	15	20	25	30	30	30	30

(a) Plot the graph of the volume oxygen against time.

(b) From the graph, determine the rate of chemical reaction between 5 and 25 s.

(c) Why was the volume of oxygen constant between 60 and 90 s?

Rate law

17. State the overall order of each reaction represented by the following rate laws:

(a) $r = k\,[NO_2]^2\,[O_2]^0$ (b) $r = k\,[NO_2]^2\,[O_2]$ (c) $r = \frac{[O_3]^2}{[O_2]}$ (d) $r = \frac{[SO_2]}{[SO_2]^{1/2}}$

18. Obtain the integrated rate laws of the reactions represented by the following rate laws:

i. $r = k\,[A]^n$ ii. $r = k\,[A][B]$

19. A second-order reaction has a rate constant of 0.77 dm^3 mol^{-1} s^{-1}. How long would it take 1.85 M of the reactant to reduce to 0.232 M?

20. The concentration of a particular reactant falls to 0.76 M in 2.0 min. Calculate its initial concentration if the reaction is zero-order. Assume the rate constant to be 1.5×10^{-4} mol dm^{-3} s^{-1}.

21. What concentration of 2.50 M of cyclopropane would remain after an hour following its first-order decomposition to propene, at a temperature at which the rate constant is 5.5×10^{-4} s^{-1}?

22. The decomposition of dinitrogen monoxide is represented by the rate law $r = k[N_2O]$. Given that the decomposition is first-order and that the concentration of the oxide reduced from 1.5 M to 0.29 M in 30.0 s, determine the rate of decomposition at the prevailing temperature.

23. The following data were obtained for the reaction $C_2H_6(g) \rightarrow 2CH_3(g)$ at 300°C:

t (min.)	0	10	20	30	40	50

[C_2H_6] (M)	0.96	1.34	1.85	2.58	3.59	5.00

(a) Confirm that the reaction is first-order.
(b) What is the rate constant at 300°C?
(c) Predict the concentration of ethane after 25 min. of the experiment.
(d) At what time would the concentration of ethane fall to 0.50 M?

24. The following data were obtained for the reaction $2ICI(g) + H_2(g) \rightarrow I_2(g) + 2HCl(g)$ at a particular temperature:

t (min.)	0	5	10	15	20	25	30
[H_2](M)	2.50	2.48	2.46	2.44	2.42	2.40	2.30

Confirm that the reaction is first-order in H_2.

25. The following data were obtained during the decomposition of nitrogen dioxide at a certain temperature:

t (s)	0	600	1200	1800	2400	3600
[NO_2](M)	2.50	3.08×10^{-3}	3.86×10^{-3}	2.57×10^{-3}	7.70×10^{-4}	5.14×10^{-3}

(a) Confirm that the reaction is second-order and calculate the reaction rate.
(b) At what temperature was the experiment performed if the rate constant at 300°C is 0.54 mol dm^{-3} s^{-1}?

26. The following data were obtained for the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$ at 600 K, with the same initial concentrations of hydrogen and iodine:

t (s)	0	10	20	30	40	50

$[H_2]$ (M)	1.50	0.77	0.52	0.39	0.31	0.26

(a) What is the order of the reaction and rate constant at 600 K?

(b) What concentration of iodine will remain after 1.5 min.?

27. (a) What is meant by the statement: the half-life of a chemical reaction is 1.5 min.?

(b) The decomposition of nitrogen dioxide is represented by the rate law $r = k\,[NO_2]^2$. What concentration of the oxide would remain after 62.23?

$$(k = 0.050\ \text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1})$$

(c) How long would it take 0.54 M of hydrogen iodide to fall to 0.0675 M, given that the decomposition is second-order?

$$(k = 1.8\ \text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1})$$

28. Obtain the relations for the half-lives of the following:

i. First-order reactions ii. Second-order reactions

29. How long would it take 5.20 M of a compound undergoing a first-order decomposition to reduce to one-sixteenth its initial concentration?

$$(k = 0.25\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$$

30. (a) What is the half-life of a first-order reaction whose rate constant is $1.7 \times 10^{-3}\,\text{s}^{-1}$?

(b) The half-life of a first order reaction is 17.2 hours; what is its rate constant in s^{-1}?

31. The following data were obtained for the reaction $2ICl(g) + H_2(g) \rightarrow I_2(g) + 2HCl(g)$:

[ICl] (M)	*$[H_2]$ (M)*	*r (mol dm^{-3} s^{-1})*
0.20	0.15	4.50
0.20	0.30	9.00
0.15	0.15	3.38

(a) Obtain the rate law and overall order of the reaction.

(b) Calculate the rate constant at the prevailing temperature.

(c) What is the rate of reaction when $[H_2]$ increased from 0.30 M to 0.60 M, with [ICI] kept constant at 0.20 M?

32. The following data were obtain for the reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$:

[NO] (M)	*$[O_2]$ (M)*	*r (mol dm^{-3} s^{-1})*
0.10	0.20	3.00
0.15	0.20	6.75
0.15	0.40	13.50

Obtain the rate law and evaluate the rate constant.

33. The following data were obtained for the reaction $2SO_2(g) + O_2(g) \xrightarrow{Pt} 2SO_3(g)$:

$[SO_2]$ (M)	*$[SO_3]$ (M)*	*r (mol dm^{-3} s^{-1})*
0.15	0.10	0.71
0.15	0.20	0.50
0.30	0.20	1.01

Obtain the rate law and evaluate the rate constant.

34. The following data were obtained during a reaction of the form A + B + C → Products:

[A] (M)	*[B] (M)*	*[C] (M)*	*r* ($mol\ dm^{-3}\ s^{-1}$)
1.20	1.20	1.50	2.84×10^{-3}
1.20	1.20	2.50	4.73×10^{-3}
2.40	1.20	2.50	1.90×10^{-2}
1.20	2.80	2.50	7.20×10^{-3}

Obtain the rate law and evaluate the rate constant.

35. The following data were obtained during an experiment on the rate of a reaction:

T (K)	1500	2000	2500	3000	3500	4000
k ($dm^{3}\ mol^{-1}\ s^{-1}$)	7.73×10^{10}	8.41×10^{11}	3.87×10^{12}	1.12×10^{13}	2.44×10^{13}	4.43×10^{13}

(a) What is the activation energy?

(b) Predict the rate constant at 3700 °C?

(R = 8.314 J mol^{-1} K^{-1})

36. The following data were obtained for the reaction $CH_3{-}CN(g) \rightarrow CH_3{-}NC(g)$:

T (°C)	227	247	267	287	307	327
k ($dm^{3}\ mol^{-1}\ s^{-1}$)	0.077	0.034	1.4	4.8	16	47

(a) What is the activation energy?

(b) Predict the rate constant at 3700°C?

(R = 8.314 J K^{-1} mol^{-1})

37. The rate constant of a reaction is 9.14×10^{-3} s^{-1s} at 27°C. Predict the rate constant at 50°C.

(E_a = 88 kJ mol^{-1}, R = 8.314 J K^{-1} mol^{-1})

38. The rate constant of a reaction is 6.63×10^{-14} s^{-1} at 227°C. At what temperature would the rate constant be 2.50×10^{-7}?

(E_a = 250 kJ mol^{-1} R = 8.314 J K^{-1}mol^{-1})

39. The rate constants of a reaction are 1.75×10^{-55}s^{-1} and 1.78×10^{-33}s^{-1}at 27°C and 127°C respectively. What is the activation energy of the reaction?

(R = 8.314 J K^{-1} mol^{-1})

40. The rate constant of a reaction is 2.26×10^{-32} s^{-1} at 27°C. Predict the temperature at which the rate constant would be 2.50×10^{-30}s^{-1}.

(E_a = 184 kJ mol^{-1},R = 8.314 J K^{-1}mol^{-1})

41. (a) What is a catalyst?

(b) State and explain the two types of catalysts.

42. The addition of a catalyst reduces the activation energy of a reaction from 150 kJ mol^{-1} to 88 kJ mol^{-1}. By what factor is the reaction rate increased?

43. The addition of a catalyst reduces the activation energy of a reaction from 384 kJ mol^{-1} to 100 kJ mol^{-1}. By what factor is the reaction rate increased?

44. (a) How would you obtain the activation energy of a reaction from the Arrhenius plot of the reaction data?

(b) Show that the reaction rates at two different temperatures are related by the equation

$$\ln\frac{k_2}{k_1} = \frac{E_a}{RT}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

where k_1 and k_2 = The rate constants at temperatures T_1 and T_2 respectively.

E_a = The activation energy in J mol^{-1}.

R = The universal gas constant.

45. Calculate the rate constant of the reaction $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$ at 327°C.

(E_a = 250 kJ mol^{-1}, $A = 8.0 \times 10^{11}$ dm^3 mol^{-1}s^{-1}, R = 8.314 J K^{-1}mol^{-1})

46. The rate constant of a reation is 3.6×10^{-4} dm^3 mol^{-1} s^{-1} at 30°C. What is the activation energy of the reaction?

($A = 1.5 \times 10^{15}$ dm^3 mol^{-1} s^{-1}, $R = 8.314$ J K^{-1} mol^{-1})

Answers

1. C 2. A 3. C 4. D
5. D 6. C 7. B 8. E
9. C 10. C 11. C 12. D
13. (b) 0.036 mol dm^{-3} min.$^{-1}$ (c) 1 g min.$^{-1}$
17. (a) 2 (b) 3
(c) 1 (d) ½
19. 4.9 s 20. 0.78 M 21. 0.35 M 22. 1.8 mol dm^{-3} s^{-1}
27. (a) It would take 1.5 minutes for the initial concentration of the reactant to fall to half its initial value.
(b) 0.281 g (c) 7.21 s
29. 11.1 s
30. (a) 6.8 min. (b) 6.72×10^{-4} s^{-1}
31. (a) $r = k[\mathrm{ICI}][\mathrm{H_2}]$, 2 (b) 150 dm^3 mol^{-1} s^{-1}
(c) 18 mol dm^{-3} s^{-1}
32. $r = k[\mathrm{NO}]^2[\mathrm{O_2}]$, k = 1.5×10^3 dm^6 mol^{-2} s^{-1}
33. $r = k[\mathrm{SO_2}][\mathrm{SO_3}]^{-1/2}$ or $\frac{k[\mathrm{SO_2}]}{[\mathrm{SO_3}]^{1/2}}$, $k = 1.5$ mol$^{1/2}$ dm$^{-3/2}$ s^{-1}
34. $r = k[\mathrm{A}]^2[\mathrm{B}]^{1/2}[\mathrm{C}]$, $k = 1.2 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}
37. 0.112 dm^{-3} mol^{-1} s^{-1} 38. 395°C
39. 506 kJ mol^{-1} 40. 47°C
45. 1.4×10^{-10} s^{-1} 46. 108 kJ mol^{-1}

14

Chapter Nuclear Chemistry

14.1 RADIOACTIVITY

Radioactivity is the spontaneous emission of radiations from the nuclei of atoms. Elements whose atoms behave in this way are called radioactive elements. Examples include polonium, uranium, radium, radon, curium, etc. Radioactivity was discovered by Henri Becquerel in 1896. Very prominent among pioneer researchers in this branch of chemistry were Pierre and Marie Curie (Figure 14.2). Marie Curie (née Sklodowska) discovered radium and polonium. The radioactive element curium is named after Pierre and Marie Curie.

Figure 14.1 Henri Becquerel, French chemist and physicist. Becquerel was the doctoral advisor to Marie Curie. He was awarded half the Nobel Prize for Physics in 1903.

There are three main types of radiations: a (alpha) particles, b (beta) particles and g (gamma) radiation. The properties of these radiations are summarized in Table. 14.1. Common devices used for detecting radiations are Geiger-Muller counter, diffusion cloud chamber and scintillation counter.

Table 14.1 Properties of nuclear radiations

Property	a *particle*	b *particle*	g *radiaion*
Nature	Helium nucleus ($^{4}_{2}$He)	Electron ($^{0}_{-1}$He)	Photon or electromagnetic radiation
Penetration	Not penetrating, relative penetration of 1	Moderately penetrating, relative penetration of 100	Highly penetrating, relative penetrative penetration on of 10000
Velocity	$\frac{1}{20}$ of c[1]	Varies from 3-99%	c c
Ionization	Highly ionizing	Moderately ionizing	Not ionizing
Absorber	Thin sheet of paper	Metal sheet	Thick block of lead
Effect of electrostatic field	Deflected towards the positive plate	Deflected towards the negative plate	Not deflected
Mass	4 amu	Mass of electron, i.e.	None
		$\frac{1}{1840}$ amu	
Charge	+2	−1	None

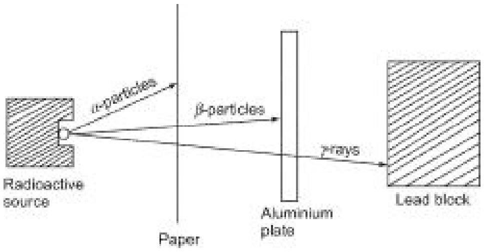

Figure 14.3 The penetrating powers of the nuclear radiations.

[1] Speed of light = 3.00×10^{8} ms^{-1}.

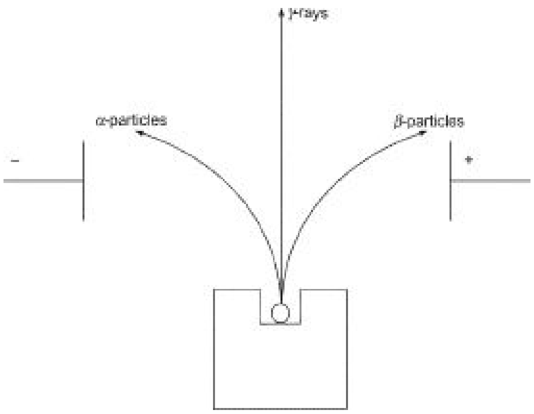

Figure 14.4 Behaviour of the three types of radiations in electrostatic field. This shows alpha particles as positively charged, beta particles as negatively charged and gamma radiation as uncharged.

Great care must be taken when dealing with sources of radiations as nuclear radiations are dangerous. They cause death or serious illness, such as cancer, by interferring with physiological processes when absorbed above safe limits. Measures that should be taken include wearing of protective clothings, undergoing routine medical check-up, and surrounding sources of radiations with materials, such as lead bricks or thick concrete for g rays, that can absorbed radiations. Moreover, nuclear wastes must be properly processed into harmless substances, or disposed properly by following applicable safety regulations.

Radioactive elements are used in medicine for the sterilization and treatment of cancer. They are also used for pest control, dating, testing pipelines for leakages, controlling and testing the thickness of materials, etc.

14.1.1 Radioactive Decay and Nuclear Equations

A nucleus is said to have decayed or disintegrated when it emits a or b particle. The lighter nucleus formed from radioactive decay is called the daughter nucleus.

The identity of the daughter nucleus depends on the radioactive nucleus and the type of radiation emitted. When a nucleus emits an a particle, its mass and atomic number decrease by 4 and 2 respectively. Thus an alpha particle corresponds to a helium nucleus. Consequently, an alpha decay is balanced with a helium nucleus in nuclear equations:

$$ {}^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}Y + {}^{4}_{2}He $$

When a nucleus emits a b particle, its atomic number increases by 1 but its mass number is unaltered. In writing a nuclear equation, a beta decay is balanced by adding an electron to the daughter nucleus:

$$^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z+1}\mathrm{Y} + {}^{0}_{-1}\mathrm{e}$$

The mass and atomic number of a nucleus remain unchanged when it emits g rays.

Radioactive nuclei undergo spontaneous disintegration until they produce stable nuclei, i.e., nuclei that are not radioactive. This process is called radioactive series. For example, uranium-238 undergoes spontaneous decay until lead-206, a non-radiocative nucleus, is formed.

Radioactive decay obeys the first-order rate law called the law of radioactive decay *r*, which is proportional to the mass or number of the radioactive atoms or nuclei originally present in a sample:

$r = \mathrm{g} \times N$ or $r = \mathrm{g} \times m$ (14.1)

where m = The mass of the radioisotope (radioactive element).

N = The number of radioactive nuclei or atoms.

The differential rate law for the decay is given by

$$r = -\frac{\mathrm{d}N}{\mathrm{d}t} \quad (14.2)$$

The minus sign indicates that the mass or number of the radioactive atoms or nuclei decreases with time.

We now equate Equations (14.1) and (14.2) to obtain

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = \mathrm{l}N \quad (14.3)$$

Cross-multiplying we have

$$\mathrm{d}N = -\mathrm{l}N\mathrm{d}t \quad (14.4)$$

Dividing Equation (14.4) by *N* we have

$$\frac{\mathrm{d}N}{N} = -\mathrm{l}\mathrm{d}t \quad (14.5)$$

We now integrate Equation (14.5) within the limits $N = N_0$ at $t = 0$, and $N = N$ at $t = t$:

$$\int_{N_0}^{N} \frac{1}{N}\,\mathrm{d}N = \mathrm{l}\int_{0}^{t} \mathrm{d}t$$

So $[\ln \mathrm{N}]^{\mathrm{N}\ \ 0}_{\ \ \mathrm{N}} = \mathrm{l}$

Thus $\ln N - \ln N_0 = -\mathrm{l}t$ (14.6)

which now simplifies to

$$\ln \frac{N}{N_0} = -\mathrm{l}t \quad (14.7)$$

We can as well write Equation (14.7) in terms of mass:

$$\ln \frac{m}{m_0} = -\mathrm{l}t \quad (14.8)$$

where N_0 = The initial number of radioactive nuclei or atom present, i.e., at time $t = 0$.

N = The number of radioactive nuclei or atoms present any particular time t.

m_0 = The initial mass of the radioisotope, i.e., at time $t = 0$.

m = The mass of the radioactive nucleus at any particular time t.

l = The decay constant of radioisotope.

Equations (14.7) and (14.8) are used for calculating the mass or number of a radioactive material that would be left after any length of time.

Example 1 Uranium-238 disintegrates to thorium($^{234}_{90}\mathrm{Th}$). Write the balanced equation for the decay if the atomic number of uranium is 92.

Solution Since the decay involves the emission of a particle, then we have to add a helium nucleus to the daughter nucleus, thorium:

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$$

Example 2 A bismuth nucleus ($^{210}_{83}\mathrm{Bo}$) emits b particle to become polonium nucleus ($^{210}_{84}\mathrm{Po}$). Write the balanced nuclear equation for the decay.

Solution Since a b particle is emitted, then we have to add an electron to the daughter nucleus, polonium:

$$^{210}_{83}\mathrm{Bi} \rightarrow {}^{210}_{84}\mathrm{Po} + {}^{0}_{-1}\mathrm{e}$$

Example 3 A uranium-238 nucleus emits an a particle and a b particle to produce protactinium. Write the balanced nuclear equation for the decay.

Solution When a uranium-238 nucleus emits an particle, its mass and atomic number decrease by 4 and 2 respectively. Thus its mass and atomic numbers becomes 234 and 90, respectively. The nucleus also emits a b particle, which has no effect on the mass number. Thus the mass number of the daughter nucleus is 234. However, the atomic number is increased by 1, making the atomic number of the daughter nucleus to be 91.

Since the disintegration involves the emission of an a particle and a b particle, then we have to add a helium nucleus and an electron to the daughter nucleus:

$$^{238}_{92}\text{U} \rightarrow {}^{234}_{91}\text{Pa} + {}^{4}_{2}\text{He} + {}^{0}_{-1}\text{e}$$

Example 4 What quantity of 2.0 g of strontium-90 would remain if kept for 50 years?

(l = 0.0247 yr^{-1})

Solution We have to apply the relation

$$\ln \frac{m}{m_0} = lt$$

m_0 = 2.0 g

t = 50 yrs

l = 0.0247 yr^{-1}

m = ?

Substituting we have

$$\ln \frac{m}{2.0\text{ g}} = -\frac{0.0247}{1\text{ yr}} \times 50\cancel{\text{yrs}}$$

Then $\ln \frac{m}{2.0\text{ g}} = -1.235$

Taking the natural antilogarithms of both sides we have

$$\frac{m}{2.0\text{ g}} = e^{-1.235} = 0.291$$

Cross-multiplying we have

m = 2.0 g × 0.291

= 0.58 g

Example 5 Calculate the mass of 1500 g of carbon-15 that would be left after 1 min.?

(l = 0.288 s^{-1})

Solution We have to apply the equation

$$\ln \frac{m}{m_0} = -lt$$

$m_0 = 1500$ g
$t = 1$ min.= 60 s
l $= 0.288$ s^{-1}
$m = ?$

Substituting we have

$$\ln \frac{m}{1500\text{ g}} = \frac{0.288}{1\cancel{s}} \times 60\cancel{s}$$

Thus $\ln \frac{m}{1500\text{ g}} = -17.28$

Taking the natural antilogarithms of both sides we have

$$\frac{m}{1500\text{ g}} = e^{-17.28} = 3.1 \times 10^{-8}$$

Cross-multiplying we have

$m = 1500 \text{ g} \times 3.1 \times 10^{-8}$
$= 4.7 \times 10^{-7}$ g

Example 6 A rock sample is estimated to contain 120 g of uranium-238. How long would it take the mass of this mass of uranium to reduce to 110 g.

(l $= 1.54 \times 10^{-10}$ yr^{-1})

Solution We have to apply the relation

$$\ln \frac{m}{m_0} = -lt$$

$m_0 = 120$ g
$m = 11$ g
l $= 1.54 \times 10^{-10}$ yr^{-1}
$t = ?$

Substituting we now obtain

$$\ln \frac{115\,\cancel{g}}{120\,\cancel{g}} = -1.54 \times 10^{-10}\ \text{yr}^{-1} \times t$$

Then $0.0426 = -1.54 \times 10^{-10}\ \text{yr}^{-1} \times t$

$$\therefore\ t = \frac{-0.0426 \times 1\ \text{yr}}{-1.54 \times 10^{-10}}$$

$$= 2.78 \times 10^{8}\ \text{yrs}$$

Example 7 0.67 g of tritium was left of a 1.0-g sample of the element after being stored for 7.0 yrs. What is the decay constant of the element?

Solution We have to apply the relation

$$\ln \frac{m}{m_0} = -\,\mathrm{l}t$$

$m_0 = 1.0$ g
$m = 0.67$ g
$t = 7.0$ yrs
$\mathrm{l} = ?$

Substituting we have

$$\ln \frac{0.67\,\cancel{g}}{1.0\,\cancel{g}} = -\mathrm{l} \times 7\ \text{yrs}$$

Then $-0.40 = -\mathrm{l} \times 7\ \text{yrs}$

$$\therefore\ \mathrm{l} = \frac{-0.40}{-7\ \text{yrs}}$$

$$= 0.057\ \text{yr}^{-1}$$

Practice Problems

1. A thorium nucleus ($^{234}_{90}$Th) emits a b particle to form a proctatinium nucleus ($^{234}_{91}$Pa).Write the balanced nuclear equation for the decay. [*Answer:* $^{234}_{90}$Th + $^{0}_{-1}e$]
2. A radium ($^{226}_{88}$Ra) nucleus emits an a particle to become a nucleus of radon ($^{222}_{86}$Rn). Write the balanced nuclear equation for the decay. [*Answer:* $^{226}_{88}$Ra

$\rightarrow {}^{222}_{86}\text{Rn} + 42\text{He}]$

3. What mass of fermium would remain if a 2.50-g sample of the element is stored for
   2.0 ms?

   $(l = 210\ \text{s}^{-1})$ [*Answer:* 1.64 g]

4. The mass of a sample of radium-226 was reduced to 4.85 g after 10 days. What is the initial mass of the sample?

   $(l = 8.61 \times 10^{-2}\ \text{day}^{-1})$ [*Answer:* 11.3 g]

5. How long would it take a 50.0-g sample of carbon-14 to reduce to 4.50 g?

   $(l = 1.2 \times 10^{-3}\ \text{yr}^{-1})$ [*Answer:* 2.0×10^{3} yrs]

6. 0.97 g was left of a 1.0-g sample of a radioisotope after 100.0 ms. What is the decay constant of the isotope? [*Answer:* $0.30\ \text{s}^{-1}$]

14.1.2 Half-life

The half-life $t_{1/2}$ of a radioactive isotope is the time required for a given sample of the element to disintegrate to half its initial value. The equation for radioactive half-life is derived by substituting $N = 1/2\ N_0$ or $m = 1/2 m_0$ at $t_{1/2}$ into Equation (14.7) or (14.8) above. Substituting $N = 1/2\ N_0$ into Equation (14.7) we have

$$\ln \frac{1/2\ \cancel{N_0}}{\cancel{N_0}} = -\lambda t_{1/2}$$

So $\ln \frac{1}{2} = -\lambda t_{1/2}$

Then $-0.693 = -\lambda t_{1/2}$

$\therefore\ t_{1/2} = \frac{0.693}{\lambda}$

Thus the half-life of a radioisotope is the same as the first-order half-life, we encountered earlier in Chapter 13.

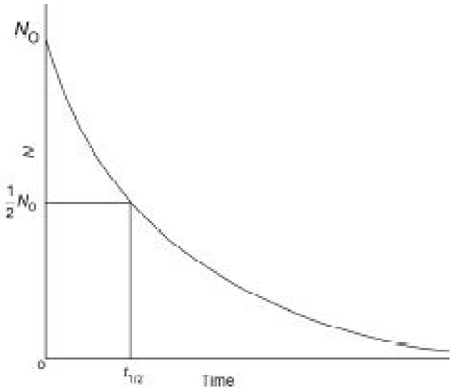

Figure 14.5 Radioactive decay curve showing the half-life of a radioactive substance. All radioactive substances have a constant half-life.

Example 1 How long would it take 8.00 g of carbon-15 to disintegrate to 0.0625 g if the half-life of the radioisotope is 2.4 s?

Solution Since the half-life of a radioisotope is constant, then all we need to do is to find out how many half-lives it would take the sample to disintegrate to 0.0625 g, and multiply the result by the half-life of the isotope. Thus we have to continue halving successive masses of the isotope until we obtain 0.0623 g:

After first half-life, $m = 4.00$ g
After second half-life, $m = 2.00$ g
After third half-life, $m = 1.00$ g
After fourth half-life, $m = 0.500$ g
After fifth half-life, $m = 0.250$ g
After sixth half-life, $m = 0.125$ g
After seventh half-life, $m = 0.0625$ g

Thus it requires 7 half-lives for 8.00 g of the radioisotope to decay to 0.625 g. Since the half-life of the isotope is 2.4 s, then

$$t = 7 \times 2.4 \text{ s}$$
$$= 16.8 \text{ s}$$

Example 2 Calculate the half-life of uranium-238, given that its decay constant is 1.54×10^{-10} yr^{-1}.

Solution We have to apply the relation

$$t_{1/2} = \frac{0.693}{\lambda}$$

$l = 1.54 \times 10^{-10}$ yr^{-1}

$t_{1/2} = ?$

Substituting we obtain

$$t_{1/2} = \frac{0.693 \times 1\text{yr}}{1.54 \times 10^{-10}}$$

$= 4.5 \times 10^{9}$ yrs

Example 3 The half-life of lead-210 is 194 years. Calculate its decay constant.

Solution We have to apply the relation

$$t_{1/2} = \frac{0.693}{\lambda}$$

$$\therefore\ l = \frac{0.693}{t_{1/2}}$$

$t_{1/2} = 19.4$ yrs

$l = ?$

We now substitute to obtain

$$l = \frac{0.693}{19.4\ \text{yrs}}$$

$= 0.0357$ yr^{-1}

Example 4 The half-life of polonium is 138 days. What would be left of a 10.5-g sample of the element if it is stored for a year?

Solution We have to apply the relation

$$\ln \frac{m}{m_0} = -lt$$

We must first work out the decay constant from the relation

$$t_{1/2} = \frac{0.693}{\lambda}$$

$$\therefore\ l = \frac{0.693}{t_{1/2}}$$

$t_{1/2}$ = 138 days

l = ?

Substituting we have

$$l = \frac{0.693}{138\ \text{days}}$$

$= 5.02 \times 10^{-3}\ \text{day}^{-1}$

m_0 = 10.5 g

t = 1 yr = 365 days

m = ?

Finally, we now substitute to obtain

$$\ln \frac{m}{10.5\ \text{g}} = \frac{5.02 \times 10^{-3}}{1\ \cancel{\text{day}}} \times 365\ \cancel{\text{days}}$$

Then $\ln \frac{m}{10.5\ \text{g}} = -1.83$

We now take the natural antilogarithms of both sides and obtain

$$\frac{m}{10.5\ \text{g}} = e^{-1.83} = 0.160$$

Cross-multiplying we have

m = 10.5 g × 0.160

= 1.68 g

Practice Problems

1. The half-life of bismuth is 5 days. How long would it take 5.00 g of the element to disintegrate to 0.625 g? [*Answer:* 15 days]
2. Calculate the half-life of radon if its decay constant is 0.182 day^{-1}. [*Answer:* 3.81 days]
3. The half-life of uranium-234 is 2.5×10^5 years. Calculate:

(a) the decay constant;
(b) the mass of the isotope that would remain if 5.0 g sample of it is stored for 2.0×10^4 years. [*Answers:* (a) 2.8×10^{-6} yr^{-1} (b) 4.7 g]

14.2 NUCLEAR REACTIONS

Nuclear reaction leads to the formation of new nuclei or elements called daughter nuclei. The formation of new nuclei from existing ones is called nuclear transmutation or nucleosynthesis. Nuclear transmutation could be natural or induced (artificial). Examples of natural transmutation are alpha and beta decays. The process of producing new nuclei or elements by bombarding existing nuclei with other particles or nuclei is called artificial transmutation. Artificial transmutation is effected through the nuclear reactions of nuclear fission and fusion.

14.2.1 Nuclear Fission and Fusion

Nuclear fission is the process in which a heavy nucleus is split into two nuclei of roughly equal mass with a release of energy and radiations. Nuclear fission could be spontaneous or induced. A spontaneous nuclear fission occurs as a result of the oscillations of the nucleus. An induced nuclear fission is effected by bombarding a heavy nucleus with neutrons. An example is the bombardment of uranium-235 by neutrons to produce fragments of barium and krypton, with a release of energy and radiations:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{142}_{56}\mathrm{Ba} + {}^{92}_{26}\mathrm{Kr} + 2\,{}^{1}_{0}\mathrm{n}$$

A nucleus in which nuclear fission can be induced is termed a fissionable nucleus. Once nuclear fission is initiated, it could become self sustaining such that the neutrons produced as a result of the fission of a nucleus induce nuclear fission in other nuclei. This process, which is the principle of the atomic bomb, is called chain reaction. The minimum amount of the fissile material required to sustain a chain reaction is called its critical mass.

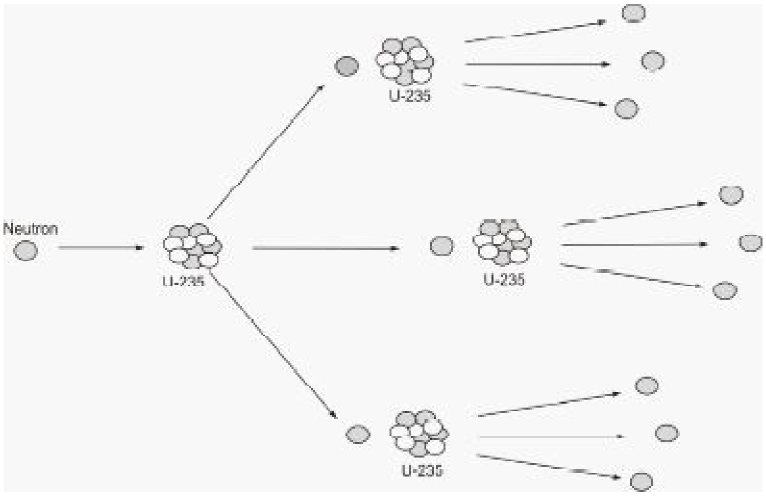

Figure 14.6 A nuclear chain reaction.

Controlled nuclear fission is harnessed for power generation. This is carried out in a nuclear reactor or atomic pile. A nuclear reactor contains the fuel elements, which is the fissile material; moderators, such as graphite and heavy water for reducing the speeds of neutrons; and control rods, such as cadmium and boron steel, for absorbing neutrons.

Nuclear fusion is the process in which two or more light nuclei fuse to form a heavier nucleus with a release of energy and radiations. This process leads to the release of higher amount of energy than nuclear fission. For example, the enormous heat energy produced by the sun is due to nuclear fusion reactions.

Extremely high temperature is required to effect nuclear fision because the two nuclei must approach each other with enough speed to overcome the repulsive forces between them. Reactions that require very high temperature to occur are called thermonuclear reactions.

14.2.2 Binding Energy

The binding energy of an atom is the amount of energy released when neutrons and protons are bonded together to form a nucleus. The energy released leads to a reduction in mass, such that the mass of the resulting nucleus or atom is always slightly different from the combined masses of the nucleons (neutrons and protons).

The binding energy per nucleon is the binding energy divided by the total number of nucleons.

14.2.3 Nuclear Energy

Unlike ordinary chemical reactions, mass is not conserved in nuclear reactions.

In other words, the combined mass of the substances undergoing a nuclear reaction vary slightly from that of the products. This difference in mass, termed mass defect, is due to the conversion of some atoms to energy.

The energy released during nuclear reactions is given by the Einstein's equation:

$$E = \Delta mc^2$$

where E = The energy released in joules.

Δm = The change in mass or mass defect in kg.

c = The velocity of light = 3.00×10^{8} ms^{-1}

The mass defect is converted to the SI unit of the kg as follows:

$$1 \text{ amu} = 931 \text{ MeV (mega electron volt)} = 1.6605 \times 10^{-27} \text{ kg}$$

Example 1 Uranium-235 undergoes nuclear fission as shown by the following reaction:

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{92}_{36}\text{Kr} + {}^{141}_{56}\text{Ba} + 3\,{}^{1}_{0}\text{n} + \text{energy}$$

Calculate the amount of energy released when 2.5 g of uranium undergoes nuclear fission.

(^{235}U = 235.040 amu, ^{92}Kr = 91.910 amu, ^{141}Ba = 140.910 amu, ^{1}n = 1.009 amu, N_A = 6.02×10^{23} mol^{-1}, $c = 3.00 \times 10^{8}$ m s^{-1})

Solution We have to apply the relation

$$E = Dmc^2$$

The mass defect is calculated from the relation

Δm = mass of reactants – mass of products

Mass of reactants = mass of ^{235}U + mass of ^{1}n

Mass of ^{235}U = 235.040 amu

Mass of ^{1}n = 1.009 amu

Mass of reactants = ?

Substituting we have

Mass of reactants = 235.040 amu + 1.009 amu = 236.049 amu

Mass of products = mass of ^{92}kr + mass of ^{141}Br + (3 × mass of ^{1}n)

Mass of ^{92}Kr = 91.910 amu

Mass of ^{141}Br = 140.910 amu

Mass of ^{1}n = 1.009 amu

Mass of products = ?

Substituting we have

Mass of products = 91.910 amu + 140.910 amu + (3 × 1.009 amu)

= 232.820 amu + 3.027 amu

= 235.847 amu

Δm = ?

Substituting we have

Δm = 236.049 amu – 235.847 amu = 0.202 amu

$= 0.202\,\cancel{\text{amu}} \times \frac{1.6605 \times 10^{-27}\ \text{kg}}{1\,\cancel{\text{amu}}} = 3.35 \times 10^{-28}\,\text{kg}$

$c = 3.0 \times 10^{8}\ \text{m s}^{-1}$

E = ?

Substituting we obtain

$E = 3.35 \times 10^{-28}\,\text{kg} \times (3.00 \times 10^{8}\ \text{m s}^{-1})^{2}$

So $E = 3.35 \times 10^{-28}\,\text{kg} \times 9.00 \times 10^{16}\ \text{m}^{2}\ \text{s}^{-2}$

$= 3.0 \times 10^{-11}\ \text{J}$

This is the energy released during the fission of 1 atom of uranium-235. The energy released in the fission of 2.5 g of the isotope is obtained by multiplying the energy released per atoms by the number of atoms in 2.5 g of the element. Thus we must first work out the number of moles in 2.5 g of the isotope:

$n = \frac{m}{M}$

m = 2.5 g

$M = 235\ \text{g mol}^{-1}$

n = ?

Substituting we have

$n = \frac{2.5\ \text{g} \times 1\ \text{mol}}{235\ \text{g}}$

= 0.11 mol

The number of atoms in 0.11 mol is obtained from the relation

$N = n \times N_{A}$

$N_{A} = 6.02 \times 10^{23}\ \text{mol}^{-1}$

$N = ?$

Substituting we have

$$N = 0.11\,\cancel{\text{mol}} \times \frac{6.02 \times 10^{23}}{1\,\cancel{\text{mol}}}$$

$$= 6.6 \times 10^{22}$$

Thus the total amount of energy released during the fission of 2.5 g of uranium-235 is

$$E = 3.00 \times 10^{-11}\ \text{J} \times 6.6 \times 10^{22}$$

$$= 2.0 \times 10^{12}\ \text{J}$$

Example 2 The masses of 1 mol of carbon-12 atom, proton and neutron are 12.011 amu, 1.0078 amu, 1.008 amu respectively. Calculate the binding energy of the carbon atom. Hence determine the binding energy per nucleon of the atom.

$$(Z = 6,\ A = 12,\ c = 3.00 \times 10^{8}\ \text{m s}^{-1})$$

Solution We have to apply the relation

$$E = \Delta mc^{2}$$

Δm = mass of nucleons – mass of atom or nucleus

The number of neutrons in an atom of carbon-12 is obtained from the relation

$$A = Z + \text{n}$$

$$\therefore\ \text{n} = A - Z$$

$A = 12$

$Z = 6$

$\text{n} = ?$

Substituting we have

$$\text{n} = 12 - 6 = 6$$

Since an atom of carbon-12 contains 6 protons and 6 neutrons, then the total mass of the nucleons is

$$m = 6 \times m_p + 6 \times m_n$$

So m = (6 × 1.0078 amu) + (6 × 1.0087 amu)

Thus m = 6.0468 amu + 6.0522 amu = 12.099 amu

For the atom we have

m = 12.011 amu

Δm = ?

Substituting we have

$\Delta m = 12.099\text{ amu} - 12.011\text{ amu} = 0.088\text{ amu}$

We $= 0.088\,\cancel{\text{amu}} \times \dfrac{1.6605\times10^{-27}\text{ kg}}{1\,\cancel{\text{amu}}} = 1.5\times10^{-28}\text{ kg}$

Also, $c = 3.0\times10^{8}\text{ m s}^{-1}$

E = ?

We now substitute to into the Einstein equation to obtain

$E = 1.5\times10^{-28}\text{ kg}\times(3.00\times10^{8}\text{ m s}^{-1})^{2}$

So $E = 1.5\times10^{-28}\text{ kg}\times9.00\times10^{16}\text{ m}^{2}\text{ s}^{-2}$

$= 1.4\times10^{-11}\text{ J}$

Note that $1\text{ kg m}^{2}\text{ s}^{-2} = 1\text{ J}$.

The binding energy per nucleon is obtained from the relation

$$\text{Binding energy per nucleon} = \frac{\text{Binding energy}}{\text{Number of nucleons}}$$

Since the atom contains 6 protons and 6 neutrons, then the atom has 12 nucleons.

Thus

$$\text{Binding energy per nucleon} = \frac{1.4\times10^{-11}\text{ J}}{12}$$

$= 1.2\times10^{-12}\text{ J}$

Practice Problems

1. Calculate the energy released in the fission of 1.0 g of uranium-235. The equation of reaction is

$${}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{142}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 2\,{}^{1}_{0}\text{n}$$

(^{235}U = 235.04 amu, ^{92}Kr = 91.91 amu, ^{142}Ba = 141.92 amu, ^{1}n = 1.009 amu, N_A =

6.02×10^{23} mol^{-1}, $c = 3.00 \times 10^{8}$ m s^{-1}) [*Answer:* 7.7×10^{10} J]

2. Calculate the nuclear binding energy of beryllium-7 atom.

(*Z* = 4, ^{1}n = 1.0087, ^{1}P = 1.0078 amu, ^{7}Bc = 7.016 amu, $c = 3.00 \times 10^{8}$ m s^{-1} = 1.0078 amu) [*Answer:* 6.2×10^{-12} J]

SUMMARY

- Radioactivity is the spontaneous emission of radiations from the nucleus of an atom. The three main types of radiations are a particles, b particles, and g rays.
- Radiations are detected by Geiger-Muller counter, scintillation counter and ionization cloud chamber.
- Radioactive decay series refers to the process by which an unstable nucleus undergoes successive disintegration by emitting radiations until a stable nucleus is formed.
- The quantity of a radioactive substance that is left after a period of time is calculated from the relation

$$\ln \frac{N}{N_0} = -lt \text{ or } \ln \frac{m}{m_0} = -lt$$

- The half-life of a radioactive substance is the time required for a given sample of that substance to decay to one-half its original mass or number of atoms. The half-life of a radioisotope is the first-order half-life:

$$t_{1/2} = \frac{0.693}{\lambda}$$

- Artificial transmutation is the process of producing new nuclei or elements by bombarding existing nuclei or elements with other particles or nuclei.
- Nuclear fission is the process by which a heavy nucleus is split into two lighter nuclei of nearly equal mass with a release of radiations and energy.
- Chain reaction is a self-sustaining nuclear fission in which the neutrons that are produced from the fission of a nucleus induce fission in other nuclei.
- A nuclear reactor or atomic pile is a reactor for carrying out controlled chain reaction.
- Nuclear fusion is the process by which two light nuclei fuse or combine to form a heavier nuclei.
- Nuclear binding energy is the energy released when neutrons and protons fuse to form a nucleus.

- The binding energy per nucleon is the binding energy divided by the total number of nucleons or particles in a nucleus.
- Mass is not conserved in a nuclear reaction because some atoms are converted to energy. The energy released during a nuclear reaction is calculated using the Einstein's equation:

$$E = \text{D}mc^2$$

EXERCISE

MULTIPLE-CHOICE QUESTIONS

1. What does B represent in the following nuclear equation?

$${}^{238}_{92}\text{U} + \text{B} \rightarrow {}^{239}_{92}\text{U}$$

A. ${}^{0}_{1}\text{n}$ B. ${}^{e}_{-1}$
C. ${}^{1}_{1}\text{p}$ D. ${}^{4}_{2}\text{He}$
E. ${}_{1}\text{e}$

2. What mass of a 2.0-g sample of potassium-42 would remain after 25.0 hours, given that the half-life of the radioisotope is 12.5 hours?

A. 0.050 g B. 0.10 g
C. 0.25 g D. 0.50 g
E. 1.0 g

3. What is the decay constant of cobalt-60 if it has a half-life of 5.29 years?

A. 0.0130 yr^{-1} B. 0.0234 yr^{-1}
C. 0.0240 yr^{-1} D. 0.131 yr^{-1}
E. 0.240 yr^{-1}

4. Which nuclear radiation corresponds to a helium nucleus?

A. a particle B. ${}_{-1}\text{e}$
C. b particle D. g particle
E. ${}^{1}_{0}\text{n}$

5. What would be left of 2.50 g of a radioactive isotope after 5 half-lives?

A. 0.0391 g B. 0.0781 g
C. 0.0980 g D. 0.163 g
E. 0.625 g

6. What is the half-life of curium-245 if it has a decay constant of 6.93×10^{-6} yr^{-1}?

A. 1.00×10^{3} yrs B. 2.50×10^{3} yrs
C. 1.50×10^{4} yrs D. 2.13×10^{4} yrs
E. 1.00×10^{5} yrs

ESSAY TYPE QUESTIONS

Radioactive decay and nuclear equations

7. Balance the following nuclear equations.

(a) ${}^{24}_{11}\text{Na} \rightarrow {}^{24}_{12}\text{Mg}$

(b) ${}^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \rightarrow {}^{17}_{8}\text{O}$

(c) ${}^{227}_{89}\text{Ac} \rightarrow {}^{223}_{87}\text{Fr}$

(d) ${}^{208}_{82}\text{Pb} \rightarrow {}^{209}_{82}\text{Pb}$

(e) ${}^{108}_{42}\text{Ag} \rightarrow {}^{103}_{45}\text{Rh}$

8. What mass of 15.0-g sample of barium-139 would be left if stored for an hour?

(g = 0.0082 min.^{-1})

9. 5.00 g was left of a sample of strontium after 50 years of storage. What is the initial mass of the sample?

($t_{1/2}$ = 28 yrs)

10. How long would it take a 1.0-g sample of neptunium to decay to 0.15 g if the half-life of the element is 2.2×10^{6} years?

11. The half-life of iodine-131 is 81 days. How long would it take 5.0 g of the radioisotope to decay to 0.63 g?

12. Determine the half-life of each of the following radioisotopes:

(a) Iodine-128, with a decay constant of 0.028 min.^{-1}.
(b) Barium-140, with a decay constant of 0.054 min.^{-1}.
(c) Promethium, with a decay constant of 0.267 yr^{-1}.
(d) Strontium-89, with a decay constant of 0.0136 day^{-1}.
(e) Silver-110, with a decay constant of 0.0924 day^{-1}.

13. Determine the decay constant of each of the following elements:

(a) Curium-245, with a half-life of 1.0×10^{4} years.
(b) Lead-209, with a half-life of 3.3 hours.
(c) Phosphorus-32, with a half-life of 14.5 hours.

(d) Potassium-42, with a half-life of 12.5 hours.

(e) Tritium, with a half-life of 12.3 years.

14. Show that the rate of radioactive decay is given by the equation

$$\ln\frac{N}{N_0} = -\mathrm{l}t$$

where N_0 = The initial number of atoms in a sample of a radioactive substance.

N = The number of atoms left after a time t.

l = Decay constant.

15. (a) What do you understand by the half-life of a radioactive element?

(b) Show that the half-life of a radioactive substance is given by the relation

$$t_{1/2} = \frac{0.693}{\lambda}$$

Nuclear reactions

16. Define the following:
    (a) Nuclear fission.
    (b) Nuclear fusion.
    (c) Binding energy.
    (d) Artificial transmutation.

17. Determine the binding energy of the nucleus N.

(^{1}n = 1.0087 amu, ^{1}p = 1.0078, ^{14}N = 14.010 amu, $c = 3.00 \times 10^{8}$ m s^{-1})

18. Determine the binding energy per mole of the nucleus $^{4}_{2}$He.

(^{1}n = 1.0087 amu, ^{1}p = 1.0078,^{4}He = 4.003 amu, $c = 3.00 \times 10^{8}$ m s^{-1})

19. Calculate the binding energy per nucleon of oxygen.

($Z = 8$, ^{16}O = 15.9949 amu,^{1}p = 1.0078, ^{1}n = 1.0087 amu, $c = 3.00 \times 10^{8}$ m s^{-1})

20. Calculate the energy released when 1.0 g of uranium-235 undergoes nuclear fission as follows:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{142}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 2\,{}^{1}_{0}\mathrm{n}$$

(^{235}U = 235.04 amu, ^{92}Kr = 91.91 amu, ^{142}Ba = 141.92 amu, ^{1}n = 1.009 amu, N_A = 6.02×10^{23} atom mol^{-1}, $c = 3.00 \times 10^{8}$ m s^{-1})

21. Calculate the energy released when 2.0 g of helium-3 is converted to helium-4 according to the reaction:

$$^{3}_{2}\mathrm{He} + {}^{2}_{1}\mathrm{D} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{1}\mathrm{p}$$

(^{3}He = 3.0160 amu, ^{2}D = 2.0141 amu, ^{4}He = 4.0026 amu, ^{1}p = 1.0078, $N_A = 6.02 \times 10^{23}$ mol^{-1},
$c = 3.00 \times 10^{8}$ m s^{-1})

22. Calculate the energy released when a carbon-12 nucleus is converted to a carbon-13 nucleus according to the reaction:

$$^{12}_{7}\mathrm{C} + {}^{1}_{1}\mathrm{p} \rightarrow {}^{13}_{7}\mathrm{N}$$

(^{12}N = 12.000 amu, ^{13}N = 13.0057, amu, ^{4}He = 4.0026 amu, ^{1}p = 1.0078, $c = 3.00 \times 10^{8}$ m s^{-1})

Answers

1. A
2. D
3. B
4. A
5. B
6. C
7. (a) $^{24}_{11}\mathrm{Na} \rightarrow {}^{24}_{12}\mathrm{Mg} + {}_{-1}\mathrm{e}$
   (b) $^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{P}$
   (c) $^{227}_{87}\mathrm{Ac} \rightarrow {}^{223}_{87}\mathrm{Fr} + {}^{4}_{2}\mathrm{He}$ (d) $^{208}_{82}\mathrm{Pb} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{209}_{82}\mathrm{Pb}$
   (e) $^{108}_{47}\mathrm{Ag} \rightarrow {}^{103}_{45}\mathrm{Rh} + {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n}$
8. 9.2 g
9. 17.2 g
10. 6.0×10^{6} yrs
11. 240 days
12. (a) 25 min. (b) 13 min. (c) 2.6 yrs (d) 51 yrs (e) 7.5 yrs
13. (a) 6.9×10^{-5} yr^{-1} (b) 0.21 hr^{-1}
   (c) 4.78×10^{-2} hr^{-1} (d) 5.54×10^{-2} hr^{-1}
   (e) 5.63×10^{-2} yr^{-1}
17. 1.58×10^{-11} J
18. 2.73×10^{12} J mol^{-1}
19. 1.28×10^{-12} J

20. 7.7×10^{10} J
21. 1.2×10^{12} J
22. 3.14×10^{-13} J

Appendices

Appendix 1: Conversion factors

Quantity	*Common units*	*SI Unit*
Length	1 m (micron)	10^{-6} m
	1 Å (Angstrom)	10^{-8} cm
	A light year = 1.52 ¥ 10^{13} mi	9.46 ¥ 10^{12} km
Mass	1 ton = 2000 Ib	1000 kg
	1 amu = 1.66 × 10^{-24} lb	1.66 ¥ 10^{-27} kg
	10 oz = 16 Ib	28.4 g
	2.205 Ib	1 kg
Area	1 ft^2 = 144 in^2	0.0929 m^2
	1 in^2 = 0.00694 ft^2	6.452 cm^2
Volume	1 dm^3 (L) = 1.05679 t (quartz) = 0.353 ft^3	1000 cm^3 (mL)

Time	1 min = 0.0167 h	60 s
	1 h = 60 min.	3600 s
	1 day = 24 hr = 1440 min.	86400 s
	1 wk 7 days = 168 hr = 10080 min.	604800 s
	1 year = 52 wks = 365 days = 8760 hr = 525600 min.	3.2 × 10^{7} s
Velocity	1 mi hr $^{-1}$ = 1.62 km hr^{-1} = 1.47 ft s^{-1}	0.447 m s^{-1}
	1 mi min $^{-1}$ = 88 ft s^{-1} = 60 mi hr^{-1}	26.82 m s^{-1}
Acceleration	1 ft s $^{-2}$ = 5280 ft s^{-2}	0.3048 m s^{-2}
Energy	1 ft Ib = 1.36 × 10 $^{-7}$ erg	1.3557 J
	1 erg	1.0 ¥ 10^{-7} J
	1 ev = 1.6 ¥ 10^{-12} erg = 3.28 ¥ 10^{-20} Ca	1.6 ¥ 10^{-19} J
	1 Ca = 2.6 ¥ 10^{-19} ev	4.184 J
	1 amu = 931.5 Mev	1.5 ¥ 10^{-16} J
Power	1 ft Ib s $^{-1}$ = 0.00182 hp	764 W (J s^{-1})
	1 erg s $^{-1}$ = 7.3 ¥ 10^{-8} ft Ib s^{-1}	1.0 ¥ 10^{-7} W
Pressure	1 atm = 760 mm Hg = 760 Torr	101.325 kPa (N

		m^{-2})
	1 bar = 1.013 atm = 770.1 mm Hg = 14.89 Ib in $^{-2}$	100 kPa
	1 atm = 14.70 Ib in $^{-2}$ = 1.0 ¥ 10^{16} dynes cm^{-3}	101.325 kPa (N m^{-2})
Temperature	°C = (5/9°F − 32) = (9/5°C + 32) °F	(°C + 273.17) K

Appendix 2: Multiples of SI units

Prefix	*Symbol*	*Value*
kilo-	k	10^{3}
mega-	m	10^{6}
Giga-	G	10^{9}
Tera-	T	10^{12}

Appendix 3: Sub-multiples of SI units

Prefix	*Symbol*	*Value*
deci-	d	10^{-1}
centi-	c	10^{-2}

milli-	m	10^{-3}
micro-	µ	10^{-6}
nano-	n	10^{-9}
pico-	p	10^{-12}
femto-	f	10^{-15}
atto-	a	10^{-18}

Appendix 4: Sub-multiples of SI units

Quantity	*Unit*	*Symbol*
Length	Metre	m
Mass	Kilogram	kg
Time	Second	s
Electric current	Ampere	A
Temperature	Kelvin	K
Amount of substance	Mole	mol

Appendix 5: Standard reduction potentials

Reduction half-equation	*E°* *(V)*
$H_4XeO_6 + 2H^+ + 2e^-$ Æ $XeO_3 + 3H_2O$	+3.0
$F_2 + 2e^-$ Æ $2F^-$	+2.87
$O_3 + 2H^+ + 2e^-$ Æ $O_2 + H_2O$	+2.07
$S_2O_8 + 2e^-$ Æ	+2.05
$Ag^{2+} + e^-$ Æ Ag^+	+1.98
$Co^{2+} + e^-$ Æ Co^+	+1.81
$H_2O_2 + 2H^+ + 2e^-$ Æ $2H_2O$	+1.78
$Au^+ + e^-$ Æ Au	+1.69
$Pb^{4+} + 2e^-$ Æ Pb^{2+}	+1.67
$2HClO + 2H^+ + 2e^-$ Æ $Cl_2 + 2H_2O$	+1.63
$Ce^{4+} + e^-$ Æ Ce^{3+}	+1.61
$2HBrO + 2H^+ + 2e^-$ Æ $Br_2 + 2H_2O$	+1.60
$MnO_4^- + 8H^+ + 5e^-$ Æ $Mn^{2+} + H_2O$	+1.51
$Mn^{3+} + e^-$ Æ Mn^{2+}	+1.40

$Cl_2 + 2e^-$ Æ $2Cl^-$	+1.36
$Cr_2O_7^- + 14H^+ + 6e^-$ Æ $2Cr^{3+} + 7H_2O$	+1.33
$O_3 + H_2O + 2e^-$ Æ $O_2 + 2OH^-$	+1.24
$O_2 + 4H^+ + 4e^-$ Æ $2H_2O$	+1.23
$ClO_4^- + 2H^+ + 2e^-$ Æ $+ H_2O$	+1.23
$Pt^{2+} + 2e^-$ Æ P_t	+1.20
$Br_2 + 2e^-$ Æ $2Br^-$	+1.09
$Cd^{2+} + 2e^-$	+0.99
$Pu^{4+} + e^-$ Æ Pu^{3+}	+0.97
$NO_3 + 4H^- + 3e^-$ Æ $NO + 2H_2O$	+0.96
$2Hg^{2+} + 2e^-$ Æ Hg_2^{2+}	+0.92
$ClO^- + H_2O + 2e^-$ Æ $Cl^- + 2OH^-$	+0.89
$NO_3^- + 2H^+ + e^-$ Æ $NO_2 + H_2O$	+0.80
$Ag + e^-$ Æ Ag	+0.80
$Hg_2^{2+} + 2e^-$ Æ $2Hg$	+0.79

Reduction half-equation	*E^{o} (V)*
$AgF + e^-$ Æ $Ag + F^-$	+0.78
$Fe^{3+} + e^-$ Æ Fe^{2+}	+0.77
$BrO^- + H_2O + 2e^-$ Æ $Br^- + 2OH^-$	+0.76
$Mn_4^{2-} + 2H_2O + 2e^-$ Æ $MnO_2 + 4OH^-$	+0.76
$MnO_4^{2-} + 2H_2O + 2e^-$ Æ $MnO_2 + 4OH^-$	+0.60
$MnO_4^- + e^-$ Æ MnO_4^{2-}	+0.56
$I_2 + 2e^-$ Æ $2I^-$	+0.54
$Cu^+ + e^-$ Æ Cu	+0.52
$I_3^- + 2e^-$ Æ $3I^-$	+0.53
$Ni(OH)_2 + H_2O + e^-$ Æ $Ni(OH)_2 + OH^-$	+0.49
$IO^- + H_2O + 2e^-$	+0.49
$O_2 + 2H_2O + 4e^-$ Æ $4OH^-$	+0.40
$ClO_4^- + H_2O + 2e^-$ Æ $ClO_3^- + 2OH^-$	+0.36
$Cu^{2+} + 2e^-$ Æ Cu	+0.34

$BiO^+ + 2H^+ + 3e^-$ Æ $Bi + H_2O$	+0.32
$Hg_2Cl_2 + 2e^-$ Æ $2Hg + 2Cl^-$	+0.27
$AgCl + e^-$ Æ $Ag + Cl^-$	+0.22
$Bi^{3+} + 3e^-$ Æ Bi	+0.20
$SO_4^{2-} + 4H^+ + 2e^-$ Æ $H_2SO_3 + H_2O$	+0.17
$Cu^{2+} + e^-$ Æ Cu^+	+0.15
$Sn^{4+} + 2e^-$ Æ Sn^{2+}	+0.15
$AgBr + e^-$ Æ $Ag + Br^-$	+0.07
$NO_3^- + H_2O + 2e^-$ Æ $NO_2^- + 2OH^-$	+0.01
$Ti^{4+} + e^-$ Æ Ti^{3+}	0.00
$2H^+ + 2e^-$ Æ H_2	0
	(Reference electrode)
$Fe^{3+} + 3e^-$ Æ Fe	−0.04
$O_2 + H_2O + 2e^-$ Æ $HO_2^- + OH^-$	−0.08
$Pb^{2+} + 2e^-$ Æ Pb	−0.13
$In^+ + e^-$ Æ In	−0.14

$Sn^{2+} + 2e^-$ Æ Sn	−0.14
$AgI + e^-$ Æ $Ag + I^-$	−0.15

Reduction half-equation	*E°* *(V)*
$Ni^{2+} + 2e^-$ Æ Ni	−0.23
$2H_2O + 2e^-$ Æ $H_2 + 2OH^-$	−0.83
$SnO_2^- + H_2O + 2e^-$	−0.91
$Cr^{2+} + 2e^-$ Æ Cr	−0.91
$Mn^{2+} + 2e^-$ Æ Mn	−1.18
$V^{2+} + 2e^-$ Æ V	−1.19
$Zn(OH)_2 + 2e^-$ Æ $Zn + 2OH^-$	−1.25
$Ti^{2+} + 2e^-$ Æ Ti	−1.63
$Al^{3+} + 3e^-$ Æ Al	−1.66
$U^{3+} + 3e^-$ Æ U	−1.79
$Be^{2+} + 2e^-$ Æ Be	−1.85
$Mg^{2+} + 2e^-$ Æ Mg	−2.36

$Ce^{3+} + 3e^-$ Æ Ce	−2.48
$La^{3+} + 3e^-$ Æ La	−2.52
$Na^+ + e^-$ Æ Na	−2.71
$Mg(OH)_2 + 2e^-$ Æ $Mg + 2OH^-$	−2.69
$Ca^{2+} + 2e^-$ Æ Ca	−2.87
$Sr^{2+} + 2e^-$ Æ Sr	−2.98
$Ba^{2+} + 2e^-$ Æ Ba	−2.91
$Ra^{2+} + 2e^-$ Æ Ra	−2.92
$Cs^+ + e^-$ Æ Cs	−2.93
$Ba(OH)_2 + 8H_2O + 2e^-$	−2.97
$K^+ + e^-$ Æ K	−2.98
$Sr(OH)_2 + 8H_2O + 2e^-$	−2.99
$Ca(OH)_2 + 2e^-$	−3.03
$Li^+ + e^-$ Æ Li	−3.05

Appendix 6: The elements

Element	*Symbol*	*Atomic number (Z)*	*Relative atomic mass (A)*
Actinium	Ac	89	227*
Aluminium	Al	13	26.98
Americium	Am	95	243*
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210*
Barium	Ba	56	137.34
Berkelium	Bk	97	249*
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Boron	B	5	10.81
Bromine	Br	35	79.91
Cadmium	Cd	48	112.40
Caesium	Cs	55	132.91

Calcium	Ca	20	40.08
Californium	Cf	98	251*
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Curium	Cm	96	247.07
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	254.09
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	257*
Fluorine	F	9	19.00

Element	*Symbol*	*Atomic number (Z)*	*Relative atomic mass (A)*
Francium	Fr	87	223*
Gadolinium	Gd	64	157.25
Germanium	Ge	32	72.59
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Helium	He	2	4.00
Holmium	Ho	67	164.93
Hydrogen	H	1	1.01
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.20
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	260*

Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Mendelevium	Md	101	258*
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	237*
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.01
Nobelium	No	102	259*
Osmium	Os	76	190.2

Oxygen	O	8	16.00

Element	*Symbol*	*Atomic number (Z)*	*Relative atomic mass (A)*
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.09
Plutonium	Pu	94	244*
Polonium	Po	84	210*
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	146.92
Protactinium	Pa	91	231.04
Radium	Ra	88	226.03
Radon	Rn	86	222*
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.91

Rubidium	Rb	37	85.47
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulphur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	99*
Tellurium	Te	52	127.60
Terbium	Tb	65	158.93
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93

Tin	Sn	50	118.69
Titanium	Ti	22	47.90

Element	*Symbol*	*Atomic number (Z)*	*Relative atomic mass (A)*
Tungsten	W	74	183.83
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

*The specified values are the relative atomic masses of the most stable isotope.

Appendix 7: Some physical constants

Constant	*Symbol*	*Value*
Gravitational constant	G	6.670 ¥ 10^{-11} N m^{2} kg^{-2}

Velocity of light	c	2.9979 ¥ 10^{8} m s^{-1}
Atomic mass unit	amu	1.6605 ¥ 10^{-27} kg
Avogadro’s number	N_A	6.0221 ¥ 10^{23} mol^{-1}
Boltzmann’s constant	k	1.3807 ¥ 10^{-23} J K^{-1}
Mass of electron	m_e	9.109 ¥ 10^{-31} kg
Mass of neutron	m_n	1.6726 ¥ 10^{-27} kg
Mass of proton	m_p	1.6726 ¥ 10^{-27} kg
Faraday’s constant	F	9.64870 ¥ 10^{4} C mol^{-1}
Electron charge	e	9.1096 ¥ 10^{-31} kg
Gas constant	R	8.314 J K^{-1} mol^{-1}
		0.08206 dm^{3} atm K^{-1} mol^{-1}
		62.37 dm^{3} Torr K^{-1} mol^{-1}
Molar volume of gases at s.t.p.		22.4136 dm^{-3} mol^{-1}
Electron radius		2.8177 ¥ 10^{-15} m
Rydberg’s constant	R_H	1.0974 m^{-1}
Acceleration due to gravity	g	9.8066 m s^{-2}

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