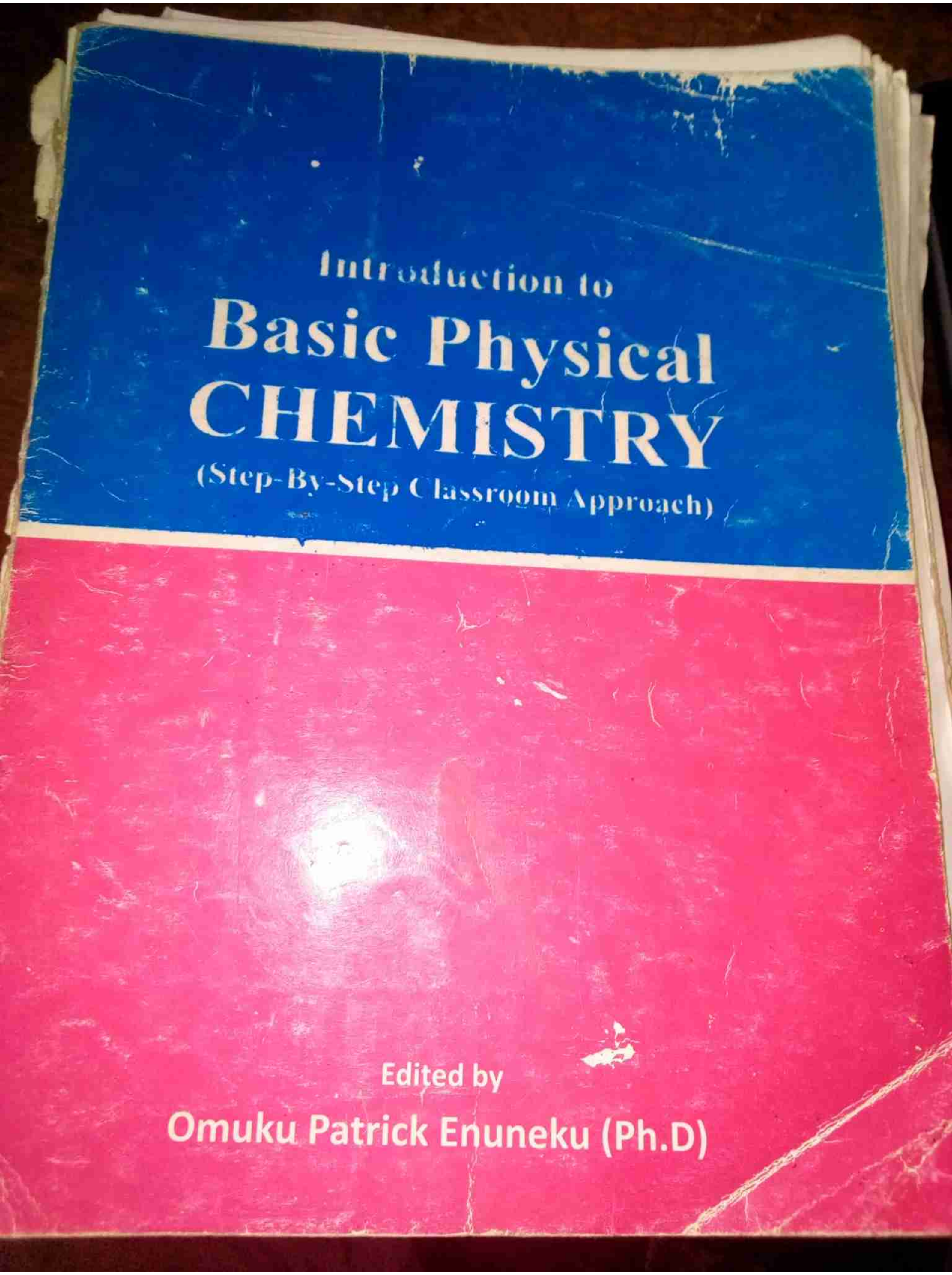

Introduction to

Basic Physical CHEMISTRY

(Step-By-Step Classroom Approach)

Edited by

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Chapter one

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1.1: General Introduction

Basic Physical Chemistry is an interesting aspect of chemistry that students hitherto dislike due to lack of interest in any mathematically oriented courses. Recently, students in the higher institutions have started developing interest in this aspect of chemistry, "Basic Physical Chemistry: Teach Yourself Approach"

This book is aimed at presenting to the students simple but classified ways of understanding some important aspect of physical chemistry visa-vis: the gas laws: Boyle's law, Charles law, the General Gas Equation, Gay-bussac's law, Gas Constant. Dalton's law of Partial Pressures, Graham's law of Gaseous Diffusion. The kinetic theory of matter. Derivation from the deal gas law; Van Der Waal's equation, liquefaction of gases, the Joule-Thompson effect properties of Dilute solutions with respect to concentration terms such as molarity, molality, mole fractions vapour pressure and lowering of vapour pressure. Raoult's law in relation to elevation of boiling point, lowering of vapour pressure and osmotic pressure.

The second aspect deals with the introduction to Thermodynamics and Thermochemistry in a view to elucidating terms such as systems, state variables, isothermal and adiabatic processes. The first law of thermodynamics, work done for state changes (PV type). Heat changes, heats of reaction, law of thermochemistry (Lavoisier and Laplace laws and Hess' law of constant heat summation). Bond energy etc.

Finally, chemical equilibrium and reversible reactions. The law of mass action, equilibrium constant, factors affecting chemical equilibrium, equilibrium between ions in the solid and liquid phases. Solubility product. Effects of a common ion in solubility and solubility product. Chemical kinetic, rate of chemical reaction, factors affecting the rate of a chemical reaction and activation energy were also properly examined.

1.2 The Gas Laws

Elements that are gases at room temperature are all non-metals such as He, Ar, N_2 and O_2 Compounds that are gases at room temperature are all covalent compounds e.g. CO_2, $S0_2$, NH_3, that contain two or more non-metals. Common gases at room temperature include H_2, O_2, etc.

Generally, these gases have relatively small atomic or molecular weights.

There are four major parameters or measurable properties that can be used to characterize a gas sample which are

- the volume (v)
- the pressure (P)
- the temperature (T) and

- the number of moles of the gas in the container (n). Gas laws are used to describe the relationship that exist among pressure, temperature and volume which can be used to characterize the general behaviour of gases.

1.3 Gases

In Chemistry, there are three major states of matter; solid, liquid and gas. Under certain conditions of pressure and temperature, most substances can exist in any of the states of matter for instance water (H_2O) can be solid ice (0^0C), liquid water (40°C) or steam or water vapour ($>1\,00^0C$).

Our discussion will be based on Gas. The name Gas was derived from a Greek word "chaos" meaning disorder. Gases exist in a state of disorder of collection of particles which are in constant and random motion. Gases are easily expandable and compressible unlike solids and liquids. Gases have a measurement of pressure. Pressure is defined as force exerted per unit area of surface. Gases has a low density because its molecules are spread apart over a large volume. A gas will fill whatever container that it is in for instance, if a bottle of Ammonia (NH_4) is being opened in a room, it is seen that the smell (odour) travels throughout the room.

The kinetic molecular theory is the bases of the many properties of gases which are:

(1) Gases are composed of molecule's whose size is negligible

compared to the average distance between them.

(2) Molecules of gases move randomly in straight lines in all directions and at various speeds, until collision.

(3) The force of attraction or repulsion between molecules in a gas are very weak or negligible except when they collide.

(4) When molecules collide with one another, the collisions are elastic, no kinetic energy is lost.

(5) The average kinetic energy of a molecule is proportion to the absolute temperature. Gases are much simpler than liquids or solids in many ways such as follows:

- In terms of temperature and pressure, gases behave more predictable than solids and liquids.
- Motion in gases is totally random and the forces of attraction between gas molecules are so small that each molecule moves freely and essentially independently of other molecules.

It is very important to know the kind of element or compounds that are gases at room temperature, they are thus:

NH_3 (ammonia)

N_2 (Nitrogen)

O_2(Oxygen)

F_2 (fluorine) and Ne(Neon)

Properties of Gases

(1) They expand to fill their container

(2) They are easy to compress

(3) They occupy far more space than liquids or solids under normal atmospheric conditions.

(4) Gases have much lower densities than solid and liquids

(5) Gases will mix evenly and completely, unlike some solids or liquids which may be immiscible.

Many scientist ventured into explaining our everyday life using temperature, volume and pressure as equipment to expatiate activities of gas. Scientists like Boyle's, Gay-Lussac, Charles Jaques and so on of which we are going to look into.

1.4 Boyle's Law

This law was postulated by Robert Boyle. He studied the behaviour of gases systematically and quantatively. It was published in 1622. Boyle's law describes the inverse proportional relationship between the absolute pressure and volume of a gas.

Boyle's law states that at constant temperature for a fixed mass, the absolute pressure and the volume of gas are inversely proportional.

$$P = \frac{k}{V}$$

$$P = Pk \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad (2)$$

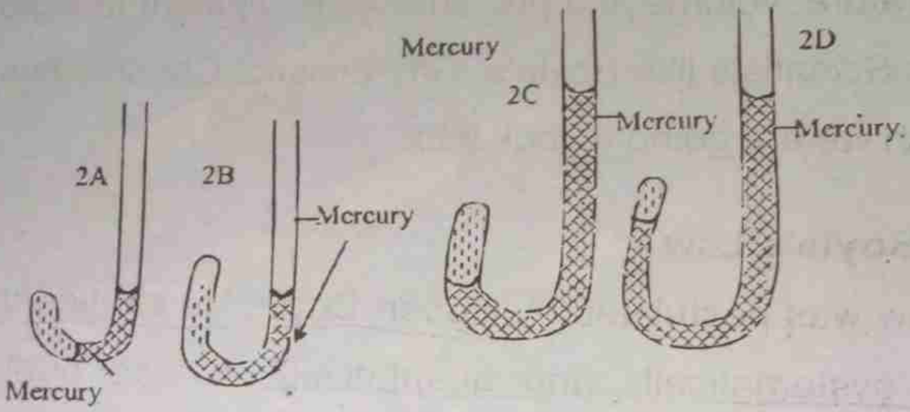
Where k = constant value representative of the pressure and volume of the system.

P = the pressure of the system

V = the volume of the gas.

Boyle's Derivation

Boyle's derived the equation above experimentally where he investigated the pressure-volume relationship of a gas sample using J-tube apparatus (i.e. a J-shaped tube) as shown below



Boyle added a mercury in a tube and found out that the pressure exerted on the gas by the mercury added to the tube as equal to atmospheric pressure in 2A. As more of the mercury is added, he found out that the volume was decreased and in unequal levels of mercury in the tube. This he also noticed in 2C and 2D that there is increase in pressure when more mercury was added and consistently, the volume decreased. Also if the pressure was decreased the volume will increase. This lead to the derivation of the below equation

$P = \alpha -$

and $P = \frac{k}{V}$

So long as the temperature remains constants the same value and the same amount of energy given to the system persists throughout its operation and therefore theoretically, the value of K will remain constant. However, due to the derivation of pressure as perpendicularly applied, force and the probable or likelihood of collision with other particles through collision theory, then predictions can be made.

Boyle's law is used to predict the result of introducing a change in volume and pressure, only, to the initial state of a fixed quantity of gas. Then before and after amount of gas, where before, and after temperatures are the same (heating and cooling will be required to meet this condition) which related by the equation.

$P_1V_1 = P_2V_2$.

1.5 Charles law

Just as Robert Boyle made effort to keep all properties of the gas constant except for the pressure and volume, so Charles Jacques took care to keep all properties of the gas constant except for temperature and volume. This law was prompted because hot air balloons were extremely popular at that time and scientist were eager to improve the performance of their balloons.

Charles used the same J-tube apparatus as Robert Boyle. A quantity of gas trapped in a J-shaped glass tube that was sealed at one end, his tube was immersed in a water bath of changing the temperature of the water, Charles was able to change the temperature of the gas. The pressure was held constantly by adjusting the height of the mercury so that the two columns of mercury had equal height and thus the pressure was always equal to the atmospheric pressure.

Charles law states that the volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature of the gas.

$$V \propto T$$

$$V = KT$$

where V = volume of the gas

T = Temperature of the system

We can compare 2 sets of volume- temperature conditions for a given sample of gas at constant pressure, we can write

$$\frac{V_1}{T_1} = K_1 \quad \text{and} \quad \frac{V_2}{T_2} = K_1 \quad \text{but } K_1 \equiv K_2$$

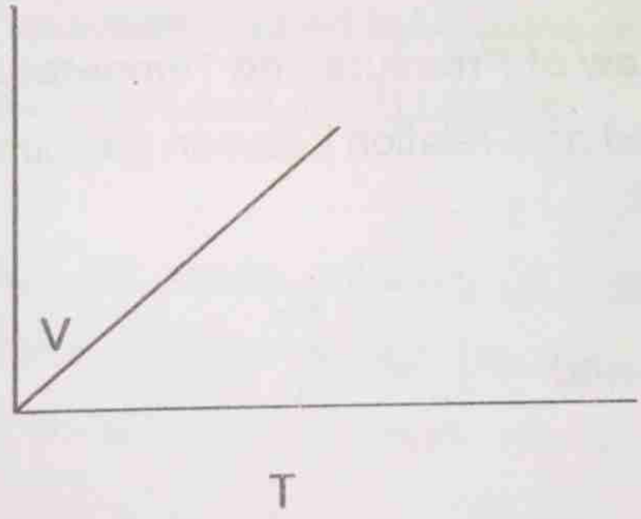
$$\therefore \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Where V_1 and V_2 are the volume of the gases at temperatures T_1 and T_2.

Charles law described the direct relationship between temperature and volume of a gas. A drop of absolute temperature brings about a proportional drop in volume. The volume of a gas increases by $\frac{1}{273}$ of its volume at 0^0C for every degree Celsius that the temperature rises.

To explain why this happens, let's explore temperature and volume in terms of gases. Temperature is an average of molecular motion. This means that while all of the gas molecules are moving around their container in different directions at different speeds, they will have an average amount of energy that is the temperature of the gas. The volume of the gas is the size of its container because the molecules will move in a straight line until they come in contact with something with (another molecule). However, to move as they do, the molecules requires kinetic energy which is measured by temperature. So, the volume and temperature are very closely related. If the temperature was not sufficient, the molecules would not be able to overcome the weak forces of attraction among them and would not be able to fill the container.

A plot of volume against temperature will give a straight line graph from origin thus:



Charles law only work when the pressure is constant.

1.5 Gay-Lussac's Law of Combining Volumes

It is used for each of the law relationship named after the French

Chemist. Joseph Loues Gay-Lussac and which concern the properties of gases. It is more usually applied to law of combining volume which states that: the law of combining volumes states that when gases reach, together to form other gases where all volumes are measured at the same temperature and pressure. The ratio between the volumes of the reactant gases and the products can be expressed in simple whole numbers.

This reflects the fact that (by Avagadroe law) equal volumes of gas contain equal numbers of molecules (at the same temperature and pressure) and also that in chemical reaction, the molecules combine in a ratio of whole numbers. This is known as stiochiometry of the chemical reaction and is expressed through the chemical equation for the reaction.

$$V \quad \alpha \quad \text{number of moles}$$

Gay-Lussac's Law of Pressure and Temperature

He also postulated as a relation between pressure and temperature.

i.e. $P \alpha T$

$$P_1 = \frac{K_1}{T_1} \quad \text{and} \quad P_2 = \frac{K_2}{T_2}$$

But $K_1 \equiv K_2$

Where P = Pressure

T = Temperature

K = Constant of proportionality

t is commonly written as

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Where P_1 and T_1 are the original values pressure and temperature of the gas, while P_2 and T_2 represents its final values. In addition to the pressure being constant, the same factors considered in any ideal gas laws apply here. These results apply for systems where an equilibrium state has been reached, the gas is not too dense and pressure is around atmosphere pressure.

1.7 Dalton's Law

It states that the total pressure exerted by a gaseous mixture is equal to the sum of the partial pressure of each individual component in the gas mixture. This law was observed by John Dalton in 1801 and is related to the ideal gas laws. This law explains that in a container of two gases A and B, pressure exerted by A alone and also B alone is equal to the pressure exerted by A and B together.

1802
1801

i.e. $P_T = P_1 + P_2 + P_3 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots P_n$

This law is useful for calculating volumes of gases collected over water. The compositions of gaseous mixtures are often expressed in percent by volume. In some cases, we found ourselves using it to work with partial volumes, which is also acceptable. The partial volume of each component in a gaseous mixture is the volume in which the component alone would occupy if it were present alone at the total pressure of the mixture. The total volume of a gaseous mixture is the sum of the partial volumes of its components.

$$V_{tot} = V_A + V_B + \dots\dots\dots\dots\dots\dots\dots\dots V_n$$

1.8: General Gas Equation

Thus as composed of the laws already discussed, that is Boyle's law, Charles Law, Avogadre's law.

Combining them prompts up what is called ideal gas equation.

Boyle's law = $V \alpha \,{}^1/_P$

Charles law = $V \alpha T$

Avogadros law = $V \alpha n$

We combine all the three expression to form a single master equation for the behaviour of gases

$$V \alpha \frac{nT}{P}$$

$$\therefore \quad V = \frac{nRT}{P}$$

$$PV = nRT \quad - \quad - \quad - \quad - \quad - \quad \text{Gas equation}$$

Where R = proportionality constant (Gas constant) with value of ($8.314472JK^{-1}mol^{-1}$). This equation describes the relationship among the four variables, i.e. pressure (P), volume(V), temperature (T) and no of moles (n).

It is used in solving many problems concerning gases. Because it covers most of the variables present in gases that is how the gases behave. We can drive the unit of R to enable us apply it to any other problems.

$$PV = nRT$$

$$R = \frac{PV}{NT}$$

Substituting the molar volume of gas at STP (Standard Temperature and Pressure),22.414L

$$1 \text{ atm} \times 22{,}414\text{L} = \frac{0.08205\text{Latm}}{\text{mol K}}$$

$$R = \frac{PV}{NT} \quad \frac{1 \text{ atm} \times 22.414\text{L}}{1 \text{ mole} \times 273.15\text{K}}$$

$$=$$

$$= \quad 0.08205\text{Latom.mol}^{-1}\text{K}^{-1}.$$

R can now be expressed as:

Litre atmosphere per mole per Kelvin

i.e. Latm $\text{mol}^{-1}\text{K}^{-1}$

we can also generate a formula that convert two different sets of condition.

Final

$P_2V_2 = n_2RT_2$

Initial

$P_1V_l = n, RT_1$

Final

$P_2V_2 = n_2RT_2$ $\qquad \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} =$ For 2 sets of conditions

initial

(2) A ballon is inflated to a volume of 2.50L in a warm living room (24^0C). Then it is taken outside on a very cold winter's day (-30^0C). assume that the quantity of air in the balloon and its pressure both remain constant, what will be the volume of the balloon when it is outdoors.

Solution:

Applying Charles's law

$$K = \frac{V}{T}$$

We write it twice because of the initial and final temperature given i.e.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = K$$

$T_1 = 24^0C = 24+273 = 297K$

$T_2 = 30^0C = -30+273 = 243K$

$V_1 = 2.50L$

$$\therefore \quad V_2 = \frac{V_1T_2}{T_1} = \frac{2.50L \times 243K}{297K}$$

$V_2 = 2.054\text{Litres}$

Exercis

(1) If an aerosol can contains a gas at 1.52atm pressure at 22°C, what will be the gas pressure "in the can if it is dumped into an incinerator at 935^0C (Hint: for a fixed amount of gas in a constant volume, pressure is directly proportional to Kelvin

temperature)

(2) A 125-g piece of solid carbon dioxide ("dry ice) sublimes (evaporates without first melting) into $CO_2(g)$. What is the volume of this gas at STP, in litres'

(3) A 1.00L flask of 02(g), first at STP and then at 100^0C what is the pressure at 100^0C.

1.9 Pressures of an ideal gas •

Consider one molecule of mass M moving towards face 1 and the X-components of its velocity is Cx. It momentum in the x-direction is MC_x. At face one there is a perfectly elastic collision so that the reverse of the momentum is - MC_x. This result in a momentum change. Changé in momentum= MCx - ($-MC_x$) = $2MC_x$. After colliding with face one, the molecule travels a distance 2L (i.e 2 transfer one) before it could collide ~~again~~ with face one again. This takes a time t, which is given by =2L1Cx. we need to get the pressure but we need to know the force and we can work it out by Newton II, consider the impulse which is the change of momentum. Change in II, consider the impulse which is the change of momentum. Change in momentum = Impulse $\Delta = F\,T$

Rearranging gives us $F = \dfrac{\text{change in momentum}}{\text{change in time}}$

Time interval is the time taken for the molecule to move up the box to the far end, bounce off and come back again.

$$\text{Time} = \frac{\text{Distance}}{\text{Speed}} = \frac{2L}{Cx}$$

$$F = \frac{2MCx}{\Delta T} = \frac{2MCx.\ Cx}{2L} = \frac{MC_x^2}{L}$$

pressure on face I. They are of face 1 = L_2

Since pressure is $\frac{\text{Force}}{\text{Area}}$, we can work out

Pressure on face I. They area of face 1 = L^2

$$P = \frac{\text{Force}}{\text{Area}} = \frac{MC_x^2}{L.L^2} = \frac{MC^2{}_x}{L^3}$$

Suppose we have N molecule of gas, the pressure will be

$$P = \frac{NMC^2{}_x}{L^3}$$

Now L^3 is the volume of the gas, so we can rewrite the equation as

$$L^3 \equiv \text{Volume (V)}$$

$$\therefore \quad P = \frac{NmC^2}{V}$$

Where N = number of molecules

M = mass of one molecule

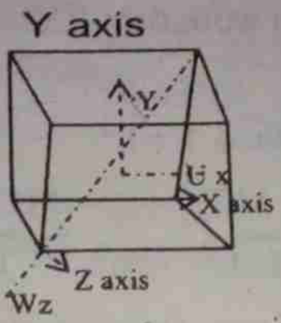
Recall that Nm = M = molecular mass

The term (C_{2x}) (square bar') is called the mean square speed of molecules in the x-direction. The bar is written over the C^2. However, the molecules are moving randomly in the container and very few would be moving exacting parallel to x-axis. However, we can consider each molecule's velocity to be the resultant of three component C_x, C_y, C as in two dimensions, the three component can be combined by Pythagoras to the resultant velocity

$$C^2 = C_x^2 + Cy^2 + C_z^2$$

Similarly we can combine the mean square velocities

$$\overline{C}^2 = \overline{C}_x^2 + \overline{C}_y^2 + \overline{C}_z^2$$



Since there are a large number of molecules one can assume that there are equal numbers moving in each of the co-ordinate direction

$$\overline{C}_x^2 = \overline{C}_y^2 = \overline{C}_z^2$$

So we can rewrite

$$\overline{C}^2 = 3\overline{C}_x^2 = \overline{C}_x^2 = {}^1/_3\overline{C}^2$$

So our final equation becomes

$$P = \frac{⅓NMC^2}{V} \rightleftarrows PV = ⅓NMC^2$$

Where N = total number of molecules

M = mass of one molecule

However, we can go ahead since Nm is the total mass of the gas and V is the volume we can express the pressure in terms of the density.

$$\text{Density} = \frac{\text{[redacted] mass}}{\text{Volume}} = \frac{Nm}{V}$$

This gives us the equation $P = \frac{1}{3}P\overline{C}^2$

Note: Be careful of the difference between the square of the mean $(<c>)^2$ ("c-bar squared) and the mean square $<C^2>$ ['C-squared bard']. Consider 1+2+3 = 6. The average is 2 and the square of the mean is $4(1^2+2^2+3^2) \div 3 = 4.67$ so there is quite a difference. The most probable speed is that which the greatest number of molecules are moving. The mean speed is the average value of all the speeds. The root mean square speed is square root of the mean square speed of the molecules.

1.10 Avogardo's Law

We can illustrate this law by considering a balloon containing a certain mass of gas. If we add more of the gas to the balloon while keeping the temperature (T) and pressure (P) constant, the volume of the gas (V) will increase. It was found that the amount of gas in moles is proportional to the volume at constant P and T.

$n \ \alpha \ V$ (T and P constant)

$V = nK$ (K = proportionality constant)

$$\frac{V}{n} = K$$

for any two gases with volumes V_1, V_2 and moles n_1, and n_2 at constant T and P

$PV = Nmc^2$

$P = \frac{Nmc^2}{V}$

$$\boxed{PV = \frac{1}{3}Nmc^2 \qquad P = \frac{\frac{1}{3}Nmc^2}{V}}$$

$$\boxed{P = \frac{1}{3}\rho c^2}$$

$P =$

$\frac{V_1}{n_1} = K_1$ also $\frac{V_2}{n_2} = K_2$ where $K_1 \equiv K_2$

Then

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad \text{if } V = V_2 \text{ then } n_1 = n_2$$

For equal volumes of the two gases at fixed T and P, number of moles is also equal. This leads to the statement of Avogadro's law which states that equal volumes of gases at the same temperature and pressure contain equal number of moles or molecules.

1.1'1 Graham's law of Diffusion

The law states that at constant temperature and pressure, the rate of diffusion of any gas is inversely proportional to the square root of its density or

molecular weight of the gas.

Recall that $PV = \frac{1}{3}MnC^2$ or ideal gas equation

$$C^2 = \frac{3PV}{Mn}$$ where Mn = total mass of the gas

but $\frac{Mn}{V}$ = density (e) of the gas

$$\therefore C^2 = \frac{3P}{e} \qquad C = \sqrt{3P/e}$$

or

root mean square speed of a gas in terms of pressure (P) and density (e) can be $PV = \frac{1}{3}MN\overline{C}^2$ (fundamental gas equation)

$$P = \frac{\frac{2}{3}mN\overline{C}^2}{V} = \frac{1}{3}(mN/v)\,\overline{C}^2$$

$$P = \frac{2}{3}\left(\frac{\text{mass of one molecule x number of molecule}}{\text{Volume of gas}}\right)C^2$$

$$P = \frac{2}{3}\left(\frac{\text{mass of gas}}{\text{Volume of gas}}\right)C^2$$

$$P = \frac{2}{3}eC^2$$

$$P = \frac{2}{3}\left(\frac{\text{Density of gas}}{\text{mass of gas}}\right)C^2$$

$$\therefore \sqrt{C^2} = \sqrt{3p/e}$$

Root mean square speed in terms of molar mass (M) and temperature (T)

$$PV = \frac{2}{3}mNC^2 \quad \text{Fundamental gas equation}$$

$PV = nRT$ (Ideal qas equation)

$nRT = {}^1/_3\, mNC^2$

but $n = \frac{L}{N}$ where $L =$ Avogadro's number

$N =$ No of molecules

$$NRT = \frac{1}{3}mNC^2$$

$$C^2 = \frac{N3RT}{mL} = \frac{3\,RT}{M} \quad \text{where } M = \text{molar mass}$$

1.12 Deduction for Kinetic Theory

If the kinetic energy of N molecules is directory proportional to the absolute temperature at constant pressure

K E of N and T

So that $\frac{1}{3}NmC^2 = KT$

Introducing $^3/_2$ so that when it cancel $\frac{1}{3}MN^1C^2$ you get back $\frac{1}{2}MN^1C^2$ which is kinetic energy

$$^3/_2(\tfrac{1}{3}NmC^2) = {}^3/_2KT$$

1.13 Daltons Law of Partial Pressure

The law states that the total pressure exerted by a mixture of gases in definite body is equal to the sum of partial pressure which each gas will exert if temperature remain constant.

$$P = P_1 + P_2 + P_3$$

Recall $P = \dfrac{\frac{1}{3}NmC^2}{V}$

$$\therefore \quad P_1 = \frac{\frac{1}{3}Nm_1C_1^2}{V}; \quad P_2 = \frac{\frac{1}{3}Nm_2C_2^2}{V}; \quad P_3 = \frac{\frac{1}{3}Nm_3C_3^2}{V}$$

The deduction of gas law from kinetic theory showed that I3Y = 1-/3mn $^1C^2$ is in concordance with the ideal gas equation

$$PV = nRT$$

$$n^1 = nN$$

Where n^1 = Number of molecules

n= number of moles

N = Avogardo's number

Substituting nN for n^1 from $PV = \frac{1}{3}Mn^1C^2$ we have

$$PV = \tfrac{1}{3}mnNC^2 = nRT$$

Note $mN = M$ = molecular weight.

By definition, molar mass of a gas is mass of one mole multiplied by Avogadro's number

$= \frac{1}{3} nmC^2$

Derivation from Ideal gas law:

$$\frac{PV}{T} = K \text{ (for a forced mass of gas)}$$

The above equation is from continued gas law. In Avogardo's law V and n or V=kn. We can go ahead to multiply the combine of gas law with n which depicts the number of moles and if that is done, the equation can be written as $\frac{PV}{T} = nR$

.With R, the universal constant in place of K

$\therefore \quad PV = nRT$ (ideal gas law)

The equation can be rearrange to *solve* for R

$$R = \frac{PV}{nT}$$

With the above equation one could determine the number of moles (n) if P,V and T are known.

1.14 Kinetic Energy of Translation

The kinetic energy of molecule is given by $\frac{1}{2} MC^2$ where m represents the mass of the molecule. The total kinetic energy (E_k) of all the molecules is given by

$$E_k = \frac{1}{2} n_1 mC^2$$

$E_k = {}^3/_2({}^1/_3 n_1 mC^2)$

If $^1/_3 n_1 mC^2 = nRT$

Then $E_k = {}^3/_2 nRT$

For one mole $Ek = {}^3/_2 RT$

From the above equation it can be deduced that the translational motion is directly proportional to the absolute temperature, hence, the average kinetic energy can be obtained by dividing with the Avogardon's constant.

$$E_k = \boxed{\frac{3RT}{2N}}$$

Where $K = R/N$

K = Boltzmann constant

1.15 Boltzmann Distribution

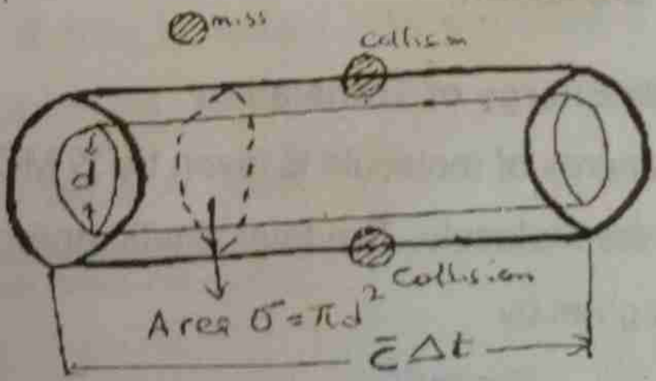
An isolated molecule may be in any one of the energy states such as E_1, E_2, E_3, ...etc. For a group of molecules at equilibrium, the no of molecules in various energy states i is given by Ni.

Where $Ni = Ae^{Ei/kT}$

But the total no of molecules is N.

where $N = \Sigma Ni$

$$\frac{Ni}{N} = \frac{Ae^{Ei/kT}}{\Sigma e^{Ei/kT}}$$



Where $\frac{Ni}{N}$ gives the fraction of the molecules in energy state: while the summation □$e^{Ei/kT}$ signifies the molecular partition function because molecules are partitioned among the various energy states.

1.16 Intermolecular Collision

We count a collision whenever the centres of two molecules come within some distance (d) of each other where d is taken as the diameter. The approach to the problem is to freeze the positions of all the atoms except the atom of interest and observe what happens as the force one transcends times Δt by so doing it sweeps out a 'collision tube' of area $\delta = \pi d^2$, length $C\Delta t$ and hence of volume $\delta C\Delta t$. δ which is labeled the collision cross-section. The number of molecules with centres inside this volume is $\delta C\Delta tN$, where N is the number of molecules per unit volume and so the number of molecules per unit volume while the number of collision is $\delta C\Delta tN$. Also collision frequency (no of collision per unit time) is $\delta C\Delta N$.

Error arises from the supposition that more than one or all the molecules are static in position then the C in the equation should be the average relative speeds of the colliding molecules. If this is taken into account it will then turn out that C should be replace with $\sqrt{2}\bar{C}$ making the collision frequency to be $Z = \sqrt{2\delta\bar{C}\frac{N}{V}}$

The above equation represent the number of collision a single molecule makes. We can go ahead to get the total collision made by multiplying by ½ N (this is to ensure that the collision A, A^1 are counted as only one collision.

:. Collision per unit volume per unit time is given as

$$Z_{AA} = \frac{1}{2} . 2\frac{N}{V} = \delta C\,(N/v)^2\sqrt{2}$$

The value of C to be used here is

$$C = (V) = \int_0^\infty f(v)dc = \left(\frac{8KT}{\pi m}\right)^{1/2}$$

Hence we conclude that

$$Z_{AA} = \boxed{\pi d^2(4KT/\pi m)^{1/2}\,(N/v)^2.}$$

1.17 Collision with Walls and Surfaces

Lets look at a wall of area A perpendicular to the X-axis. In the container there are N molecules per unit volume, If the molecules has a velocity V_x lying between (x) and as, it will strike the wall in a time Δt of it lies within a distance. $V_x\Delta t$ of it (note if the molecule has a V_x lying between 0 and ∞ it is a wrong direction). So all molecules in the volume $Av_x\Delta t$ with velocity in the right direction, will strike the wall in the interval $\underline{\Delta t}$. The total number of collision is No of collision = $A\Delta t$

$$\int_0^\infty V_x f(v_x)dv_x$$

0 and ∞ → wrong direction
Δt → right direction.

The integral can be evaluated using the explicit form of the velocity distribution

$$\int_0^{\infty} V_x f(v_x) dv_x = (m/2\pi KT)^{1/2} \int_0^{\infty} V_x \exp(-mv^2x/2kT)\, dvx = (KT/2\pi m)^{1/2}$$

$\therefore$ No of collision per unit time per area is

$$Z_w = (KT/2\pi m)^{1/2} N/V = 1/4\, C\, N/V$$

Note: the number of density N/V can be converted into an expression in terms of the pressure by writing.

$$N/V = P/KT \text{ and so}$$

$$Z_w = 1/4\, PC/KT = P/t_2\pi mKT)^{1/2}$$

1.8 Vander Waal's Equation

This is equation of state for a fluid composed of particles that have non- zero size and perwise attractive inter-particle force (such as Vander Waal force). This equation approximates the behavior of real fluids taking into account the non-zero size of molecules and the attraction between them.

The first form of the equation is

$$\left(P + \frac{a^1}{v^2}\right)\left(V - b^1\right) = KT$$

Where P = pressure of fluid

V = volume of the container holding the particle divided by the total number of particle.

K = Boltzman constant

T = Absolute Temperature

a^1 = Measure of attraction between the particles

b = Average volume excluded from a particle

Upon introduction of Avogardro's constant N_A, the number of moles n, and the total number of particle (nN_A) the equation can be taken into the second form.

$$\left(P + \frac{a^1}{v^2}\right)\left(V - nb\right) = nRT$$

Where P = pressure of fluid

V = total volume of the container containing the fluid

a = measure of attraction between the particle

a = $N_A{}^2a^1$

b = volume excluded by a mole of particle

b = N_Ab^1

n = number of moles

R = gas constant

R = N_AK

T = absolute temperature

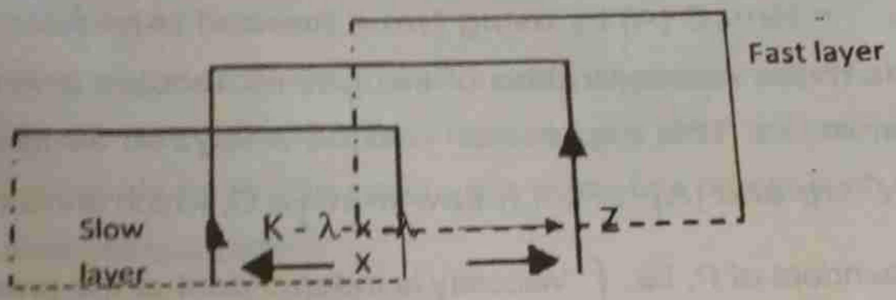
A careful destruction must be made between the volume available to particle and the volume of a particle in particular. In the 1st equation, refers to free space available per particle. This V is volume of the container divided by the total number (nN_A) of particle.

The parameter b^1 on the other hand is proportional to proper volume of a single particle. The volume bounded by the atomic radius. This is the volume to be subtracted from V because of the space taken up by one molecule. In Vander Waals equation, we can derive various relationships.

Note: The pressure P goes to infinity when the container is completely filled with particles so that there is no void space left for particles to move. This occurs when V = nb.

1.19 Viscosity

Viscosity is the measure of frictional resistance that layer of fluid in motion offer to another. The reciprocal of viscosity is fluidity.



Now from the above structure, molecules travelling from the right (i.e. from the fast layer to a slower one), transport a momentum $MV_x(\lambda)$ to their new layer at Z = 0 while travelling from the left transport a momentum $MV_x(-\lambda)$. Assume the density is uniform, the collision fluix is ¼ NC.

Those arriving from the right on average, carries a momentum.

$$MV_x(\lambda) = mV_x(0) + M\lambda \left(\frac{dV_x}{dz}\right)_0$$

The net flux of X-momentum in the z-direction is $J = \left[\frac{1}{4} NC, vx(0)\, m\lambda\right]\left[-\ \right]$

$$= \frac{1}{4} NC. ([mV_x(0)]-$$

$$= -\frac{1}{2} NM\lambda C \left(\frac{dV_x}{dz}\right)_0$$

If we compare this expression with (components of momentum) n $\left(\frac{dv_x}{dz}\right)$

= (from transport property of perfect gas) and multiplied by $^2/_3$ we will get

$$n = \tfrac{1}{3}Nm\lambda C$$

we can go ahead to convert the above equation into

$$n = \tfrac{1}{3}m\lambda C\,[A] \text{ by using } Nm = nm \text{ and } [A] = n/v$$

where A is molar concentration of the gas molecules and m is their molar mass. This expression can be analyzed as flows:

(1) $\lambda \propto 1/p$ and $[A] \propto P$, it follow that $\int \alpha C$, which shows that $\int$ is independent of P, i.e. $\int$ viscosity is independent of the pressure.

(2) C and $T^{1/2}$ i.e. $\int \alpha T^{1/2}$ the viscosity of a gas increase with temperature.

1.20: Law of Equipartition of Energy

This law' makes it possible for the thermal equilibrium for the total energy possessed by the molecules of a gas to be distributed evenly into translational kinetic energy and vibrational potential energy. Recall that the velocity in space is related to component velocity. So that we have

$$C^2 = C^2_x + C_y^2. + C_z^2$$

Multiplying both side by ½ M we have $\frac{1}{2}MC^2 = \frac{1}{2}MC^2 + \frac{1}{2}MC^2_y + \frac{1}{2}MC_2^2$

∴ the total kinetic energy (KT) of the gas molecule is $\frac{1}{2}MC^2$ while $(K.EY)^x$ $(K.E)_y$ and $(K.E)_z$ represents the average kinetic energy me. The x, y and z velocity component making total kinetic energy (ET) = K.E)x + (K.E)y +

(K.E)z since the x, y and z directions are all equivalent, by principle of equipartition of energy ($C^2_x = C^2_y = C_2^2$) which is same as $K.E_x = K.E_y = K.E_z$

$K.E_x = ½ KT$, $K.E_y = ½ KT$ and $K.E_z = ½ KT$

From the above equation, the average kinetic energy associated with each translational degree of freedom is ½ KT and it applies for other types of motion.

1.21 Liquefaction of Gases.

The liquefaction of gases deals on the number of phases used to convert a gas into a liquid state. Many gases can be put into a liquid at normal atmospheric pressure by simple cooling but some few others such as carbon dioxide requires pressuration.

Liquefaction is used for analyzing the fundamental properties of gas molecules (intermolecular force) for storage of gases as in refrigeration and air conditioning. There the gas is liquefied in the condenser, where the heat of vapourization is released and exporated in the evaporator where the heat of vapourization is absorbed.

Liquid oxygen is provided to hospital for conversion for patients suffering from breathing problems and liquid nitrogen is used to freeze semen. Liquified chlorine is used for water purification, sanitization of industrial waste, sewage and swimming pool treatment. Liquified chlorine could also be used for bleaching of pulp and textiles and manufacturing of carbontetrachloride, glycol and many other organic compounds as well as phosgene gas.

Questions

Calculate the average speed and root mean speed for the following sets of molecules

10 molecules moving at 5×10^2m/s

7 Molecules at 7×10^2m/s

5 molecules moving at 10×10^2m/s

$$C_x = \frac{C_1 + C_2 + C_3}{N}$$

N = number of molecules

$$= \frac{10(5\times10^2)+7(7\times10^2+5(10\times10^2)}{22} \cdot \frac{149000}{22}$$

$$= 6772.7$$

Root mean square speed

$$C\sqrt{\frac{c_1^2 + c_2^2 + c_2^2}{N}} = \frac{10(5\times10^2)+7(7\times10^2+5(10\times10^2)}{22}$$

$$= 18341.4\text{m/s}$$

What is the density of a gas at a pressure of 10^5 N/M when the root mean square velocity of its molecules is 3.x10 = M/S recall $Pv = \frac{1}{3}mnC^2$.

$$\text{Density} = \frac{mn}{v} = \frac{3p}{c^2}.$$

$$= \frac{3(10^5)}{(3\times10^2)^2} = 3.33\times10^{-1}\text{kg/m}$$

3. viscosity of hydrogen at 0^0C is 5.41×10^{-5} poise, determine the mean free path of the molecule at this temperature and 1 atm of pressure

$$n = \frac{1}{3}mn^{1}C\lambda$$

$$n = \frac{1}{3}eC\lambda$$

To determine density e since at 0^0C and 1 atm 2.016g of hydrogen occupy the volume at S.T.P. which is $2400cm^3$ or $22.4dm^3$

$$\therefore \quad e = \frac{m}{v} = \frac{2.016}{22400Cm^3} = 9.0 \times 10^{-5} g/cm^3.$$

For the root mean speed (c)

$$C = \frac{8RT}{\pi M}$$

$$= \frac{8 \times 8.314 \times 10^7 \times 273K}{3.14 \times 2.016g} = 2.869x1011$$

Where

$n = 5.41x10-5$

$e = 9.0x10-5$

$C = 2.869x1011$

$\lambda = 7$

So $\lambda = \frac{37}{eC}$ noting the original formula $7 = \frac{1}{3}eC\lambda$

We have $$\frac{3 \times 5.41 \times 10^{-5}}{9.0 \times 10^{-5} \times 2.869 \times 10^{11}} = 6.285 \times 10^{-12}.$$

NOW ATTEMPT THIS

1. Consider the most probable speed, mean velocity and root mean speed for oxygen molecule at 10°C.

   Note: mean velocity = mean speed

   Probable speed = probable velocity

   Most of 02 = 2 x 16 = 32.

2. The observed speed of 10 particles at a particular instance are shown in the table blow.

No of particle	1	2	4	1	1	1
Speed (m/s)	5.0	7.0	9.0	12.0	14.0	15.0

A. What is the most probable speed.

B. What is the mean speed

C. What is the root mean square speed of the molecules .

3. N gas is kept in a closed container at a temperature of 27°C and pressure of 1.0×10^{-5} bar. The density of N is $1.25 kgm^{-3}$. Calculate

I. The root mean square of the molecule.

II. Temperature at which the molecules travels twice as fast as it was.

Chapter Two.

By Omuku, P.E.

PROPERTIES OF DILUTE SOLUTIONS

2.1 Dilute Solution

A solution is a mixture of two or more chemically non-reactive substance whose relative amount can vary within certain limits. A solution can also be defined as a homogenous mixture of two or more substances consisting of a single phase. Based on the size of the particles of the various substances present in a mixture, we can classified mixtures into homogenous or heteroqenous mixture. Homogenous mixture is a mixture in which the molecular size of the constituent particles ranges, from 1 milimicron (1 mμ) to 5μ with a uniform distribution. They cannot be separated from one another by ordinary mechanical, means. They form "true solution", e.g. solution of sugar in water.

The molecular size of the particles in heterogenous mixture is greater than 200mμ. They may not be uniformly distributed and the, particles may be separated by simple mechanical means.

Generally, the two major components of a solution are **SOLVENT** and **SOLUTE**. The solute is the substance that dissolves in the solvent while the solvent is the medium in which the dissolution takes place. A solution may exist in solid, liquid of gaseous phase. The solid phase of a solution exists when the solution is frozen. The liquid phases of the solution occur when the solute is completely soluble in the solvent at room temperature. The vapour phase of a solution is noticeable when the solution is vapourised. A binary solution is composed of two substances while ternary solution is made of three main components.

A dilute solution is a solution that is made up of relatively low amount of the solute in a given solvent.

2.1.1 Composition of a dilute solution

Solvent	**Solute**	**Solution**
(1) Gas	Gas	Air
(2) Liquid	Gas	Carbonated drinks e.g. CO_2 in H_2O, O_2 in H_2O
(3) Solid	Gas	Adsorption of H_2 by palladium
(4) Liquid	Liquid	Alcohol in water
(5) Solid	Liquid	Mercury in silver
(6) Liquid	Solid	Salt in water
(7) Solid	Solid	Metal alloys

2.1.2 Dilute Solution Expressions

The composition of a dilute solution can be expressed in different ways each having its significant for a particular purpose.

(a) percentage by weight

(b) molarity

(c) molality

(d) mole fractions

(e) normality

2.1.2.1 Percentage by Weight

This is the weight of the solute as a percent of the total weight of the solution. This is applicable when the molecular mass of the solute is unknown during chemical analysis.

$$\% \text{ by wt of solute} = \frac{\text{wt of solute}}{\text{wt of solute + wt of solvent}} \times \frac{100}{1}$$

e.g. if a solution of NaCl is 48% NaCl by weight (w). it means wt of NaCl = 48. wt of solvent = 52

Problem: What is the % by weight (wt) of $CaCl_2$ if 5.60g of Cacl, is dissolved in 25.50g of H_20

Solution:

$$\% \text{ wt} = \frac{\text{wt of } CaCl_2}{\text{Wt of } CalCl_2 + \text{wt of } H_2O} \times \frac{100}{1}$$

$$= \frac{5.60}{5.60+25.50} \times \frac{100}{1} = 18\%$$

2.1.2.2 Molarity

Molarity is used in volumetric analysis to show the amount of solute per dm^3 of a solution. It is the no of mole of the solute present in 1000ml of the solution

$$M = \frac{\text{Mass}}{\text{Molar mass}} \times \frac{1000}{\text{Reg.V.(in ml)}}$$

$$M = \text{molartiy} = \frac{\text{Moles of solute}}{\text{Litres of solution}}$$

Problem

Determine the molarity of a solution prepared by dissolving 68g of pure HCl in 650ml of distilled water.

Molality

Molality are generally used in physical chemistry to express mass concentration. It is the number of mole of the solute present in 1kg of the solvent

2.1.2.4 Mole Fraction

Mole Fraction of a substance in a solution is the no of moles of the substance divided by the total no of moles of all the substance present in the solution. It is basically used in physical chemistry. The % by wt, molarity, molality, normality, mole fraction, do not change with change in temperature of the solution.

For a binary solution, the mole fraction of a solute is equal to number of moles of the solute divided by the total number of moles of the solute and the solvent.

$$X_{solute} = \frac{\text{No of moles of solute}}{\text{No. of moles of solute} + \text{No of moles}} \times \frac{100}{1}$$

$$X_1 = \frac{n_1}{n_1 + n_2}, \qquad X_2 \frac{n_2}{n_1 + n_2}$$

X_1 =, mole fraction of solute

X_2 = mole fraction of solvent

n = no of moles of solute

n_2 = no of moles of solvent

In general $X_1 + X_2 = 1$ for a binary solution and the sum of all the mole fractions of a particular substance is unity i.e. $X_1 + X_2 + X3 + \quad = 1$

Question

Determine the mole fraction of NaCl in a solution of NaCl in water containing 22% NaCl by wt.

$$n_1 = \frac{\text{mass}}{\text{molar mass}} = \frac{22}{58.5}$$

$$n_2 = \frac{78}{18}$$

$$X_1 = \frac{0.3761}{0.3761 + 4.3333}$$

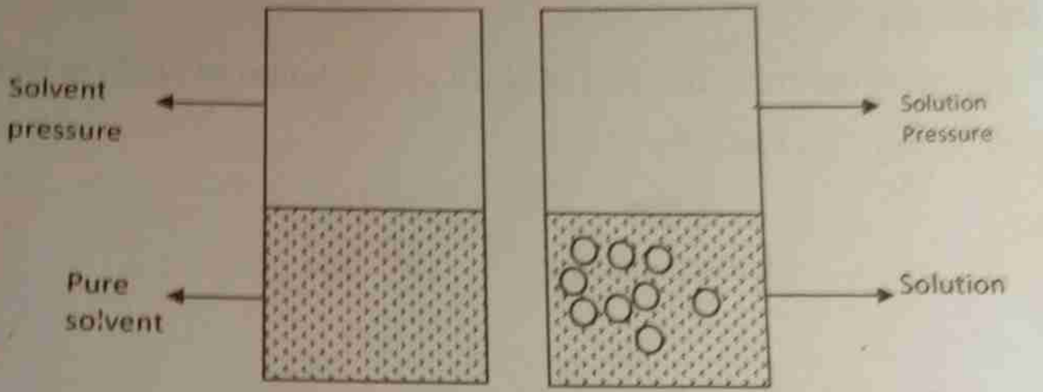
2.2. Colligative Properties

Colligative properties are properties of a dilute solution that depend on the number of solute particles present in a given solvent. The four basic colligative properties are

1. Vapour pressure lowering of the solvent
2. Boiling point elevation of the solution
3. Freezing point depressing of solution
4. Development of osmotic pressure.

2.2.1 Vapour Pressure Lowering of the solvent

Vapour pressure is the pressure generated when a number of molecules evaporating from the surface of the solvent or solution hit the wall of the containing vessel. Vapour pressure lowering of the solvent is the decrease in vapour pressure of a pure solvent (P^0) when a non-volatile solute is dissolved in it.



P^0 = vapour . Pressure of pure solvent

P = vapour of pressure of solution ($P^0 > P$)

Raoult's Law

States that the partial vapour pressure (V.P) of a non volatile solute is equal to the vapour pressure (V.P) of the pure solvent multiplied by the mole traction of the solute.

$P_1 = X_1 p^0$, $P_2 = X_2 P^o$

P_1 = partial V. P. of the solute

P_2 = V.P. of the solute

P^0 = V.P. of the pure solvent

X_1 = mole fraction of the solvent

X_2 = mole fraction of the solute

This shows that for real solution, the partial vapour pressure (V.P) of any of the constituent is directly proportional to its mole fraction.

$P_1 \alpha X_1$ and the constant of proportionality is the vapour pressure of the pure solvent. $P_1 = X_1 P^0$

but total pressure $P = P_1 + P_2$ from Daltons law of particle pressure

$P = P_1 + P_2 = X_1 P_1^0 + X_2$

P_2^0

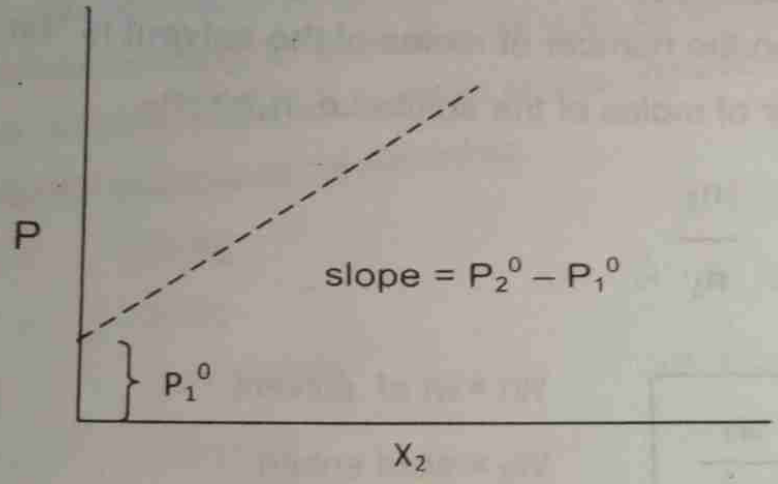
$P = X_1 P_1^0 + X_2 P_2^0$

$P = P_1^0(1 - X_2) + X_2 P_2^0,$

$P = P_1^0(1 - X_2) + X_2 P_2^0,$

$' = P_1^0 + X_2(P_2^0 - P_1^0)$

A plot of V.P. above a solution against mole fraction of the solute is shown below



Relative lowering of V.P.

Raoult carried out an experiment which gave an empirical relationship between relative lowering of V.P. and the concentration of the solute in dilute solutions. Hence Raoults's' law can also be stated as the relative lowering of ·V.P. of a dilute solute is equal to the mole fraction of the solute.

$0.950 = \frac{760-P}{760}$

$722 = 760-P$

$$\boxed{X_2 = \frac{P^0 - P}{P^0}}$$

X_2 = mole fraction of solute

p^0 = V.P of pure solvent

P = V.P of dilute solution

but

$$\boxed{X_1 = \frac{n_2}{n_1 + n_2}}$$

n_1 = number of mole of solvent

n_2 = number of mole of solute

For a very dilute solution the number of moles of the solvent is "far far" greater than the number of moles of the solute i.e. $n_1 >>> n_2$.

$$\therefore X_2 \frac{n_2}{n_1 + n_2} \cong \frac{n_2}{n_1}$$

$$\boxed{n_1 = \frac{w_1}{mm_1} = \frac{w_1}{m_1}}$$

W_1 = wt of solvent

W_2 = wt of solute

M_1 = molar mass of solvent

M_2 = molar mass of solute

$$\boxed{n_2 = \frac{w_2}{M_2}}$$

From Raoults law $X_2 = \frac{P^0\text{-}P}{P^0} \cong \frac{n_2}{n_1}$

$$\frac{P^0\text{-}P}{P^0} \simeq \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1}$$

$$\boxed{\frac{\Delta P}{P^0} = \frac{w_2M_1}{w_1M_2}}$$

$$M_2 = \frac{W_2M_1P^0}{W_1\Delta P}$$

Question: 20.5g of an organic compound was dissolved in 250g of ethanol leading to lowering of V.P. of ethanol by 0.005mmHg. Determine the molecular mass of the organic compound if the V.P of ethanol soluble is 16.5mmHg.

W_2 = 20.5g

W_1 = 250g

ΔP = 0.005mm/g

M_1 = 46g/mol

P^0 = 16.5mmHg

$$M_2 = \frac{W_2M_1P^0}{W_1\Delta P}$$

$$M_2 = \frac{16.5 \times 20.5 \times 46}{250 \times 0.005}$$

2.2.2 Boiling Point Elevation of Solution

The rise in temperature of a liquid via heating brings about an increase in the vapour pressure of the liquid. For a continual rise in temperatures as a result of continuous heating, the vapour pressure of the liquid will also continue to rise until it becomes equal to the atmospheric pressure. When the vapour pressure of the liquid is equal to the atmosphere. The boiling point of a liquid is the temperature at which the vapour pressure of the liquid is at equilibrium with the atmospheric pressure. When a non-volatile solute is added to the liquid, the vapour pressure of the liquid decreases, it would require higher temperature to raise the vapour pressure to become equal to the atmospheric pressure. This means increase in boiling point as a non-volatile solute is added to the pressure, then the liquid boils. Boiling point elevation is the difference between the boiling point of the pure solvent and that of the solution formed by addition of a non volatile solute.

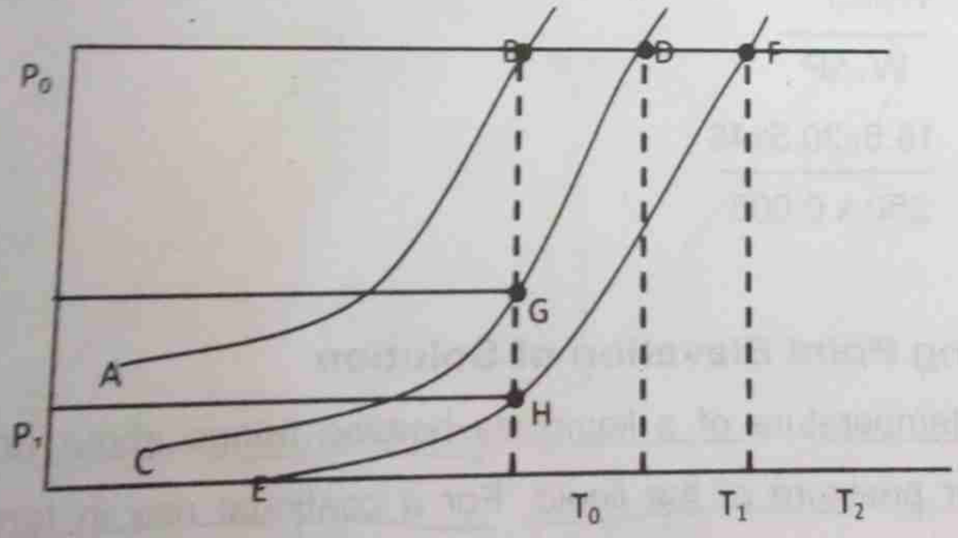
$$\boxed{\Delta T_b = T_{b1} - T_{b0}} \quad \text{or} \quad \boxed{\Delta T_b = T_1 - T_0}$$

$\Delta T_b = T_1 - T_0$

T_{b1} = boiling point of solution 1.

T_{b0} = boiling point of pure solvent

By plotting the graph of vapour pressure against the temperature, we have.



Graph of vapour pressure against boiling point

Curve AB is curve of Pure Solvent

Curve CD is curve of solution I

Curve EF is curve of solution II

T_o = boiling point-of pure solvent

T_1 = boiling point of pure solution I

T_2 = boiling point of solution II

P^0= vap. Pressure of pure solvent

P_1= vap. Pressure of solution I

P_2 = Vap. Pressure of solution II

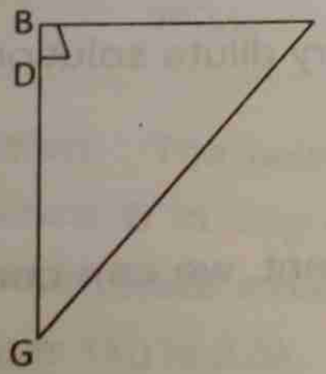
Elevation of boiling point of solution I $\longrightarrow \Delta T_1 \quad = \quad T_1 - T_0 = BD$

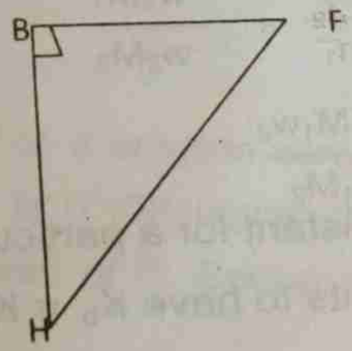
Elevation of boiling point of solution II $\longrightarrow \Delta T_2 \quad = \quad T_2 - T_0 = BF$

At To, the vapoure pressure of pure solvent, represented by B, G, and H respectively.

Lowering of V.P. of solution I - $\longrightarrow$ $P^O - P_1$ = /BG/

Lowering of VP of solution II $\longrightarrow$ $P^O - P_2$ = /BH/





From similar triangle formula

$$\frac{DB}{BF} = \frac{EG}{EH} \rightarrow \frac{T_1 - T^o = P^o - P_1}{T_2 - T^O \; P^o - P_2}$$

$$\frac{\Delta Tb_1}{\Delta Tb_2} = \frac{\Delta P_1}{\Delta P_2}$$

Dividing the numerator and the denominator of the right angle side of equation above by P^0

$$\frac{\Delta Tb_1}{\Delta Tb_2} = \frac{\Delta P_1/P^0}{\Delta P_2/P^0} \quad - - - \quad - \quad - \qquad (2)$$

Equation 2 shows that the boiling point elevation for the two solutions are in the same ratio as their relative lowering of vapour pressure and hence of vapour pressure of a dilute solution.

$$\Delta T_b \ \alpha \ \frac{\Delta P}{P^0} \ \alpha \ X_2 \quad - \quad - \quad - \quad - \quad - \qquad (1)$$

$$\Delta T_b \ \alpha \ X_2$$

$\Delta T_b = kX_2$ K = constant of proportionality

Recall

$$X_2 = \frac{n_2}{n_1+n_2}$$

$X_2 \sim \frac{n_2}{n_1} = \frac{w_2M_1}{w_2M_2}$ for a very dilute solution

$\therefore$

$$\Delta T_b = \frac{KM_1w_2}{W_1M_2}$$

Since M_1 is constant for a particular solvent, we can combine the two constants to have K_b = KM

K_b = ebullioscopic constant or boiling point elevation constant

$$\Delta Tb = KM.\ w_2 \ \frac{1}{W_1M_2}$$

$$\Delta T_b = \frac{K_b\ w_2}{M_2 w_1}$$

If one mole of the solute is dissolved in one gram of the solvent, then

$\Delta T_b = K_b$.

i.e. Ebullioscopic constant is equivalent to the boiling point elevation of a solution formed by dissolving one mole of the solute in 1g of the solvent. Molar ebullioscopic constarnt is produced when 1 mole of the solute is dissolved in 1000g of the solvent i.e. In terms of molality,

$$\Delta T_b = \frac{1000 K_b w_2}{W_1 M_2}$$

Unit of K_b = ^{0}Ckg/mol

But if 1 mole is dissolved in 100g of the solvent then

$$\Delta T_b = \frac{100 K_b w_2}{W_1 M_2}$$

Question: The boiling point of a solution containing 0.5g of a substance B in 50g of ether is 0.15K higher than that of pure ether. Calculate molecular mass of B. Boiling point constant of ether per 1kg is 2.5k

Solution

W_2 = 0.5

W_1 = 50g

ΔT_b = 0.15k

$$M2 = \frac{100 K_b W_2}{W_1 \Delta T_b}$$

K_b = 2.5k (M_2 in g/mol).

2.2.3 Freezing point Depression of Solution

Freezing point is the temperature at which the solid and the liquid state of a pure substance are at equilibrium. The freezing point can also be described as the temperature at which a liquid substance changes to its solid state at a given pressure. When a solute is added to the solvent, the vapour pressure lowers leading to a decrease in freezing point.

Freezing point depression of a solution is the decrease in the freezing point of the solution when a non-volable solute is dissolved in it. The lowering of freezing point depends on the molecular concentration of the solute and the nature of the solvent.

The process of determining the molecular wt of the solute from the freezing point depression of the solution is, called Cryoscopy.

Generally, freezing point depression is the difference between the freezing point of a pure solvent and that of its dilute solution. A plot of the vapour pressure against the temperature of solutions can be used to obtain the relationship between the freezing point and that of the molecular mass of the solute. From similar deduction as in the boiling point above, we arrive at

$$\Delta T_1 = K_1 \frac{W_2}{M_2} \times \frac{1}{W_1}$$

$\Delta T_1 = T_0 - T$ = freezing point depression of the solution

K_1 = Cryoscopic constant or freezing point depression constant.

Freezing point depression of a solution is equivalent to the cryoscopic constant when one mole of the solute is dissolved in 1g of the solvent.

Molar depression constant is the freezing point depression produced when 1 mole of the solute is dissolved in 1000g of the solvent.

$$\Delta T_f = 1000K_f \quad \frac{w_2}{M_2.} \times \frac{1}{W_1}$$

ΔT_f = freezing point depression

K_t = freezing point depression constant or cryoscopic constant

Question: 2.05g of napthelene was dissolved in 80cm3 of benzene and the freezing point of the solution was found to be 250.50k while the freezing point of benzene is 252.55k. Density of benzene is 0.85g/cm2. If cryoscopic constant is 4.21k per 100g of benzene, calculate the molecular weight of the natphelene.

Solution

W_2 =2.05g = W_2

$V_1 = 80cm^3 = V_1$

T_1 = 250.50k = T1

T_0 = 252.55k = T_o

D_b= 0.85g/cm^3

K_f = 4.21 k/100g

$$D_b = \frac{w_1}{V_1}$$

$$W_1 = D_b \; V_1$$

$$= 0.85x80$$

$$\Delta T_f = 100K_f \frac{W_2}{M_2} \times \frac{1}{W_1}$$

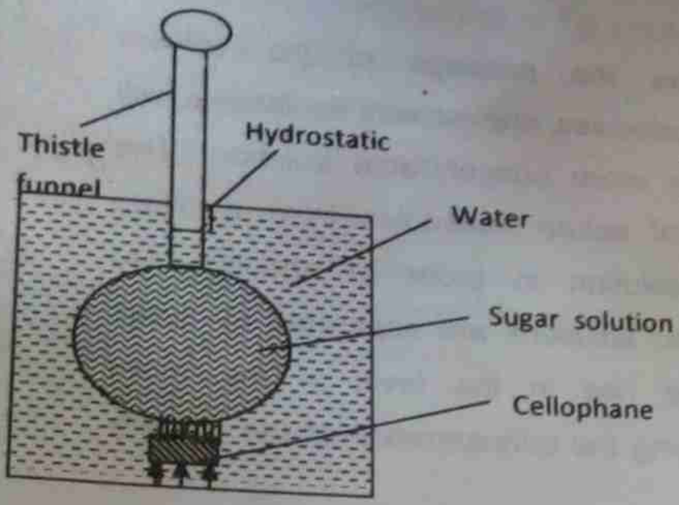
$$M_2 = \frac{100K_fW_2}{W_2\Delta T_f} \times W_2$$

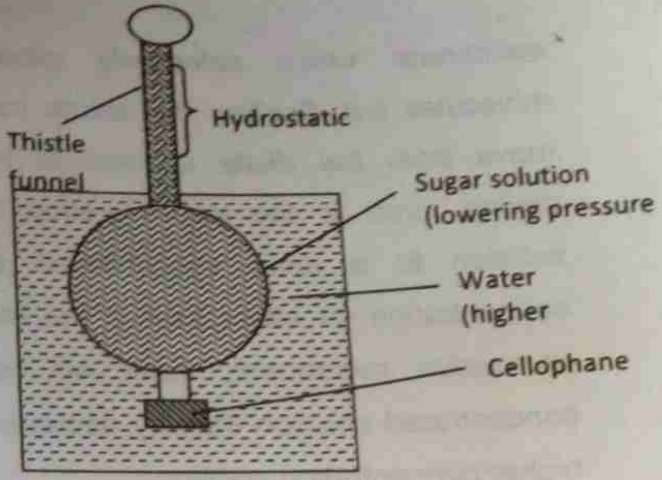
$$M_2 = \frac{100 \times 4.21 \times 2.05}{0.85 \times 80 \times (252.55-250.50)}$$

2.2.4 Osmotic Pressure

Osmosis is the movement of solvent molecules through semi-permeable from a region of lower concentration to a region of higher concentration (solution). This occurs when pure solvent is separated from its solution by a semi-permeable membrane. In this case, some molecules of the solvent move across the semi-permeable membrane to the solution. No molecules of the solute will be allowed to move across the membrane of the pure solvent. Generally, osmosis involves two solutions which are separated by a semi-permeable membrane that will only allow the solvent molecules to pass through. E.g. of semi-permeable membrane are animal membrane, cellulose membrane, cupric ferrocyanide CU_2 [Fe $(CN)_6$] (CU_6). The membrane used depend on the nature of the solute and solvent.

We can illustrate osmosis by fastening a' piece of cellophane over a thistle funnel as shown below.





The sugar solution is contained in the thistle funnel which is immersed in the water. As osmotic is set up, water molecules begins to move across the membrane through the semi-permeable membrane (cellophane) to the thistle funnel containing the solution. Hydrostatic pressure is generated as a result of the differences in the level of sugar solution in the thistle funnel and the surface of the "pure" water in the tube. When the difference in pressure between the solvent and the solution has attained a particular value in which they are at equilibrium, there will be no more transfer of solvent molecule into the solution.

The pressure operating at this equilibrium point is the osmotic pressure. Hence we can define osmotic pressure as the pressure which must be applied on the solution to prevent the passage and the solvent molecule into the solution when the solvent of the solution are separated by a semi-permeable membrane. Osmotic pressure depends on the nature of the solvent and the amount of solute but not in the nature of the semi-permeable membrane.

When two solutions of unequal concentration are separated by a membrane which selectively allows the passage of the solvent molecules but disallow the solute molecules, the solvent molecules will move from the dilute solution to a more concentrated solution. The driving force is the net migration of solute molecules from a dilute solution to a more concentrated solution in order to equalize the concentration on either side. If the two solutions are separated by semi-permeable membrane, there will be rise in the level of the more concentrated solution thereby decreasing the concentration of the .initially higher concentration solution.

The driving force can be attributed to the greater vapour pressure of the solvent to that of its solution. In attempt to equalize the pressure, solvent molecules with higher vapour pressure will move to the solution which has a lower pressure.

Hence, osmosis can be described as movement of solvent molecules from a region of higher vapour pressure to a region of lower vapour pressure through semi-permeable membrane. This means osmotic pressure can - also be defined as the external pressure applied to the more concentrated solution to stop the movement of solvent molecules from a region of higher vapour pressure to a region of lower vapour pressure.

Osmotic pressure can be determined by measuring the difference in height (or levels) of the solution and the solvent. It is represented by n from ideal gas equation, it can be observed that n is directly proportional to the molar concentration. i.e. $\pi \alpha C$

$\pi = CRT$

π = osmotic pressure

C = molar concentration of the solute

R = gas constant

T = absolute temperature

From PV = nRT

Where $P \equiv \pi$

Then $\boxed{\pi V = nRT}$

But n $\frac{w}{M}$

Hence, $\frac{\pi V}{M} = mRT$

$$\boxed{\pi V = \frac{wRT}{M}}$$

W = mass of solute = w

M = molar of the solute = M

V = volume of pure solvent.

Question

When 5.0g of myoglobin found in the muscle was dissolved in 60ml of water, the osmotic pressure of the solution at 25^0C was found to be 15.5mmHg. Calculate the molecular weight of myoglobin ($R = 0.050$atm $mol^{-1}K^{-1}$)

Solution:

= 0.0850x760mmHg

V = 60ml = 0.6L

$$\therefore \quad M = \frac{mRT}{\pi V}$$

= 5 x 0.0850 x 760x 298.

Chapter Three

By Awachie, O.M and Okoye, I.E.

INTRODUCTION TO THERMODYNAMICS

- System
- State variables
- Equilibrium
- Isothermal and Adiabatic processes
- The 1st law of thermodynamics
- work done for state change (PV- Type)

3.1 Introduction to Thermodynamics

Energy changes in physical and chemical reactions owe its study towards the term "thermodynamic". Thermodynamics is based on experimental facts which do not contain time as a variable. During a reaction, there is a change from one state to another which is a factor of law of conservation of energy. Thermodynamcis on its own can be defined as the study of interconversion of energy which occurs in physical and chemical processes. Thermodynamics can be classified under three basic laws which are:

(a) The 1st law of thermodynamic which is based on the equality of different forms of energy.

(b) The 2nd law of thermodynamics which is based on direction of chemical changes/transformation and conditions for equilibrium to occur.

(c) The 3rd law of thermodynamic which attempt to simplify thermodynamic parameters.

The 1st law of thermodynamics shall be our main area of concentration in this course but before that, some thermodynamic terms need to be explained for easy understanding of the topic.

3.1.1 System

A system can be said to be that part of the universe in which the properties of our interest is under investigation or study for every system, there is a link to the surrounding through the boundary. The part of the universe apart from the system is called the 'surrounding' and the separation between the surrounding universe and the system is known to be the 'boundary'. This boundary or wall may be rigid, impermeable, permeable, adiabatic or diathermal by structure. Meanwhile, a system is affected by some properties which are calculated via experiments. The system can also be in different states. The state of a system is the nature by which all the properties that make up the system has a definite define value. There are different types of systems which is determined simultaneously by type of wall or boundary present.

(i) **A Closed System:** A closed system enclosed by an impermeable wall is a system whose energy may change but mass always remains constant e.g. volatile liquid in a closed metal vessel.

(ii) **An Open System:** An open system enclosed by a permeable wall is a system in which matter and energy are both exchanged e.g. a volatile liquid in a beaker.

(iii) **An Isolated System:** An isolated system enclosed by an adiabatic wall is a system in which neither energy nor mass can be exchanged. The boundary prevents different forms of interaction with the surrounding.

3.1.2 State Variables

This can be defined as those measurable factors .that explains the state of a system wholly. These factors includes number of moles (n) temperature (t), pressure (p), volume (v), etc. They are likewise called "state function" or "thermodynamic variables.

As the changes move from one state to another, the state variables are independent of the pathway of the system but depends on the initial and final states of the system. However, they are independent of how changes are attained and are exact differentials e.q P, V, T, E, (internal energy), H (enthalpy), .A (free energy». In state functions, there is always an equation of state which brings' about the interrelationship between - the state functions or state variables. Variables which depend on the pathway of the system in going, from one state to another is refre to as path function e.g. heat (q) and work (w). The path functions have an inexact differential unlike the sate variables path functions can be a exact differential if and only if the path is specified. Nevertheless, under state variable, or thermodynamic variables, there are two types of thermodynamics properties which include

(a) Intensive properties ✓

(b) Extensive properties ✓

3.1.2.1 Extensive properties are thermodynamics properties which depends on the totality of all the substance that make up or constitute the system e.g mass, no of moles, enthropy, enthalpy, heat capacity, etc.

3.1.2.2 Intensive Properties

Are thermodynamic property which are not dependent on the totality of all the substance that make up the system e.g. boiling and freezing points, pressure, viscosity, density, surface, tension, specific heat, free energy per mole. etc.

Other thermodynamic processes include isothermal, adiabatic, isobaric, isochoric, cyclic, reversible and irreversible processes.

- Isothermal process → changes occurring at constant temperature
- Isochoric process → the volume of the system is kept constant during changes
- Isobaric process → the pressure of the system is kept constant during changes.
- Adiabatic process → no exchange of heat between the system and surrounding. Heat change is zero. This accompanies changes in temperature.
- Reversible process → here, properties of the system at every moment remains uniform but at a quite very slow rate. They are also ideal.
- Irreversible process → the system have no change to reach equilibrium. All natural process are irreversible and spontaneous in action.

During the study of thermodynamic as a topic, we shall also introduce certain sign convention for heat (q) and work (w). e.g. Heat (q) absorbed by the system is positive i.e. $+q$, $dg > 0$. Heat released by the system is -ve i.e $-q$, $dq < O$; work done by the system is positive (expansion) i.e. $+w$, $dw > 0$: is tual, $dul > O$; work done on the system is -ve (compression) ie $-w$, $dw < 0$.

3.2. The 1st Law of Thermodynamics

Thermodynamics as we said earlier is the study of energy changes in physical and chemical processes. The 1st law of thermodynamics is also based on the law of conservation of energy. "The first law of thermodynamic simply states that energy can be transformed from one form to another but can neither be created nor destroyed". The total energy of the universe, is equal to the sum of energy of the system and that of the surrounding

$E_{total} = E_{system} + E_{surrounding}$

The energy of the surrounding can be grouped into thermal and mechanical sub divisions.

$E_{surrounding} = E_{thermal} + E_{mechanical}$

Where E_{mech} is the energy of the mechanical part owing to compression or expansion of the system while $E_{thermal}$ is the energy of the thermal part of the surrounding.

Therefore, the total energy of the universe can be written as

$E_{total} = E_{system} + E_{thermal} + E_{mechanical}$

$E_{total} = 0$ if and only if energy is conserved.

Eq1: In the expansion of a real gas it was found that 200J of heat was given out by the gas when work done by the gas was proportional to 1450J. Calculate the change in interval energy of the system.

Solution

Since heat is lost by the system, the quantity becomes -ve and also since work is done by the system then work is +ve .

$E_{total} = E_{system} + E_{surrounding}$

$E = -200 - (1450) = (1, 650J) = -1,650J$

E.g 2: During the course of an experiment, the change in heat energy was found to be 150J which was given out to the surrounding and the work-done on the system via the mechanical part is 400J. Calculate the energy of the surrounding and determine the total energy, if the energy of the system was

found to be 950J.

Solution:

$E_{total} = E_{system} + E_{thermal} + M_{echanical}$

Where $E_{thermal}$ = change in heat energy and is equivalent to q

E_{mech} = change in mechanical energy of the surrounding

equivalent to W

∴ since heat is given out, q = -ve

work is done on system, w = -ve

∴ $E_{surrounding} = E_{thermal} + E_{mech}$

$= -(q) + -(w)$

$= -(150) + -(400)$

$= -550J$

To get the total energy, we substitute into the above equation

$E_{total} = E_{system} + E_{surrounding}$

$= 950J + -(550)J$

$= 950J - 550J$

$= 400J$

$\Delta G = -RT\ln k$

However, the first law can be represented as

$dE = dq - dw$

Where dE is change in internal energy, dq is change in amount of heat absorbed and dw is the small amount of external work done by the system at a given time. It can also be represented as

$\Delta E = q - W$

Which implies that the change in internal energy of the system is equal to the energy absorbed from the surrounding' in form of heat minus energy lost in the form of external work done by the system. The 1st law of thermodynamics does not hold for nuclear reactions where there is energy mass conversion.

3.2.1 Internal Energy

Lets consider 3 factors involved in the 1st law of thermodynamics which are internal energy, heat and work.

Internal energy is energy which includes all the microscopically diverse forms of energy such as kinetic and potential energies of molecules, atoms, ions, energy of attraction and repulsion. The internal energy is the same as the energy of the system. The actual value of the internal energy is specifically not known but our primary concern is with energy change ΔE which are measurable quantities. For ideal gases, change in internal energy $\Delta E = 0$ is at constant temperature. This is so owing to the fact that at constant temperature, kinetic energy is constant and since ideal gas molecules have no attractive forces, there is no change in potential energy during expansion i.e. $\Delta E = 0$.

$$\Delta E = q - w$$

$$0 = q - w$$

$$q = W$$

Its very vital to note that internal energy is a state function and exact differential equal to zero for a cyclic process.

3.3 Heat Change in Thermodynamics

In thermodynamics heat is a path function but under certain conditions or terms, it can become a state function

→ Heat change at constant volume (q_v)

From 1st law,

$\Delta E = q - w$

$q = \Delta E - w$

$q = \Delta E + P\Delta V$

If the work is that done for expansion at constant pressure, then $\Delta V = 0$ (constant volume process).

$q_v = \Delta E$

$\therefore \quad q_v = \Delta E$

Therefore, internal energy which is a state function is now equal to the heat absorbed at constant volume. Therefore, q_v is a state function.

→ Heat change at constant pressure: Enthalpy (H)

→ $dE = q - w$

When P-V work is done at constant ΔP, $E = q_p - PV$ - - -(1)

$E_2 - E = q_p - P(V_2 - V_1)$ where $\Delta E = E^2 - E^1$,

$q_p = (E_2 + PV_2) - (E_1 + PV)$

$\Delta V = V_2 - V_1$.

Heat absorbed is equal to difference of 2 quantities and a new state function known as enthalpy (H) is introduced as

$H = E + PV$

Such that $q_p = H_2 - H_1 = \Delta E$ where q_p is heat at constant pressure. Hence, it is a state function since its function of E,P and V which are all state function.

So, $\Delta H = \Delta E + \Delta(PV)$

At constant P, $\Delta H = \Delta E + P\Delta V$ -- - - - (2)

Combination of equation (1) and (2) gives Δq_p = H from the earlier equations,

$q_v = \Delta E$ where q_v is heat at constant volume and $\Delta E = q_p - P\Delta V$

combine them gives $q_p = q_v + P\Delta V$.

This implies that the heat absorbed occurring at constant pressure surpasses that at constant volume by $P\Delta V$ (i.e. by the external workdone at constant pressure). this is to say that constant pressure processes are common owing to the fact that most operation are carried out at atmospheric pressure (either in open vessels).

3.4 Heat Capacity in Thermodynamics

This is the rate of change of heat with temperature. It's the amount of heat needed to change the mass of substance. Heat capacity may be in form of specific heat which is that capacity of 1g of substance, or molar specific heat capacity which is heat capacity of 1mole of the substance. Heat capacity at constant P, Cp = heat capacity at constant V,Cr = $\frac{dqp}{dT} = \left(\frac{\delta H}{\delta T}\right)$ $\frac{dq_p}{dT} = \left(\frac{\delta H}{\delta T}\right)_V$

It is vital to note some symbol such as $\bar{C}v$ and $\bar{C}p$ which represent heat capacity per mole at constant volume and pressure respectively. Thus $\bar{C} = n\bar{C}v$ and $\bar{C}p = n\bar{C}p$.

Molar heat capacities of gases (in joule/deg.mole) at 25^{0}C

Gas	$\bar{C}p$	$\bar{C}v$	$\bar{C}p = \sigma \bar{C}v$
Argon	20.79	12.47	1.67
Helium	20.79	12.47	1.67
Hydrogen	28.87	20.54	1.41
Oxygen	29.50	21.13	1.40
Chrome	34.52	25.69	1.34
Nitric oxide	2.75	21.38	1.39
Hydrogen chloride	29.50	20.96	1.41
Ammonia	36.11	27.49	1.31
Methane	35.98	27.57	1.31
Dimethyl ether	66.48	57.53	1.16

It can be shown from all indication that under kinetic theory, that monoatomic ideal gases are given by $^3/_2K$ i.e. 12.47, $Jdeg^{-1}mol^{-1}$ ideal/mog which is the value for argon, helium. For diatomic gases, Cv is given by $^5/_2K$ is 20.79J/deg/mol which is the value for O_2, HCl.

From all statistical and experimental clarification, heat capacity is dependent on temperature so far as thermodynamic is concerned.

3.5. Dependence of Internal Energy on Temperature and Volume.

$\Delta E = f(T,v)$

Change in internal energy dE is given as

$$dE = \left(\frac{\delta E}{\delta T}\right) dT + \left(\frac{\delta E}{\delta v}\right)_T^{dv}$$

but Cv =

$$\frac{dqv}{dT} = \left(\frac{\delta E}{\delta v}\right)_v$$

∴ Substituting for Cv,

$$dE = Cv\ dT + \left(\frac{\delta E}{\delta v}\right)_v^{dT}$$

where $\left(\frac{\delta E}{\delta T}\right)_T$ is known as internal pressure and depends on intermolecular forces.

For ideal gases in which the internal pressure is zero has the internal energy equal to temperature as its only function, i.e. E = f(T) only. But for real gases, that is not quite true though they are quite small.

3.6. Enthalpy as a Function of Temperature and Pressure

$H = F(T,P)$

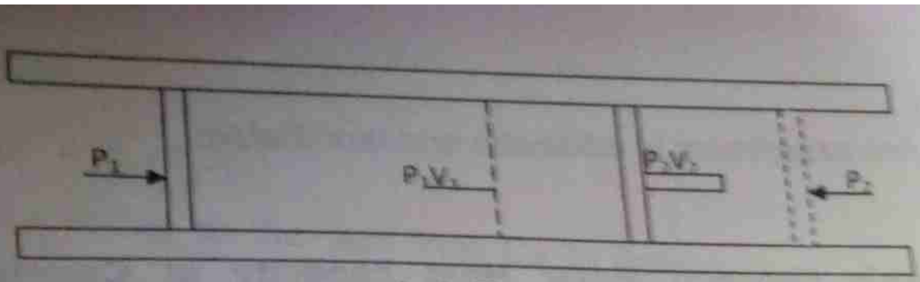
Taking the derivative of H gives

$$dH = \left(\frac{\delta E}{\delta T}\right)_p^{dT} + \left(\frac{\delta E}{\delta v}\right)_T^{dT}$$

but $Cp = \left(\frac{\delta E}{\delta v}\right)_P$

$$\therefore dH = Cp\ dT + \left(\frac{\delta H}{\delta P}\right)_T^{dP}$$

However, its vital to note that calculation of Cp is easy but evaluation of $(dH/dp)_r$ is hard. Solids and liquids have negligibly small $(dH/dp)_T$ but for gases, ideal gases, $(dH/dp)_r = 0$. Real gases, $(dH/dp)_T$ is quite small and can be measured by joule. Thompson experiment.



Joule-Thompson experiment

The experiment was carried out of which temperature change was measured when a gas expand via a porous plug under adiabatic condition. As the enclosed gas pours initially from volume 1 (V_1) to The p volume 2, (V_2) it was observed that for real gases, the final at con temperature, T_2, differ from the initial temp, T_1 of which P_1 and P_2 are Cp, is constant P_1 is slightly greater than P_2.

For Joule- Thompson experiment, $\Delta H = 0$ i.e. work done on the gas in forcing it through the plug is $W_1 = P_1V_1$ and work done by the gas in expanding to the other side is given as $W_2 = P_2V_2$.

$W_T = W_1 + W_2$ = total work done

$= P_2V_2 = P_1V_1$

$\Delta E = E_2 - E_1$

From 1st law of thermodynamics,

$\Delta E = q = W$

Under adiabatic condition, $q = 0$

$\therefore \Delta E = -W$

$\Delta E + W = 0$

$E_2 - E_1 + P_2V_2 - P_1V_1 = 0$

$(E_2 + P_2V_2) - (E_1P_1V_1) = 0$

i.e. $H_2 - H_1 = \Delta H = 0$

Therefore, Joules experiment is adiabatic and isonthalpic

3.7 Relationship between Molar Heat capacity at Constant Pressure and Volume (Cp and Cv)

The pressure volume work is always done when a substance is heated at constant pressure. That is why heat capacity at constant pressure, Cp, is always larger than heat capacity at constant volume. For a mole of an ideal gas

$$Cp - Cv = \left[\left(\frac{\delta E}{\delta v}\right)_T + P\right] \left[\left(\frac{\delta v}{\delta t}\right)_P\right]$$

But if ideal gases, $\left(\frac{\delta E}{\delta v}\right)_T = 0$

But $PV = RT$

Differentiating gives

$Pdv + Vdp = RdT$

$\therefore$ $(dV/dT)p = R/P$ (note $Vdp = 0$ at constant P)

$\therefore$ $Cp - Cv = R$

3.8. Heat Capacity of an ideal gas and thermodynamic expression

C_v $\delta E/\delta T$

i.e. $dR = C_v dT$

But E is independent of volume

$\therefore$ For a finite change,

$$\Delta E \int_{T_1}^{T_2} C_v dT = C_v (T_2 - T_1)$$

$\Delta E = C_v (T_2 - T_1)$

But owing to the fact that Cv is independent of temperature, ideal gases are likewise given as

$Cp = (dH/dT)_p$

$dH = CpdT$

$\Delta H = \int_{T_1}^{T_2} CpdT.$

From all indications, we now know that

$Cp - Cv = R$ therefore,

$\Delta q = dw + dE$

Taking that p=v work only is done. Under 1 mole of ideal gas.

$\Delta q = pdv + CvdT$ - - - - - (3)

$Pv = RT$

$\therefore Pdv = RdT$ (P = constant)

Substituting into equation (3) and dividing by dT gives

$\Delta q_p/dT = C_v + R$

But $q_p/dT = C_p$

$C_p = C_v + R$

e.g. during an isothermal process, the heat absorbed by the system is 952J and the change in volume is $30cm^3$. What is the total pressure of the system?

Solution: At isothermal process $\Delta E = 0$

$\therefore \Delta E = q - w$

$0 = q - w \longrightarrow w$

But $w = P\Delta V$

$\therefore q = P \Delta V$ where $q = +952J$

$\Delta V = 30cm^3$

$952 = P(30)$

$P = 31.73mmHg$

e.g. the heat capacity at constant pressure per mole was found to be 1300J/mol if 5 moles of all the reactants are involved. Calculate the heat capacity at constant volume of heat capacity per mole at constant volume is not given.

Solution: from the equation below,

$\bar{C}p = \bar{C}i + R$

Where $\bar{C}p$ = molar heat capacity per mole at constant pressure

$\bar{C}v$ = heat capacity per mole at constant volume.

$\bar{C}v$ = heat capacity at constant volume

And K = gas constant 8.314J/mol/K

$\therefore \bar{C}v = \bar{C}p - R$

= 1300J/deg/mol – 8.314J/mol/K

= 1291.6deg/K

But $nC_v = C_v$

$Cv = nC_v$

= 5mol x 1.2916deg/K

= 6.458joule/deg.

Problem

What is the internal energy of a system given that heat capacity at constant volume is 150J/deg and temperature change of 50^0C.

Solution

Cv = nCv

But dE = C_vdT

dE = 150g/deg x (50+273)

= 150x323

= 48.450J

e.g. One mole of an ideal gas is expanded isothermally and reversibly at 27^{0}C from a volume of 5dm^3. Calculate ΔE, ΔH and W, q

Solution:

V_1 = 5dm^3 V_2 = 14dn, T = 300K

W = 2.30enRT log (V_2/V_1).

2.303 x 1 x 8.314 x 300log ($^{15}/_3$)

= 2740.65J/mol.

ΔE = E_2-E_1 = 0 since E_1 = E_2

q = ΔE + w where ΔE = 0

∴ q = w = 2740.65J/mol

ΔH = ΔE + Δ(PV)

But for 1 mole of ideal gas

PV = RT

ΔH = ΔE + Δ(RT)

Where Δt = 0 and T = 0

ΔH = $H_2 - H_1$ = 0

e.g. Calculate the heat released from a system under operation given that heat capacity at constant volume is 120J/deg and the temperature change was 78°C and the work done by the system was 280J.

Solution:

$\Delta E = q - w$

but $\Delta E = nC_v\Delta T = \bar{C}_v dT$

$\therefore C_v dT = q - w$

$120 \times 351 = q - 280$

$42.120 + 280 = q$

$42.400 = q$

Since heat is released by the system

$q = -42.400J$

$q = -42.4KJ$

3.9 Work Done For State Changes (Pv-Type)

During the course of energy changes in physical and chemical process, work is done either on the system or by the system making it dynamic. For a workdone on the system has a negative convention and that done by the system have a positive convention. Work as all know is the outcome of action against an opposing force.

W = FXS

Where F = Force against which work has to be done.

S = displacement or distance

For mechanical work, $P = F/A \longrightarrow F = PA$

Where P = pressure exerted for the work done

A = Area of contact

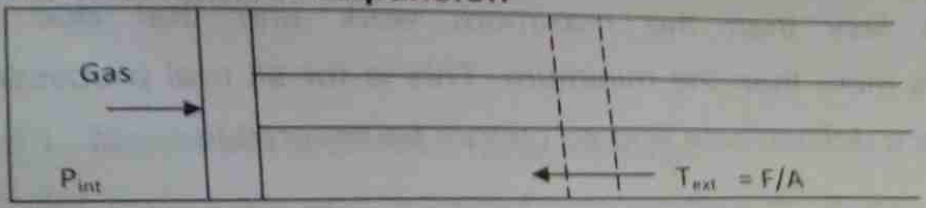
F = force

$\therefore W = P.A.$

But area x ΔL = volume

$\therefore W = Pdv.$

Reversible work of Expansion



Where P_{int} = internal pressure while P_{ext} = external pressure.

For a gas in a cylinder of cross-sectional area, A and fitted with a piston which is frictionless and weightless. Let P_{int} be internal pressure expanding against an external pressure, P_{ext}. However, if

$P_{int} > P_{ext}$: expansion work is against P_{ext}.

$P_{int} < P_{ext}$: compression work is against the P_{int}.

$P_{int} = P_{ext}$: equilibrium reversible work of expansion

The workdone against the environment is given by

$dw = pdv$

$dw = P_{ext} dv$

but $P_{ext} = P_{int} - pd$

$dw = (P_{int} - dp)dv \qquad (4)$

$dw - P_{int} dv$

Equation (4) is for reversible work of expansion which is greater than the actual work (i.e. P_{ext} dv). Maximum work is obtained under reversible condition. For minimum work to be achieved, reversible work of compression is undergone. i.e. $P_{ext} - P_{int} + dp$

Work of compression $dw_c = P_{ext}dv = P_{int}dv + dpdv$ where dpdv is negligibly small.

$dwc = P_{int}dv$ - - - - - - - - (5)

Equation (3) is less than the actual work of compression. Work due to expansion is less than the maximum work and that due to compression is more than the minimum. This is for all real processes which occurs at a defined rate and so cannot be reversible.

3.10 Work as a Path Dependent

For a well defined process,

$$W = \int_{V_1}^{V_2} Rdv = \int_{V_1}^{V_2} (P)(V)dv$$

Work as a path function can be consider under 3 conditions

(a) Expansion towards a constant external pressure

$$W = P_{ext}(V2 - V1) = P_{ext}\Delta v$$

(b) Expansion into a vacuum

If P = 0 which gives W = pdv = 0

(c) Expansion toward reversible and isothermal conditions

$$P_{int} \approx P_{ext}$$

$$W = \int_{V_1}^{V_2} P_{int}dv$$

From ideal gas law, PV = nRT

$$P_{int}\ V = nRT$$

$$P_{int} = nRT/V$$

Substituting and integrating

$W \quad nRT \text{ in } V_2/V_1$

Or $W = 2.303nRT \log V_2/V_1$.

The 3 above processes are a property that show that work is a path dependent function it shows the different amount of work done by the system.

3.11 Maximum work in Phase Change

Under reversible and constant temperature conditions, the processes of melting, vapourisation, boiling, freezing, crystallization etc can occur. For sublimation, vapourization, workdone is maximum and for condensation, minimum work is done.

$W \ P\Delta V$ where ΔV = volume change

P = vapour pressure of the system

$\Delta V = V_v - V_L$ where V_v and V_L are vapour and liquid volumes

$W = PV_v$ $\quad V_v >>> V_L$ for temperature not too close the initial temperature

But for ideal gases.

$PV = nRT$

$PV_1 = nRT$

$$V_v = \frac{nRT}{P}$$

$W = PV_v$

$= PV_v = nRT$

$$V_v = \frac{nRT}{P}$$

$W = nRT$

Where n = number of moles of liquid vapourised or formed. The above consideration is applicable to a one directional transition i.e. (condensation, sublimation process) from solid to liquid, solid to gas or liquid to gas and never vice versa.

e.g. 15moles of an ideal gas is isothermally and reversibly expanded at 250°C from a volume of $13dm^3$ to $20dm^3$. Calculate the work done by the system.

Solution:

$W = nRT \text{ in } V_2/V_1 = 2.303 \text{ nTR logn } (V_2/V_1)$ where n = 15moles $V_1 = 13dm^3$, $V_2 = 20dm^3$.

$T = 1500c + 273K = 423K$

:. $W = 15 \times 8.314 \times 423x \text{ in } 1.5384$

$= 52,75.33 \times 0.407$

$= 22,772.5J/mol.$

E.g. when nitrogen reacted with hydrogen expansion against a constant exterior pressure was found to 230atm given that change in volume was $80cm^3$. Determine the work done by the system.

Solution

$W = P_{ext} (V_2 - V_1) = P_{ext} dv$

$\Delta V = 80cm^3$

:. $W = 120atm \times 80cm^3$.

$= 9,699J$

E.g. 2mole of ethanol is converted reversibly into vapour at its boiling point 98°C by heating. The vapour expands against the pressure of 6atm. The heat of vapourization of ethanol is 201J/g. Calculate q ΔE, w and ΔH for the operation.

Solution

Heat released to vapourize 2mole of ethanol = q molar mass of ethanol

= 46g/mol

T = 78 + 273 = 351K

:.q = 201J/g x 46g

= 9.246J

W = $P\Delta V = P(V_1 - V_2)$ since U >>>U

:.W = PV_v

But PV_v = nRT

$$V_v = \frac{nRT}{P}$$

:. W = nRT

= 2x8.314x351

= 5836.43J

Δt = q – w

= 9,246 - 5836.43

= 3,409.57J

$\Delta H = \Delta E + \Delta(PV)$

$= \Delta E + P\Delta V$ (constant pressure process)

$\Delta H = q = 9{,}246J$

E.g. Determine the minimum work required to compress 349 of nitrogen at $35^{0}C$ from a pressure of 8atm to a pressure of 70atm.

Solution

P_1 = 8atm; P2 = 70atm, T = 35 + 273 = 308K

N = 34/28 = 1.214

:. $W = 2.303nRT \log P_1/P_2$.

$= 2.303 \times 11.214 \times 8.314 \times 308 \times \log 0.114$

= - 6,751.94J

E.g. Calculate the actual work of compression in an isothermal reversibly process given that the pressure is 29 atm and the volume change work found to be $75cm^3$.

Solution

For an operation which involves compression, actual work of compression is gotten under reversible condition.

:. $dwc = P_{int} W$

Where P_{int} = 29atm

$\Delta V = 75cm^3$

Δwc = 75cm3 x 29atm

= 2,175J

3.12 Isothermal and Adiabatic Process

Isothermal Process: This is a thermodynamic process in which temperature is kept constant throughout the operation. It is attained by removal of heat from the system or supply of heat to the system. Isothermal process can be under:

(a) Reversible expansion of an ideal gas

(b) Reversible free expansion of ideal gas

(c) Irreversible actual expansion of an ideal gas.

3.13 Isothermal-Reversible Expansion of an Ideal Gas

Under this condition, $P_{int} \approx P_{ext}$, V_1 = initial volume, V_2 = final volume, T is temperature and is constant.

→ For workdone by the gas: $dw = Pdv$

$$W = \int_{V_1}^{V_2} pdv$$

$$PV = nRT \text{ i.e. } P = \frac{nRT}{V} \text{ for ideal gas}$$

$$W = nRT \int_{V_1}^{V_2} dv = nRT\,Ln\,(V_0/V_1) = 2.303nRT\,\log(v_2/v_1)$$

Also $W = 2.303nRT\,\log(P_1/P_2)$ since P_1V_1 P_2V_2 for ideal gas under isothermal reversible condition, workdone is maximum

→ Change in internal energy ΔE

Since internal energy is a function of temperature and under isothermal process, T is constant and equal to zero is $T_2 = T_1 = dT = 0$

$$\therefore \quad \Delta E = E_1 - E_2 = 0$$

→ Heat change (q)

$\Delta E = q - w$

$q = \Delta E + w$

but $\Delta E = 0$

$q = w = 2.303\,nRT\,\log(V_2/V_1)$

enthalpy change (Δ)H

since we know that $\Delta H = H_2 - H_1$

$\Delta H = (E_2 + P_2V_2) = (E_1 + P_1V_1)$

$= (E_2 - E_1) + (P_2V_2 - P_1V_1)$

$+ 0 + 0$ for $P_1V_1 = P_2V_2$ (Boyles law) or we know that $E = H - PV \rightarrow H = E + PV$

$\Delta H = \Delta E + \Delta(PV)$

$PV = RT$ (Ideal gas law)

$\Delta H = \Delta E + \Delta(RT)$

3.14 Isothermal Free Expansion (Irreversible) of an Ideal

For Isothermal process, $T_1 = T_2$; P_1 and V_1 be initial pressure and $w = \int_{V_1}^{V_2} P_{ext}\,dv$ volume while P_2 and V_2 be final pressure and volume against vacuum, $P_{ext} = 0$.

Internal energy change (ΔE): $\Delta E = 0$ (isothermal process)

Heat change of:

$q = \Delta t = w$

$= 0 + 0 = 0$

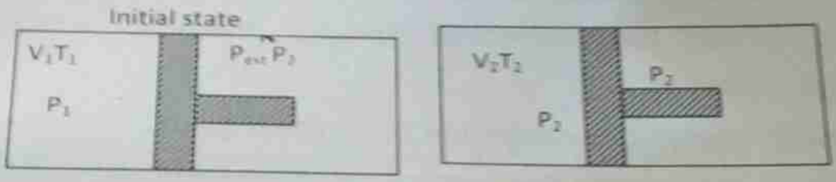
Enthalpy change ΔH

$\Delta H = \Delta E + \Delta\,(PV)$

$= \Delta E + \Delta(RT)$ (ideal gas relation)

$BH = 0x0$ (due to the isothermal process)

3.15 Isothermal Irreversible actual expansion of an ideal



Removing the pin, the external pressure is released suddenly to a final pressure P_2 i.e gas expand against P_2, $T_1 = T_2$.

$$w = \int_{V_1}^{V_2} P_{ext}\, dv = \int_{V_1}^{V_2} P_2 dv = P_2 \int_{V_1}^{V_2} dv$$

$$W = P_2 (V_2 - V1)\ P_2 = \left(\frac{nRT}{P_2} - \frac{nRT}{P_2}\right) = nRT\left(1 - \frac{nRT}{P_2}\right)$$

Internal energy change ΔE: At T constant and for ideal gases, $\Delta E = E_2 - E_1 = 0$

Heat change q : $q = \Delta E + W$

$$= 0\ nRT\left(1 - \frac{P_2}{P_1}\right)$$

Enthalpy change ΔH:

$\Delta E = \Delta H - \Delta (PV)$

$\Delta H = \Delta E + \Delta (PV)$ RT is a constant

$\Delta H = 0\text{-}0 = 0$

3.16 Adiabatic Processes:

This is a thermodynamic process in which there is no exchange of heat between the system and the surrounding, and q is always equal to zero. Every adiabatic process accompanies a change in temperature just like isothermal process, adiabatic process can be classified under:

(a) Adiabatic reversible expansion of an ideal gas

(b) Adiabatic irreversible free expansion of an ideal gas

(c) Relationship between T, V, and P for reversible expansion under adiabatic condition.

$q \quad = 0$

$\Delta E = q - w$ i.e. $\Delta E = -W$

$= \Delta E = W$

3.17 Adiabatic Reversible Expansion:

$W \quad = \quad -\Delta E \ (q = 0)$

$$\Delta E = nCv\,dT + \left(\frac{\Delta E}{\Delta v}\right)_T dv$$

$$\text{But}\left(\frac{\Delta E}{\Delta v}\right)_T = 0 \text{ for ideal gas}$$

$$\int_{E_1}^{E_2} dE = \int_{T_1}^{T_2} nC_v dT$$

$\Delta E = E_2 - E_1 = nC_v dT$

$\therefore W = nC_v (T_2 - T_1)$

Enthalpy change, (ΔH): $\Delta H - H_2 - H_1 = (E_2 + P_2V_2) - (E_1 + P_1V_1)$

$\Delta H = (E_2 - E_1) + (P_2V_2 - P_1V_1)$

$= \quad \Delta E + nRT (T_2 - T_1)$

$\Delta H = nC_v (T_2 - T_1) + nRT (T_2 - T_1)$

$= n(T_2 - T_1)(C_v + R)$

$\therefore \Delta E = H = nC_p(T_2 - T_1)$

3.18 Relationship Between P,V and T for Reversible Adiabatic Expansion of an Ideal Gas

(i) Pressure and volume: $P_1V_1T1 = P_2V_2T_2$

(ii) $\frac{P_2V_2}{P_1V_1} = \frac{T_2}{T_1}$ but $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$

(iii) $\therefore$ $\frac{P_2V_2}{P_1V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$

Simplifying gives $\boxed{\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \frac{V_1}{V_2}}$

$\therefore PV\ \alpha = \text{constant}$

(ii) Temperature and volume $dE = nCvdT$

$dW = pdv$ but $q = 0$

$dE = pdv = nCvdt$

$\frac{C_v}{R} \ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_1}{V_2}\right)$

After long calculations,

$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$

(iv) Pressure and Temperature = $q = 0$

$\therefore\ dE = -W = -pdv$

$Pv = nRT$ (ideal gas law)

Differentiating gives $pdv + vdp = nRdT$

$dE = -nRdT + vdp = nCvdt$

$dt = -nRdT. + vdp = nCvdt$

$n(Cv + R)dt = vdp = \frac{nR}{T} dP$

Integrating and rearranging

$$\frac{C_p}{R} \ln \frac{T_2}{T_1} = \ln \frac{P_2}{P_1}$$

Antilog gives $\left(\frac{T_2}{T_1}\right)^{\frac{Cp}{R}} = \frac{P_2}{P_1}$

Adiabatic irreversible free expansion: $q = 0$ expansion into a vaccum produces no work therefore $w = 0$

$\Delta E = q - w = 0 - 0$

$\Delta E = nC_v (T_2 - T_1) = 0$

Since $C_v \neq 0$ It means that $(T_2 - T_1) = 0$

$\therefore T_2 = T_1$

And $\Delta H = nC_p (T_2 - T_1) = 0$

$\therefore$ W,q, ΔE and ΔH are all zero for adiabatic free expansion of an ideal gas. E.g. during the combustion of nitrogen, the heat capacity per mole at constant pressure is 99atm of which 3moles of the product was formed. Determine the enthalpy change given that there is a temperature rise from 25^0C to 30^0C.

Solution

$\Delta H = C_p dT$

$= nC_p (T_2 - T_1)$

Where $n = 3$moles; $T_1 = 25^0C = 298K$

$\therefore C_p = 99$atm $T_2 = 300C = 303K$

$\Delta H = 3x99 (303 - 298)$

$= 297(5)$

$= 1,485J$

e.g. under a reversible adiabatic expansion of an ideal gas, there was a change in pressure from 30atm to 70atm. If the volume initially was $15cm^3$, determine the final volume (Take r to be 1.51).

Solution

$PV^{\propto} = \text{constant}$

i.e. $\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\propto -1}$

where $P_1 = 30atm$; $V_1 = 15cm^3$; $P_2 = 70atm$; $\infty = 1.51$ and $V_2 = ?$

$$\therefore \frac{70}{30} \left(\frac{15}{V_2}\right)^{1.51}$$

$$2.333 = \frac{(15)^{1.51}}{(V_2)^{1.51}} = S\ 2.333(V_2)^{1.51} = (15)^{1.51}$$

$$(V_2)^{1.51} = \frac{(15)^{1.51}}{2.333} \qquad \therefore (V_2)^{1.51} = \frac{59.689}{2.333}$$

$(V_2)^{1.51} = 25.584$

E.g The change in enthalpy of a reaction in which a molecule of oxygen reacted with phosphorus to give a phosphorus oxide is 640J. If the temperature change was found to be 55°C. What is the total number of molecules involves if the heat capacity per mole at constant pressure was 17atm.

Solution:

$\Delta E = q - W$

$q = \Delta E + W$

but $qp - \Delta G \therefore \Delta H = C_p dT$

$n = \Delta H / C_p dT = 640/17 \times 328$

$= 0.11$mole

3.19: Thermodynamics Equilibrium

The statement which says that for every action there is equal and opposite reaction manifests itself during the course of a chemical reaction. Due to the reversible nature of chemical reactions, there hardly go to completion and is analogous even to that of physical processes. For example freezing is the reverse of melting and condensation the reserve of vapourization.

$$H_20(\text{gas}) \underset{\text{Condensing by cooling}}{\overset{\text{Vapourising heating}}{\rightleftharpoons}} H_20(\text{liquid})$$

Chemical reaction can be reversed by altering the conditions of the reaction

$$\underset{\text{Low heat}}{\overset{\text{Strong heat}}{\rightleftharpoons}}$$

$2HgO \longrightarrow 2Hg + O_2$

$H_2 + \frac{1}{2} O_2 (g) \xrightarrow[\text{Electrolysis}]{} H_2O(L)$

In chemical reactions, equilibrium can occur when the rate of forward reaction is equal to that of backward reaction such that the reactants are reacting to give the wanted product and the product reacting to give back the initial reactions. Equilibrium can be static or dynamic and when it does so, we say that the reaction is in equilibrium.

3.19.1 Equilibrium Changes in Physical Processes

During physical processes, equilibrium do occur of which sometimes is due to some certain terms which are not naturally instinct. Physical processes include vapourization and condensation processes, melting and freezing process, sublimation processes etc. when a liquid is placed in a closed container, vapourization and condensation may occur and at a stage, the rate of vapourization gets to equal that of condensation. We say its now at equilibrium because the rate at which the vapour liquid is leaving the container is proportional to the rate at which the liquid is formed back from the vapour.

3.19.2 Equilibrium in Chemical Processes

During the course of a chemical reaction, equilibrium occurs due to the fact that most chemical reaction hardly go to completion.

3.19.3 Chemical Equilibrium and its Reversibility

For a reversible reaction, when the product and resultants are enclosed in a verssel, a time is reached when the reactant react to give the product and the product react to give back the reactant. At such a point we say a dynamic equilibrium is reached since its characterized by continual exchange but not change. So, when the concentration of reactant and product in a reaction no longer change with time a state of chemical equilibrium is attained.

How to Determine Chemical Equilibrium

To determine when equilibrium is attained, changes in concentration with time has to be monitored. If concentration no longer change with time, i.e. proceed with a zero rate, then equilibrium is said to be attained. Though it would fail for a reaction that proceed slowly.

$$A + B \rightleftharpoons C + D$$

If 1 mole of A and 1mole of B or 1mole of C and 1mole of D are reacted under some conditions, the same final state of equilibrium is reached in the reverse as in the forward reaction. If concentration of D is measured at regular interval during reaction, the same equilibrium concentration of B would be obtained in each.

3.20 Laws that Governs Chemical Equilibrium

(a) Homogenous Equilibrium:- Waage and Guldberg in their study of chemical equilibrium and reversible reaction applied the law of mass action to a system in equilibrium and found the occurrences of a definite relationship between equilibrium concentration of the reaction species. For a simple relationship of the type

$$A + B \rightleftharpoons C + D$$

may be called the law of chemical equilibrium

$$K = \frac{(C)\,(D)}{(A)\,(B)}$$

where (A), (B), (C), and (D) are equilibrium concentration of gaseous reactant and K is equilibrium constant.

For reaction involving number of moles

$$aA + bB \rightleftharpoons cC + dD$$

the equilibrium law is written as

$$K = \frac{(C)^c\,(D)^d}{(A)^a\,(B)^b}$$

Where each concentration is raised to a power of equal to the co-efficient in overall balanced equation for the reaction. E.g. in the reaction between nitrogen and hydrogen to form ammonia the following equilibrium concentrations were determined at 725k

$[H_2] = 0.51 mol/dm^3$

$[N_2] = 2.0 mol/dm^3$.

$[NH_3] = 0.095 mol/dm^3$

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Solution

Using the equilibrium law,

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{[0.095]^2}{[2.0][0.61]^3}$$

$$= \frac{0.009025}{[2.03][0.3369]}$$

$$= \frac{0.00902J}{0.45396}$$

$= \quad 0.0198 \quad \therefore \quad K = 1.98 \times 10^{-2}$.

The equilibrium constant numerical value depends on the particular reaction and temperature. If equilibrium constant at a known concentration and temperature of the reactants are known, it will be easy to determine the equilibrium concentration of the product from the mass action law.

(c) **Heterogeneous Equilibrium:** These are equilibrium that involves 2 or more phases i.e. a reaction to taking place in gaseous phase with a liquid phase with gaseous phase present.

For example, $2C_{(s)}, + O_{2(g)} \rightleftharpoons 2C_{O(g)}$

Which involves solid and gaseous phases and its equilibrium conditions is given as

$$K = \frac{(CO)^2_g}{[C_{(s)}]^2 (O_2)_g}$$

The concentration of CO and O_2 are variable while that of C will not be changed. If more of CO is introduced, its volume which is the volume of the vessel remains unchanged and its concentration increase, since number of molecules has increased that is same with solid carbon. However, at steady temperature, concentration of any substance as a

known
ΔT
M2W1

pure solid or liquid cannot be changed and is constant. Thus, the equilibrium constant can be combined with the constant concentration to give a new equilibrium constant so that the equilibrium law do not involve the pure condensed phase i.e.

$$K(C)^2_s = \frac{(CO)^2}{(O_2)}$$

Where $(CO)^2_s$ is a constant and if represented with equilibrium constant K; it becomes

$$K = \frac{(CO)^2}{(O_2)}$$

. For heterogeneous equilibrium, pure solid and liquid are omitted from the equilibrium law expression e.g.

At 1200⁰C $H_{2(g)} + S_{(g)} \rightleftharpoons H_2S_{(g)}$ $K_1 = \frac{[H_2S]}{[H_2][S]}$

At 200⁰C $H_{2(g)} + S_{(g)} \rightleftharpoons H_2S_{(g)}$ $K_2 = \frac{[H_2S]}{[H_2]}$

At 150⁰C $H_{2(g)} + S_{(g)} \rightleftharpoons H_2S_{(g)}$ $K_3 = \frac{1}{[H_2]}$

Multiple Equilibrium: For equilibrium reactions that leads to an overall reaction, the equilibrium constant of the overall reaction is the product of the equilibrium constant of the individual reaction e.g.

$A + B \rightleftharpoons C$ - - - - - - - K_1

$X \rightleftharpoons D + B$ - - - - - - K_2

Overall reaction: $A + x \rightleftharpoons C + D$ - - K

The equilibrium expression is given as

$$K = \frac{(C)\,(D)}{(A)\,(X)}$$

$$K_1 = \frac{(C)}{(A)\,(B)}$$

$$K_2 = \frac{(D)\,(B)}{(X)}$$

$$K_1 x K_2 = \frac{(C)}{(A)\,(B)} \times \frac{(D)(B)}{(X)} \quad K = \frac{(C)\,(D)}{(A)(X)}$$

Equilibrium constant K can be grouped under various categories

(a) K is a factor of the reaction and varies only with change in temperature. Its independent of the initial concentration of A,B,C and D at a fixed temperature.

(b). If $K>1$, it indicates that the reaction do not proceed far from left to right and if $K<1$, then the reaction proceeds far from left to right and to completion.

(c) In equilibrium law expression, via convention, concentration of reactant appear in the numerator and concentration of product in the denominator.

(d) For reversible reactions, equilibrium constant of a new equation is equal to the reciprocal of that of the original chemical reaction.

(e) For a reaction that is times by n, the equilibrium constant is raised to the nth term, e.g. $2A + 2B = 2C + 2D$ ....(1)

$$K^2 = \frac{(C)^2 (D)^2}{(A)^2 (B)^2}$$

$$K^2 = \left(\frac{(C)(D)}{(A)(B)}\right)^2$$

(f) If 2 chemical equations are added to get a new equation, its equilibrium constant will be equal to the product of equilibrium constant of the original equation.

e.g. $SO_2 + \frac{1}{2} O_2 \rightleftharpoons SO_3$ (i) $K_1 = \frac{[SO_2]}{[SO_2][O_2]^{1/2}}$

$CO_2 + CO + \frac{1}{2} O_2$ (2) $\rightleftharpoons$ (ii) $K_2 = \frac{[CO_2][O_2]^{1/2}}{[CO_2]}$

$2SO_2 \rightleftharpoons CO + SO_3$ (3) (iii) $K_3 = \frac{[CO][SO_3]}{[SO_2][CO_2]}$

Derivation of the Equilibrium Law from Mass Action Law

The law of mass action states that the driving force of a chemical reaction is proportional to the active masses of the reacting substance. the law of chemical equilibrium is infact an experimental fact and empirical which is however proven by using principles of kinetics as stated in the law of mass action above.

$A + B \rightleftharpoons C + D$ for homogenous reaction

Rate $= K^1 [A][B]$ forward reaction rate (K^1)

Rate $= K^{ii} [C][D]$ backward reaction rate (K^{ii})

Where K and K^1 are rate constants for forward and backward reactions

At equilibrium K and K^1 are equal. Thus,

$$\frac{K}{K^1} = \frac{(C)\,(D)}{(A)\,(B)}$$

Calculations based on equilibrium

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI(g)$ with a value of K at 45.9 and temperature 490°C.

e.g. 1 mole of H_2 and 2 mole of T_2 are introduced into a $1dm^3$ box at a temperature of 490^0C. What will be the final concentration in the box at equilibrium.

Solution: Let x moles of H_2 be converted at equilibrium

	H_2	$T_2 \rightleftharpoons$	$2HI$
Initially	1	2	0
At equilibrium	1-x	2-x	2x

$$\therefore\ 45.9 = \frac{[H_1]^2}{[H_2][I_2]}$$

$$\therefore\ 45.9 = \frac{[2x]^2}{[1-x][2-x]}$$

$$41.9x^2 - 137x + 91.8 = 0$$

:. Two solutions are gotten where x = 0.93 or 2.36. The value of x is substituted but the latter value is 2.36 is not used because its chemically impossible.

:. x = 0.93

So at equilibrium, $H_2 = 1\text{-}x = 0.07\text{mol/dm}^3$

$T_2 = 2\text{-}x = 1.07$

HI = 2x = 1.86

e.g. 2mole of HI are injected into a 2dm^3 container at 490^0C. Calculate the concentration of each specie in the container at equilibrium.

Solution: As usual, let x moles of HI be decomposed at equilibrium

	H_2	$I_2 \rightleftharpoons$	$2HI$
Initially	0	0	2
At equilibrium	$^x/_2$	$^x/_2$	2x

$$\frac{[HI]^2}{[H_2][T]}$$

$$:.\quad 45.9 = \frac{[2\text{-}x]^2}{[^x/_2][^x/_2]}$$

Which after calculations gives x as 0.456

∴ At equilibrium, $H_2 = {}^{x}/_{2} = 0.228 mol/dm^3$

$I_2 = {}^{x}/_{2} = 0.228$

$HI = 2 - x = 1.644$

3.21 The Vitality of the Expression ($\Delta G^0 = -RTlnk$)

The equilibrium $\Delta G^0 = -RTlnk$ connects the standard Gribbs free energy change (ΔG^0) for a reaction with its equilibrium constant. Its important for reaction that proceeds slowly of which direct measurement of equilibrium can't be made for situation that are hard to experimentally achieve.

If ΔG^0 = negative ~~positive~~, k will be greater than 1 and reactant react fast to give product. If $\Delta G^0 = 0$, k will be equal to 1 and reactant will be in equilibrium with the product. If G^0 = positive, k will be less than 1 and reactant react slowly to give product.

It is always mandatory for the Gribbs free energy change to be negative for the reactants to react fast to give the wanted product, e.g. the formation of ammonia at 673K according to the reaction.

$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$ has equilibrium constant of 1.64×10^{-4} calculate G^0 for the reaction at 673K. ⑦

Solution $\Delta G^0 = RTlnk$

$= -(8.314J/mol/K) \times (673K \times 2.503\log 1.64 \times 10^{-4})$

$= 48.78KJ/mol.$

Equilibrium Change and Factors that Affect it:

Concentration of reactant, temperature, volume pressure and relative weight of reactant are factors that determine the yield and point of equilibrium. There is a need for the chemical reaction to re-establish equilibrium in certain reactions.

Calculated Production of Equilibrium Change

Le Chatelier Principles

Le Chatelier principle states that if anything be done to a system in dynamic equilibrium, that would normally result in a change in any of the factors that determine the state of equilibrium, the system will adjust itself in such a way to minimize that change. These factor that affect equilibrium of a reaction and are adjusted or annulled are temperature, concentration, pressure, volume, etc.

(a) Effect of Temperature: For a reaction in which there is an absorption of heat energy from the environment that is endothermic reaction, the forward reaction is favoured while for a reaction in which there is release of energy to the environments which is exothermic reaction, the backward reaction is favoured. E.g. (i)

$2SO_2 + O_2 \rightleftharpoons 2SO_3 - Qcal$ (exoethermic)

(ii) $N_2 + O_2 \rightleftharpoons 2NO + Qcal$ (endothermic) in (i), backward reaction is favoured i.e. formation of more of SO_2 and O_2 while for

(ii) forward reaction is favoured i.e. formation of NO.

(b) **Effect of volume** Change in volume do not affect liquid and solids but affect gases. Increase in pressure decreases volume of the system and vice versa. Decrease in pressure increases volume (i.e. reduces concentration) and hence favours forward reaction in which more molecules are produced. E.g. $CH_{4(g)}$ + $H_2O(g)$ $CO_{(g)}$ + $3H_{2(g)}$

For a decrease in pressure, there increase in volume and the rate of formation of CO and H_2 is increased and at an increase in pressure, a decrease in volume occur in which less of CO and H_2 are formed and more of CH_4 and H_2O produced.

(c) **Effect of Concentration:-** Increasing mass of one substance by addition of more of it to the reacting system in equilibrium increases the concentration of this substance relative to that of all the other ones. By Le Chatelier principle, a shift is made to annual the defect.

An excess of steam will direct the equilibrium to the right, increasing yield of CO and H_2. A decrease in concentration of 1 of the reactant favours its formation. The equilibrium shift can be continued till the wanted reaction goes to completion by removing the product as they are formed.

(d) **Effect of Catalyst:** A catalyst change the rate of reaction by reducing the activation energy of the forward reaction rate. The net outcome won't change the heat of reaction which determines the equilibrium constant. However, a catalyst does not alter the equilibrium constant.

3.22 Spontaneity of Chemical Reactions and Equilibrium Constant

If ΔG^0 = $-RT\ln k$, similarly $\Delta G^0 = \Delta H^0 - T\Delta S^0$ and we substitute for ΔG^0

$-RT\ln k = \Delta H^0 - T\Delta S$

$RT\ln k = -\Delta H + T\Delta S$

$RT\ln k = T\Delta S - \Delta H$

$$\ln k = \ln k = \frac{T\Delta S}{RT} + \frac{\Delta H}{RT}$$

Taking antilog gives

$K = e^{\Delta S/R} - e^{\Delta H/RT}$

From (3), we can determine the sign and magnitude of ΔS^0 and ΔH^0 needed for K>1 i.e. for reactants to be converted spontaneously to give the product. When ΔH^0 = negative, ΔS^0 = positive, K is greater than 1 and reaction will be spontaneous, if ΔH^0 = positive, ΔS^0 = negative, K < 1 and reaction won't be spontaneous if ΔH^0 and ΔS are positive, K>1 at low temperature but at enough high temperature K> 1. If ΔH^0 and ΔS^0 are negative (where bonds are formed in a reaction), K>1 at sufficient low temperature and K< 1 at sufficient high temperature. The thermodynamic basis for spontaneous of a process is ΔG and not ΔG^0 because most reaction are not carried out at standard conditions i.e. 25^{0}C and 1atm.

$$\Delta G = \Delta G^0 + RT\ln k$$

If ΔG^0 is positive, ΔG may be negative and the reaction thus proceeds spontaneously by increasing the pressure or concentration of reactants or decreasing the pressure or concentration of the product; either K<1 and ΔG is negative, e.g. the standard Gibbs free energy changes (ΔG^0) for the reaction $N2O_{4(g)} \rightleftarrows 2NO_{2(g)}$ is + 4857.6 Joules at 25^0C, the reaction is non-spontaneous at this temperature. If NO_2 is withdrawn by some means to keep its partial pressure say at 1atm while that of N_2O_4 is maintained at 10atm.

therefore, during $\Delta G = \Delta G^0 + RT\ln k$

$\Delta G = 4857.6 + (8.314)(298)\ln {}^1/_{10}$.

$= -847$Joules ⟶ spontaneous reaction

3.23: Chemical Production and the Chemical Equilibrium:

For the economic manufacture of any desired product, great attention should be paid to the kinetics and equilibrium state of the chemical reaction. It is a very imperative for every manufacturer or producer to produce his product at the shortest possible time and at large quantity. However, the effect of temperature which fastens attainment of equilibrium may have an undesirable effect in position of equilibrium i.e. lower yield of the product.

For example, $N_{2(g)}$. + $3H_{2(g)} \rightleftarrows 2NH_{3(g)}$ ΔH_2 - 90.5kg. At 150°c and 250atm, the yield of NH_3 from the reaction of H_2 and N_2 is 90% but the rate of formation of NH_3 is slow.

At 700°C and 250atm, the yield of NH_3 is only 10% but the rate of its formation is high. Thus, lower temperature favours yield and higher temperature favour rate.

Also, a catalyst on its own do not increase the yield of the product. This is so because the catalyst only reduce _the potential energy barrier in the two opposing reaction in a proportionate manner. It raises the rates of both reactions to the same degree thereby making the equilibrium concentration of reactants and product· to remain unchanged.

However, temperature and catalyst can be combined, and a good yield may be achieved. For example, in the making of H_2S0_4, the main stage is the oxidation of $S0_2$ to $S0_3$ which is an exothermic process.

$$2S0_2 + O_2 \longleftrightarrow 2S0_3 \quad \Delta H = -172kJ$$

Meanwhile, at high temperature, there is a fast reaction leading to the formation of NH_3 but a slow reaction towards the yield of $S0_3$. Thus abnormally is corrected using a solid catalyst e.g. vanadium compound or platinum. The gases are passed over a part of the catalyst at about 500-600°C under which 70 - 80% of $S0_2$ is fastly converted to $S0_3$ and to cool the gases till the temperature when passing over the last portion of catalyst is about 400°C. At 400°C, the equilibrium yield of $S0_3$ is high

E.g. $HCl + NaOH_{(aq)} \longrightarrow NaCl_{(g)} + H_2O(c)$

Determine the equilibrium constant of the reaction above given that the concentration of HCl is 3.45mol/dm^3, NaOH is 5.0mol/dm^3, NaCl is 0.7mol/dm^3 and that of H_2O is 1.2mol/dm^3.

Solution

From the equilibrium law expression

$$K = \frac{[A][B]}{[C][D]} = \frac{[NaCl][H_2O]}{[HCl]NaOH]}$$

$$= \frac{0.84}{17.25} = \frac{(a7)\,(1.2)}{(5)\,(3.45)} = 0.0486$$

$K = 4.86 \times 10^{-2}$

e.g. $2C_{(s)} + 20_{2(g)} \longrightarrow 2C0_2(0)$

The concentration of 2moles of carbon is 3.01 mol dm^{-3} and it reacted with oxygen with a concentration of 6.2mol/dm^3 it form CO_2 with concentration of 0.5 mol/dm^3, Find the equilibrium constant of the reaction.

Solution: for a reaction in this form,

$2A + 2B \longrightarrow 2C$ in equilibrium constant law expression is ,given as

$$K = \frac{(C)^2}{(A)^2\,(B)^2}$$

For the reaction between carbon and oxygen

$$K = \frac{(CO_2)^2}{(C)^2\,(O_2)^2} = \frac{(0.5)^2}{(2)^2\,(3.01)^2} = \frac{0.25}{36.24}$$

$K = 0.00689$

273 28

K = $6.89\text{x}10^{-3}$

e.g. 28^0C, a reaction was carried out at an equilibrium constant of 0.00456. Determine the standard free energy change and the free energy change of the reaction.

Solution: $\boxed{\Delta G^0 = RTInk}$

$= -(8.314)(301)(In\ 0.00456)$

$= (13,49=89.63).$

To get the free energy change, DG we use the formula, $\boxed{DG = DG^0 + RTInk}$

$= \quad 13,489.63 + (8.314 \times 301 \times In\ 0.00456)$

$= \quad 13,489.63 + (13,489.633)$

ΔG = 0 is reactant and are in equilibrium with the product.

water and carbondioxide gas ΔH is 781.0kcal at 25^0C (298K) calculate the heat of this reaction at constant volume at same temperature.

Solution

$C_6H_{6(L)} + 7\frac{1}{2}\ O_{2(g)} \longrightarrow 3H_20_{(L)} + 6H_20_{(g)}$

Write and balance your equation. It is very important ΔH_{298} = - 789.0kcal

The number of moles N_A of gaseous reactants is 7.5 while the number of mole N_B of gaseous products is 6 so that

$\Delta n = N_B - N_A = -1.5$

Temperature T = 298K and R may be taken as 2cal (or 2×10^{-3}) $deg^{-1}mol^{-1}$

Hence from equation $\Delta H = \Delta E + RT\Delta N$ (your formula)

$\Delta E=H = \Delta E - (2x10^{-3} \times 298x1.5)$

$= \quad 789 = \Delta E - 0.894$

$\therefore \Delta E = 788$kcalorie.

We have different types of heat reaction:

(i) Heat of formation

(ii) Heat of combustion

(iii) Heat of solution

(iv) Heat of neutralization

(v) Heat of formation of ions in solution

4.5 Heat of Formation:- This is referred to as standard heat of formation because reactants and products are in standard state (281K and 1atm) this heat change involved in the formation of 1mole of a substance from its elements and is known as the heat of formation of the substance.

During this process of heat of formation, some problem were encountered so to get around it, some assumption is made which is that the enthalpies of all elements in their standards state at 250C are arbitrarily taken to be zero. If we have a reaction like this, $2Mg_{(s)} + O_{2(g)} \longrightarrow 2Mg0$ q = xkj to calculate this heat of formation, the equation tells you that the reaction above have the formula of two moles so the SHF (standard heat of formation will be x/2kJ. But in the case $C(s) + O_{2(g)} \longrightarrow CO_{2(g)}$ q = -393.51J.

Also

$$H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)} \longrightarrow \Delta H = 51.7kgmol^{-1}$$

$$\text{Heat of formation HF} = \frac{\Delta E}{2} = \frac{51.9}{2} = 25.9kJmol^{-1}.$$

Some compounds and their heat of formation

Compounds	Standard heat of formation
$H_2O_{(g)}$	241.82
$SO_{2(g)}$	-296.8
$HCl_{(g)}$	-92.31
$NH_{3(L)}$	-46.11
$NO_{2(g)}$	-33.2
$NaOH_{(L)}$	-425.6
H_2SO_4	-811.3
HNO_3	174.1

Problem 1:

Calculate the standard heat of reaction of ferric oxide by Aluminum which proceeds according to the following reaction

$2AL + Fe_2O_3(s) \quad 2Fe(s) + Al_2O_3(s)$

The heat of formation of $Fe_2O_3(s)$ and $Al_2O_3(s)$ as $-196.5calmol^{-1}$ and $399.akcal\ mole^{-1}$ respectively.

Solution: Let the heat of reduction of ferric oxide by aluminum be xkcal.

$2AL(s) + Fe_2O_3(s)$ $2Fe+AlO_3\Delta H$ = xkcal using formula $\Delta H = \Sigma H_p - \Sigma H_R$ so if you have aA+ bB cC + dD you will have $(c\Delta H^0_fC + d\Delta H_f^0D) - (a\Delta H^0_fA + b\Delta H^0_fB)$

$[(2H^0Fe(s) + H^0Al_2O(s)] - [2H^0Al + H^0Fe_2O_3(s)]$

(0-399.1) – (0-196.5).

-202.6Kcal hence the standard heat of reduction = 202.6kcal.

Problem 2: Calculate the heat of reaction for the equation $CO(g) + H_2O(1) = CO_{2(g)} + H_2(g)$.

-94.7

$f = \frac{HR}{2}$ Given that $H_2O_{(L)}$ = -68.3 ΔHf ($kcalmol^{-1}$)

$68.3 = \frac{HR}{2}$ CO(s) = - 26.4Hkcal $mole^{-1}$.

$H = P - R$

$HR = 136.6$

Solution:-

$CO_{(g)} + H_2O_{(2)} = CO_{2(g)} + H_{2(g)}$

- 26.4 – 68.3 = -94.00

Given that

ΔH reaction = H product – H reactants i.e. $\Delta H_1 - \Delta H_p - \Delta H_R$

Where ΔH_r = heat of reaction

ΔH_f $(H_p - H_r)$

ΔHp = heat of product

ΔHR = heat of reactant

ΔH_{Rxn}

= -94.0[-26.4] + [-68.3]

= -94.0 – (-94.7)

= -94.0 + 94.7 = 0.7kcal

ΔH reaction = 0.7kcal at 25^0C.

4.6 Heat of Combustion

This heat depends on the conditions of burning. The heat of combustion is the change in heat when one mole of a substance i.e. element or compound is completely burnt in oxygen at a constant pressure if reactants and products are kept at standard value of 298k and 1atm while burning 1 mole of a substance completely in oxygen the heat evolved is referred to as the standard heat of combustion (SHC) using equation we will have something like this

$C_6H_6 + 7\frac{1}{2} 0_2 \longrightarrow 6C0_2 + 3H_20$ $\Delta H = 781.0$ kcal.

Heat of combustion are very much experienced in organic chemistry when fuels are combusted for energy and few also get burnt inside the body to produce heat in form of energy.

4.7 LAWS OF THERMOCHEMISTRY

These laws are derived from the principle of conservation of energy. The 1st law was given by Lavoiserand Laplace in 1980, which states that "The quantity of heat which must be supplied to decompose compounds into its elements is equal to the heat evolved when the compound is formed from it element.

Using this form to explain more

$H_{2(g)} + \frac{1}{2} O2_{(g)} \longrightarrow H_2OL$ $\Delta H - 68300$ cals

$H_20(1) \longrightarrow H_2(g) + \frac{1}{2}\ 0_{2(g)}$ $\Delta H' + 68300$ cals

$SO_{2(g)} \longrightarrow S(g) + O_{2(g)}$ $\Delta H - 70960$cals

$S0_{2(g)} \longrightarrow S(g) + 0_{2(g)} =$ $\Delta H + 70960$

The beauty of this law is that we can reverse thermochemical equation provided the sign of the equation is changed and the magnitude remains the same. Another law is the Hess law of constant heat summation (1840) "It states that the overall heat charge in a chemical reaction carried out either at constant pressure or at constant volume is the same irrespective of the fact whether the reaction proceeds in one or several stages. This law enables thermochemical equation to be added or substracted like algebriae equation. As a result heat of reaction that cannot be obtained experimentally are obtained by calculation from other thermochemical data.

Hess's law may also be stated that if different processes are used to bring about the same change, the heat change is same for all of them. Hess law are also applied as follows:

(i) Heat of formation reaction of some compounds

(ii) Calculation of lattice energies of conic crystals

(iii) Study of multistep reactions..

(iv) Determination of calorific values of food and feels. Let try determining ΔH for the reaction

$2C + 2H_2 \longrightarrow C_2H_4 \longrightarrow \Delta H26^0C$

Given the experimental results

$C + O_2 \longrightarrow CO_2 \longrightarrow \Delta H_{25}{}^0C = -94kcal$ (i)

$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O \longrightarrow \Delta H_{25}{}^0C = 68.3kcal$ (ii)

$C_2H_4 + 3O_2 \longrightarrow 2CO_2 \longrightarrow 2H_2O = \Delta H_{25}{}^0C = -342$ (iii)

Solution

Multiply equation 1 and (ii) 2 and add

$2C + 2O_2 \longrightarrow 2CO_2 \; \Delta H_{25}{}^0C = -2x94kcal$

$2H_2 + O_2 \longrightarrow 2H_2O \; \Delta H_{25}{}^0C = -2x68.3kcal$

$2C + 2H_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta H_{25}{}^0C = 324.6kcal$ (iv)

Substituting equation (iii) from equation (ii) to obtain a desired equation.

$2C + 2H_2 \longrightarrow C_2H_4 \quad \Delta H_{25}{}^0C = (-324.6 + 342) = +17.4$ kcal.

4.8 Bond Energy

At first one will say what those bond and energy has to do with thermochemistry but looking at it that way is not bad but if you look at it from this chapter point of view you will actually know that there is no heat changes without bond being broken or bond being formed in a reaction. Bond energy means average amount of energy per mole necessary to rupture a particular bond in a molecule and this effects a complete separation of the resulting atoms or radical from one another. For diatomic molecules like H_2, O_2 Cl_2 its energy is called bond dissociation energy. In poly atomic molecule, the energy required to break a given bond will depend to some extent on the nature of the remainder of the molecule and will vary from compound to compound for instance energy needed to break O-H bond in alcohol is not same amount of energy needed to break it in organic acids therefore the bond energy in poly atomic compound is the average amount of energy required to break a particular bond in one mole of the compound. Example in water we have

$H_20 \longrightarrow H_{(g)} + OH_{(g)} \quad \Delta H = 119.95\ \text{kcalrnol}^{-1}$ to break O-H bond

in hydroxyl radical requires a different heat quantity.

$OH(g) = O(g) + H(g) \quad \Delta H = 101.19\text{kcal}$

$$\text{Bond energy} = \frac{\text{average of the two values}}{2}$$

$$e^{O-H} = \frac{119.95 + 101.17}{2} = 11\,0.57\text{kcal mole}^{-1}$$

In diatomic molecules such as H_2 the bond energy and the bond dissociation energy are identical for both, refer to the following reaction. $H_2(g) = 2H(g)$ H - H = ΔH_{298} ^0C = 104.18kcal

To determine bond energy for a particular bond like C-H bond we will first find the enthalpy change for the following reaction. CH_4 = C + 4H using eC˙H to represent bond energy of C-H we have eC˙H

$$= \frac{\Delta H}{4}$$

because there are four C˙H bonds and all the bonds are identical so from heat of combustion data ΔH for CH_4 was found to be 398. 0kcal.

Therefore eC-H $\frac{398.0}{4}$ 99.5 kcalmol^{-1}.

Similarly, bond energies of H-O, H-N, H-S bond can be determined from the heats of reactions in which the molecules H_20, NH_3, and HS are formed from their atoms.

Note that when bond break, bond enthalpy is positive but when a bond is formed bond enthalpy is negative.

The symbol H_2,Cb and N_2 is referred to as the mole of a substance which contains 6.023 x 10^{23} molecules. This one mole of Hel contains 6.023 x 10^{23} linkages while ammonia has 3 x 6.023x 10^{23} linkages. The energy to break one bond of H-H actually means the energy to break all the linkages in a mole of gas.

454

C - H = 4×(99) + [illegible](58)
396 + 58
454 kJ/mol
3(99) + 78 + 103
478 kJ/mol

157 - 127

-C-Cl

BB - BF
454 - 478 = (-24 kJ/mol)

Here are some bound and their energy

Bond		Bond Energy	
C-C	348	N-N	861
C=C	610	0-0	140
C≡C	826	O-H	463
H-H	436	Cl-Cl .	243
N-H	331		

Uses of bond energies

(a) Comparing strength of bonds
(b) ·Understanding structure and bonding
(c) Estimating the enthalpy changes in a reaction
(d) Understating the mechanism of chemical reaction

The one we will look into in this chapter is the most important use, which is estimating the enthalpy changes that is taking place in a chemical reaction.

Problem 1

Given that bond enthalpies for C-H, Cl-Cl, C-Cl and H-Cl are respectively 99, 58, 78 and 103 calculate the moles, determine ΔH for the reaction

$CH_4 + Cl_{2(g)} \longrightarrow CH_3Cl + HCl$

Solution:-

$\Delta H = \Sigma_{B.E}$ (breaker) $-\Sigma_{B.E.}$ (formed) where Σ = summation, B.E. bond energy

In the reaction above CH_4 has 4 C-H bond that exist but only one is affected and are H-H bond in H_2 which are broken in turn, one C-Cl bond in CH_3Cl and one H-Cl bond in HCl are formed therefore, $\Delta_{25}{}^0C$ = - (eC-Cl + eH – Cl) + (eC-H + eCl – Cl) inserting the various values we get

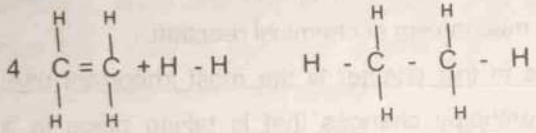
$\Delta H_{25}{}^0C = -(78 + 103) + (99 + 58)$

$\Delta H_{25}{}^0C = -24kcal$

(57) -187

Problem 2

Calculate the enthalpy change for the reaction hydrogenation of ethane $CH_2 = CH_2 + H \longrightarrow CH_3 - CH_3$ gives the following B.E in kjmol^{-1} C-H = 410,87, C=C 606.68. H-H = 431.79, C-C = 336.81.



$$4 \quad H_2C{=}CH_2 + H{-}H \qquad H{-}CH_2{-}CH_2{-}H$$

Bond Broken are

(1) (C = C) + 4(C - H) + 1(H - H)

606.68 + 4(410.87) + 1 (431.79) = 2681.95kJmol

Bond Formed

1(C-C) + 6 (C- H)

(336.81) + 6 (410.87) = 2882.03kJmol.

ΔH = ΣB.E. for breaking - ΣB.E. for bound formation

2681.93 - 2802.03 = 120.0kJmol^{-2}.

fats / Carbohydrates — organisms

4.9 Bond Energy in Fuels and Food:-

Hydrocarbons compound and coal are most common fuel for machines whereas those for organisms are fats and carbohydrates. Both are made up of large molecules mainly C-H and C-C bond. Utilization of fuels brings about bond breaking and atoms become bonded to oxygen atom. The waste product of these fuels are CO_2 and H_2O. Fuels with many weaker bonds will yield more energy than fuels with stronger bonds. During utilization fuel are burned in the presence of oxygen to give C-O and O-H bond which decreases the usefulness of the fuel.

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Chapter Five

By Onuigbo, U.A.

CHEMICAL EQUILIBRIUM

Chemical equilibrium applies to reaction that occur in both direction. In a reaction such as $CH4(g) + H_2O_{(g)} \rightleftarrows CO_{(g)} + 3H_{2(g)}$.

The reaction can happen both ways. So after some of the .product we created the products begins to react to form the reactants. At the beginning of the reaction, the rate that the reactant are changing into the product is higher than the rate that the product are changing into the reactants. Therefore, the net change is a higher number of products. Even though the reactants are constantly forming product and vice-versa the amount of reactants and product does become steady (not equal but constant).

So when the net change of the product and reactant is zero, the reaction has reached equilibrium. The equilibrium is dynamic.

5.1 Dynamic Equilibrium:- The word "dynamic" applies to something in motion that is something that is moving. Therefore dynamic equilibrium when the movement of reactant to product and movement of product to reactant is constant. This can only be possible in a closed system. So what we are saying is that chemical dynamic equilibrium takes place in a closed system.

- **Closed System:-** When we say the word "system" it can be anything a cup of water, a balloon, a laboratory planet, thus for discussion purposes we define a isolated portion of the universe as a system. Anything outside the system is called environment.

When a system is under observation it is isolated from its environment in such a way that there is no energy or mass transferred into or out of the system, the system is said to be a closed system.

Note: In a closed system, changes occur but eventually there is no net change over time. Such a state is called an equilibrium state.

Discussion about chemical equilibrium we earlier mention that the reaction goes in both ways forward and backward reaction as much as possible. The reaction that possess this ability is called reversible reaction

Reversible reaction:- Reversible reaction is a reaction that can proceed in both direction according to experiment condition.

$$A + B \longleftrightarrow C + D$$

A, B, C, D, can be any compound atom or molecule A and B in above are the two reactant which react to give the product. C and D if the product are not allowed to escape, then as soon as they accumulate they react to form the reactants. So does C and D.

We have two types of reversible reaction

(i) Reversible reaction under the same condition e.g. reaction between

$$3Fe_{(s)} + 4H_2O_{(g)} \longrightarrow Fe_3O_4 + 4H_{2(g)}$$

(ii) $CaCO_{3(s)} + H_2O + CO_{2(g)} \longrightarrow Ca(HCO_3)_2$.

In (i) the median and condition for forward and backward reaction are the same but in (2) the mode for forward reaction is different from the mode for backward reaction.

5.2 Law of Mass Action

This law was proved by Guldberg and Waage in 1864 when they hydrolyzed sucrose. It was found that the rate of hydrolysis was proportional to the amount of sucrose unreacted. The law state that at constant temperature the rate of a chemical reaction is directly proportional to the product of the "active mass" of the reactant Guldberg and Waage used the term "active mass" rather than concentration, which is for tortuously. Closer to the correct description of activity. This law helps us to find the relation between the concentration of reactant and products at equilibrium in chemical reactions.

Active mass in the above is a chemodynamic "quantity and is given that

$A = CF$ where A = active mass, C = concentration of molecules and F = the activity co-efficient.

Considering the equation below

$aA + bB \rightleftarrows cC + dD$

According to law of mass action the rate of forward reaction R_f

$R_f = K_f [C]c [D]d$ - - - - - (1)

Where K_f is the proportionately rate constant for forward reaction. Similarly for backward (reverse) reaction, the rate is R_b.

$R_b = K_b (A)^a (B)$ - - - - - (2)

Kf = rate constant for forward reaction

Kb = rate constant for backward reaction

(A) = Concentration of A

(B) = Concentration of B

(C) = Concentration of C

(D) = Concentration of Q

At equilibrium $R_f = R_b$ - - - - - (3)

Therefore, $K_f (A)^a (B)^b = K_r (C)^c (D)^d$ - - - (4)

$$\frac{K_f}{K_b} = \frac{(C)^c (D)^d}{(A)^a \ (B)^b} = \frac{C_c \ C_D}{C_A \ C_R} \quad - - - \quad -(5)$$

$\therefore$ At equilibrium the equilibrium constant (K_c).

$$K_c = \frac{Kf}{Kb}$$

$$\therefore K_c \quad \frac{(C)^c (D)^d}{(A)^a \ (B)^b} \quad - - - \quad -(6)$$

Where c,d,a and b are the number of moles of reacting species

So to write the equilibrium constant; it just the product over the reactant e.g.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(ag)}$$

$$Kc = \frac{(HI)^2}{(H_2)(I_2)}$$

5.3 Equilibrium Constant Expressed in Different Units

When the reaction involve gases it is easier to express concentration of any gas at any given temperature in terms of its partial pressure: to define the equilibrium constant in terms of the partial pressure of the reactants and products, consider the general gaseous reaction

$aA + bB + \ldots\ldots \rightleftharpoons cC + dD + \ldots\ldots\ldots$

Assuming, PA, PB, PC and PD are the partial pressure of the various gaseous species at equilibrium, equilibrium constant may be written as

$$K_p = \frac{P_C^{c} P_D^{d}}{(P_A^{a} . P_B^{b}} \qquad (7)$$

Where K_p is the equilibrium constant in terms of partial pressure, and is constant at a given temperature. It should be noted that equation (7) is only for ideal gas.

From the above we can express the equilibrium of a reaction, mathematically, and we can explain it theoretically but these thing have no foundation if we on not know the principles and factor affecting the system.

Le-Chatelier's Principles: The principle states that when a system in chemical equilibrium is disturbed by a change of temperature, pressure or a concentration. The system shifts in equilibrium composition in a way that tends to counteract this change of variable. This principle is useful in determining the effect of variation in temperature, pressure and concentration on the position of equilibrium of a reversible reaction. It was fundamental base on second law of thermodynamics.

Factors Affecting Chemical Equilibrium

(1) Concentration: If the concentration of one of the reacting component of the system is increased, the equilibrium will change in such a way so as to decrease the concentration of that particular component, e.g.

$CO_{2(g)} + H_2O_{(g)} \rightleftarrows CO_{(g)} + H_2O_{(g)}$.

Increase in concentration of the reactant will shift equilibrium to the right. More product is forward. If the concentration of the product is increased the equilibrium will shift to the left, more reactant is produced. If the concentration of reactant is decrease the equilibrium shift to the left to produce more of the reactant and vice versa.

(2) **Temperature:-** generally, temperature affect equilibrium position negatively or positively. If the reaction is exothermic (heat is evolved from the reaction) then decrease in temperature will follow the forward reaction. However, if the reaction is endothermic (heat is absorb for the reaction) increase in temperature will favour the forward reaction

$N_2 + 3H_{2(g)} \rightleftarrows 2NH_3$ - exotherm

(a$2NH_{3(g)} \rightleftarrows N_{2(g)} + 3H_{2(g)} + 91.8KJ$

Equation A is exothermic and equation B is endothermic but both processes occurs in the equilibrium system. If temperature is increased the equilibrium will shift to the left because heat is required. If the temperature is decreased the equilibrium will shift to the right because heat is given off.

Pressure:- The effect of pressure on the system depends on the two conditions.

(i) The reactants and products must be gases

(ii) The total number of moles of reactant and the total number of moles of product must not be the same.

(iii) $M_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ no effect

$Cs + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$. no effect

Considering the equation below

$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$.

2 mole 4 moles

2 volumes 4 volumes

Increase in pressure decrease the volume so the equilibrium shift to the left to produce more reactant which has lesser volume. Decrease in pressure, increases the volume, so the equilibrium shift to the right, more product is forward. Catalyst: The catalyst does not alter the value of equilibrium constant for any reversible reaction. It simply helps in approaching the equilibrium at an earlier stage by catalyzing equal both in forward and the backward reaction.

Types of Chemical Equilibrium

The plural of equilibrium is equilbria, we have two types.

(i) **Homogenous Equilibria:** which only one phase occur. For example, a system containing only gases or a single liquid or solid phase.

(ii) **Heterogeneous Equilibria:** which more than a single phase appears. For example, equilibrium between solid and gas, liquid and gas, solid and liquid, solid and solid etc. the word "phase" used in the above applied to any homogenous and physically distinct part of a system which is separated from other part of the system by definite boundary surface. Equilibrium between ions in the solid and liquid phases (equilibria in heterogeneous system). Heterogeneous reaction involves two or more phases, one of which is a solid and liquid. The application of law of mass action to heterogeneous equilibria is based on the face that activity of a pure solid or liquid is always taken as unity at all temperature up to a fairly high pressure.

Consider the dissociation of mercuric oxide

$$HgO_{(s)} \longrightarrow H_{g}^{2+}{}_{g(aq)} + O^{2-}{}_{(aq)}$$

So the equilibrium constant for the above reaction is

$$Kc = \frac{(Hg^{+2})\ (O^{-2})}{H_gO}$$

Kc is the equilibrium constant for ionic dissociation. It is important to know for this equilibrium to be possible, there must be dissociation in aqueous medium to produce ions. There are also many types of these to be discuss in further chapters.

5.4 Solubility:

When we say solubility three things comes to our mind, solute, solvent, solution. Mathematically, solute + solvent = solution.

Solute: This is the smallest part of the solution. It does not determine the states of matter.

Solvent: This is the largest part of the solution it determines the states of matter whether, solid, liquid or gas. The solute is dissolved in the solvent.

Solution: This is homogeneous mixture of solute and solvent.

Solubility of a substance can be defined as the amount of the substance that dissolve in 1000cm^3 of the excess solvent. The solubility of a substance strongly depends on the used solvent as well as the temperature and pressure. the extent of the solubility of a substance in a specific solvent is measured as the saturation concentration where adding more solute does not increase the concentration of the solution.

Solubility occur under dynamic equilibrium, which means that solubility results from the simultaneous and opposing processes of dissolution and phase separation (e.g. precipitation of solids). The solubility equilibrium occurs when the two processes proceeds at a constant rate.

5.5 Factors Affecting Solubility

(a) **Temperature**: Solubility of a given solute in a given solvent typically depends on temperature. It is generally known that as the temperature of the system increase, the solubility of the system will also increase. For example, sugar dissolve faster in hot water than in cold water so also other substances.

(b) **Pressure:-** Pressure have negligible effect on solubility. It only affect gases slightly in most cases, when the pressure is increased, the molecules react faster so tend to dissolve more than at normal pressure.

5.6 Application of Solubility

(i) it is used to determine the substance polarity

(ii) is it also useful when separating mixture that it help in separation.

Considering a fairly soluble salt

$$A_x B_{y(s)} \rightleftharpoons A^{+y}_{(aq)} + B^{-x}_{(aq)}$$

Since it is not a very soluble salt i.e. it is partial ionization

$$Kc = \frac{[A^{+y}][B^{-x}]}{A_xB_y}$$

$$Kc = [A^{x-}B^{y}] - [A^{+y}][B^{-x}]$$

$$Kc = [A^{+y}]\,[B^{-x}]$$

Where Ksp is the solubility product equilibrium constant

Solubility product (Ksp) is the equilibrium constant for the equilibrium that exist between a slightly soluble salt and its ions in a saturated solution. It is defined as the product of concentration of the ions of a fairly soluble salt in saturated solution raise to power of the co-efficient. It is also called ionic product.

$$PbCl_2 \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$$

$$K_{sp} = [Pb^{2+}]\,[Cl^{-}]^2$$

Solubility product is literally the product of the solubility of the ions in units of molarity. So the unit of solubility is $moldm^{-3}$ or mol/dm^3.

$Hg(IO_3)_2 = 3.0\times10^{-13}\ moldm^{-3}$

$Pb\,(OH)_2 = Pb^{2+} + 2OH^{-}$

$Hg(IO_3)_2 = 3.0\times10^{-13} moldm^{-3}$

$Pb(OH)_2 = Pb^{2+} + 2OH^-$

$Hg(IO_3)_2 = Hg^{2+} + 2IO_3^-$

From the above $Hg(IO_3)$ is more soluble than $Pb(OH)_2$.

5.7 Common Ion Effect on Solubility and Solubility Product

Common ion effect refers to the fact that solubility equlibria shift in accordance with Le-chatelier principle. (considering $AgCl_2 = Ag^+_{(aq)} + Cl_{(aq)}$.

Suppose NaCl is added to AgCl, the concentration of Cl^- is increased, the addition of the common ions (Cl^-) will reduce the solubility and this will lead to precipitation.

$$CaSO_4 \rightleftharpoons Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

The addition of sulfate ions (e.g. Na_2SO_4) to a saturated solution of calcium sulfate causes (SO_4 to precipitate until the concentration of the ions in solution are such that they again satisfy the solubility product.

Note that when this common ion have effect on the solubility of substance it will also affect the solubility product.

Salt effect:- The salt effect refers to the fact that in presence of another salt, even though there is no common ion, has an effect on the ionic strength of the solution and hence on the activity coefficients of the ions, so that solubility changes even though solubility product (Ksp) remain constant (assuming that the activity of the solid remain unity).

Solubility Constant

Solubility constant has been experimentally determined for a large number of compounds and tables are readily available. For ionic compounds the constant are called solubility products.

(a) Barium carbonate: 2.60×10^{-9} moldm^{-3} for $BaSO_4$

(b) Copper (i) chloride 1.72×10^{-7} for CuCl

(c) Lead (ii) sulfate 1.81×10^{-8} for $PbSO_4$.

Question

(1) How can one say that a chemical reaction is in equilibrium?

(2) For a system to be in equilibrium what conditions must be present and define these conditions?

(3) What is the difference between a phase and a closed system?

(4) State the law of mass action and its uses?

(5) State Le-chatelier principle and its effects?

(6) How does catalyst affect the equilibrium of reaction?

(7) How can we compare the contrast between solubility and solubility product?

(8) What is common ion effect?

(9) Calculate the solubility of $Ce(IO_3)4$ if the Ksp at 25^0C is 5.0×10^{-17} in mol dm^{-3}?

$Ce(IO_3)_4(g) \longrightarrow Ce_{(aq)} + 4(O^-_3)_{(aq)}$

Answer: 1.81 NO^{-14}mol dm^{-3}.

$5.0\times10^{-17} = [x][4x]^4$

$5.0\times10^{-17} = 256x^5$

$x^5 = \frac{5\times10^{-17}}{256}$

$x^5 = 1.953125\times10^{-19}$

$x = 1.81\times10^{-4}$ mol dm^{-3}

Extract Information

Relationship between Kp and Kc

Kp and Kc for a given reaction are not the same numerically. We can obtain a relationship between these two constants at any point of temperature provided the gases in the reaction obey the ideal gas laws.

For idea gas, the pressure is given by

$$PV = nRT$$

$$P = \frac{nRT}{V} = \frac{n}{V} RT$$

We know that concentration of 1mol is

$$C = \frac{n}{V} = \frac{\text{no of moles}}{\text{volumes}}$$

Replacing in equation (I) we have P = CRT

Substituting this value of P in equation (7)

$$Kp = \frac{[C]^c [RT]^c [D]^d [RT]^d}{[A]^a \{RT\}^a [B]^b [RT]^b}$$

$$Kp = \frac{[C]^c [D]^d \ldots\ldots [RT]^{c+d}}{[A]^a \{B\}^b \ldots\ldots [RT]^{a+b}}$$

$$Kp = \frac{[C]^c [D]^d}{[A]^a [B]^b} RT^{(c+d+\ldots) - (a+b+\ldots}$$ Equation

$$Kc = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Therefore, equation (8) becomes

$$Kp = Kc\,(RT)^{\Delta n}$$

$$Kp = Kc\,(RT)^{\Delta n}$$

$$Kc = \frac{Kp}{(RT)^{\Delta n}}$$

Where Δn = [c+d+...) – [a+b+...] is equal to difference in the total number of moles of gaseous products and $\overset{\text{reactants}}{\text{resultants}}$ during the reaction Δn can be zero, positive or negative. If Δn is zero, it means that the number of moles of product is equal to the number of mole of the reactant, therefore, it follows the equation $K_p = K_c$.

e.g. $H_{2(g)} + CO_{2(g)} \qquad H_2O_{(g)} + CO_{(g)}$

if Δn is positive it means that number of moles of product is greater than number of moles of reactant

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$..................$K_p > K_c$

When Δn is negative, it means that the number of moles of product < number of mole of the reactant.

$K_p < K_c$

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$..................$K_p < K_c$

Mathematically solubility of substance (salt) is given as

$$= \frac{\text{Mass of salt}}{\text{Molar mass of salt}} \times \frac{1000}{\text{volume}}$$

CHAPTER SIX

By Omuku, P.E. and Nwigwe, A.C.

CHEMICAL KINETICS

6.0 Definition

Chemical Kinetics is the study of the speed with which a chemical reaction occurs and the factors that affect this speed. This information is especially useful for determining how reactions occur. For e.g. at home, you might be interested in the rate at which you can bake a cake or boil an egg, in Industries, engineers and other workers might wait to determine the rate at which ammonia can be obtained from nitrogen and hydrogen.

6.1 Features of a Chemical Reaction

Three distinct features are present for a reaction to occur they are:

1. The direction:- getting the desired products.
2. Its velocity or rate: How fast the desired products are obtained.
3. Its extent or yield: - How much of the desired products are obtained at the end of the reaction.

Conditions

The direction of a chemical reaction is determined by the additions under which it is carried out. E.g. Ethyla1chol can be converted into different products under different conditions as follows:

$$C_2H_5OH \xrightarrow{300\ -\ 40^0C} C_2H_4 + H_2O$$

$$C_2H_5OH \xrightarrow[M]{350^0C} -CH_3\,CHO + H_2$$

6.2 The Speed of a Reaction

The speed of a reaction is the rate at which the concentration of the reactants and products change with time.eg. Consider the hypothetical example the letters A,B and C represent chemical species suppose the following imaginary reading occurs.

$A + 2B \longrightarrow 3C.$

The stoichiometric coefficient for specie B is twice that of specie A, then the concentration of B will decrease twice as fast as that of specie A. Similarly, the concentration of specie C increases 3 times as fast as the concentration of A decreases. Conceptually, there should be a single unambiguous rate for a reaction. How might such a rate be defined given the highly varied rates of change for the various specie in the reaction.

6.3 Reaction Rate

The rate of change ~ɒ concentration of the reactants and products can be used to characterize the rate of a chemical reaction. The rate of a reaction R is defined as the slope of the concentration time plot for species divided by the stoichiometric co-efficient of that species. Additionally, if the species in a reactant, the negative value of the slope as the slope is negative and a positive rate is desired.

Consider the equation by experiment

$aA + bB \longrightarrow cC$

The rate of reaction $R = -1 \frac{d(A)}{a.dt} \quad \frac{d(B)}{b.dt} \quad \frac{d(C)}{c.dt}$

The rate may be define by $- \frac{d(A)}{dt}$ (decrease in A) or $\frac{-d(B)}{dt}$

(decrease in B) or $+d \frac{d(E)}{dt}$ (increase in C)

Thus, the rate of reaction can be expressed unambiguously in terms of any specie dividing the concentration change of the selected species by the stochiometric coefficient of that species in the balance chemical reaction.

e.g. $2H_2 + O_2 \longrightarrow 2H_2O$.

the rate can be expressed as $\frac{-d(H_2)}{dt}$ or $\frac{-d(O_2)}{dt}$ or $\frac{-d(H_2O)}{dt}$

but since $\frac{-d(H_2)}{dt} = \frac{-d(O_2)}{2dt}$ as required by the chemistry of the

reaction, the rate would be different: that H_2 is used up twice as much as O_2.

Note however, that $\frac{-2d(H_2)}{dt} = \frac{-d(O_2)}{2dt}$

Therefore, for the equation $A + 2B \longrightarrow 3C$

$R = \frac{d(A)}{dt} = -1 \frac{d(B)}{2dt} = 1 \frac{d(C)}{3dt}$

Notice that this definition produces the same rate of reaction irrespective of which species in the reaction is used to perform the calculation.

6.4 Rate Laws (Differential Rate Laws)

In many reaction, the rate of a reaction changes as the reaction progresses. Initially, the rate of a reaction is relatively large while at very long times, the rate of reaction decreases to zero (at which point the reaction is complete) incidentally characterize the kinetic behavior of a reaction. It is desirable to determine how the rate of a reaction varies as the reaction progresses.

A rate law is a mathematical equation that describes the progress of the reaction. In general, rate laws must be defined experimentally. Unless a reaction is an elementary reaction, it is not possible to predict the rate law from the overall reaction rate/chemical equation. There are two forms of a rate law for chemical kinetics,

(1) The differential rate law and (2) The integrated rate law

6.4.1 Differential Rate Law

The differential rate law relates the rate of reaction to the concentration of the various species in the system. They can take on many different forms especially for complicated chemical reactions. However, most chemical reactions obey one of the three differential rate laws. Each rate law contains a constant K_o called the **rate constant.** The units for the rate constant depend upon the rate law because rate always has unit of mol L^{-1} sec and they cone always has units of mole L^{-1}.

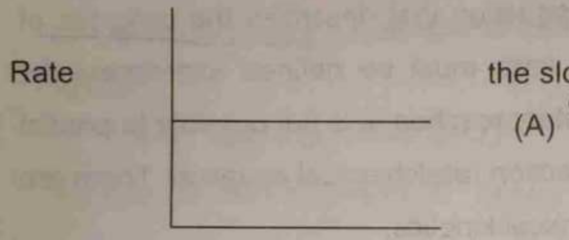
Zero – order reaction

For a zero-order reaction, the rate of reaction is a constant. When the limiting reactant is completely consumed the reaction abrupt stops. The rate is not affected by changes in the concentration of one or more reactant because it is determined by some limiting factor other than concentration.

$$\text{Rate} = \frac{-d(A)}{dt} = K_o(A)^0 = K_0 \text{ since } (A)^0 = 1$$

Differential rate law; R = k.

The rate constant, k has units of mole $L^{-1}sec^{-1}$.



the slope of the graph is zero

e.g decomposition of HI on a golden surface it

$$2HI \xrightarrow[\text{High pressure}]{\text{golden surface}} I_2(g) + H_{2(g)}$$

At high pressure, the golden surface is saturated such that any further increase in pressure will not increase the reaction rate.

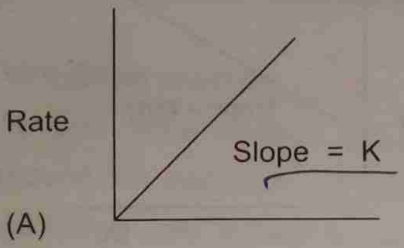
First- Order Reaction

For a 1st order reaction, the rate of a reaction is directly proportional to the concentration of one of the reactants.

$$\text{Rate } \frac{-d(A)}{dt} = K_1(A)$$

Differential rate law, $R = k(A)$

The rate constant K has units of sec^{-1}.



e.g. decomposition of H_2, O_2, radioactive decays etc.

Second Order Reactions

For a second order reaction, the rate of reaction is directly proportional to the square of the concentration of one of the reactants. They are of two types.

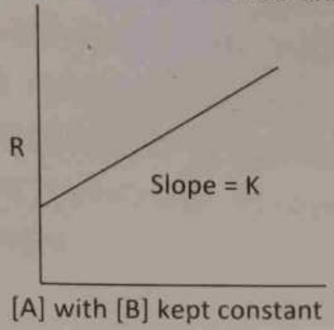
(i) $R = [A]^2$ e.g. $A + B \longrightarrow$ Product $\longrightarrow$ for homogeneous

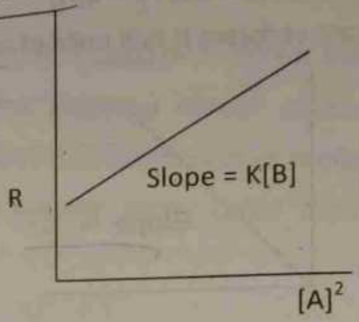
Reactants

$$\text{Rate} = \frac{-d}{dt} = K[A]^2.$$

(ii) $R = K[A]\ [B]$ for heterogeneous reactant

The rate constant K has units of $Lmol^{-1} sec^{-1}$.





Observation from Graph

- In examining the plots, bear in mind that as the reaction progresses the reactant decreases. This corresponds to moving from left - right on the plot of reaction rate against concentration.

1. For a 1st order reaction, the rate of reaction is constant as the reaction progresses.
2. For a 1st order reaction, the rate of a reaction is directly proportional to the concentration. As the reactant is consumed during the reaction, the concentration drops and so does the rate of reaction.
3. For a second order reaction, the rate of a reaction measures with - the square of the concentration producing an upward curving line in the rate concentration plot. For this type of reaction, they rate of reaction decreases rapidly (faster than linearly) as the concentration of the reactant decreases.

Consider the following reaction between formic acid (HCOOH) and bromine $HCOOH_{(aq)} + Br_{2(aq)} \longrightarrow 2H^{+}_{(aq)} + 2Br^{-}_{(aq)} + CO_{2(aq)}$.

Spectrophotometry

In this chemical system, the only specie that absorbs visible light is bromine thus spectrophotometry can be employed to determine how the concentration of .bromine varies with time during the reaction.

Third-Order reaction

The third order reaction are quite rare in the gas phase reaction because the probability of three of the reacting molecules to come together at one instant is low -in solution however the 3rd order reactions are not uncommon because of considerable reduction in intermolecular distance, moreso if the solvent is itself one of the reactants.

6.4.2. Integrated Rate laws

These relationships can be found by Integrating the rate law. If we assume that the concentration of reactant A is $[A]_0$, at t = 0 and [A] at time 1. A reaction of type. A $\longrightarrow$ products, we can separate the variables in the rate equation and integrate. The details of the integration differ depending on the order of species in the reaction. The table below gives the rate expression for 0th ,1st and 2nd order reaction.

Order Rate Expression Integrated Rate Law

0th rate = $k[A] = [A]_0 - Kt$

1st rate = $K[A]/\ln([a]_0) - \ln([A]) = kt$

2nd rate = $K[A]_2$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

6.5 Molecularity of an Elementary Reaction

This is the number of molecules taking part on each intermediate elementary reaction in the overall reaction sequence of a complex reaction. Eg for the decomposition of ozone to oxygen; $20_3 = 30_2$. Studies have established is mechanism to involve the following elementary reactions.

$0_3 \longrightarrow 0_2 + 0$

$0 + 0_3 \longrightarrow 20_2$.

Rate law	molecularity	order
Rate = $K(0_3)$	1	1
Rate = $K(0)(0_3)$	2	2

Thus for an elementary reaction, the order is equal to the molecularity. The molecularity of a reaction must be a whole number and in fact is found to be one, two or rarely three, but the order of a reaction can be an integer or fraction. Half-life: [T½]:- This is the time required for half of the initial amount to react Half-life is the time taken for a substance to reduce to one half of its original mass.

T½ of a zero order reaction

At T ½ $[A] = \frac{[A_0]}{2}$

$$[A]_0 - \frac{[A_0]}{2} = K_0\, T½$$

$$\boxed{T½ = \frac{[A_0]}{2K_0}}$$

Where T½ is the half-life for a first order reaction

$$\therefore \quad T½ = \frac{[A]_0}{2K}$$

T½ of 2nd order reaction

Initial concentration A_0.

At half-life, half of an initial concentration would have gone

At T½ $[A] = \frac{[A_0]}{2}$

$$\frac{1}{\frac{[A_0]}{2}} = \frac{2}{[A_0]} = kT½ + \frac{1}{A_0}$$

$$2 \quad \frac{2}{A_0} - \frac{1\,K}{A_0} = kT½$$

$$T½ = \frac{1}{[A]_0}$$

Order of a Reaction

The order of a reaction is the sum of the exponents of the concentration terms in the experimental rate law.

$$2O_3 \rightleftarrows 3O_2$$

Rate = $K[O_3]^2[O_2]^{-1}$

= $K(O_3)^2(O_2)^{-1}$

Order with respect to O_3 is two while with respect to O_2 is – 1.

Overall order is therefore one. It must be re-emphasized that unless the reaction is an elementary reaction, an order of reaction with respect to a given substance has no relation whatsoever to the stochometric coefficient of the substance in the chemical equation for example, in the generalized reaction below:

$$aA + bB \longrightarrow cC.$$

The coefficient of A is a. we cannot infer from this that the order of the reaction is a unless proven.

6.6 Factors affecting Reaction Rate

1. **Nature of the reactant:** Depending upon what substances are reacting, the time varies. Acid reaction; the formation of salts, and ion exchange reactions are fast reactions. While covalent bond formation takes place between molecules and when large molecules are formed, the reactions tend to be very slow. Nature and strength of bonds in the reactant greatly influence the rate of its transformation into products. The reaction which involve lesser bond arrangement proceed faster than the reactions which involves large bond rearrangement.

2. **Physical State:** The physical state (solid, liquid or gas) of a reactant is also an important factor of the rate of change of reactant or products. When reactants are in the same phase, as in aqueous solution, thermal motion brings them into contact. However, when they are in different phases, the reaction is limited to the inter face between the reactants. Reaction can only occur at their area of contact, in the case of liquid and a gas, at the surface of the liquid. Vigorous shaking and stirring may be needed to bring the reaction into completion. This means that the more finely divided a solid or liquid reactant, the greater the surface area per unit volume and the more contact constant it makes with the other reactants, thus the faster the reaction. E.g. when one starts a fire, and use, wood chips and small branches, one doesn't start with large logs right away. In organic chemistry, water reactions are the exception to the rule that homogeneous reactions take place faster than heterogeneous reactions.

3. **Concentration:** This plays a very important role in reactions, according to the collision theory of chemical reactions, because molecules must collide in order to react together. As the concentration of the reactant increase, the frequency of the molecule colliding increases, striking each other more presently by being in closer contact at any given point in time. E.g. consider two reactant being in a closed container, all the molecules contained within are colliding constantly by increasing the amount of one or more of the reactant. It causes the collision to happen more often, increasing the reaction rate i.e. the higher the concentration, the more the molecules are closer to

each other, the shorter the time they get in contact and the faster the rate of collision which leads to faster reactions.

4. **Temperature:** This usually has a major effect on the rate of a chemical reaction. Molecules at higher temperature have more thermal energy, although collision frequency is greater at higher temperature, and this alone contributes only a very small proportion to the increase in rate of reaction. Much more important is the fact that the proportion of the reactant molecules with sufficient energy to react (energy greater than the activation actuation energy: E>Ea) is significantly higher and can be explained in detail by the Maxwell-Bottzoar distribution of molecular energies. The rule of them that the rate of chemical reactions doubles for every 10^0C temperature is a common misconception. This may have been generalized from the special case of biological systems where the Q_{10} (temperature coefficient) is often between 1.5 and 2.5.

5. **Catalysts:** The presence of a catalyst open a different reaction pathway with a lower activation energy. Catalysts are substances that can accelerate the rate of a chemical reaction but remain chemically unchanged afterwards. The catalyst increases rate of reactions by providing a different- reaction mechanism to occur with a lower activation energy.

In autocatalysis, a reaction product is itself a catalyst for the reaction leading to a positive feedback. Proteins that act as catalyst in biochemical reactions are called enzymes. Michelin-menten Kinetics described the rate of enzyme mediated reaction. A catalyst does not affect the position of the equliibria as the catalyst speeds up the backward and forward reactions equally. In certain organic molecules specific substituent can have an influence on reaction rate in neighbouring group participation Agitation or mixing a solution will also accelerate the rate of a chemical reaction, as this gives the particle greater kinetic energy, increasing the number of collision between reactants and therefore the possibility of successful collisions.

6. **Pressure:** Increasing the pressure in gaseous reaction will increase the number of collisions between reactants thereby increasing the rate of reactions. This is because the activity of a gas is directly proportional to the tot eh partial pressure of the gas. This is similar to the effect of increasing the concentration of a solution.

7. **Equilibrium:** While chemical kinetics is concerned with the rate of a chemical reaction, thermodynamics determines the extent to which reactions occur. In a reversible reaction, chemical equilibrium is reached when the rates of the forward and reverse reactions are equal with the concentration of the reactants and products are kept unaltered. This is demonstrated for e.g. by the Haber-Bosch process for combing nitrogen and hydrogen to produce ammonia.

8. **Free energy:** In general terms, the free energy change (ΔG) of a reaction determines if a chemical change will take place but kinetics describes how fast the reaction is. A reaction can be very exothermic and have a positive entropy change but will not happen in practice, if the reaction is too slow. If a reactant can produce two different products, the thermodynamically most stable one will generally form

except in special circumstances when the reaction is said to be under **kinetic reach control.**

6.7 Rate Determining Step (RDS)

This is a chemistry term for the slowest step in a chemical reaction. The rate determining step is often compared to the neck of a funnel. The rate at which water flows through the funnel is determined by the width of the neck, not the speed at which water is poured into it. In similar manner, the rate of a reaction depends on the rate of the slowest step for example,

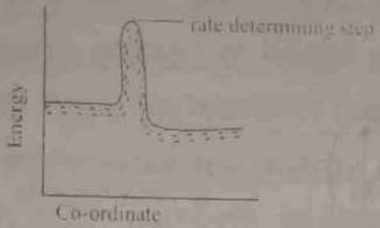
$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$ can be thought of as occurring on two elementary steps.

$NO_2 + NO_2 \longrightarrow NO + NO_3$ (slow step)

$NO_3 + NO \longrightarrow NO_2 + NO$ (fast step)

As the 2nd step consumes the N03 produced in the slow 1st steps, it is limited by the rate of the 1st step. For this reason, the rate determining step is reflected in the rate equation of a reaction. The rate determining step is one of the sequential chemical reaction leading to, a product. The rate determining step can also be the transport of reactant molecules to interact and form the product. This is referred to as diffusion control and in general, occurs where the formation of a product from the activated complex is very rapid and thus the supply of reactants which brings interaction of the reactant molecules is rate determining step.

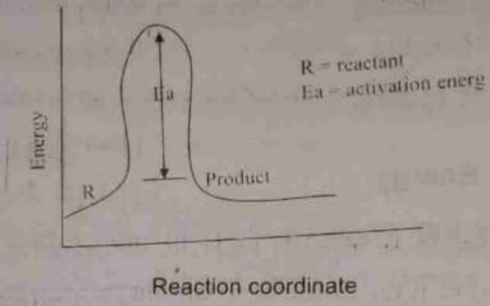
The concept of rate determining step is very important to the optimization understanding of many chemical process such as catalysis, combustion etc. in a reaction co-ordinate, the transition state with the highest energy is the rate determining step of a given reaction.



6.8 Activation Energy

This is the energy that must be overcome for a chemical reaction to occur. Its units is kJ/mol. E.g. the concept of enthalpy in physics tells us that objects in the universe tend towards their lowest energy state. This can be as simple as a ball returning to earth after being thrown in the air or a substance converting from gas to liquid. Now, obviously, there are some occasion where this principle seems to be broken, carbon for e.g. can exist in various stable forms, such as graphite, diamond and C_6O. All three forms cannot have the lowest energy state, so how does this work?.

Essentially, the various forms have the lowest local energy state and there are barriers that prevent the substance from freely moving to the other possible states. Take for instance, carbon is strictly more stable as a graphite than as diamond. However, the reason that your jewelry doesn't decay into pencil is that the crystal structures are quite different and energy is required to get the atoms in structure to rear range themselves. The reaction will still produce a small amount of energy to be put in to get the reaction going in the 1st place to activate it. This spike of energy that separates different states is known as the activation energy, it will divide two states even if one is more preferable than the other.



Activation energy is also the energy in excess over the ground state energy which must be added to an atomic or molecular system to allow a particular process to take place. It is also the minimum amount of energy required to activate atoms or molecules to a condition in which it is equally likey that they will undergo chemical reaction or transport as it is that they will return to their original state. It is amount of energy required to boost the initial material uphill to the transition state, the reaction then proceeds "downhill to form the product materials.

Catalysts (including enzymes) lower the transition state. Activation energies are determined by experiments that measure them as the constant of proportionality in the equation describing the dependence of reaction rate in temperature proposed by Svante Arrhenius. It is a well known fact that chemical reaction between two substances occur only when an atom, ion molecules of one collides with an tom, ion or molecules of the other. Only a fraction of the total collide, result in a reaction, because, using a small percentage of the substance interaction have the minimum amount of kinetic energy a molecule must possess for it to react. When the reactants collide, they may form an intermediate product whose chemical energy is higher than the combined chemical energy of the reactants. In other for this transition state in the reaction to be achieved, some energy must enter onto the reaction other than the chemical energy of the reactants. The energy is the **activation energy**. If activation energy is low, a greater proportion of the collision between reactants will result in reaction. If the temperature of the system is increased, the average heat energy is increased, heat energy is increased, a greater proportion of the collision between reactant, result in reaction and the reaction proceeds more rapidly. Catalyst increases the reaction rate by providing a reaction mechanism with a lower activation energy, so that a greater proportion of collision result in reaction. The activation energy and the rate of reaction are related by the equation K = $e^{-Ea/RT}$ where K is the rate constant.

A = temperature independent factor (often called the frequency factor)

E = activation energy

R = universal gas constant

$K = e^{-Ea/RT}$

T = temperature

e = exponential

Because the relationship of reaction rate to activation energy is exponential, a small change in temperature or activation energy causes a large change in the rate of reaction.

Negative Activation Energy

In some case, rate of reaction decreases with increasing temperature when following are approximately experimental relationship, so the rate constant can still comply to an Arrhenius expression, this result in a negative value of εa-. Reactions exhibiting these negative activation energies are typically barrierless reaction, in which the reaction proceeding relies on the capture of the molecules in a potential well. Increasing the temperature lead to a reduced probability of the colliding molecules capturing one another (with more glancing collision but not leading to reaction as the higher momentum carries the colliding particles out of the potential well) which is expressed as a reaction cross section that decreases with increasing temperature. Such a situation no longer leads itself to direct interpretations as the height of a potential barrier.

6.9 Temperature Independence and the Relation to the Arrhenius Equation:

The Arrhenius equation given the quantities basis of the relationship between the activation energy and the rate at which a reaction proceeds. From the Arrhenius equation, the Ea can be expressed as

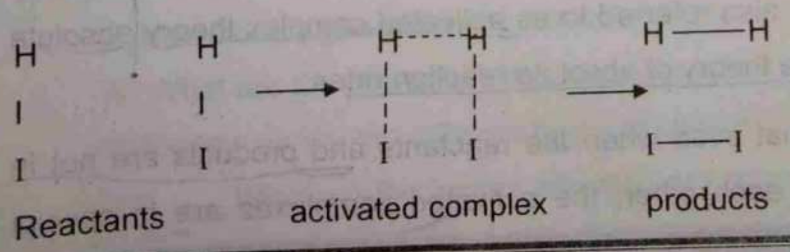
$E_a = -RT/n(K/A)$.

Where A = frequency factor for the reaction
T = temperature in Kelvin
R = universal gas constant.

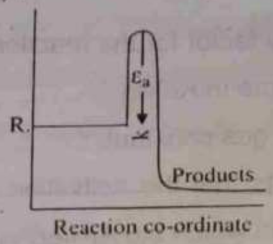
While this equation suggests that the activation energy is dependent on temperature, in regimes in which the Arrhenius equation is involved, this is cancelled by the temperature dependence of K. This εa can be evaluated from the constant at any temperature (within the validity of the Arrhenius equation).

6.10 Action Complex/Activated Complex:

Activation complex is an unstable species and is held together by loose bonds. This is the configuration of the atoms which corresponds energetically to the top of the energy barrier separating the reactants from the products. It is also the state at the top of the potential energy barrier or simply an intermediate compound such as intermediates which occur in many chemical reactions. It is a molecule in which a bond in the process separating two minima of potential of being broken or decomposition of HI.



It can be thought as the height of the potential barrier (sometimes called energy barrier).

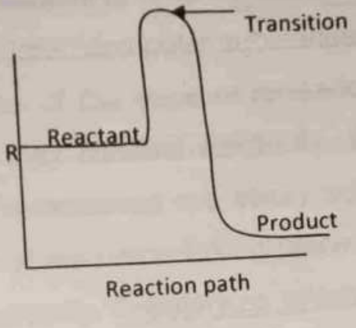


Transition State Theory (TST

This explains the reaction rates of elementary chemical reactions. Elementary chemical reactions are reactions where a single collision leads to formation of products. The theory assumes a special types of chemical equilibrium (quasi-equilibrium) between reactants and activated transition state complexes.

TST is used primarily to understand qualitatively how chemical reactions take place. It has been less successful in its original goals of calculating absolute reaction rate constants because the calculation of absolute reaction rates requires precise knowledge of potential energy surface, but it has been successful in calculating the standard enthalpy of activation (ΔH^0) and the standard entropy of activation (ΔS^0) for a particular reaction if the rate constant has been experimentally determined. It is also referred to as activated complex theory absolute rate theory or the theory of absolute reaction rates.

TST assumes that even when the reactants and products are not in equilibrium with each other, the activated complexes are in special equilibrium with the reactants. In TST, it is important to realize that when it is said that the activated complex are in equilibrium with the reactions it is referred only to those activated complexes that were reactant molecules in the immediate part. The equilibrium constant for the quais equilibrium can be written as $R = AB^T$.



Question

(1) What are the features of "chemical reaction?

(2) Define a rate law.

(3) Given the equation $NaOH + HCl \longrightarrow NaCl + H_2O$

Write the equation for the reaction rate

(4) Define order, moleclarity and rate determining step of a reaction

(5) Explain briefly the 1st order of reaction

(6) Derived the half-life equation of a zero order reaction

(7) How does a gas affect the rate of chemical reaction?

(8) What are the characteristics of catalysts?

(9) Explain vividly the different types of catalyst;

(10) What are the factors affecting activation energy?

(11) Define barrierless reactions?

(12) What is an activated complex?

(13) Functions of transition theory

(14) Define absolute theory.

Chapter Seven

By Nwigwe, A.C.

7.0 Ionic Equilibrium

Ionic equilibrium is substances that undergo ionization easily. It is also observed in polar substances in which ionization can be induced. With the availability of ions, ionic and polar substances are easily soluble in polar solvents because of the ease of ionization taking place in the solvent medium and they conduct electricity. With the availability of ions, ionic and polar substances are easily soluble in polar solvents because of the ease of ionization taking place in the solvent medium and they conduct electricity. Substances which conduct electricity are called electrolytes while those that do not conduct electricity are non-electrolytes.

7.1 Electrolytes

Electrolytes are molten form or aqueous solution of a chemical substance which conducts electricity and is decomposed in the process. There are two types of electrolytes namely:

(1) Strong electrolyte and weak electrolyte. The type of electrolyte depends only on the strength of the substance used. Strong electrolytes dissociate completely into ions in liquid form and the readily conduct electricity e.g. NaCl, NaOH, kCl etc.

(2) Weak electrolytes does not dissociate completely and do not

conduct electricity readily because its particles undergo partial dissociation/ionization in aqueous solutions or molten forms i.e. the ions are not numerous in the solution, e.g. H_2S, CH_3COOH, NH_4OH etc.

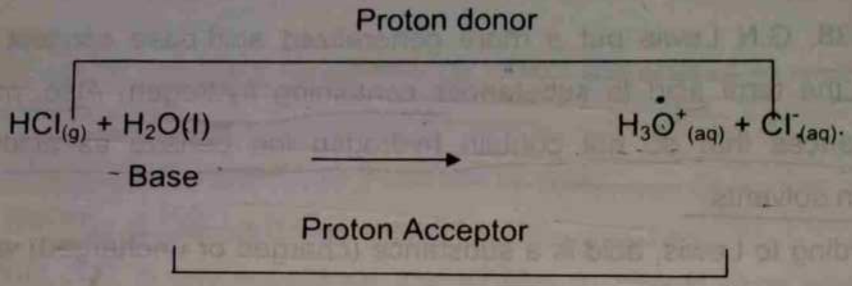
7.2 Acids and Base

Before, acids were regarded as a substance that tastes sour and able to change the colour of litmus paper. An alkali was defined as a substance with a soapy feeling and cleaning power. When acids react with alkalis, it forms salts. The name "Base" was later used instead of alkali. Now. A base is define as compound which can neutralize any acids. Substances that act as both acid and base are called amphiprotic. Not all bases are soluble in water, a solutble base is called an alkali.

7.3 Bronsted-Lowry Theories of Acids and Bases

In 1923, Johannes Bronsted and Thomas Lowry independently proposed a general theory known as the Bronsted-Lowry proton transfer theory. The Arrhenium theory is not broad enough to include acid-base hehaviour in non-aqueous solvents.

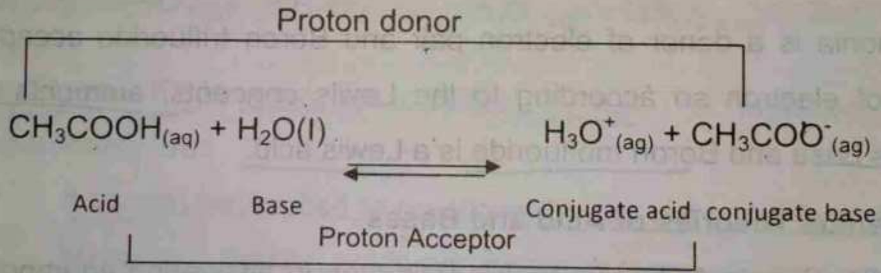
According to this concepts, any substance which is capable of donating hydrogen ion, H+ to another substance is regarded as an acid while a base is regarded as a substance that accepts the hydrogen ion H+. e.g. HCl dissociates in water to form H_3O^+ and Cl^- instead of Cl^- and H^+ ions.



$$HCl_{(g)} + H_2O(l) \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}.$$

$HCl_{(aq)}$ acts as an acid as it donates H^+ ion to water.while water acts as a s base as it accepts H+ ions. Chemists name H^+ a proton or an hydrogen ion. Bronsted-Lowry acids are known as hydrogen ion donors or acceptors.

When Bronsted-Lowy acid gives up a proton, it is converted to a conjugate base and when a Bronsted-Lowry base accepts a proton, it is converted to a conjugate acid.



$$CH_3COOH_{(aq)} + H_2O(l) \rightleftharpoons H_3O^+_{(ag)} + CH_3COO^-_{(ag)}$$

The strength of an acid is its ability to donate H^+ ions, and the strength of base is its ability to accept H^+ ions. Generally, the stronger the acid, the weaker is its conjugated base. The stronger the base, the weaker its conjugate acid.

7.4 Lewis Theories of Acids and Bases

In 1938, G.N Lewis put a more generalized acid-base concept but limits the term acid to substances containing hydrogen. Also, many substances that do not contain hydrogen ion behave as acids in certain solvents.

According to Lewis, acid is a substance (charged or uncharged) which can accept a pair of electrons in a chemical reaction while a base is a substance (charged or uncharged) which can donate a pair of electron in the formation of a covalent bond.

A Bronsted-Lowry acid is not a Lewis acid though the proton it gives out is a Lewis acid e.g. HCl is a Bronsted-Lowry acid but not a Lewis acid.

$$\underset{\text{Base}}{H_3N:} + \underset{\text{acid}}{BF} \rightleftharpoons \underset{\text{product}}{H_3N: \quad BF_3}$$

Ammonia is a donor of electron pair and Boron trifluoride accepts a pair of electron so according to the Lewis concepts, ammonia is a Lewis base and Boron triofluoride is a Lewis acid.

Arrhenius Theories of Acid and Bases

In 1884, Svante Arrhenius took a bold step in answering an important question about determining whether a compound is an acid or a base where he define an acid as a substance that ionize when dissolved in water to give H^+ ion and its corresponding negative ions, e.g. HCl is an Arrhenius acid because it ionizes when it dissolves in water to give (H^+) and chloride ion (Cl^-).

$$HCl_{(g)} \xrightarrow{H_2O} H^+_{(ag)} + Cl^-_{(ag)}$$

He also defined a base as substance which dissociates in water to give hydroxide ion (OH-) and its positive ion when dissolved in water

$$NaOH_{(s)} \xrightarrow{H_2O} Na^{+}_{(ag)} + OH^{-}_{(ag)}$$

Arrhenius acid is any substance that ionizes to give H^+ ions when it dissolves in water e.g., HCl, HNO_3, H_2SO_4 and HCN. Arrhenius base is any substance that gives OH^- ions when it dissolves in water e.g ionic compounds that contain OH, NaOH, $Ca(OH)_2$, KOH.

Polyprotic acids are acids which form more than one proton per molecule. H_2SO_4, H_2S etc are diprotic acids while H_3PO_4 and $C_6H_8O_7$ are triprotic acids. They usually lose one H^+ at a time in a reaction.

1st loss e.g. $H_2SO_{4(ag)} + H_2O_{(l)} \quad H_3O^{+}_{(ag)} + HSO^{-}_{4(ag)}$ k1 is gre

2nd loss e.g. $H_2SO^{-}_{4(ag)} + H_2O_{(l)} \quad H_3O^{+}_{(ag)} + HSO_2{}^{-}_{4(ag)}$ k2.

Where K_1 and K_2 is ionization constant $K_1 > K_2$. The limitations of Arrhenius theory are:

(1) It cannot be applied to reactions that do not occur in water, because it defines acids and bases in terms of ions formed when they dissolve in water.

(2) The definition of an acid is valid as there can never be free protons in aqueous solutions.

$$H^{+}_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^{+}_{(aq)}.$$

This reaction is highly exothermic, therefore, no free hydrogen ion, H^+ will exist in the solution. Instead, hydroxonium ion, H_3O^+ characterizes the acid.

(3) The base definition is only valid for hydroxides but not for other compounds which exhibit basic properties.

E.g. ammonia and sodium carbonate can also neutralize hydrochloric acid but they do not contain OH^- ions.

$$\underset{\text{Base}}{NaCO_{3(s)}} + \underset{\text{acid}}{2HCl_{(ag)}} \longrightarrow 2NaCl_{(ag)} + H_20_{(l)} + CO_{2(g)}$$

$$HCl_{(ag)} + NH_{3(g)} \longrightarrow NH_4Cl_{(ag)}$$

7.5 pH and Dissociation Constant

In 1909, Sorensen introduced the concentration of hydrogen ions (H^+), which gave an idea about the acidic and basic characters of the aqueous solution. The term is called pH which means the power of hydrogen and it can be defined as the negative logarithm of the hydroxonium ion (H_3O^+) concentration in mol dm^3 or mol per litre. The definition enables the avoidance of negative values as much as possible.

Consider two aqueous solutions O.I.M of HCl and O.IM of NaOH, then hydrogen ion (H_3O^+) concentration are O.1moles/dm^3 and $1x10^{-13}$ moles/dm^3 respectively. The latter is obtained as follows (OH^-) = O.IM but $[OH^-][H_3O^+] = 1x10^{-14}$.

$$\therefore \quad [H^+] = \frac{1 \times 10^{-14}}{0.1} = 1 \times 10^{-13}M$$

The concentration of H^+ ion in these two solutions differ by a factor of 10-^{12}.

$$pH = -\log [H_30^+{}_{(aq)}]$$

$POH = -\log [OH^-_{(aq)}]$

Note that the higher the pH values, the lower the acidity of the hydrogen ion concentration and the more alkaline the solution.

At 25°C, $(H_3O^+_{(ag)} = [OH^-_{(ag)}] = 1.0 \times 10^{-7}$ mol dm^{-3}

$$\begin{aligned} pH &= -\log [H_3O+_{(ag)}] \\ &= -\log[H_3O^+_{(ag)}] \\ &= -\log [H_3O^+_{(ag)}] \\ &= -\log[1\times10^{-7}] \\ &= 7 \end{aligned}$$

For alkaline solution, $[H_3O^+_{(ag)}] < [OH_{(ag)}]$

$$\begin{aligned} [H_3O^+_{(ag)}] &< 1.0 \times10^{-7} \\ \log [H_3O^+_{(ag)}] &< -7 \\ -\log [H_3O^+_{(ag)}] &> 7 \\ pH &> 7 \end{aligned}$$

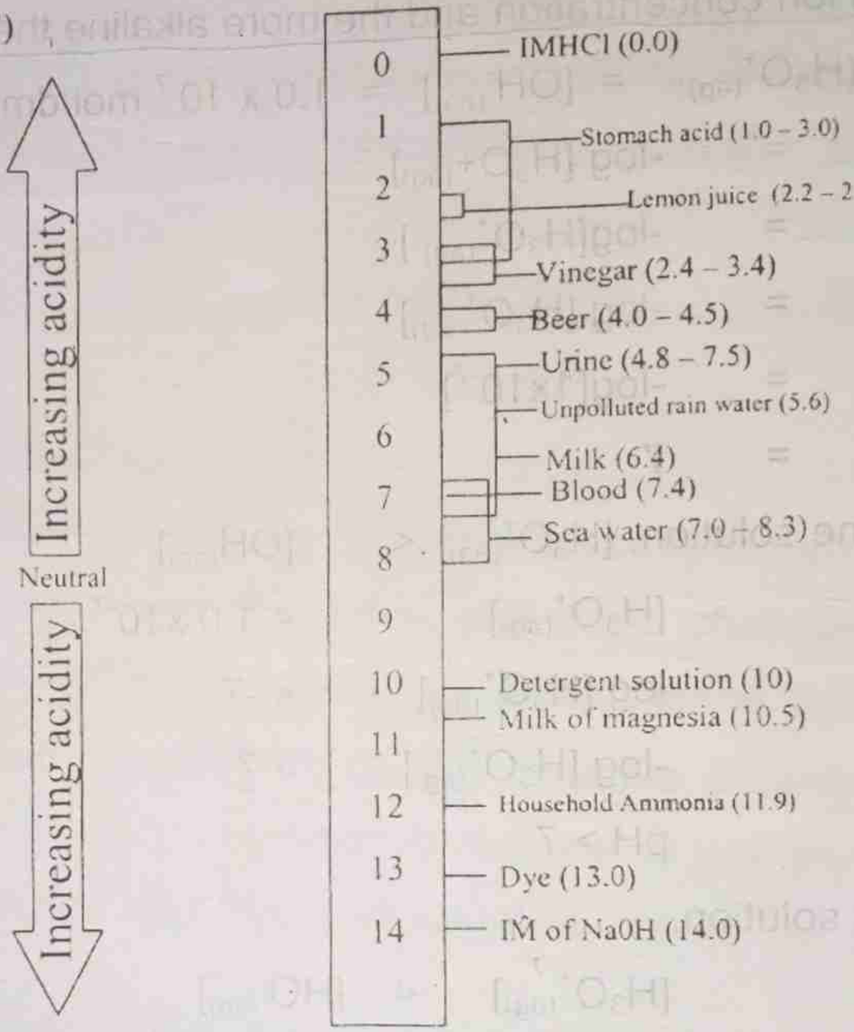
For acidic solution,

$$\begin{aligned} [H_3O^+_{(ag)}] &< [HO^-_{(ag)}] \\ [H_3O^+_{(ag)}] &> 1 \times 10^{-7} \\ \log [H_3O^+_{(ag)}] &< -7 \\ -\log [H_3O^+_{(ag)}] &< 7 \\ pH &< 7 \end{aligned}$$

The pH scale can reflect the acidity and alkalinity of solution. A solution of pH –7 is neutral, pH less than 7. is acidic. The lower the pH, the higher its H= concentration and the more acidic the solution. A solution of pH greater than 7 is alkaline.

The ionic product kw, increases with temperature. Pure water at 50°C is neutral, its pH is less than 7. The relationship between the pH and degree of acidity and alkalinity of solutions is shown below.

(moldm^{3}) [H+]	(moldm^{-3}) [0H^{-}]
1	10^{-4}
10^{-1}	10^{-13}
10^{-2}	10^{-12}
10^{-3}	10^{-11}
10^{-4}	10^{-10}
10^{-5}	10^{-9}
10^{-6}	10^{-8}
10^{-7}	10^{-7}
10^{-8}	10^{-6}
10^{-9}	10^{-5}
10^{-10}	10^{-4}
10^{-11}	10^{-3}
10^{-12}	10^{-2}
10^{-13}	10^{-1}
10^{-14}	1



It is not always easy to calculate the pH of a solution by finding how much hydrogen ions there are in a solution. pH meter and universal indicator (pH paper) can be used to measure the pH of a solution directly.

7.6 Dissociation Constant

Dissociation is a process by which the compound or ion split into two components that are also ions or compounds. A general example is the dissociation of the compound.

In lower level, we learnt that strong acid is an acid which dissociates completely in water while weak acid dissociates slightly in water. The strength of acids and bases can be determined by electrical conductivity measurements. pH provides some measure about the strength of an acid which varies with the concentration of solutions and therefore, it is used in limited term, but dissociation constant provides a better alternative and it is applicable to equilibrium law, and to state the strength of acids.

Strong and weak acids. When an acid is dissolved in water, it will dissociate to form a H^+ ion and an anion. This result is in dynamic equilibrium, e.g.

$$HA_{(ag)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(ag)} + A^-_{(ag)}$$

$$Kc = \frac{[H_3O^+]\,[A^-]}{[HA]\,[H_2O]}$$

As a result, the amount of water molecules remains relatively constant, the concentration of water $[H_2O_{(l)}]$ can be considered as a constant to give another constant known as dissociation constant, ka.

$$Ka = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

Dissociation constants can also be called equilibrium constants. It is only affected by changes in temperature. Strong acids ionize completely to almost moderate dilutions. They have high dissociation constant, ka value while week acids ionizes slightly or exist mainly as covalently bonded molecules. They have small dissociation constant ka.

Pka can be used to compare strengths of acids. Pka can be expressed as

$$Pka = -\log ka$$

Weak acids have large Pka than strong acids. Some common acids and their ka and Pka values

Acid	KaC mol $2m^{-3}$	Pka	Strength
HBr	1×10^{9}	-9.00	Very strong
H_2SO_4	1×10^{3}	-3.00	Very strong
HNO_3	28	-1.45	Strong
Benzoic acid	1.8×10^{-16}	15.74	Very weak

For strong and weak bases, when a base is dissolved in water, it will accept a proton from water to form hydrogen ion and hydroxide ion e.g.

$$B_{(aq)}{}^{+} H_20_{(L)} \rightleftharpoons HB^{-}_{(aq)} + 0H^{-}_{(aq)}$$

$$Kc_{\times} = \frac{[HB^{-}]\,[OH^{-}]}{[B]\,[H_20]_{\times}}$$

Where B is the base

Combining k_c and $H_20_{(l)}$ gives another constant known as dissociation constant of base (K_b).

$$Kb = \frac{[HB^{+}_{(aq)}]\,[OH^{-}_{(aq)}]}{[B_{(aq)}]}$$

Weak bases have small Kb values while strong base have high K_b

values. The smaller the Pka value, the stronger the base and vice versa.

Acid	Kb (mol dm-3)	Pkb	Strength
$C_6H_5NH_2$	4.27×10^{-10}	9.37	Weak
NH_3	1.7×10^{-5}	4.37	Weak

Ionization of Water

It is noted that highly pure water is a low but measureable conductor of electricity. And it only dissociates slightly into ions. E.g. a weak acid HA and a strong base such as sodium hydroxide. Because the acid is weak, an equilibrium is achieved.

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant exist as

$$Ka = \frac{[H_2O^+_{(aq)}]\,[OH^-_{(aq)}]}{[H_2O(L)]^2}$$

In an aqueous medium, HA can be treated as constant and combining with the constant, ka it gives a new constant known as Ionic product, $Kw = (H_3O^+)(OH^-)$.

Water dissociates into equal amount of H3O+ and OH- at the temperature of about 25°C, it will give 1.0×10^{-14} i.e.

$$\begin{array}{llll} 2H_{2(1)} & \rightleftharpoons H_30+_{(ag)} & + 0H^-_{(ag)} & \\ 10^{-7} & 10^{-7} & 1 \times 10^{-7} \,.\, 1 \times 10^{-7} & \\ & & 1 \times 10^{-14} \text{ moldm}^{-3} & \end{array}$$

When an acid is added to water, the (H_30^+) increases above 1×10^{-7}M. But the ionic product must remain equal to 1×10^{-14} consequently, hydroxide ion (OH^-) will decrease below $1.0x10^{-7}$moles. Consequently when a base is added to water, the concentration of OH^- increase above $1x10^{-7}$ moles and the concentration of H_30^+ decrease below $1x10^{-7}$ moles.

Note that the equation which is the ionic product constant K_w where $K_w = [(H_3O^+_{(aq)}] \cdot [OH^-_{(ag)}]$ is not limited to pure water only but involves aqueous solutions.

7.7 Hydrolysis of Water

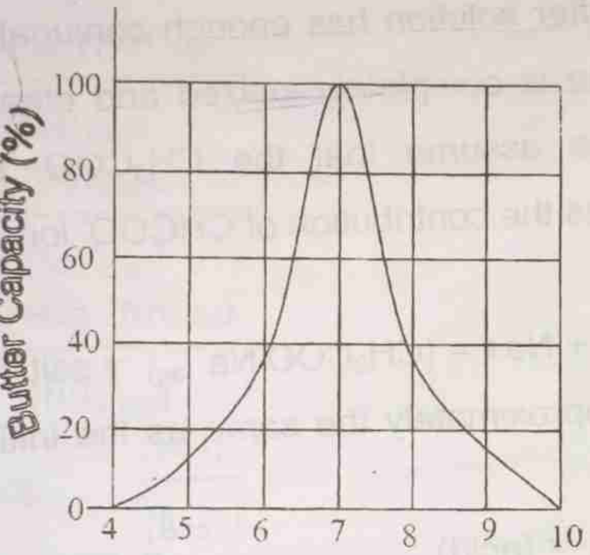
Hydrolysis is a chemical reaction during which one or more water molecules are split into hydrogen and hydroxide ions in the process of a chemical mechanism. It is the type of reaction that is used to break down certain polymers, especially those made by step growth polymerization, such polymer degradation is usually catalysed by either acid e.g. hydrogen textraozosulphate (VI) ($H2SO4$) or alkali e.g. sodium hydroxide (NaOH) attack, often increasing with their strength or pH. Hydrolysis is different from hydration. In hydration the hydrated molecules does not break into two new compounds while in hydrolysis, two new compounds are formed.

Method of hydrolysis

Hydrolysis can be achieved using 9v battery, 2 electrodes and small guage wire. A small amount of salt is added to increases the conductivity of the water and an acid/base indicator to visualize the reaction.

7.8 Buffer Solutions and Buffer Capacity

A butter solution is an aqueous solution consisting of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid. A buffer solution is a solution that tends to resist changes in pH when a small amount of acid or base is added to it. Many life forms thrive only in a relatively small pH range. An example of a butter solution is blood.



Buffer capacity is a quantitative measure of the resistance of a buffer solution to pH change on addition of hydroxide ion. It can be defined as follows:

$$\text{Buffer capacity} = \frac{\Delta n}{\Delta pH}$$

Where Δn is an infinitesimal amount of added base and Δ(pH) is the resulting infinitesimal change in pH.

Two types of buffers

- Acidic buffer is prepared by mixing a strong acid and a weak acid, the strong acid serves as the salt, e.g. ethanoic acid and sodium ethanoate. The solution is used to resist pH in an acidic medium.

$CH_3COO^-Na^+_{(ag)} \longrightarrow CH_3COO^-_{(ag)} + Na^+_{(ag)}$ - - (1)

Ethanoic acid is slightly ionized

$CH_3COOH_{(ag)} + H_20_{(l)} \longrightarrow CH_3COO^-_{(ag)} + H_3O^+_{(ag)}$ - - (2)

The presence of ethanoic acid in the system is to have enough amount of undissociated CH_3COOH molecules to cope with the addition of the base. Hence, a buffer solution has enough conjugate acid-base pair. As sodium ethanote is completely ionized and ethanoic acid is only slightly ionized, we assume that the CH_3COO^- ions come from $CH_3COO^-Na^+$ only as the contribution of $CHCOO^-$ ions from CH_3COOH is negligible.

$$[CH_3COO^-_{(ag)}] + Na+ = (CH_3COO^-Na^+_{(ag)} = salt$$

$[CH_3COOH_{(ag)}]$ is approximately the same as the initial concentration of the acid

$$[CH_3COOH_{(ag)}] = (acid)$$

Substituting (salt) for $[CH_3COOH^-_{(ag)}]$ and (acid) for $[CH_3COOH_{(ag)}]$, the general equation to calculate the pH of an acidic buffer would become.

$$pH = Pka + \log\frac{(salt)}{(acid)}$$

Reaction of weak base and its salt of a strong acid makes a basic buffer e.g. aqueous ammonia and ammonium chloride.

It resist pH changes in a basic medium

$NH_4Cl_{(ag)} \rightleftharpoons NH_4^+{}_{(ag)} + Cl^-{}_{(ag)}$ - - - (1)

$NH_{3(ag)} + H_20_{(l)} \rightleftharpoons NH_4^+{}_{(ag)} + OH^-{}_{(aq)}$ - - (2)

When an acid example $[H_3O^+{}_{(ag)}]$ is added to the system it reacts with OH^-. The equilibrium position of equation (2) will shift to the right.

$(NH_{3(aq)} + H_20_{(l)} \qquad NH_4^+{}_{(aq)} + OH^-{}_{(ag)}$

Supplementing loss of OH- ions, when a base is added, the position of equilibrium shifts to the left so that the effect of additional OH^- is removed.

$$NH_{4(ag)} + H_20_{(l)} \rightleftharpoons NH_4^+{}_{(ag)} + OH^-{}_{(ag)}$$

$$K_b = \frac{[NH_4^+{}_{(ag)}]\,[OH^-{}_{(ag)}]}{[NH_{3(ag)}]}$$

$$[OH^-{}_{(ag)}] = \frac{K_b + [NH_{3(ag)}]}{[NH^+{}_{4(ag)}]}$$

$$[POH = \frac{PK_b + \log\ [NH_{4(ag)}]}{[NH_3^+{}_{(ag)}]}$$

$$POH = PK_b + \log \frac{[Salt]}{[Base]}$$

Since pH = 14 - POH, then,

$$pH = 14 - PK_b + \log \frac{[Salt]}{[Base]}$$

Buffer capacity of a weak acid reaches its maximum value when pH = Pka. At pH = Pka ± 1, the buffer capacity falls to 33% of the maximum values. This is the approximate range within which buffering by a weak acid is effective.

Buffer solutions are necessary to keep the correct pH for enzymes in many organisms to work. Many enzymes work only under a specific condition; if a pH goes too far out of a margin, the enzymes slow or stop working and can be denatured, thus permanently disabling its catalystic activity.

Industrially, buffer solutions are used in fermentation processes and in setting the correct condition for dyes used in colouring fabrics. They are used in chemical analysis and calibration of pH meter.

Note that Buffer capacity is directly proportional to the analytical concentration of the acid.

Example 1: calculate the pH and percentage dissociation of (HI040) in a 0.5M aqueous solution. Given that ka of acid is 2.3×10^{-2} mofldm $^{-3}$

Solution

$$HI0_{4(aq)} + H_20 \rightleftharpoons H_20+(aq) + IO_3^-{}_{(aq)}$$

At equilibrium (0.5 –x)mol x mol (in $1dm^3$)

$$K_a = \frac{[H_20^+{}_{(ag)}\,[IO_4^-{}_{(ag)}]}{[HIO_{4(ag)}]}$$

$$2.3 \times 10^{-2} = \frac{X . X}{0.5 - x}$$

$$X_2 = 0.023 \times (0.5 - x)$$

$$X_2 + 0.023 \times 0.051 = 0$$

$$\therefore \quad X = 0.0964$$

$$\therefore \quad pH = -\log[H_30^+{}_{(aq)}]$$

$$= -\log (0.0964)$$

$= \quad 1.02$

∴ % dissociation $=$

$$K_a = \frac{0.096 \times 100}{0.5}$$

$= \quad 19.28\%$

2. 10.0cm^3 of IMHCl is added to 1dm^3 of a solution of 0.1M acetic acid and 0.1M sodium acetate (Ka = 1.82 x 10^{-5}). Calculate the pH of the system.

Solution:

In absence of HCL

Since [CH_3COOH] = [CH3COONa].

$PH = Pka = -\log 1.82 \times 10^{-5} = 4.74$

In the presence of HCl, the reaction below occurs

$$\underset{\text{(from HCl)}}{\underset{\downarrow}{H^+}} + CH_3COO^- = \underset{\text{(from salt)}}{\underset{\downarrow}{CH_3COOH}}$$

$$H^+ \text{ from HCl} = \frac{(1.0)\,M\,(10)}{1000} = 0.01 \text{ moldm}^{-3}$$

$(CH_3COO-) = 0.1 - 0.01 = 0.09$

and $(CH_3COOH) = 0.1 + 0.01 = 0.11$

$p^H = 4.74 - 4.64 = 0.09$

3. How many grams of Ammonium Chloride (NH_4Cl) is required to prepare a basic buffer solution of p^H 9.0 If $100Cm^3$ of 0.1M $NH_{3(aq)}$ is added to it? (K_b (NH_3) = 1.74×10^{5} $moldm^{-3}$; molar mass of NH_4Cl = 53.5g mol^{-1})

Solution

$$POH = Pk_b = \log \frac{[salt]}{[base]}$$

Let x M be the concentration of ammonium chloride in the buffer system.

$$14 - 9 = -\log(1.74 \times 10^{-5}) + \log \frac{X}{0.1}$$

$$5 = 4.76 + \log \frac{X}{0.1}$$

$X = 0.174$

Number of moles of NH_4Cl used $= 0.174 \times \frac{100}{1000}$

$= 0.0174$ moles

Mass of NH_4Cl used $= 0.0174 \times 53.5$

$=$ **0.93g**

4. Calculate the degree of ionization, the P^H and the pOH in a 0.10M solution of HCN, with ka equal to 7.2×10^{-10}

Solution

Substituting in the oswaltd's dilution law gives

$$\frac{0.10\,\alpha^2}{1 - \alpha} = 7.2 \times 10^{-10}$$

This is a quadratic equation which can be solved algebraically. However, if α is assumed small compared to unity, then:

$Ka = \alpha^2 C$

$\therefore \alpha = (Ka/C)^{½} = \left(\frac{7.2 \times 10^{-10}}{0.1}\right)^{1/2} = 8.5 \times 10^{-5}$

$(H^+) = \alpha C = (8.5 \times 10^{-5})\ (0.1) = 8.5 \times 10^{-6}$

$\therefore\ P^H = -\log(H^+) = -\log 8.5 \times 10^{-6}$

$= 5.1$

$_pOH = 14 - P^H = 14 - 5.1$

$\therefore pOH = 8.9$

A buffer is made by adding 4.1g of sodium ethanoate to 1dm^3 of 0.1M of ethanoic acid. What is the pH of the buffer? (Ka(CH_3COOH) = 1.74×10^{-5} moldm^{-3}, molar mass of sodium ethanoate = 82gmol^{-1}.

$$P^H = PKa + \log \frac{[H_3C00^-_{(ag)}]}{[CH_3C00H_{(ag)}]}$$

Number of moles of CH_3C00Na

$$= \frac{4.1}{82} = \mathbf{0.05mol}$$

$$\therefore [CH_3C00\text{-}_{(aq)}] = \frac{0.05}{1} = \mathbf{0.05M}$$

$$PH = -\log(1.74 \times 10^{-5}) + \log \frac{0.05}{0.01}$$

$$= 4.76 + 0.70$$
$$= 5.46$$

General Questions

1. Calculate the change in pH after 0.01mole of gaseous HCL is added to 250.0cm^3 of a solution containing 0.05M NH_3 and 0.15M of NH_4Cl ($K_b(NH_3)$ = 1.7×10^{-5}moldm^{-3}).
2. The concentration of hydrogen ion in a solution is 0.001 mol per dm^3
   (a) Calculate the grams of hydrogen ion per dm^3
   (b) The volume of solution in dm^3 containing one mole of

hydrogen ion.

(c) The pH and POH values.

3. A solution of dimethyl arsenic acid (a monobasic acid) was titrated with a solution of sodium hydroxide in order to determine the ionization constant of the acid. After addition of $17.3cm^3$ of NaOH, the pH was 6.23. It was found that $27.6cm^3$ was required to neutralize the acid solution completely. Calculate the Pka value..

4. Calculate the change in pH after $2cm^3$ of 0.02M NaOH is added to $200.0cm^3$ of a 0.08M CH^3COONa ($K_a(CH_3COOH)$ = $1.7x10^{-5}moldm^{-3}$.

5. An acid dissociates according to the equation H_2A H+HA-.A 0.100M solution of the acid is 1 percent ionized. What is the value of K_a?

6. The Kb values for ammonia and methylamine at 250C are 1.8x10-5 $moldm^{-3}$ and 4.4 $x10^{-5}$ $moldm^{-3}$ respectively. Which of their conjugate acids is stronger?

7. In pure water, the following equilibrium exists: $H_2O_{(l)}+H_20_{(ag)}+OH^-_{(ag)}$.

Water thus behaves both as acid and as a base, according to the Bronsted-Lowry theory, explain and comment on the above equilibrium equation.

Chapter Eight.

BY Ogor, S.O

8.0 CRYSTALS

A crystal or crystalline solid is material, whose constituent atoms molecules, or ions are arranged in an orderly repeating pattern extending in all three spatial dimensions.

Crystals can also be defined are solids that are formed by a regular repeating pattern of connecting together.

In crystals, however, the collections of atoms called the "unit Cell" is repeating in exactly the same arrangement over and throughout the in all entire material. Because of repetitive nature, crystals can take on strange and interesting looking forms, naturally.

The scientific study of crystals and crystal formation is "crystallogragh". The process of crystal formation via mechanisms of crystal growth is called crystallization or solidification. The process of forming a crystalline structure from a fluid or from materials dissolved in the fluid is often referred to as" crystallization.

Crystalline structures occur in all classes of materials, with all types of chemical bounds. Almost all metal exists in all classes of materials, with all types of chemical bounds. Almost all metal exists in a polycrystalline state; amorphous or single-crystal metals must be produced synthetically, often with great difficulty. Ironically, bonded crystals can form upon solidification of salts, either from a molten fluid or upon crystallization from a solution. Covalently bounded crystals are also very common, notable examples being diamond, silica and graphite. Polymer materials generally will form crystalline regions, but the lengths of the molecules usually prevent comp crystallization. Van Der Waal forces can also play a role in a crystal structure for example, this type of bonding loosely holds together this hexagonal patterned sheets in graphite.

8.1 Types of Crystals

There are seven crystal systems:-

1. **Triclinic:-** Usually not symmetrical from one side to the other, which can lead to some fairly strange shapes.
2. **Monoclini:-** Like skewed tetragonal crystals, often forming prisms and double pyramids.
3. **Orthorhombic:-** like tetragonal crystals except not square in cross section (when viewing the crystal on one end), forming rhombic prisms or dipyramids (two pyramids stuck together).
4. **Tetragonal:-** similar to cubic crystals, but longer along one axis than the other, forming double pyramids and prisms.
5. **Trigonal:-** posses a single 3-fold axis of rotation instead of the 6-fold axis of the hexagonal division.
6. **Hexagonal:-** six sickle prisms. When you look at the crystal on end, the cross section is a hexagon.
7. **Cubic:-** not always cube shaped.

Note:- You will also find octahedrons (eight false) and dodecahedrons (10 false).

Lattices can either be primitive (only one lattice point per unit cell) or non-primitive (more than one lattice point per unit cell). If you combine the seven crystal systems with the two different types of lattices, you end up with 14 Bravias lattices (named after Auguste Bravais who figured all this out in 1850).

Another way to answer this question (types of crystals) is to categorize crystals by their physical/chemical properties. In this classification you have four types of crystals:-

1 **Covalent Crystals:-** this is a crystal which has real chemical covalent bond between all of the atoms in the crystals so really a single crystal of a covalently bonded crystals is really just one big molecule. An example of this is a crystal like diamond or zinc sulphide. Covalent crystals can have extremely highly melting points.

2 **Metallic Crystals:** individual metal atoms sit on lattice site while the other outer electrons from these atoms enable them to flow freely around the lattice. Metallic crystals normally have high melting points and densities.

3 **Ionic Crystals:-** this is a crystal where the individual atoms don't have covalent bonds between them, but are held together by electrostatic forces. An example of this type of crystal is sodium chloride (NaCl). Ionic crystals are hard and have relatively high melting point.

4 **Molecular Crystals:-** this is a crystal where there are recognizable molecules in the crystal which are held together by non-covalent interactions like Van De Waals forces or hydrogen bonding. An example of this crystal would be sugar. Molecular crystals tend to be soft and have lower melting points (2).

8.2 crystalline Phases

8.2.1Polymorphism:- is the ability of a solid to exist in more than one crystal form. For example, water ice is ordinarily found in the hexagonal form ice, I_h, but can also exist as the cubic ice, I_c the vhonibhedral ice I_i, and many other forms.

8.2.2 Amorphous:- phases are also possible with the same molecules, such as amorphous ice. In this case, the phenomenon is known as polymorphism. For pure chemistry elements, polymorphism is known as allotropy. For example, diamond, graphite, and fullevenes are different allotropes of carbon.

Why do different crystals have different shapes and sizes?

This depends on two factors:

(a) The internal symmetry of the crystal

(b) The relative growth rates along the various direction in the crystal.

For example, suppose you have mutually perpendicular axis, a,b and c, suppose the crystal grows at equal rates along a,b and c, then the crystal shape will be a cube. Now suppose a different crystal grows in the c direction. The crystal will then grow as thin plates with the face of the plate being perpendicular to c. These are only simple examples.

More complicated cases (and shapes) happen when the crystal doesn't have mutually perpendicular axis, and when the fastest directions of growth corresponds to face or body diagonals (or even other directions) in the crystal.

Some crystalline materials may exhibit specifically electrical properties such as the ferroelectric effects or the piezoelectric effect. Additionally, light passing through a crystal is often refracted or bent in different directions, producing an array of colors; crystal optics is the stage of these effects. In periodic dialectic structures a range of unique optical properties can be expected as seen in photonic crystals.

8.3 How crystals get their colour

The pressure of different chemicals causes the variety of colours to different gemstones. Many gems are simply quartz crystals colored by the environment to which they are exposed. Amethyst gets its color from iron found at specific points in the crystalline structure.

Topaz is an aluminum silicate: it comes in many colors due to the presence of different chemicals. The color of any compound (whether or not it is a crystal) depends on how the atoms and or molecules absorb light. Normally white light (what comes out of light bulbs) is considered to have all wave lengths (colors) of light in it. If you pass a white light through a colored compound some of the light is absorbed, (we don't see the color which is absorbed, but we see the rest of the light) as it is reflected off the surface. This gives rise to the idea of "complementary colors". If a compound absorbed light of a certain color the compound appears to be the complimentary color. Here is a table of colors and their compliments

Colors	compliments	wavelength (color nm)
Violet	green-yellow	400-424
Blue	yellow	424-491
Green	red	491-570
Yellow	blue	570-585
Orange	green-blue	585-647
Red	green	647-700

So if you have a crystal which absorbs red light, it will appear green and if the crystal absorbs green light, it will appear red.

8.4 growth and Formation of Crystals

The crystalline state of matter is characterized by a distinct structural rigidity and virtual resistance to deformation (i.e. changes of shape and/or volume). Most crystalline solids have values both of Young's modules and of the shear modulus of elasticity. This constants with most liquids or fluids, which have a low shear modulus, and typically exhibit the capacity for macroscopic viscous flow.

8.5 Crystal Growth

This is a major state of a crystallization process, which typically follows an initial stage of either homogeneous or heterogeneous (surface catalyzed) nucleation. It occurs from the addition of new atoms, ions or polymer stings into the characteristic arrangement of a crystalline Bravais lattice.

The action of crystals growth yields a crystalline solid whose atoms or molecules are typically close packed with fixed positions in space relative to each other. This account for the objects structural rigidity. In mineralogy and crystallography, a crystal structure is a unique arrangement of atoms in a crystal. A specific symmetry of crystal structure I composed of Bravais lattice which is typically represented by a single unit cell. The unit cell is periodically repeated in three dimension of a lattice. The spacing between unit cells in various direction is called its lattice parameters. The symmetry prosperities of the crystal are embodied in its space group. A crystals structure and symmetry play a role in determining many of its physical properties, such as cleavage, electronic band structure, and optical properties.

8.6 Formation of Crystals

8.6.1 Introduction

Crystalline solid are typically formed by cooling and solidification from the molten (or liquid) state. According to the Ehrenfest classification of first order phase transition, there is a discontinuous change in volume (and thus a discontinuity in slope of first derivative with respect to temperature, dv/dt) at the melting point. Within this context, the crystal and the melting point are distinct phases with an inter-facial discontinuity having a surface or tension with a positive surface energy. Thus, a meta stable parent phase is always stable with respect to the nucleation of small embryos or droplets from a daughter phase provided. It has a positive surface or tension. Such first-order transitions must proceed by the advancement of an interfacial region whose structure and properties vary discontinuously from the parent phase.

The process of nucleation and growth generally occurs in two different stages, small nucleus containing the newly forming crystal components must impinge on each other in the correct orientation and placement for them to adhere and form the crystal. After crystal nucleation, the second stage of growth spreads outwards from the nucleating site. In this faster process, the elements which form the motif add to the growing crystal in a prearranged system, where the crystal lattice starts the crystal nucleation. As first pointed out by Frank, perfect crystals would only grow exceedingly slowly. Real crystals grow comparatively rapidly because they contain dislocations (and other defects), which provide the necessary growth points, thus providing the necessary catalyst from structural transformation and long-range order formation.

8.6.2 Discontinuity

The conditions of a homogeneous environment are often approximated to but rarely ever realized. Crystal growth always involves some forms of transport of matter or heat (or both). And homogenous conditions for the transport process can only exist for spherical, cylindrical, infinite plane surfaces. A polyhedral crystal cannot grow (remaining polyhedral) with uniform levels of super saturation (or super cooling) over its faces. In general, the super saturation is greatest at its concentrations. This refutes the assumption that the growth rate is a function of orientation and local super saturation.

Thus, the crystal face must grow as a whole. The growth rate of the entire face is determine by the driving force (level of super saturation). The point of emergence of the predominant point of growth (e.g. a dislocation, a foreign particle acting as catalysts, or crystal twine. The defect-free habit face can thus resist a finite level of super saturation without any growth at all.

Gibbs himself was the first to point out that in the growth of a perfect crystal, the first derivative of the free energy with respect to mass becomes periodically indefinable at each time that an additional layer on the crystal face is completed. There is discontinuity in the chemical potential at each such point.

In one sense, the crystal can then be in equilibrium with environments having a range of chemical potentials. In another sense, it is not in equilibrium. There are available states of lower free energy. But any free energy barrier must be passed by a fluctuation, or nucleation process, in order to access it. The fundamental thermodynamic effect of a screw dislocation is to eliminate this discontinuity in the chemical potentials, by making it impossible to ever complete a single crystal face.

8.6.3 Nucleation

Nucleation can be either homogeneous, without the influence of foreign participles, or heterogeneous, with the influence of foreign particles. Generally, heterogeneous nucleation takes place more quickly since the foreign particles act as a scaffold for the crystal to grow on, thus eliminating the necessity of creating a new surface and this incipient surface energy requirements.

Heterogeneous nucleation can take place by several methods. Some of the most typical path-way are small inclusion, or cuts, in the container the v is being grown on. This includes scratches on the side and bottom of glassware. A common particle in crystal growing is to add a foreign substance, such as a string or a rock, to the solution, thereby providing a nucleating site for the project and speeding up the time it will take to grow a crystal.

The number of nucleating sites can also be controlled in this manner. If a brand-new piece of glassware or a plastic container is used, crystals may not form because the container surface is too smooth to allow heterogeneous nucleation. On the other hand, a badly scratched container will result in many lines of small crystals. To achieve a moderate number of medium sized crystals, a container which has a few scratches works best. Likewise, adding small previously made crystals, or seed crystals, to a crystal growing project will provide nucleating sites to the solution. The addition of only one seed crystal should resist in a larger single crystal.

Some important features during growth are the arrangement, the origin of growth, the interface form (important for the drilling force), of the final size. When origin of growth is only in one direction for all the crystals, it can result in the material becoming very anisotropic (different properties in different directions). The interface form determines the additional free energy for each volume of crystal growth.

Lattice arrangement in metals often takes the structure of body centered cubic, face centered cubic, or hexagonal closed packed. The final size of the crystal is important for mechanical properties of materials. (for example, in metals it is widely acknowledged that large crystals can stretch further due to the longer deformation path and thus lower internal stresses).

8.6.4 Crystal Systems

Every crystal class is a member of one of the six crystal systems. These systems include the isometric, hexagonal, tetragonal, orthorhombic, monoclinic, and triclinic crystal system. The hexagonal crystal system is further broken into hexagonal and rhombohedra division.

Every crystal class which belongs to a certain crystal system will share a characteristic symmetry element with the other members of its system. For example, all crystals of the isometric system posses four 3 fold axis of symmetry which proceed diagonally from corner to corner through the center of the cubic unit cell. In contrast, all crystals of the hexagonal division of the hexagonal system possess a single six-fold axis of rotation.

In addition to the characteristic symmetry element which are not necessary present in all members of the same system. The crystal class which possesses the highest possible symmetry or the highest number of symmetry elements within each system is termed the "Holomorphic class" of the system.

For example, crystals of the holomorphic class of the isometric system possess inversion symmetry, three 4-fold axis of rotational symmetry, the characteristics set of four 3-fold axis of rotational symmetry which is indicative of the isometric crystal system, six 2-fold axis of rotational symmetry, and nine different mirror planes. In contrast, a crystal which is not a member of the holomorphic class yet sill belongs to the isometric system may possess only three 2 - fold axis of rotational symmetry and the characteristic four 3-fold axis of rotational symmetry.

The crystal system of a mineral species may sometimes be etermined in the field by visually examining a particularly well formed crystal of the species.

1. Isometric

The isometric crystal system is also known as the "Cubic system". The crystallographic axis used in this system are of equal length and are mutually perpendicular, occurring at right angles to one another. All crystals of the isometric system posses four 3-fold axis of symmetry, each of which proceeds diagonally from comer to comer through the center of the cubic unit cell. Crystals of the isometric system may also demonstrate up to three separate 4 - fold axis of rotational symmetry. These axis; if present, proceed from the center of each face through the origin to the center of the opposite face and correspond to the crystallographic axis. Furthermore crystals of the isometric system may posses six 2-fold axis of symmetry which extend from the Center of each edge of the crystal through the origin to the centre of the opposite edge. Minerals of this system may demonstrate up to nine different mirror plane. Examples of minerals which crystallize in the isometric system are halite, magnetite, and garnet. Minerals of this system tend to produce crystals of equidimensional or equant habit.

2. Hexagonal

Minerals of the hexagonal crystal system are referred to three crystallographic axis which intersect at 120^0 and a fourth which is perpendicular to the other three. This fourth axis is usually depicted vertically [7].

The hexagonal crystal system is divided into the "hexagonal and rhombohedral or trigonal" divisions. All crystals of the hexagonal division possess a single 6- fold axis of rotation. In addition to the single 6- fold axis of rotation, crystals of the hexagonal division may possess up to six 2-fold axis of rotation. They may demonstrate a center of inversion symmetry and up to seven mirror planes.

Mineral species which crystallize in the hexagonal division are apatite, beryl, and high quartz. Minerals of this division tend to produce hexagonal prisms and pyramids. Example species which crystallize in the rhomboidal division are calcite, dolomite, low quartz and tourmaline. Such minerals tend to produce rhombohedral and triangular prisms.

3. Tetragonal

Minerals of the tetragonal crystal system are referred to three mutually perpendicular axis. The two horizontal axis are of equal length, while the vertical axis is of different and may be either shorter or longer than the other all posses single-4 fold symmetry axis. They may possess up to four 2-folds axis of inversion, and up to five mirror planes. Minerals species which crystallize in the tetragonal crystal system are Zircon and cassiterite. These minerals tend to produce short crystals of prismatic habit.

4. Orthorhombic

Minerals of the orthorhombic crystal system are referred to three mutually perpendicular axis, each of which is of a different length than the others.

Crystals of this system uniformly possess three 2-fold rotation axis and/or three mirror planes. The holomorphic class demonstrate three 2-fold .symmetry axis and three mirror planes as well as a center of inversion. Other classes may demonstrate three 2-fold axis of rotation or one 2-fold rotation axis and two mirror planes. Species which belong to the orthorhombic system are olivine and barite. Crystals of this system tend to be of prismatic, tabular, or a circular habit.

5. Monoclinic

Crystals of the monoclinic system are referred to three unequal axis. Two of these axis are inclined toward each other at an oblique angle; these are usually depicted vertically. The third axis is perpendicular to the other two. The two vertical axis therefore do not intersect one another at right angle, although both are perpendicular to the horizontal axis.

Monoclinic crystals demonstrate a singles 2-fold rotation axis and/or a single mirror plane. The holomorphic class possesses the single 2-fold rotation axis, a mirror plane, and a center of symmetry. Other classes display just the 2-fold rotation axis or just the mirror plane.

Mineral species which adhere to the monoclinic crystal system include pyroxew, amphibole, orthoclase, azurite, and malachite, among many others. The minerals of the monoclinic system tend to produce long prisms.

6. Triclinic

Crystals of the triclinic system are referred to three unequal axis, all of which intersect at oblique angles. None of the axis are perpendicular to any other axis.

Crystals of the triclinic system may be said to possess only a l-fold symmetry axis, which is equivalent to possessing no symmetry at all.

Crystals of this system possess no mirror planes. The Holomorphic class demonstrates a cener of hiversion symmetry.

Mineral species of the triclinic class include plagioclase and axinite; these species tend to be of tabular habit.

Miller Indices

Miller indices are a notation system in crystallography for planes and directions

in crystal (Bravais) lattices

In particular, a family of lattice planes is determined by three integers L, M and n, which are the miner indices. They are written (him) and each index denotes an intersection of a plane with a direction {l,m,n) in the basis of the reciprocal lattice vectors. By convention, negative integers are written with a bar, as in 3 for -3. The integers are usually written in lowest terms, i.e their greatest common divisor should be 1. Miller index 100 represents a plane Orthogonal to direction l, index' 01'0 represents a plane orthogonal to direction m, and index 001 represents a plane orthogonal to n. There are also several related notations.

The rotation {lmn} denotes the set of all planes that are equivalent to (lmn) by the symmetry of the lattice. In the context of crystal directions (not planes), the corresponding notations are: [lmn], with square instead of round brackets, denotes a direction in the basis of the direction lattice vectors instead of the reciprocal lattice; and similarly, the notation <1mn> denotes the set of all directions that are equivalent to (1mn) by symmetry.

Miller indices were introduced in 1839 by the British mineralogist William Hallowes miller. The method was also historically known as the millerian system, and the indices as millerian, although this is now rare [6].

The precise meaning of this notation depends upon a choice of lattice vectors for the crystal, as described below. Usually, three primitive lattice vectors are used. However, for cubic crystal systems, the cubic lattice vectors are used. Even when they are not primitive (e.g, as in body - centered and face –centered crystals).

I.

Definition

There are two equivalent ways to define the meaning of the miller indices: via a point in the reciprocal lattice, or as the inverse intercepts along the lattice vectors. Both definitions are given below. In either case, one needs to choose the three lattice vector a, a2, and a, as described above. Given these, the three primitive reciprocal lattice vectors are also determined (denoted b., b_2, and b_3). Then, given the three miller indices l,m,n, (lmn) denotes planes orthogonal to the reciprocal lattice vector:

$$g_{lmn} = 1b, + mb_2 + nb,$$

That is, (1mn) simply indicates a normal to the planes in the basis of the primitive reciprocal lattice vectors. Because the co-ordinates are integers, this normal is itself always a reciprocal lattice vector. The requirement of lowest terms means that it is the shortest reciprocal lattice vector in the given direction.

Equivalently, (lmn) denotes a plane that intercepts the three points $a_1/1$. a_2/m, and a_3/n, or some multiple thereof. That is, the, Miller indices are proportional to the inverses of the intercepts of the plane, in the basis of the lattice vectors. If one of the indices is zero, it means that the plane do not intersect that axis (the intercept is "at infinity").

Considering only (lmn) planes intersecting one 'or more lattice points (the lattice planes), the perpendicular distance "d" between adjacent lattice plane is related to the (shortest) reciprocal lattice vector orthogonal to the planes by the formula:

$$d = \frac{2\pi}{1g1mn1}$$

The related notation (1mn) denotes the direction

$\therefore 1a_1 + ma_2 + na_3$

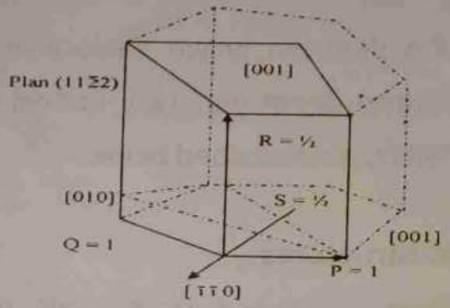
That is, it uses the direction lattice basis instead of the reciprocal lattice. Note that (1mn) is not generally normal to the (1mn) planes, except in a cubic lattice as described below.

8.7 Case of Cubic Structures

For the special case of simple cubic crystals, the lattice vectors .are orthogonal and of equal length (usually denoted a); similarly for the reciprocal lattice. So, in this common case, the Miller indices (lmn) and [lmn] both simply denote normal/directions in Cartesian coordinates. For cubic crystal with lattice constant a the spacing d between adjacent (1mn) lattice planes is (from above).

$$d_{lmn} = \frac{a}{\sqrt{L^2 + m^2 + n^2}}$$

Because of the symmetry of Cubic Crystals, it is possible to change the place and sign of the integers and have equivalent directions and planes. => Coordinates in angle brackets such as < 1 00> denotes family of directions which are equivalent due to symmetry operations, such as [100], [010], [001] or the negative of any of those directions. For face-centered cubic and body- centered cubic lattices, the primitive lattice vectors are no orthogonal. However, in these cases the miller indices are conventionally defined relative to the lattice vectors of the cubic "super cell" and hence are again simply the cartesran directions. Case of Hexagonal and Rhombohedral structures.



Miller – Bravais Tuder

With "hexagonal and rhombodhedral lattice system", it is possible to use the Brauais-Miller Index which has 4 numbers (h k i l).

$$i = -h - k$$

here h, k and l are identical to the Miller index, and "I" is a redundant index. This four-index scheme for labeling planes in a hexagonal lattice makes permutation symmetric apparent. For examples, the similarity between

(110) = (1120) and

(120) = (1210) is more obvious when the redundant index is shown.

In the figure at right, the (001) plane has a 3-fold symmetry: it remains unchanged by a rotation of 1/3 ($2\pi/3$ rad, 120^0). The (100), (010) and the (I I0) directions are really similar. If "S" is the intercept of the plane with (I I 0) axis, then $i = 1/S$.

There are also adhoc schemes (e.g. in the transmission electron microscopy literature) for indexing hexagonal lattice vectors (rather than reciprocal lattice vectors or planes) with four indices. However, they don't operate by similarly adding a redundant index to the regular three-index set.

For example, the reciprocal lattice vector (hkl) as suggested above can be written as $ha^* + kb^* + 1c^*$ if the reciprocal-lattice basis-vectors are a^*, b^*, and c^*. For hexagonal crystals this may be expressed in terms of direction lattice basis-vectors a,b and c as (6).

$(hk1) = ha^* + kb^* + 1c^* = 2/3a^2\,(2h+h)\,a + 2/a^2\,(h+2k)\,b + i/c^2$ ---(1)

Hence zone indices of the direction perpendicular to plane (hkl) are, in suitably - normalized triplet form, simply $[2h+k,\ h+2k,\ 1(3/2)\ (a/C)^2]$. When four indices are used for the zone normal to plane (hkl), however, the literature often uses $[h,\ k,\ -h\ -k,\ l\ (3/2)\ (a/C)^2]$ instead. Thus as you can see, four - index zone indices in square or angle. brackets sometimes mix a single direct - lattice index on the right with reciprocal - lattice "indices (normally in round or curly brackets) on the left [6].

8.8 LATTICE AND CRYSTAL STRUCTURE

Simple lattices and their unit cells.

(1) Simple Cubic (SC):

There is one host atom ("Lattice point") at each coner of a cubic unit cell. The unit cell is described by three edge length a=b=c = 2r (r is the host atom radius), and the angles between the edges, alpha = beta = gamma = 90 degrees. There is one atom wholly inside the cube (Z = 1). Unit cells in which there are host atoms (or lattice points) only at the eight comers are called primitive.

(2) Body Centered Cubic (BCC)

There is one host atom at each corner of the cubic unit cell and one atom in the cell cluster. Each atom touches eight host atoms along the body diagonal of the cube (a = 2.3094r,Z = 2)

(3) Face Centered Cubic (FCC)

There is one host atom at each corner one host atom in each face, and host atoms touch along the face diagonal (a = 2.8284r, X = 4). This lattice is "closest packed "because spheres of equal size occupy the maximum amount of space in this arrangement (74.05%); since this closest packing is based on a cubic array, it is called "cubic closest packing". CCP = FCC.

4. Face Centered Cubic primitive (FCC Primitive):

It is also possible to choose a primitive unit cell to describe the FCC lattice.

The Cell is a rhombohedron, with a = b = c = 2r, and alpha = beta = gamma = 60 degrees. [A cube is a rhombohedron with alpha = beta = gamma = 90 degrees].

5. Simple Hexagonal [SH]

Spheres of equal size are most densely packed (with the least amount of empty space) in a plane when each sphere touches six other spheres arranged in the form of a regular hexagon. When these hexagonally closest packed planes (The Plane through the centers of all sphere) are stacked directly on top of one another, a simple hexagonal array results; this is not, however, a three - dimensional closest packed arrangement. The unit cell, outlined in black, is composed of one atom at each comer of a primitive unit cell (Z = I), the edges of which are: a = b = C = 2r, where cell edges a and b lie in the hexagonal plane with angle a - b = gamma = 120 degrees, and edge C is the vertical stacking distance.

6. Hexagonal closet Packing (HCP):

To form a three-dimensional closest packed structure, the hexagonal closest packed planes must be stacked such that atoms in successive planes nestle in the triangular "grooves" of the proceeding plane. Note that there are six of these "grooves" surrounding each atom in the hexagonal plane, but only three of them can be covered by atoms in the adjacent plane. The first is labeled "B" and the perpendicular interlinear spacing between plane A and plane B is 1.633r (compared to 2.00r for simple hexagonal). If the third plane is again in "A" orientation and succeeding planes are stacked in the repeating patter ABABA.... = (AB). This resulting closest packed structure is HCP.

HCP coordination: Each host atom in an HCP lattice is surrounded by a touches 12 nearest neighbors, each at a distance of 2r. six are in the planar hexagonal array (B layer), and six (three in the A layer below) form a trigonal prism around the central atom.

7. Cubic Closest Packing (CCP)

If the atoms in the third layer lie over the three grooves in the A layer which were not covered by the atoms in the B layer, then the third layer is different from either A or B and is labeled "C". If a fourth layer then repeats the A layer orientation, and succeeding layers repeat the pattern ABCABCA.... – (ABC), the resulting closest packed structure is CCP = FCC. Again, the perpendicular spacing between the two successive layers is 1.633r.

CCP Coordination

Each host atom in a CCP lattice is surrounded by and touches 12 nearest neighbors, each at a distance of 2r: six are in the planar hexagonal (B) plane, and six (three in the C layer above and three in the A layer below) form a trigonal anti-prism (also known as a distorted octahedron) around the central atom.

8. Rhombohedral (R) Lattice

If, in the (ABC) layered lattice, the inter-planar spacing is not the closest packed value (1.633r 1, then the primitive (Z = 1) unit cell is a rhombohedron with a = b = c < or> 2r and alpha = beta = gamma < or> 60 degrees. The non-primitive hexagonal unit cell (Z = 3). May also be chosen.

2 and 3 - layer repeats: There is only one way to produce a repeat pattern (crystal lattice) in two layers of hexagonally closest packed planes: (AB) = HCP. Likewise, there is only one way to produce a repeat pattern in three layers of hexagonally closest packed planes: (ABC) = CCP.

4 - **layer repeats:** However, there are two way to produce a closest packed lattice in four layers: (ABAC) and (ABCB). By extension there are increasing numbers of ways to produce closet packed lattices in five layers, six layers, e.t.c, up to and including non repeating random stacking. Thus, there are many closest (and pseudo - closest) packings in natural and artificial materials. Holes (:Interstices") in closest packed Arrays. Tetrahedral Hole: Consider any two successive planes in a closest packed lattice. One atom in the A layer nestles in the triangular groove formed by three adjacent atoms in the B layer, and the four atoms touch along the edges of length 2r) of a regular tetrahedron; the center of the tetrahedron is a cavity called the tetrahedial (or Td) holes; a guest sphere will just fill this cavity (and touch the four host spheres) if its radius is 0.2247r.

Octahedial Holes: Adjacent to the Td hole, three atoms in the B layer touch three atoms in the A layer such that a trigonal antiprismatic polyhedron (a regular octahedron) is formed; the center of the octahedron is a cavity called the octahedral (or Oh) hole. A guest sphere will just fill this cavity (and touch the six host spheres) if its radius is 0.412r, it can be shown that there are twice as many Td as Oh holes in any closet packed bi layer.

8.9 Symmetry Properties and Symmetry Elements of Crystals

Symmetry

Crystals, and therefore minerals, have an ordered internal arrangement of atoms. This ordered arrangement shows symmetry, i.e. The atoms are arranged in a symmetrical fashion on a three dimensional network referred to as a "lattice", When a crystal forms in an environment where there are no impediments to its growth, crystal faces form as smooth planar boundaries that make up the surface of the crystal. These crystal faces reflect the ordered internal arrangement of atoms and thus reflect the symmetry of the crystal lattice. To see this, let's first imagine a small 2-dimensional crystal composed of atoms in an ordered internal arrangement as shown below. All of the atoms in this lattice are the same. If we rotate the sample crystals by 90° notice that the lattice and crystal look exactly the same as what we started with. Rotate it another 90° and again it's the same. Another 90° rotation again results. in an identical crystal, and another 90^0 rotation returns the crystal to its original orientation. Thus, in one 3600 rotation, the crystal has repeated itself, or looks identical four times. We thus say that this object has 4 fold rotational symmetry.

8.10 Symmetry Operations and Elements

A symmetry operation is an operation that can be performed either physically or imaginatively that results in 'no change in the appearance of an object. Again it is emphasized that in crystals, the symmetry is internal, that is it is an ordered geometrical arrangement of atoms and molecules on the crystal lattice. But, since the internal symmetry is reflected in the external form of perfect crystals, we are going to concentrate on external symmetry because this is what we can observe.

There are 3 types of symmetry operations rotation, reflection, and inversion.

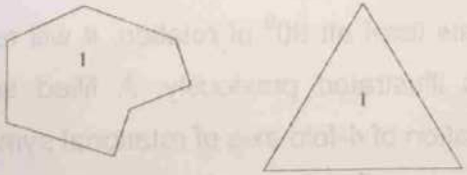
We will look at each of these in turn.

Rotational Symmetry

As illustrated above, if an object can be rotated about an axis and repeats itself every 90^0 of rotation then it is said to have an axis of 4 - fold rotational symmetry. The axis along which the rotation is performed is an "element of symmetry" referred to as a "rotation axis". The following types of rotational symmetry axis are possible in crystals.

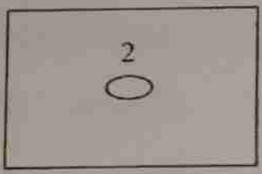
i. 1 - FOLD ROTATION AXIS

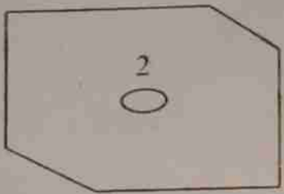
An object that requires rotation of a full 360^0 in order to restore it to its original appearance has no rotational symmetry. Since it repeats itself one times every 360^0 it is said to have a l-fold axis of rotational symmetry.

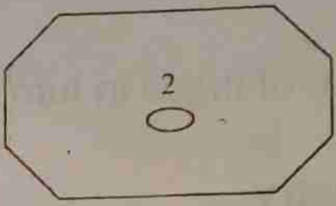


ii 2- Fold Rotation Axis

If an object appears -identical after a rotation of 180°, that is twice in a 360° rotation, then it is said to have 2-fold rotation axis (3601180 = 2). Note that in these examples the axis we are referring to are imaginary lines that extend toward you perpendicular to - the page or blackboard. A filled oval shape represents the point where the 2-fold rotation axis intersects the page.

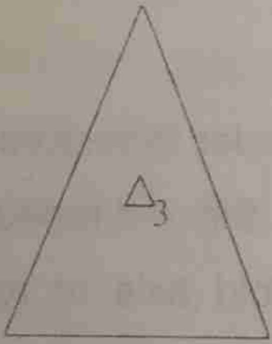


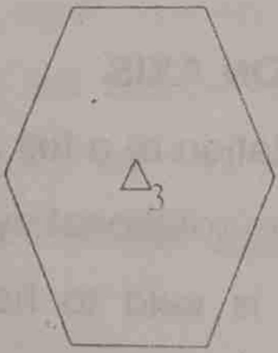




iii 3-Fold Rotation Axis

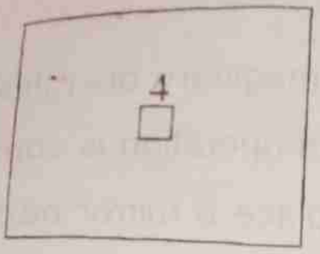
Objects that repeat themselves upon rotation of 120° are said to have a 3 fold axis of rotational symmetry (3601120 =), and they will repeat 3 times in a 360° rotation. A filled triangle is used to symbolize, the location of 3-fold rotation axis.

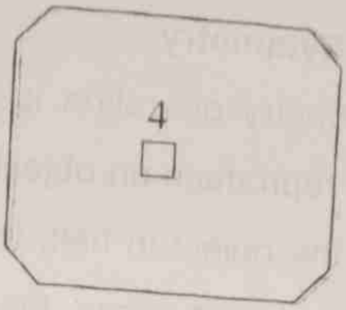




iv 4- Fold Rotation Axis

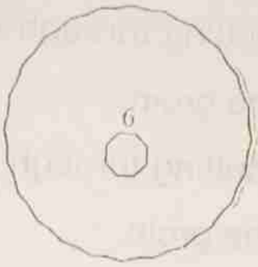
If an object repeats itself aft 90^0 of rotation, it will repeat 4 times in a 360^0 rotation, as illustrated previously. A filled square is used to symbolize the location of 4-fold axis of rotational symmetry.



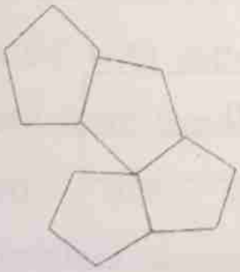


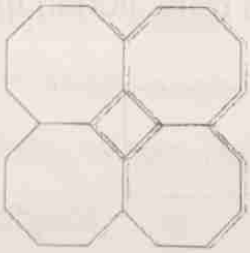
v. 6-Fold Rotation Axis

if rotation of 60^0 about an axis causes the object to repeat itself, then it has 6-fold axis of rotational symmetry ($36^0/60 = 6$). A filled hexagonal is used as the symbol for a 6-fold rotation axis.



Although objects themselves may appear to have 5-fold-7-fold-8-fold, or higher – fold rotation axis, these are not possible in crystals. The reason is that the external shape of a crystal is based on geometric arrangement of atoms. Note that if we cannot combine them in such a way that they completely fill space, as illustrated below,



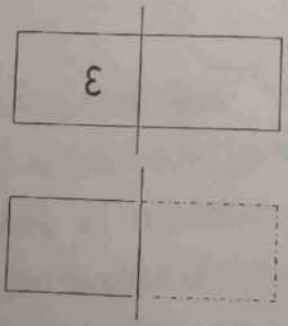


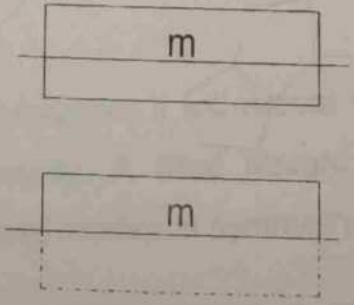
8.11 Mirror Symmetry

A mirror symmetry operation is an imaginary operation that can be performed to reproduce an object. The operation is done by imagining that you cut the object in half, then place a mirror next to one of the halves of the object along the cut. If the reflection in the mirror reproduces the other half of the object then the object is said to have mirror symmetry. The plane of the mirror is an element of symmetry referred to as a "mirror plane" and is symbolized with the letter M. As an example, the human body is an object that approximates mirror symmetry with the mirror plane cutting through the center of the head, the center of nose and down to the groin.

symmetry, with the mirror plane cutting through the center of the head, the centre of nose and down to the groin.

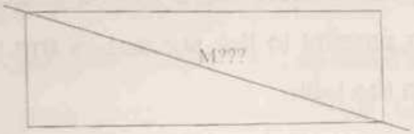
The rectangles shown below have tow planes of mirror symmetry. The Rectangle on the left has a mirror plane that runs vertically on the page and is perpendicular to the page. The rectangle on the right has a mirror plane that runs horizontally and is perpendicular to the page. The dashed parts of the rectangles below show the part the rectangles that would be seen as a reflection in the mirror.

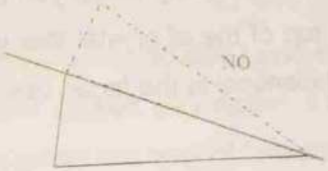




The rectangle shown above have two planes of mirror symmetry. Three dimensional and more complex objects could have more. For example, the hexagon shown above, not only has 6-fold rotation axis, but has 6-mirror planes [5].

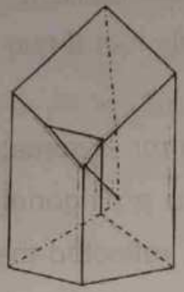
Note that a rectangle does not have mirror symmetry along the diagonal lines. If we cut the rectangle along a diagonal such as that labeled "m" as shown in the upper diagram, reflected the lower half in the mirror, then we would see what is shown by the dashed lines in lower diagram. Since this does not reproduce the original rectangle, the line "m" does not represent a mirror plane [5].

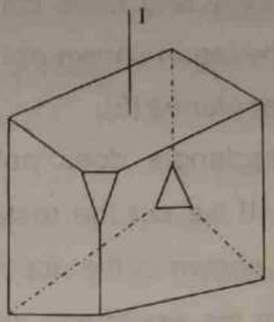




Center of Symmetry

Another operation that can be performed is inversion through a point. In this operation lines are drawn from all points on the object through a point in the centre of the object, called a "symmetry Center" (symbolized with letter "i"). The lines each have lengths that are equidistant from the original points. When the ends of the lines are connected, the original object is reproduced inverted from its original appearance. In the diagram shown here, only a few such lines are drawn for the small triangular face. The right hand diagram shows the object without the imaginary lines that reproduced the object [5].





If an object has only a center of symmetry, we say that it has a 1-fold votoinversion axis. such as an axis has the symbol I as shown in the right the property that if you place it on a table there will be a face on the top of the of crystal that will be parallel to the surface of the table and identical to the facae vesting on the table.

SECTION A

Ia State Grahams Law of diffusion and Boyles Law

b Under certain conditions of temperature and pressure, the density of oxygen gas is 1.30g/dm^3, a volume of 2.1cm^3 of O_2(gas) effuses through an apparatus in 1.0 sec and the rate of effusion of gas x through the same apparatus is 1.5cm^3/sec. calculate the density of gas x under the same experimental conditions.

c. Air has a density of 202g/dm^3 at STP what, will be the weight of 4.67dm^3 of air at 90^{0}C and 735mmHg?

2a Define Raoults law, molarlity and vapor pressure of a solution,

b. What is the molecular weight of dichlorobenze if 1.47g dissolved in 50g of benzene raised the boiling point of benzene by 0.506 (K_b = 2.53, R = 0.0205at-dm^{3}K-1 0.314J/K/mole.

c. What will be the boiling point and freezing point of a solution containing 160g of sucrose ($C_{12}CH_{22}O_{11}$) in 450g of water at 1atm pressure (MW of sucrose – 347g/mol) K_b = 0.512^{0}C.

3a. Explain the following terms with suitable examples: (a) system (ii) enthalpy (iii) bond dissociation energy.

bi State the first law of thermodynamics

ii Derive the change in internal energy. ΔE_1 for a system which absorbs heat and does work.

c. Given the heat of combustion of ethane as -1550.88KJ and the heats of formation of liquid water and carbon (IV) oxides as - 285.8 and -393.5KJ respectively. Calculate the heat of formation of ethane.

4a. State the law of mass action

b. Explain the effect of (i) pressure (ii) temperature (iii) concentration on equilibrium position.

c. For the reaction $H_2 + I_2 \rightleftharpoons 2HI$

K = 45.9 at 490^{0}C if one mole of H_2, two moles of I_2 and three mole of HI are injected into a 1dm^3 box.

Determine the equilibrium concentrations of reactants and products at 490^{0}C.

5a. Identify the acid-base conjugate pairs in the following equations

i $NH^-_2 + N_2H_4 \rightleftharpoons NH_3 + N_2H^-_3$

ii $H_2C_2C_4 + CH_3NH_2 \rightleftarrows HC_2O^-_4 + CH_3\,NH^7{}_3$.

b. Predict whether the aqueous solutions of the following salts will be acidic, basic or neutral.

(i) NaCl (ii) NH_4NO_3 (iii) $KC_2H_3O_2$.

c. Calculate the pH of a 0.10M solution of ethanoic acid if the pKa = 4.76.

6a. state three assumptions of collision theory,

b. draw an energy profile diagram for both catalyzed and uncatalyzed system for the reaction.

$$N_2 + 3H_2 \rightleftarrows 2NH_3 \qquad \Delta H = xKJmol^{-1}.$$

c. Define the half-life of a chemical reaction

(ii) Which of the factors affecting the rate of chemical reaction cannot be changed by the experimenter.

(iii) what is a buffer solution. Give one example.

(iv) Write an expression for buffer capacity

d. List three factors that can affect the rate of any chemical reaction.

ii. After five seconds, 0.1mol dm^{-3} of ethanol fermented to ethanoic acid, calculate the rate of fermentation.

NNAMDI AZIKIWE UNIVERSITY, AWKA 2008/2009 SESSION

1. The unit of equilibrium constant of reaction PbCl2(s) $\rightleftharpoons$ $Pb^{2+}_{(aq)}+2Cl^{-}_{(aq)}$ is (A) dimensionless (b) atm (c) mol^3/dm^{-9} (d) mol^3dm^{-9}.
2. One of these will affect the equilibrium constant of any reaction (a) moisture (b) temperature (c) catalysts (d) pressure.
3. The point on the phase diagram where one indistinguishable phase exists is known as (a) critical point (b) melting point (c) sublimation point (d) triple point.
4. A combination of temperatures and pressures at which liquid and gas phases can exist at equilibrium is shown by (a) melting point curve (b) sublimation curve (c) boiling point curve (d) diffusion curve.
5. The expression for the equilibrium constant of this reaction $AgCl_{(s)(aq)}$+Ag + $[(Cl)]^{-2}$ (d) 2[Cl-1] [Ag+].

6. For the equation in no 5 above, the value of the equilibrium constant at 298K is (A) l.44 (B) 14.4 (C) 0.144 (d) 144.

7. If the solubility product of the reaction $Ag+_{(aq)}+$ $cl^{-1}(sq)$ $Ag+_{(aq)}+$ is 2.0×10^{-10} mol^2/dm^6, the concentration of Ag^+ in g/dm^3 is (A) $l.52 \times 10^{-3}g/dm^{-3}$ (B) $1.52 \times 10^{-4}g/dm^{-3}$ (C) $1.5 \times 10^{-3}g/dm^3$ (d) $l.52 \times 10^4g/dm^3$

8. If these equilibrium reaction AgCl(s) $\rightleftharpoons$ $Ag+_{(aq)}$ $+Cl^{-1}_{(aq)}$g $NaCl_{(s)}$ Na+

$_{(aq)} + Cl^-_{(aq)} \rightleftharpoons$ take place in system, the effect of common ions on the

system is (a) increase in the concentration of Cl^- (b) decrease in the

solubility of AgCl (c) all of the above (d) none of the above.

9. Solubiity product, a special type of equilibrium constant applies to mainly

(a) very soluble salts (b) compound salts (c) ionizable salts

(d) springly soluble salts.

10. One of these equation is true (a) $\Delta G^o/RT = -\ln k$, (b) $\Delta G^o = -RT^2 \ln K_p$

(c) $\Delta G^o = -RT\ln Kp$ (d) $\Delta G^o = -RT\ln Kp$

11. What is the percent by weight of NaCl if 1.75g of NaCl is dissolved in

5.85g of water (a) 76% (b) 7.4% (c) 24% (d) 23% (e) 2.4%

12. The mole fraction of HCl in a solution of HCl in water

containing 36% HCi by weight is (a) 64 (b) 0.991 (c) 3.550 (d)

1.05 (e) 0.218

13. What is the molality of a solution prepared by dissolving 5 g of

toluene (C7HS) in 225g of benzene (C6H6)? (a) 0.0543m (b)

0.225m (c) 92m (d) 18m (e) 0.24m (C = 12, H=l).

14. Which one of the following has molality equal to one? (a) 36.5g

of HCl in 500ml of water (b) 36.5g of HCi in 1000ml of water (c)

36.5g of HCl in 1000g of water (d) 36.5g of HCl in 500g of water (e) None of these.

15. Calculate the vapour pressure lowering caused by the addition of 100g of sucrose (mol mass = 342) to 1000g of water if the vapour pressure of pure water at 25°C is 23.8mm Hg (a) 12.5mmHg (bO 125mmHg) (c) 1.35mmHg (d) 0.125mmHg (e) 1250mmHg.

16. The boiling point of a solution containing 0.2g of a substance x in 20g of ether is 0 . 17-K higher than that of pure ether. Calculate the molecular mass of X. Boiling point constant of ether per lkg is 2.16k (a) 1.27 x 10^2 (b) 1.27 x 10^3 (c) 1.27 X 10-^2 (d) 1.27 x 10~3 (e) 1.27 x 10^4

17. 1.25g of naphthalene was dissolved in $60cm^3$ of benzene and freezing point of the solution was found to be 277 .515K, while that of benzene 278.495K. Density of benzene is $0.88gcm\text{-}^3$, K;= 5.l per 1000g of benzene. The molecular mass of the naptheten is (a) 123 (b) 4.55 (c) 61 (d) 6.1

18. On dissolving common salt in water it is observed that (a) freezing point is raised (b) vapour pressure is increased (c) boiling point of the solution decreases (d) boiling point of the solution remained unchanged (e) none of these.

19. A solution of glycol containing 1.821g per litre-has an osmotic pressure of 51.8cm Hg at 10°C. What is the molecular mass of glycol (R=.0.0821 Latm) (a) 62.04 (b) 0.816 (c) 8.16 (d) 81.6 (e) 56.

20. For the reaction $2N2O_5 \quad 4NO_2 + O_2$, the rate is directly proportional to N2O5. At 450C, 90% of the N2O5 reacts in 3600 sec. find the value of rate constant. (a) 2.5x10-5S-1 (b) $10^{-2}S^{-1}$ (c) $1.8x10^{-1}S^{-1}$ (d) $6.4 x10^{-4}S^{-1}$ (e) $5.3 x10^{-3}S^{-1}$.

21. 50% of a first order reaction is complete in 23min. calculate the time required to complete 90% of the reaction (a) 76.4min. (b) 0.301mins (c) 30.1min (d) 301min (e) 58.2min.

22. Here is a second order reaction A P. If the initial concentration of A, is 0.0818M goes down 30% in 3.15min, what is the reaction for the reaction? (a) $0.0078Lmol^{-1}S^{-1}$. (b) $1.7L\ mol^{-1}S^{-1}$. (c) $9.1L\ mol^{-1}S^{-1}$. (d) $16L\ mol^{-1}S^{-1}$. (e) $1.6L\ mol^{-1}S^{-1}$.

23. As the temperature of a reaction is increased, the rate of the reaction increases because the (a) reactant molecules collide with greater energy (b) reactant collide less frequently (c)

reactant molecules collide less frequently. (d) activation energy is lowered (e) reactants molecules are independent of temperature.

24. Which of the following includes all the aims of Kinetics (i) to measure the rate of reaction (ii) to be able to predict the rate of reaction (iii) to be able to establish the mechanism by which a reaction occurs (iv) to be able to control a reaction (a) I, ii and iii (b) I and ii (c) ii and iii (d) ii, iii and iv (d) I, ii, iii and iv.

25. A reaction A P is a second order pcoess with T½ = 23 min at an initial concentraton of A = 0.5M. What is the concentration of A after 1 hour elapses? (a) 0.139M (b) 0.263M (c) 0.822M (d) 0.175M (e) 0.158M.

26. Molality is the number of moles of the solute that is present in ________ of the solvent (a) $1dm^3$ (b) $1000cm^3$ (c) $1m^3$ (d) $1000dm^3$ (e) 1000g.

27. The solid phase of a solution occurs when the solution is ________ (a) vapourised (b) boiled (c) saturated (d) frozen (e) none of the above

28. The adsorption of H_2 by palladium forms a solution in which

the solvent is ______________ respectively (a) gas and gas (b) gas and liquid (c) liquid and gas (d) solid and solid (e) none of these.

29. One of the following statements is incorrect (a) they are used to determine the molecular weight of the dissolves solute (b) they depend on the nature of the solute (c) they depend on the number of solute (d) they depend on the nature of the solvent (e) none of these.

30. The half-life of a second order reaction is _________ to the initial concentration of the reactant (a) directly proportional (b) independent (c) inversely proportional (d) all of these (e) none of these.

31. The major use of thermodynamics is (a) to predict the rate of chemical reaction (b) to know the yield of the product of a chemical reaction. (c) to predict whether a reaction can proceed spontaneously or not. (d) all of the above.

32. Given the following standard molar heats of formation in KJmol-1+ $CH_{4(g)}$ = 74.83m; $CO_{2(g)}$ = -393.51 and $H_20(l)$ = -285.84. Calculate the standard molar heat of combustion of

methane (a) -890.36KHmol^{-1} (b) -604.62KJmol^{-1} (c) 1040.02KJmol^{-1} (d) 754.19KJmol^{-1}.

33. A thermochemical equation consist of (a) reactants (b) products (c) reactant and products (d) a balanced chemical equation

34. The law that enables thermochemical equation to be added or subtracted is (a) Lavoisier and Laplace law (b) Hess's Law of constant heat summation (c) the heat addition and subtraction law (d) the law of mass action.

35. The mathematical statement of the first law of thermodynamics for a system that does work on the surrounding is (a) $\Delta E = q-w$ (b) $\Delta E = q+w$ (c) $\Delta E = -q-w$ (d) $\Delta E = -q+w$.

36. One of these is not a state function (a) pressure (b) temperature (c) volume (d) density

37. One of these is an intensive property (a) mass (b) volume (c) enthalpy (d) density

38. What is the heat change of the reaction $2CO_{(g)} + O_2$ $2CO_{2(g)}$ if the standard molar heats of formation of $CO_{2(g)}$ and $CO_{(g)}$ in $KJmol^{-1}$ are 3, 1 and -8.1 respectively. (a) 22.4 $KJmol^{-1}$ (b) -22.4 $KJmol^{-1}$ (c) -11.2 $KJmol^{-1}$ (d) 2.4 $KJmol^{-1}$

39. Calculate the heat of hydrogenation of propyen given the following bond energies in $KJmol^{-1}$ C-C = 336.81;C=C= 606.68; C≡C = 828.43, H-H = 431.79, C-H = 410.09. (a) 630.09 $KJmol^{-1}$ (b) -630.09 $KJmol^{-1}$ (c) 43.53 $KJmol^{-1}$ (d) 63.09 $KJmol^{-1}$

40. When bonds are formed energy is (a) given out (b) taken in (c) broken (d) formed

41. If the standard molar heat of formation of CO(g) and CH3 OH(l) in $KJmol^{-1}$ are -110.53 and -238.57 respectively, calculate the heat of the reaction $CO_{(g)} + 2H_{2(g)}$ $CH_3OH(l)$ in $KJmol^{-1}$ (a) 128.04 (b) -128.04 (c) 349.1 (d) -349.1.

42. When pressure doubles and volume is halved, deviation to the law occurs at high pressures or low temperatures as a result

of increase in intermolecular forces. This statement refers to (a) Charles law (b) Avogadros law (c) Boyles law (d) Charles law and Boyles law.

43. The gram weight of exactly $1000dm^3$ of O_2 gas at STP is (a) 145g (b) 147g (c) 143g (d) 144g.

44. Two porous containers were filled respectively with H_2 and O_2 at STP. At the end of one hour $880cm^3$ of H_2 had escaped. How much O_2 escaped during the same period of time? (a) $180cm^3$ (b) $200cm^3$ (c) $220cm^3$ (d) $240cm^3$.

45. One mole of CO_2 was found to occupy a volume of $1.32dm^3$ at 480C. calculate the pressure that would be expected from the ideal gas? (a) 18.94atm (b) 19.88atm (c) 19.94atm (d) 18.84atm.

46. The volume of container is (a) $1.5dm^3$ (b) $1.4dm^3$ (c) $1.3dm^3$ (d) $1.2dm^3$

47. The mole fraction of hydrogen in the mixture is (a) 0.860 (b) 0.865 (c) 0.870 (d) 0.875.

48. The partial pressure of hydrogen is (a) 0.875atm (b) 0.870atm (c) 0.865 (d) 0.860

49. The density of NO at STP is (a) 1.43g/dm^3 (b) 1.24g/dm3^3 (c) 1.34g/dm^3 (d) 1.13g/dm^3

50. To what temperature (^{O}C) must 1.00dm^3 of gas be heated to expand its volume to 2.75dm^3. assuming that there is no change in pressure (a) 4670C (b) 4570C (c) 4770C (d) 4770C (e) 4870C.

Prefix	Fraction	Symbol
deci	10^{-1}	d
cent	10^{-2}	C
milli	10^{-3}	m
Micro	10^{-6}	µ.
nano	10^{-9}	n
pico	$10-^{12}$	P
femto	10^{-15}	f
atto	10^{-18}	a
deca	10^{1}	da
hecta	10^{2}	h
kilo	10^{3}	k
mega	10^{6}	m
giga	10^{9}	g
tera	10^{12}	t

S/N	**Quantity**	**Symbol**	**Si Unit**
1	Atomic mass unit	Amu	1.6606x 10^{-27}kg
2	Avogadro's number	N_A	6.022x10^{23} particle/mol
3	Bohr radius	R_o	5.2918 xl0^{23}m
4	Boltzmann constant	K	1.3807 x 10^{-23}J/K
5	Change to mass	e/m	1.7588 X10^{11}C/Kg
6	Mass of electron	Me	9.1095 x 10^{-31}kg
		Me	=0.00054859 amu
		Mp	1.6726 x 10^{-27}kg
7	Mass of proton	Mp	= 1.007277amu
8	Mass of neutron	Mn	1.67495 x 10^{-27}kg
		Mn	= 1.008665amu
9	Faraday	F	96487J/cmo^{-1}

			= 96487 coulomb/smol
10	Gravitational force	,g	9.906m1s
11	Molar volume (STP)	Vm	22.414 x 10-^{3}m^3/mol
		Vm	=22.414 L/mol = 22.414dm^3/mol
12	Plancks constant	h	6.6262 x 10^{-27}kg
		h	=6.6262 xl0^{-27} ergsec
13	Speed of light	C	2.9979xl0^{8}mls
14	Rydberg constant	Rz	1.0974 x 10^{7}m^{-1}
		Rz	=2.1799 x 10^{-11}erg
		Rz	=2J 799 x 10^{-18}J

Acid dissociation constant (K_a) at 25^{0}C

Acid dissociation constant (Ka) at 25 C

	Formula	Name	ka
1	CH_3COOH	Acetic Acid	1.8 x 10^{-5}
2	H3As04	Arsenic acid	5.6 x 10^{-3}
3	H_3As0_3	Arsenious acid	6.0 x 10^{-10}
4	C_6H_5COOH	Benzoic acid	6.5 x 10^{-5}
5	H_3B0_3	Boric acid	5.8x 10^{-10}
6	H_2C0_3	Carbonic' acid	4.3 x 10^{-7}
7	$ClCH_2COOH$	Chloroacetic acid	1.4 x 10^{-3}
8	HCOOH	Forric acid	1.8 x 10^{-4}
9	HCN	Hydrogenic acid	4.9 X 10^{-10}
10	HF	Hydrofluoric acid	6.8 x 10^{-4}

13	H_2S	Hydrogen sulphide	5.7×10^{-4}
14	HBrO	Hypobronous acid	2.0×10^{-9}
15	Helo	Hypochlorous acid	3.0×10^{-8}
16	HIO	Hypoiodous acid-	2.0×10^{-11}
17	$CH_3(OH)\ COOH$	Lactic acid	1.4×10^{-4}
18	$CH_2(COOH)_2$	Melonic acid	1.5×10^{-3}
19	HNO_2	Nitrous acid	4.5×10^{-4}
20	$(COOH)_2$-	Onalic acid	5.9×10^{-2}
21	C_6H_5OH	Phenol	1.3×10^{-10}
22	H_3P0_4	Phosphoric acid	7.5×10^{-3}
23	CH_3CH_2COOH	Propionic acid	1.3×10^{-5}
24	H_2S0_4	Suphuric acid	Strong acid
25	H_2S0_3	Sulphorous acid	1.7×10^{-2}
26	$(CHOHCOOH_2)$	Tartaric acid	1.0×10^{-3}

STANDARD ELECTRODE POTENTIALS AT 25°C FOR OXIDATION REACTIONS

ELECTRODES	ELECTRODE REACTIONS	E° (VOLTS)
Li : Li	Li(s) Li + e	+3.045
K:K	K(s) = K + e	+2.9241
Ca:Ca	Ca(s) = Ca + 2e	+2.87
Na : Na	Na(s) Na + e	+2.7146
Zn : Zn	Zn(s) Zn + 2e	+0.7618
Fe : Fe	Fe(s) = Fe + 2e	+0.441
Cd:Cd	Cd(s) = Cd + 2e	+0.403
Pb:PbSO$_4$(s). SO$_4$	Pb(s) + SO$_4$ = PbSO$_4$(s) + 2e	+0.3546
Tl:Tl	Tl(s) = Tl + e	+0.3346
Ni:Ni	Ni(s) Ni + e	+0.236
Ag:AgI(s),I	Ag(s) + I AgI(s)+e	0.1522
Sn:Sn	Sn(s) Sn + 2e	-0.140
Pb:Pb	Pb(s) Pb + 2e	+0.1265
H$_2$:H	H$_2$(g, 1 atm) H + 2e	+0.0000
Ag:AgBr(s),Br-	Ag(s) + Br AgBr(s) + e	-0.0711
Pt,Sn , Sn^{4}	Sn Sn 2e	-0.14
Ag:AgCl(s), Cl-	Ag(s) + Cl AgCl(s) + e	0.2225
Hg:Hg$_2$Cl$_2$Cl-	2Hg(l) + 2Cl Hg$_2$Cl$_2$(s) + 2e	0.2680
Cu:Cu	Cu(s) Cu + 2e	-0.337
I$_2$:I	2I = I$_2$(s) + 2e	-0.337
Hg:Hg$_2$SO$_4$(s).SO$_4$	2Hg(l) + SO$_4$ Hg$_2$SO$_4$(s) + 2e	-0.6141
Pt:Fe , Fe^{3}+e	Fe Fe^{3} + e	-0.771
Ag : Ag	Ag(s) Ag + e	-0.7991
Br$_2$: Br	2Br = Br$_2$(l) + 2e	-1.0652
Pt: Tl , Tl^{3}	Tl Tl^{3} + 2e	-1.252
Cl$_2$: Cl	2Cl = Cl$_2$(g, 1 atm) + 2e	-1.3595
Pt : Ce^{3}, Ce^{4}	Ce^{3} = Ce^{4} e	-1.61
Pt :Co , Co^{3}	Co = Co^{3} + e	

Prefix

Quantity	Unit	SI Symbol
Primary Units		
Time	Second	ST
Length	Metre	M
Mass	Kilogram	Kg
Electric current	Ampere	A
Amount of substance	Mole	Mol
Temperature	Kelvin	K
Derived Units		
Area	Square metre	M^2
Volume	Cubic metre	M^3
Density	Kilogram per. cubic metre	Kgm^{-3}
Electric potential different	Volt	V
Electric resistance	Ohm	$\Omega(VA^{-1})$
Electric force	Volt	V
Energy	Joule	J(Nm)
Entropy	Joule per Kelvin	(JK^{-1})
Force	Newton	N $(kgms^{2})$
Power	Watt	W (Js^{1})
Pressure	Newton per square metre	(Nm^{-2})
Quantity of electricity	Coulomn	C (As)
Quantity of heat	Joule	J (Nm)
Specific heat	Joule per kilogram-kelvin	$O(JKg^{-1}K^{-1})$
Voltage	Volt	V
Work	Joule	J (Nm)

TABLE OF ATOMIC MASSES

Element	Symbol	Atomic no.	Atomic wt
Aluminum	Al	13	26.98
Antimony	Sb	51	121.76
Argon	Ar	18	39.944
Arsenic	As	33	74.91
Barium	Ba	56	137.36
Beryllium	Be	4	9.013
Bismuth -	Bi	83	200.00
Boron	B	5	10.81
Bromine	Br	35	79.916
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Carbon	C	6	12.011
Cerium	Ce	58	140.13
Cesium	Cs	55	132.91
Chlorine	C1	17	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Copper	Cu	29	63.54
Dysprosium	Dy	66	162.51
Erbium	Er	68	167.27
Europium	Eu	63	152.0

Fluorine	F	9	19.00
Gadolinium	Gd	64	157.26
Gallium	Ga	31	69.72
Germarium	Ge	32	72.60
Gold	Au	79	197.0
Hafnium	Hf	72	178.50
Helium	He	2	4.003
Holmium	Ho	67	164.94
Hydrogen	H	1	1.00080
Indium	In	49	114.82
Iodine	1	53	126.91
Iridium	Ir	77	192.2
Iron	Pe	26	55.85
Krypton	Kr	36	83.80
Lamthanum	La	57	138.02
Lead	Pb	32	207.21
Lithium	Li	3	6,940
Lutetium	Lu	71	174.99
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.94
Mercury	Hg	80	200.61
Molybdenum	Mo	42	95.95
Neodymium	Nd	60	144.27
Neon	Ne	10	20.183
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.008
Omsimum	O_3	76	190.2
Oxygen	O	8	16,000
Palladium	Pd	46	106.4
Phosphorus	P	15	30.975
Platinum	Pt	78	195.09
Potassium	K	19	39.100

Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.1
Samazium	Sm	62	150.35
Scandium	Sc	21	44.96
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.880
Sodium	Na	11	22.991
Stronzium	Sr	38	87.63
Sulfur	S	16	32.066
Tantalum	Ta	73	180.95
Tellurium te	Te	52	127.61
Terbium	Tb	65	158.93
Thallium	tl	81	204.39
Thorium	Th	90	232.05
Thulium	Tm	69	168.94
Tin	Sn	50	118.70
Titanium	Ti	81	204.39
Tungsten	W	74	183.86
Uranium	U	92	238.07
Vanadium	V	23	50.95
Xenen	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

The S. 1. Units stands for International system of units. It is a standard unit of measurement that is generally accepted. The S. 1. units can be grouped into two (a). base units (b) derived units.

(a) **Base Unit:** The base units are the primary units of measurement which are independent of any other units unlike the derived units. They cannot be derived at by substituting other units.

Base quantity	**Base unit**	**Symbol**
Temperature	Kevlin	K
Time	Second	S
Length	Meter	M
Mass	Kilogram	Kg
Electric current	Ampere	A
Luminous intensity	Candela	Cd
Amount of substance	Mole	Mol

(b) **Derived Units**

Derived units as the name sound are the units that are obtained by substitution of two or more of base units. They are combination of two or more primary units.

Derive quantity	**Substituent**	**Unit**
Volume	Length X breadth x height	m^3
Area	Length x breadth	m2
Density	Mass/volume	Kg/m^3
Acceleration	Length /$(time)^2$	m/s^2
Force	Mass x acceleration	$Kgms^2$. Newton (N)
Work	Force x distance	Kgm^2/S^2 x Joule (J)
Pressure	Force ÷ distance	$Kgm^2/S^2 = Nm^2$
Electrical charge	Current x time	As = Coulomb = C
Power	Work ÷ time	Kgm^2/S^3 = J/S

UNIT FACTORS

Unit factors are identical numerators and their corresponding denominator which are used for conversion from one unit to another of equal value.

UNIT FACTORS FOR TIME

Unit	60s	60min	24hrs	7 days	4 weeks	52 weeks	365 days
Equivalent	I mins	I hrs	I day	I week	1 month	I year	1 year

UNIT FACTORS FOR DISTANCE OR LENGTH

Unit	10^{-2}m	10^{-1}m	10^{-3}m	10^{-9}m	10^{-6}m	10^{-10}m
Equivalent	Icm	I dm	1mm	Inm	1μm	1A°

UNIT FACTORS FOR MASS

Unit	1	10^{3}g	10^{-3}g	10^{-6}g	10^{-9}g
Equivalent		1kg	1mg	1 μm	1ng

UNIT'FACTORS FOR PRESSURE

Unit	769mmHg	1.01xl0^{5} Nm^{-2}	14.69psi	1 Nm^{-2}	ImmHg	10^{5}Nm^{-2}
Equivalent	latm	I atm	1 atm	IPa	1 Torr	1 bar

UNIT FACTORS FOR ENERGY

Unit	10^{-7}J	4.184J	1.602 x 10^{-19}J
Equivalent	1 erg	I cal	leV

UNIT FACTORS FOR VOLUME

Unit	1μL	1dm^{3}	1L	1dm^{3}
Equivalent	10^{-9}m^{3}	1L	1000ml	1000cm^{3}

APPLICATION OF SCIENTIFIC CALCULATORS

Function	Examples	Press 1st	Press 2nd	Press 3rd	Press 4th	Press 5th	Answers
-x	-15.6	15.6	+/-	-	-	-	-15.6
√x	√28	28	√	-	-	-	5.292
1/x	1/30	30	30	1/x	-	-	0.0333
x^n	3^5	3	x^y	5	-	-	243
$X^{1/n}$	$6^{1/3}$	6	Shift	x^y	3	-	1.817
Log_x^{10}	Log_{28}^{10}	28	Log	-	-	-	1.4471
1nx	1n25	25	Ln	-	-	-	3.219
e^x	e^3	3	Shift	1n	-	-	20.086
Antilogx	Antilog 3.75	Shift	Log	-	-	-	5.623
Sin 45	Sin 45	45	Sin	-	-	-	0.7071

Note: Some calculators may differ from what we stated above, so you are expected to get familiar with the mode of operation of your own calculator.

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