Gwali notes for

Physical sciences

Name

Department

Date

COURSE OUTLINE

- Gases: The gas Law, the kinetic theory of gases, elementary derivation, deduction of th gas laws, molecular speeds.

  Derivations from ideal gas behaviour

  Van der waal's modification
- Liquefaction of gases

  Phase transition and phase equilibrium (one component system).
- Solutions: Brief survey of properties of solutions (vapour pressure, boiling point, Freezing point).

  Ideal solution, Raoult's and Henry law.
- Real Solution. Colligative properties and molecular weight determination by vapour pressure and freezing point lowering, boiling point elevation and osmotic pressu measurement.
- Aspect of 1st law of thermodynamics, thermo chemistry, chemical equilibrium, chemical energy Entropy, Free energy and spontaneous changes
- Ionic equilibria, Acids, Bases and indicators Buffers.

- Elementary chemical Kinetics; Reaction rate and factors affecting it.
  Experimental rate law, order; Molecularity and Stoichiometry Zero and 1st order reactio
- Effects of temperature on reaction rate.
  Arrhenius equation, collision and transition state theory (Qualitative treatment).

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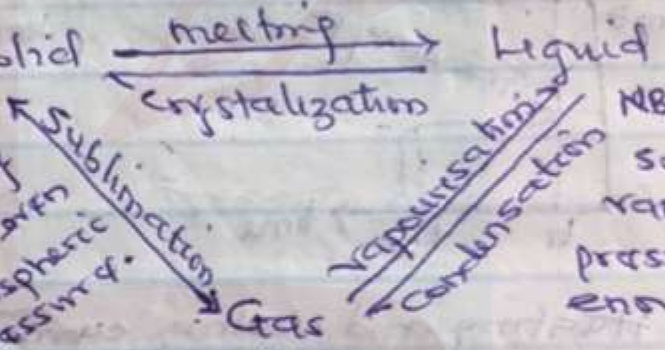
1/7/2019

PHASE EQUILIBRIA

There are three states of matter which can also be refer to as three phase of matter

a Solid state / Phrase
b Liquid state / Phrase
c Gas state / Phrase

These three phrase of matter can change from one state to another due to temperature



NB: Not all crystalline solids change into liquid on heating some like solid CO_2 changes directly into vapour even at atmospheric pressure.

NB; almost all solids can vaporised if the pressure is low enough.

Note; Evaporation occurs at all temperature.

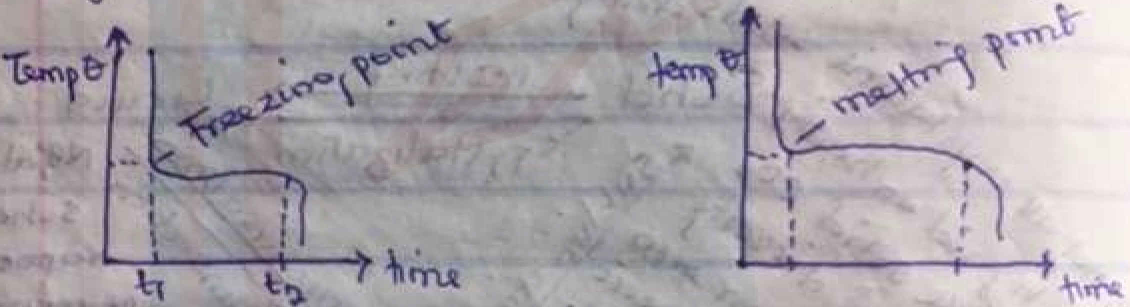
EQUILIBRIUM PHASE CHANGES

An isothermal process occurs at a constant temperature.

Vapourization, crystallization and sublimation are isothermal similarly, the processes of melting, crystallization and condensation are isothermal this is because during heating, the forces are overcome by heat. The added heat

The process of vaporization of a solid followed by its recondensation is called. Sublimation

is used to break intermolecular forces in a particular phase before phase change. Therefore, the temperature doesn't reflect during breaking of bonds. On the other hand, during condensation, crystallization or solidification, the heat removed from this system during cooling is compensated for by the heat released in the process.



Heating and cooling curve of a substance.

The liquefaction temperature of a substance is same as boiling temperature while freezing/melting temperature are the same.

LIQUEFACTION OF GASES

The temperature at which gas molecules coalesce to form a liquid is called **LIQUEFACTION TEMPERATURE**.

- Low temperature is necessary for liquefaction because it is needed to slow the gas molecules thus enhancing intermolecular attractive force that draws the molecules together to form a Liquid.

The process of vapourisation, crystallization and sublimation are equilibrium processes which are controlled by temperature and pressure condition

- High pressure promotes liquefaction as distance ~~distance~~ between molecules are smaller and intermolecular forces become greater. Thus, the higher the pressure of a gas, the easier it is to liquefy it and the higher its liquefaction temperature.

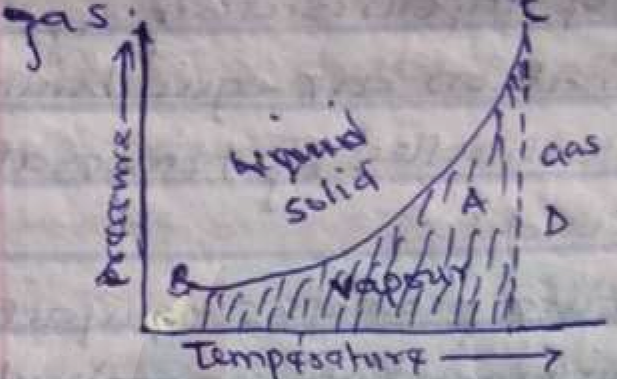
CRITICAL CONSTANT & GAS LIQUEFACTION

Above the critical temperature (T_c) the attracting forces cannot produce liquefaction no matter how high the pressure.

NB. The minimum temperature above which a gas cannot liquify no matter how high the pressure is called **CRITICAL TEMPERATURE**.

This phenomenon was demonstrated for carbon dioxide in 1869 by Andrews who showed the critical temperature of CO_2 to be 31°C

Above T_c, the substance can exist only as a



BC↑ = ~~Liquid~~ solid
A = vapour
C = Critical temperat
D = Gas

Any point in the shaded area, the substance can be liquefied (ie a point on the curve BC can be reached) by raising the pressure sufficiently or lowering the temperat sufficiently or both.
At a temperature above Tc eg at D, the substance is a gas and cannot be liquefied by raising pressure because the Liquid boundary cannot be reached.
Temperature must first be lowered to at least critical temperature.

In general, any gas may be liquefied by a suitable combination of cooling (lower temperature) and compression (higher pressure).
Substances with Tc above room temperatur eg water, sulphur dioxide exist in the

atmosphere as vapour and are liquefiable by compression only.

Substances with T_c below room temperature eg O_2 and H_2 exist as gas in the atmosphere and can only be liquefied by first cooling followed by compression.

Substances	T_c (°C)	P
Water H_2O	374	217.7
Sulphurdioxide SO_2	157	
Carbondioxide CO_2	31	73.0
Oxygen O_2	-119	49.7
Nitrogen N_2	-147	33.5
Hydrogen H_2	-240	12.8
Helium, He	-267.8	2.3

NB Gases are compressible because of their intermolecular spaces ie ~~they~~ have empty spaces inbetween molecules.

The pressure which must be exerted to produce liquefaction at the critical temperature is known as CRITICAL PRESSURE.

GENERAL METHODS OF COOLING A GAS.

There are three (3) methods of cooling a gas.

a By lowering temperature by immersion in a colder substance.

b By expansion against a pressure, causing th gas to do external work at the expenses o its kinetic energy, thus a decrease in the kinetic energy of the gas molecules is observ as a lowering of the temperature.

c By free expansion (ie against vacuum) involving no external work.

Cooling generally occurs here because as the gas expands, it molecules must spread out and to do this, they must do the work of overcoming their own mutual attraction and this again is done at the expenses of the gas internal energy and hence the observed cooling effect.

The colder the gas, the greater the forces o attraction and the greater is the cooling effe of expansion

Also, the more rapid the expansion, the less opportunity for heat to flow in from the surroundings and hence the greater the coolin of gas itself.

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INVERSION TEMPERATURE (T_i)

The temperature below which the expansion of gases brings about cooling. This temperature is about six times the critical temperature of most gases. Most inversion temperature of gases are above room temperature and for this reason, the temperature will bring about cooling however the compression of such gases will bring about warming.

NB; Expansion of gases = cooling
Compression of gases = warming

Gases like Hydrogen, He have T_i below room temperature however, when they expands they bring about warming this is because their intramolecular attractive forces are absent.

The amount of heat require to evaporate one mole of a liquid at it boiling point is called MOLAR LATENT HEAT OF EVAPORATION
It is also the amount of heat that must be supplied to just keep the temperature constant for one mole of liquid to

evaporate.

Example.

If 39.2 KJ/mol of heat is required to evaporate one mole of C_2H_5OH (ethanol) How much heat is required to evaporate 75g of it

Solution

C_2H_5OH - 46g/mol

46g = 39.2

$$75g = \frac{75 \times 39.2}{46} = 63.9 \text{ KJ/mol}.$$

When the rate of evaporation

At Equilibrium, this liquid becomes saturated with the vapour on top and this vapour on top exert pressure on the liquid below. That pressure which the vapour exert on the liquid below at equilibrium is called the "saturated vapour pressure of the liquid.

Saturated vapour pressure of the liquid is dependent on:-

1. Temperature

ii Nature of the liquid

It does not depend on the volume of the liquid neither does it depend on the space above the liquid.

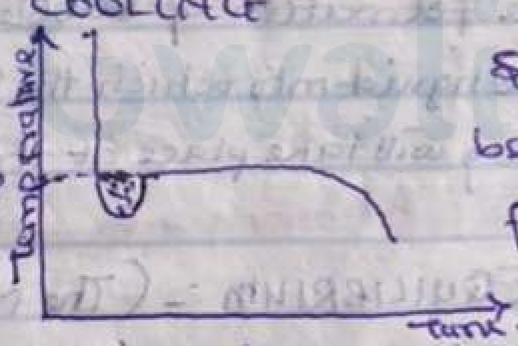
The more volatile a liquid is, the higher the equilibrium vapour pressure due to increase in escape tendency of the molecules of the liquid

Increase in temperature brings about increase in vapour pressure.

NB The vapour pressure curve terminates at the critical temperature.

SUPER COOLING & SUPER HEATING.

Cooling a liquid below its cooling point without it becoming a solid is known as SUPER COOLING



Supercooling arises because of the failure of the liquid particles to line up in characteristic crystalline arrangement and since heat continues to be removed from the system without crystallization occurring, the temperature falls below the freezing point.

The process of heating a liquid in a vessel open to the atmosphere above its boiling point is called SUPERHEATING.

This is as a result of increaced pressure arising from liquid head when the heat applied is well below the surface of the liquid. Consequently, the first bubbles of vapour will not form until the temperature is well above the boiling point. When they do form they grow very rapidly and the excess pressure ~~that~~ often bumps the liquid right out of the vessel. This can be prevented by introducing chips of porous earthenware into the liquid which will enable the formation of bubbles of air inside the body of the liquid into which the liquid will evaporate and boiling will take place at the proper temperature

PHASE EQUILIBRIUM :- (The Number of Phase (P))

A phase is a system or part of a system that is uniform throughout in chemical composition

and physical state, and it is said to be homogeneous.
For instance, ice, liquid water and water vapour constitute three different phrases of water namely solid, liquid and gaseous phases, respectively, as each is characterised by chemical and physical uniformity.

Similarly, a solution of two chemical species (eg sodium chloride and water) is considered as one phrase at macro level. A gaseous mixture will constitute a one phase system because gases are completely miscible.

A system consisting of more than one phrase is said to be heterogeneous.
Solids which have different chemical composition or the same chemical composition but different crystal structure constitute different phase. Example:- a mixture of rhombic (Sr) and monoclinic (Sm) sulphur will form two phrase because they have different crystal structures.

- Number of Component (c): This is denoted by C and it is defined as the least number of independent chemical species necessary to describe the composition of each and every phase of the system.

- The number of degree of freedom (F) is defined as the minimum number of intensive variables that must be specified to find the values of all the remaining intensive variables.

CONDITIONS FOR EQUILIBRIUM BETWEEN PHASES

For each phase to be in equilibrium in a multiphase system, it is necessary that the following equilibrium conditions are fulfilled

1 Thermal equilibrium

The temperature of all the phases must be the same otherwise heat would flow from one phase to another

2 Mechanical equilibrium

This means that all the phases are under the same pressure otherwise one phase would increase in volume at the expense of another

3 Chemical equilibrium

The chemical equilibrium, the chemical potential of any component is the same in all phases at equilibrium

8/7/2019.

THE PHASE RULE

This rule, first derived by J. Willard Gibbs (1878) gives the degree of freedom (F) of a system with C components and P phases.

According to the rule:-

$$F = C - P + 2 \quad or \quad F + P = C + 2$$

I The greater the number of components in a system, the greater is the degree of freedom or variance for a fixed number of phases

II The greater the number of phases the smaller is the number of variables such as temperature, pressure and concentration that must be specified to describe the system completely.

III For a given number of components, the number of phases ($P = C - F + 2$) is a maximum when the variance is zero. For one component system, the maximum number of phases at equilibrium is 3, and for two components, it is 4 etc

PHASE RULE FOR A ONE COMPONENT SYSTEM

For a one component system, the phase rule is given by $F = 3 - P$. The maximum degree of freedom is 2. The maximum number of phrases is 3. The separate phases are however the same substance in different physical state or different crystalline modifications.

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GASES: GAS LAW.

Definite shape and volume - Solid
No definite shape but definite volume - Liquid
No definite shape and volume - Gases

Gases has a common property which is the reason for gases law that governs them. Variables that affects gases state include;-

i Temperature
ii Pressure
iii Volume
iv Amount (n)

Law that governs Gases include;-

i Boyle's law

$V \propto 1/P$ at constant temperature & amoun ii Charles law

$V \propto T$, Pressure & amount is constant

iii Avogadro's law

$V \propto n$, Temperature & pressure constant

iv Gay Lussac's law

$P \propto T$, volume & amount constant

v Dalton law

$P_T = P_1 + P_2 + P_3$ - - - - - - -

vi Graham's law

$R \propto 1/\sqrt{d}$ or $R \propto 1/\sqrt{m}$

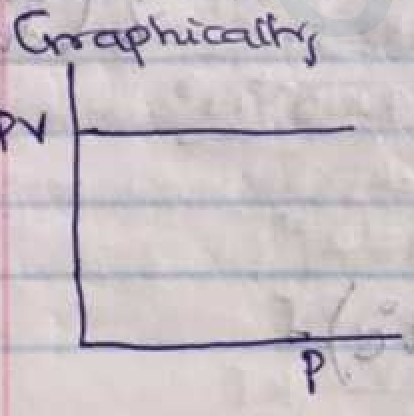
BOYLES' LAW

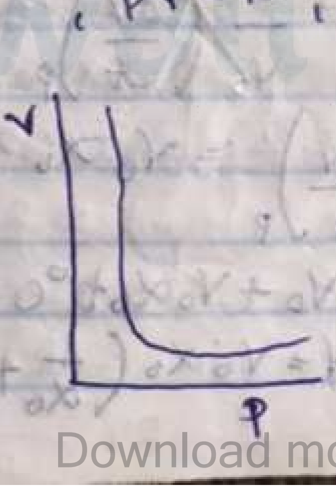
Boyles law states that the volume of a given mass of gas is inversely proportional to the pressure provided that the temperature remains constant

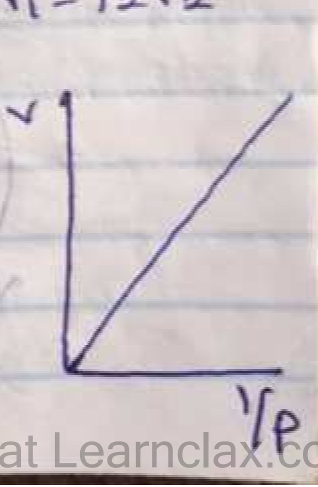
$V \propto 1/P$, (n, T)

$V = K/P$, $PV = K$, $P_1V_1 = P_2V_2$

Graphically







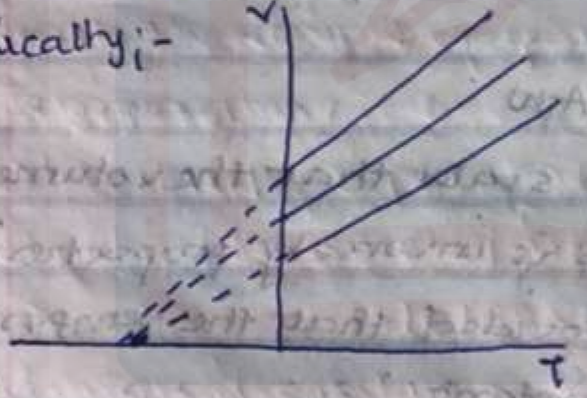
Limitation; There is limitation to low temperature and high pressure because the attraction between molecules is highly pronounced and they becomes liquid

CHARLES LAW

It states that the volume of a given mass of gas is directly proportional to the absolute temperature provided the pressure remains constant.

$V = a + bt$

Graphically;-



Mathematically,

Intercept $= V_0$

Slope $= \left(\frac{\delta V}{\delta t}\right)_P$

$V = V_0 + \left(\frac{\delta V}{\delta t}\right)_P t$

co-efficient of thermal expansion at 0°C =

$\frac{1}{V_0}\left(\frac{\delta V}{\delta t}\right)_P$ ie $\alpha_0 = \frac{1}{V_0}\left(\frac{\delta V}{\delta t}\right)_P$

$\left(\frac{dV}{\delta t}\right)_P = V_0\alpha_0$

$V = V_0 + V_0\alpha_0 t°C$

$V = V_0\alpha_0\left(\frac{1}{\alpha_0} + t°C\right)$

$$\frac{1}{\alpha_0} = 273.15$$

$$\therefore 1/\alpha_0 + t^\circ C = T$$

$$v = v_0 \alpha_0 T$$

$$\frac{v_1}{T_1} = \frac{v_2}{T_2}$$

Limitations: There is limitation to low temperature and high pressure because the attraction between molecules is highly pronounced and they become liquid.

AVOGADRO'S LAW

Avogadro's law states that equal volume of all gases under the condition of temperature and pressure contain the same number of molecules.

$V \propto n$ (T, P constant)

$n = N_A = 6.02\times10^{23}$

at stp, 1 mole of gas ~~is~~ 6.02×10^{23} is $22.4 dm^3$

GAY LUSSAC'S LAW

The pressure of a constant volume of gas varies directly at absolute temperature

$P \propto T$ (v, n)

$$P = KT$$

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

Relationship

$v \propto 1/P$ (T, n)

$v \propto T$ (P, n)

$v \propto n$ (T, P)

$$v \propto \frac{nT}{P}$$

$$v = \frac{RnT}{P}$$

$$PV = nRT$$

Universal gas law is a constant that relate with the volume of gas at a standard temperature:

Standard Temperature = 273K

Standard Pressure = 1 atm = 769mm Hg = 760tor = 101325Pa or Nm^{-2} = 101Kpa

Universal gas law = $R = \frac{PV}{nT}$

$$R = \frac{1atm \times 22.4L}{1mol \times 273K} = 0.082\text{---}\ atm\ lit\ mol^{-1}K^{-1}$$

$$R = \frac{101325Nm^{-2} \times 22.4 \times 10^{-3}m^3}{1mol \times 273K}$$

$$R = 8.314 Jmol^{-1}K^{-1}$$

Modification :- $PV = nRT$

$$PV = \frac{mole}{molarmass}RT$$

Molar mass of a substance can be calculated by using i—

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

where, M = Molar mass

m = mole

δ = Density

V = volume

P = Pressure

T = Temperature

$$PMV = mRT$$

$$PM = \frac{mRT}{V}$$

$$PM = \delta RT$$

GRAHAM'S LAW

It states that the rate of change/ diffusion of gas is inversely proportional to the square root of its density.

$$R \propto 1/\sqrt{\delta} \quad , \quad R \propto 1/\sqrt{m}$$

15/7/2018 · KINETIC MOLECULAR THEORY OF GASES

i. Gases consists of very tiny and identical molecules that are far apart each other.

ii. The molecules of gases are in rapid random and continuous motion colliding frequently with each other and the walls of the containers, they move in straight lines in between collisions

iii. The collision between the molecules of gases are perfect elastic ie there is no loss in energy rather they transform energy from one molecule to another

iv. Gases travels in a straight line after collision because there is lack of attraction between the gas molecules

v. The gases have no volume. They only occupy the space of the container in which they contain.

vi. The average Kinetic Energy of the translation of the molecule is directly proportional to the absolute temperature ie the motion of gases depend only on their temperature.

DEVIATIONS OF THE GENERAL (IDEAL) GAS LAW.

* Vander waal's modification of gas law.

- Addition of pressure increases the attraction between gas molecules causing it to liquify.
- Pressure of a gas is as a result of collision between the molecules and the wall.

Attraction between gas molecule is internal pressure and it is inversely proportional to the square root of the volume.

$$P_{int} \propto \frac{n^2}{V^2}$$

$P_{int} = \frac{an^2}{v^2}$, a = vanderwaal force of attraction (constant) between gas molecule.

The more the attraction between the gas molecule, the more the pressure.

$P_{int} = (P + an^2/v^2)$

- The volume occupied by a real gas is smaller than that occupied by an ideal gas and it is known as EXCLUDED VOLUME.

The excluded volume is directly proportional to the amount.

$V_{ex} \propto n$ b = Vander waal constant in relations to size.

$V_{ex} = bn$

$V_{int} = (v - bn)$

Modification of the gas equation

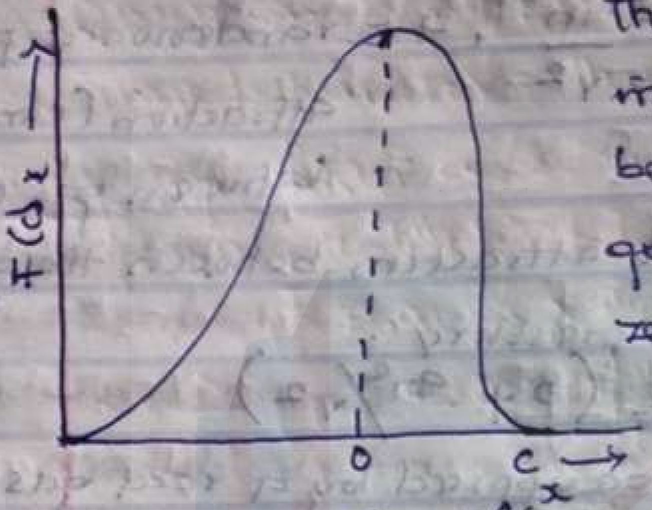
$(P + an^2/v^2)(v - bn) = nRT$

$P + a/\bar{v}^2 (\bar{v} - b) = RT$

At lower pressure, the volume of gas are far apart so that it will be negligible and at higher temperature, the volume of the gas will increase

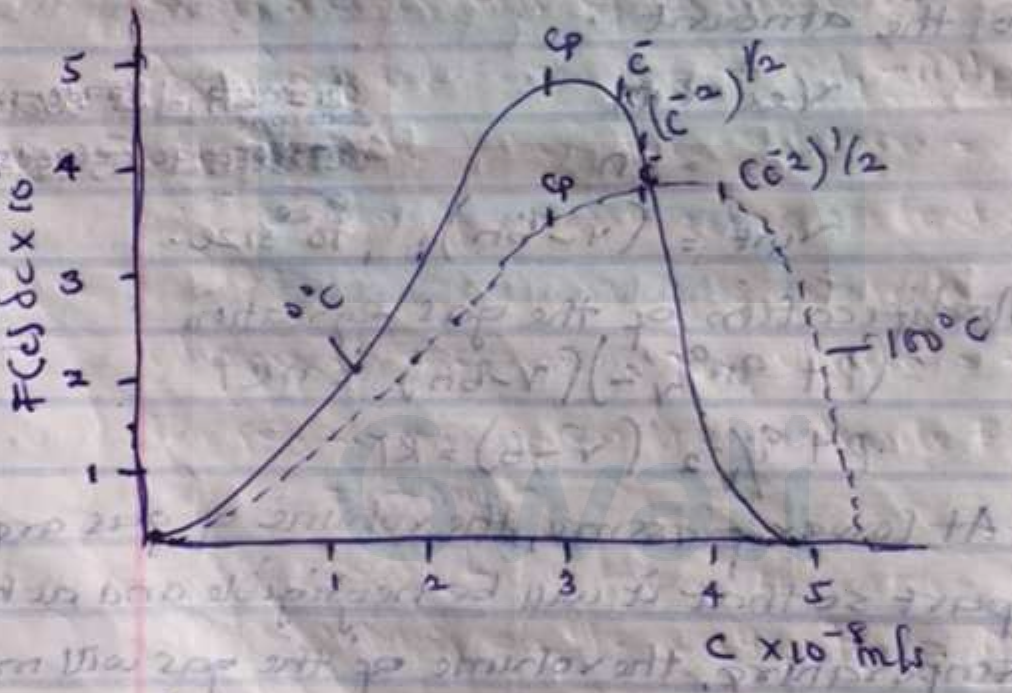
Note:- Pressure and volume is modified by vanderwaal.

DISTRIBUTION OF MOLECULAR SPEED & VELOCITY



The most probably velocity in the x value is zero (0) because the probability of going both direction is zero.

$$f(x)\delta c = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mc^2}{2kT}} \cdot 4\pi c^2 \delta c$$



3 ways of expressing velocity (speed).

1. The most probable speed (Cp) is the speed with the highest speed acquired by most of the molecu

$$C_p = \sqrt{\frac{2KT}{m}} = \left(\frac{df(c)\delta c}{dc}\right)_{c=0}$$

where K is boltzman constant .

$$= \sqrt{\frac{2RT}{m}}, \quad K = \frac{R}{N_A} = \frac{8.3147 mol^{-1}K^{-1}}{6.023\times10^{23}}$$

2. The arithmetic mean speed $(\bar{C})$: this is the total of all speed divided by the number .

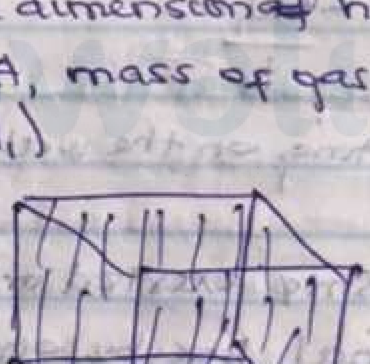
$$\bar{C} = 1/N\sum_{i=1}^{N} c_i = \sqrt{\frac{8KT}{\pi m}} = \sqrt{\frac{8RT}{\pi m}}$$

3. Root mean square speed (Rms) $(\bar{C}^2)^{1/2}$:- Summation of all the square divided by the total number

$$(\bar{C}^2)^{1/2} = \sqrt{\bar{C}^2} = 1/N\sum_{i=1}^{N} c_i^2 = \sqrt{\frac{3KT}{m}} = \sqrt{\frac{3RT}{m}}$$

17/7/2019 CALCULATING THE PRESSURE OF GASES .

Considering a gas molecule in a rectangular box in one dimension having a length L, and area A, mass of gas m, and initial velocity (u_1)



Distance covered during collision = $2L$

Time taken for collision = $\frac{2L}{u_1}$ $\left(\frac{\text{distance}}{\text{velocity}}\right)$

Recall:- velocity = $\frac{\text{Distance}}{\text{Time}}$

$$F = \text{mass} \times \text{Acceleration}$$

$$= m \times \frac{du}{dt}$$

$$= \frac{d(mu)}{dt}$$

Initial momentum of the molecule = mu_1

Final momentum of the molecule = $-mu_1$

Average momentum = $-mu_1 - mu_1 = -2mu_1$

If the time taken for collision = $\frac{2L}{u_1}$

∴ Number of collision per second = $\frac{u_1}{2L}$

Change in momentum per collision = $-2mu_1\left(\frac{u_1}{2L}\right)$

The force acting on the molecule F_1

$$= -\frac{mu_1^2}{L}$$

Force acting on the wall, $F_w = \frac{mu_1^2}{L}$

The pressure exerted on the wall of the one dimensional box by one gas molecule:-

$$P_1 = \frac{F_w}{A}$$ (Force of the wall per unit Area)

$$P_1 = \frac{Mu_1^2}{L \times A}$$

L × A = V

L = length, A = Area

$$\therefore P_1 = \frac{mu_1^2}{V}$$

V = volume.

The pressure exerted by the whole gas molecule on the wall of the one dimensional box is Px

$$P_x = \frac{m(u_1^2 + u_2^2 + u_3^2 + \cdots)}{V}$$

$$u_{Avg}^2 = \frac{u_1^2 + u_2^2 + u_3^2 + \cdots}{\text{Number of } u}$$

$$N(u^2) = u_1^2 + u_2^2 + u_3^2 + \cdots$$

$$P_x = \frac{Nm(u^2)}{V}$$

Considering the probability of the gas molecule moving randomly in the 3 dimensional box is 1/3.

$$\therefore P = \frac{\frac{1}{3}Nm(u^2)}{V}$$

$$K.E = \frac{1}{2}mu^2$$

$$P = \frac{\frac{2}{3}Nm(u^2)}{2V}$$

$$P = \frac{2/3 N(E)}{V}$$

$$PV = 2/3 N(E)$$

Recall; - $PV = nRT$

$$nRT = 2/3 N(E)$$

$$\frac{N}{n}(E) = \frac{3}{2}RT$$

$$n = \frac{N}{N_0} \left(\frac{\text{Number of particle}}{\text{Avogadro's constant}}\right)$$

$$N_0 = \frac{N}{n}$$

$$N_0(E) = 3/2 RT$$

N = Number of gas particle
n = amount of gas particle
E = Kinetic Energy

22/7/2015

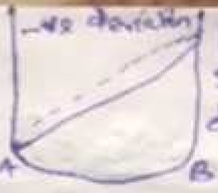
REAL SOLUTION AND COLLIGATIVE PROPERTIES

A non ideal gas is known as a real solution. Most solutions does not obey Raoult's law. They show deviation from ideality.

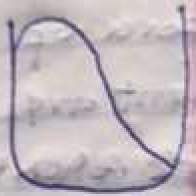
Deviation is of two (2) types - Namely; -

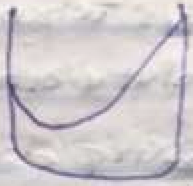
i. Negative deviation
ii. Positive deviation.

+ve (positive) deviation increase slightly with maximum



Negative deviation can slope gently or go through definite minimum deviation


+ve deviation


-ve deviation

* Hexane and Heptane have similar forces so the force of attraction is the same so it's an ideal solution.

* Trichloromethane & propand held together by dipole forces. The forces are not the same because the electronegative becomes different so, it is an not ideal solution. It is a real solution.

NB:- The more the solute solvent escapes, the more vapour pressure.

ORIGIN OF NON-IDEAL (REAL) SOLUTION.

The origin of non ideal behaviour lies in the relative strength of the interaction between the molecules of the solvents and solute.

When the attractive forces between the solvent and solute are weaker than those between the solute molecules or solvent molecules, neither the solute or the solvent particles are held tightly in the solution as they are in their pure substances. It leads to positive deviation as they escape more causing increase in vapour pressure.

Vapour pressure in solution is higher than that of their pure form in this cause.

Vapour pressure increases when the force of attraction holding the solute and solvent are weak while vapour pressure decreases when the force of attraction holding the solute and solvent are strong

Ethanol + water = +ve deviation with maximum

Methanol + water = negative deviation

Tetrachloromethane + Propanol = -ve deviation + minimum

Relative Attraction	ΔH Solution	To change when solution is formed	Deviation from Raoult's Law	Examples
A-A, B-B = A-B	0	None	ideal solution	Benzene, chloroform (heptane, hexane)
A-A, B-B < A-B	Negative exothermic	Increase	Negative	acetone/water
A-A, B-B > A-B	Positive Endothermic	Decrease	Positive	ethyl, alcohol water

COLLIGATIVE PROPERTIES

Colligative properties of a solution are the properties that depends on the number of moles present and not on the nature of the solution present

It helps to tell us the quantify of solution ·

colligative properties used to determine the molecular weight

nclude:-

I Vapour pressure lowering

II Freezing point depression

III Boiling point Elevation

IV Osmotic pressure

These four can be used to determine the molar weight (molecular weight) of a solution

- Vapour pressure lowering:- This comes from Raoult's law. It states that the vapour pres P_1 of a solvent in solution is equal to the vapour pressure of the pure solvent multiply by it mole fraction.

$$P = X_1 P^\circ \quad ------ \quad (1)$$

X_1 = mole fraction of solvent

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

n_1 = moles of the solvent

n_2 = moles of the solute

$X_1 = (1 - X_2)$ NB $X_1 + X_2 = 1$

$P = (1 - X_2)P^\circ$ X_2 = mole fraction of solute.

$P = P^\circ - PX_2$

$PX_2 = P^\circ - P$

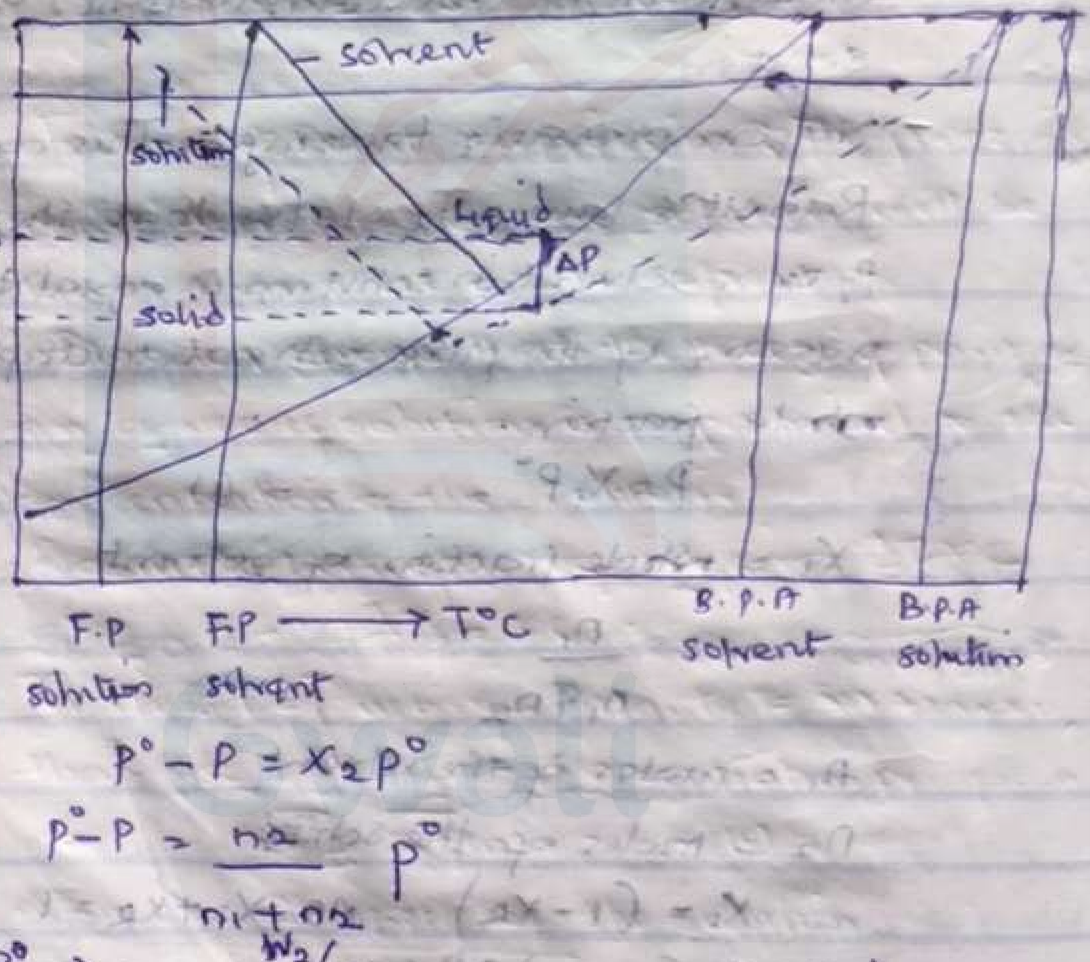
$$\therefore \; P - P^\circ = X_2 P^\circ$$

$$\Delta P = X_2 P^\circ \; ------ \; (2)$$

ΔP = vapour pressure lowering

24/7/2019

At any point in time, the vapour pressure of a solvent is always greater than the vapour pressure of the solution



$$P^\circ - P = X_2 P^\circ$$

$$P^\circ - P = \frac{n_2}{n_1 + n_2} P^\circ$$

$$\frac{P^\circ - P}{P^\circ} = \frac{w_2/m_2}{\frac{w_1}{m_1} + \frac{w_2}{m_2}} \; ------ \; (3)$$

The solution must be very dilute for an ideal solution implying that the amount of solute will be insignificant compared to the amount of solvent.

$$\frac{P^0 - P}{P^0} = \frac{w_2/m_2}{w_1/m_1}$$

$$\frac{P^0 - P}{P^0} = \frac{w_2}{m_2} \times \frac{M_1}{W_1}$$

P^0 = vapour pressure of solvent

P = vapour pressure of solution

Example:-

The vapour pressure of a solution containing 20g of a non-volatile solute in 200g of water at 27° centigrade is 27.4 torr. Calculate the molar mass of the solute assuming that the solution behaves ideally, the vapour pressure of water at this temperature is 28.065 torr.

Solution

$w_2 = 20g$

$w_1 = 200g$

$P = 27.4$ torr

$P^0 = 28.065$ torr

$M_1 = H_2O = 2+16 = 18$

$$\frac{P^0 - P}{P^0} = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$$

$$M_2 = \frac{W_2}{W_1} \times M_1 \times \frac{P^0}{\Delta P\ (P^0 - P)}$$

$$M_2 = \frac{2g \times 18\,g/mol \times 28.065\,torr}{200g \times (28.065 = 27.46)\,torr}$$

$$M_2 = 75.97\,g\,mol^{-1}$$

- Freezing Point depression: The freezing point depression of the solution will be lower than that of the solvent.

Blagden shows that the freezing point of of an aqueous solution is proportional to the concentration of the solution

Raoult's brought the idea of $\Delta T_f \propto C$

$$\Delta T_f = KC$$

Instead of using Molarity = Gramdm^{-3}, he then use molality = concentration per gram.

i.e $\Delta T_f = Km$ ---- (1)

where m = Molality of the solution

$$\Delta T_f = K_f \frac{W_2}{M_2} \times \frac{1000g}{W_1}$$

T_f is the freezing point of depression.

K_f = freezing point constant

T_f is equivalent to $\frac{\text{FP of solvent}}{\text{FP of solution}}$.

∴ ΔT_f = Freezing point of solvent − FP of solut

Example:-

The freezing temperature of benzene is 5.40°C. A solution of 1.15g of Naphthalene in 100g of benzene has a freezing point of 4.95°C calculate the molecular weight of Naphthalene if the K_f is 5.12° molar^{-1} (5.12 degree/molar)

Solution

Fp of solvent = 5.4°C

$W_2 = 1.15g$ $\quad \Delta T_f = 5.40°C - 4.95°C = 0.45dg$

$W_1 = 100g$ $\quad \Delta T_f = \frac{K_f \; W_2 \times 1000g}{M_2 W_1}$

$M_2 = ?$

$$M_2 = \frac{K_f \times W_2 \times 1000g}{W_1 \; \Delta T_f}$$

$$M_2 = \frac{5.12dgmol^{-1} \times 1.15g \times 1000g}{100g \times 0.45dg}$$

$$M_2 = 180.8g$$

29/2/19 - Boiling Point Elevation: The boiling point of a solvent is more than that of a pure solution.

$\Delta T_b = K_b m$

K_b = boiling point elevation constant

$$\Delta T_b = K_b \frac{w_2}{M_2} \times \frac{1000g}{w_1}$$

w_2 = Solution

w_1 = Solvent

$$M_2 = \frac{K_b}{\Delta T_b} \times \frac{w_2}{w_1} \times 1000$$

Example:-

1 What is the normal boiling point of a solution containing 18g of $C_6H_{12}O_6$ dissolved in 100g of water. K_b = 0.45 degmol

Solution

$w_2 = 18g$

$w_1 = 100g$

M of $C_6H_{12}O_6$ = 12×6 + 1×12 + 16×6 = 180g.

K_b = 0.45 degmol

ΔT_b = ?

$$\Delta T_b = \frac{K_b \times w_2 \times 1000}{M_2 \quad w_1}$$

$$\Delta T_b = \frac{0.45 \times 18 \times 1000}{180gmol^{-1} \times 100}$$

ΔT_b = 0.45deg.

ΔT_b = Boiling point of solution − Boiling point of solvent

$0.45 = x - 100$

$x = 0.45 + 100$

$x = 100.45°C$ //

2. The boiling point of benzene is raised from ~~it~~ it normal value of 80.1 deg, 82.4 deg by the addition of 13.76g of biphinil ($C_6H_5C_6H_5$) to 100g of benzene. What is the boiling point elevation constant according to the provided data?

Solution

~~w_1 = 80.1 deg~~ $w_1 = 100g$

Boiling point of solvent = 80.1°C

Boiling point of solution = 82.4°C

ΔT_b = Boiling point of soln − Boiling point of solvent

ΔT_b 82.4°C − 80.1°C

$\Delta T_b = 2.3°C$

$$M_2 = \frac{K_b}{\Delta T_b} \times \frac{w_2}{w_1} \times 1000$$

$$\cancel{\Delta T_b =} \; K_b = \frac{\Delta T_b \times M_2 \times w_1}{w_2 \times 1000}$$

$\Delta T_b = 2.3°C$ $w_2 = 13.76g$

$M_2 = C_6H_5C_6H_5 = 12\times6 + 1\times5 + 12\times6 + 1\times5 = 154g$

$w_1 = 100g$

$$K_b = \frac{2.3°c \times 154 \times 100}{13.76 \times 100}$$

$$K_b = 2.574° mol^{-1}.$$

∴ The boiling constant (K_b) from the provided data is $2.574° mol^{-1}$

- Osmotic Pressure ; When a solution is separat from the solvent by a semi permeable membr which is permeable to solvent not solute, the solvent will flow spontaneously into the solution through the membrane into the solution

The flow of solvent can be prevented by applying a very high pressure know as osmotic pressure

The osmotic pressure (~~π~~) is the excess pressure that must be applied to the soln to enable equilibrium and prevent osmosis

Van't Hoff introduced an equation similar to ideal equation :- $PV = nRT$

$$\pi V = n_2 RT$$

π = osmotic pressure of the solution

V = volume of the solution = volume of the solution

T = Temperature

R = constant with the same value of the general gas constant.

n = number of moles of solute =

when determining the molecular weight of macro molecule with high molecular weight ;-

$$\pi V = \frac{W_2}{M_2} RT$$

$$\pi = C \times \frac{RT}{M_2} \implies \pi = \frac{CRT}{M_2}$$

$$C = \frac{N_2}{V}$$

$$\pi = \frac{N_2 R}{V\ M_2} T$$

Example:-

The osmotic pressure of an aqueous soln of 1g of sucose (342g/mol) per 100cm³ of solution is 0.649atm at 0°c. Calculate the expected osmotic pressure.

Solution (R = 0.082dm³atmmol⁻¹deg⁻¹

$$\pi = \frac{CRT}{M_2}$$

$C = 1g$

$R = 0.082dm^3 atm/mol\ deg^{-1}$

$T = 0$

$M_2 = 342gmol^{-1}$

$$\pi = \frac{w_2}{V_2}\frac{RT}{m_2} = \frac{1}{100} \times \frac{0.082 \times 273 \times 1000}{342}$$

$$\pi = \frac{22386}{34200}$$

$$\underline{\pi = 0.655 atm}$$

31/7/2019

SOLUTION:

~~Solution is :- Homogenous and mixture~~

Solution is homogenous mixture of two or more moleculer or substances. Homogenous mean evenly distributed thing having equal representation of all the component of that system.

Water + sugar (Homogenous solution)

Water + sand (Heterogenous but not a soln.)

Solution can also be defined as the homogenous (evenly distribution) mixture of two or more group of molecules or substance in a system.

Solute + Solvent = Solution

Solute (solid)

Solvent (liquid)

When the solvent used in a solution is water, then it is an aqueous solution. Irrespective of the solvent, the solute should be in a larger quantity i.e the solute should have a higher quantity

TYPES OF SOLUTION

1 Gas - gas solution
2 Gas - Liquid solution. Example:- carbonated drinks
3 Gas - Solid solution Example:- hydrogen and Palladium
4 Liquid - Liquid solution Example Ethanol and water.
5 Liquid - Solid solution
6 Solid - Solid solution Example Alloy.

VAPOUR PRESSURE

This is the ~~force~~ pressure exerted by a vapour when the vapour is in equilibrium with the liquid or solid form or both of the same substance.

The inter-molecular forces in volatile liquid are small compared to non-volatile liquid meaning the inter molecular forces in non-

volatile liquid are large.

When a liquid is heated, it molecule obtain kinetic energy to overcome the forces holding them in the liquid and escape into the gaseous phase.

By doing, so, they generate a population of molecule in vapour phase above the liquid that produces the pressure which is known as vapour pressure.

5/8/2019 - BOILING POINT

Low boiling temperature result in increase
5/8/2019 vapour pressure while high boiling temperature result in low vapour pressure.

The temperature at which the vapour pressure equals the atmospheric pressure is known as Boiling Point.

BP = 100°C at 1atm or 760mmHg

NB: The boiling point of water remains constant no matter the heat applied

FREEZING POINT

The temperature at which a liquid solidifies is known as freezing point.

5/8/2019.

IDEAL SOLUTION

Ideal solution is a homogenous mixture of substances that has physical properties linearly related to the properties of the pure components.

The components of an ideal solution is proportional.

RAOULT'S LAW

This states that the vapour pressure of a solvent above a solution is equal to the vapour pressure of a pure solvent multiplied by the mole fraction of the solvent.

In a mixture of 2 liquids A and B of vapour pressure POA and POB respectively, NA moles of A are mixed with NB mole of B

$$P_A = \frac{N_A}{(N_A+N_B)} \times P_{OA}$$

$$P_B = \frac{N_B}{(N_A+N_B)} \times P_{OB}$$

$$P_{total} = P_A + P_B$$

$$P_{OA} \times N_A\left(\frac{n_A}{n_A+n_B}\right) + P_{OB} \times N_B\left(\frac{n_B}{n_A+n_B}\right)$$

Example:-

In a mixture at a given temperature containing 2 moles of A of POA = 60KPa and 1 mole of

B of POB = 30KPa ? Find the vapour pressure of A and B . The total pressure .

$$P_A = \frac{2}{2+1} \times 60KPa$$

$$P_A = 2/3 \times 60$$

$$P_A = 40KPa$$

$$P_B = 1/2+1 \times 30KPa$$

$$P_B = 1/3 \times 30$$

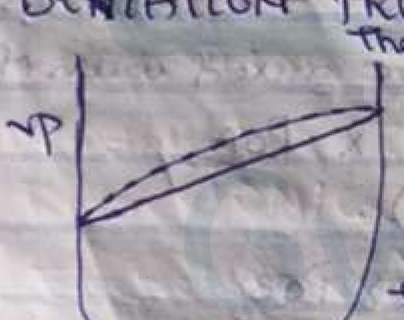
$$P_B = 10KPa$$

$$P_{Total} = P_A + P_B$$

$$= 40 + 10$$

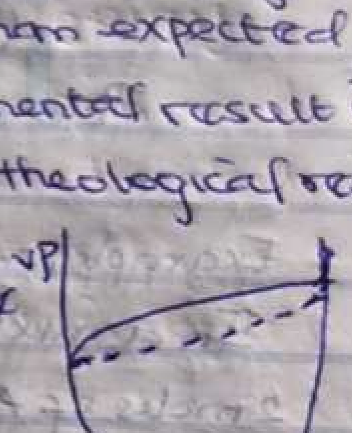
$$= 50KPa$$

7/8/2019 DEVIATION FROM RAOULT'S LAW



The diagram shows positive deviation meaning that the result gotten is more than expected i.e the experimental result is higher than the theological result .

This graph shows negative deviation



HENRY'S LAW

This studies the relationship between pressure and solubility of a gas.

The law states that the solubility of a gas is directly proportional to the pressure

$$c \propto P$$

$$C = KP$$

K = Henry's law constant (m/atm)

c = Solubility of the gas at a fixed temperature in a solvent

P = Pressure (atm).

molarity $\leftarrow M = \frac{ML}{L}$

The solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid (Henry's Law).

Example:-

The solubility of a certain gas in water is $0.745\,gL^{-1}$ at standard pressure. What is it solubility when the pressure above the solution is raised to 4.50atm? The temperature is constant at 20°c.

Solution

$$\frac{S_1}{P_1} = \frac{S_2}{P_2}$$

P_1 = Pressure at initial
S_1 = Solubility at initial
P_2 = Pressure at changed situation
S_2 = Solubility at changed situation

$S_1 = 0.745 gl^{-1}$
$P_1 = 1atm$
$P_2 = 4.50atm$
$S_2 = ?$

$$\frac{S_1}{P_1} = \frac{S_2}{P_2}$$

$$\frac{0.745}{1} = \frac{S_2}{4.50}$$

$$S_2 = 0.745 \times 4.50$$

$$S_2 = 3.35 gL^{-1}$$ //

14/8/2015

IONIC EQUILIBRIUM

Electrolyte are solute which on dissolving dissociates or break up into electrically charged fragments or Ions.

Since ions moving in solution constitute an electric current, then the measurement of electrical conductivity of the solution is all that is required to determine whether a solute dissociate into ions.

Electrolyte however differ in their degree of dissociation in a given solven All electrolyte does not dissociate equall

Example:-

1 In water, HCl, NaOH, NaCl are essentia 100% dissociation into ions. They are known as strong electrolyte because th dissociate completely.

Weak electrolyte like ethanoic acid NH_4OH are not readily dissociated.

FACTORS RESPONSIBLE FOR DISSOCIATION OF ELECTROLITES:

(1) Nature of the solute (3) Conc of $\underline{\delta}$ solute
(2) Nature of the solvent (4) Temperature

NATURE OF SOLVENT:- Remember that we have many solvent since water is not the only solvent then we will remember that the dissociating behaviour of solute in different solvent other than water can be significantly different.

Example;- HCl is 100% dissociative in H_2
but it has less than 1% dissociative in
Benzene. This shows that benzene affects
the dissociation of HCl

CONCENTRATION OF THE SOLUTE;- The %
dissociation of an electrolyte increase as
the electrolyte decreases ie the more dilute
a solution is, the higher the concentration of
dissociation.

Example;- 1 molar solution of ethanoic acid
have 0.4% dissociation while 0.0001 molar
of the same acid in the same ethanoic but
different concentration. This is because when
the molecules breaks up to form ions, the chance
that the ions will come together is very small
at high dilution (ie at infinite dilution all
electrolyte approach 100% dissociation).

From the above statement, the definition of
strong and weak electrolyte is somehow wrong
Therefore, we need to give a common basis to
define them to of more ambiguity.

So using molar solution as the basis, if
the substance in 1 molar solution is highly

dissociated, it is called strong electrolyte but otherwise called weak electrolyte.

TEMPERATURE: In some electrolyte, increase in temperature decreases the dissociate. In some also, decrease in temperature increases the dissociation.

DIFFERENCES BTW DISSOCIATION & IONIZATION

Dissociation is the breakup of substances into fragment or particle which may not or may be charged

dissociation

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$NaCl \rightleftharpoons Na^+ + Cl^-$$ ionization

But it is possible to have ionization without complete dissociation through the formation of Ion pair. This occurs in concentrated solution of strong electrolyte such as NaCl in which Na^+ and Cl^- are formed.

Ions pair are electrically pair, electrically neutral and hence do not contribute to electrical conductivity of the solution.

In concentrated solutions of ionic compound, ionization is always complete but the formation of ion pair leads to incomplete dissociation. On the other hand, in concentrated solutions of molecular electrolyte such as HCl, ionization dissociation could be incomplete in other word equilibrium is formed.

IONIZATION EQUILIBRIUM

- $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

The shift to the left leading to existence of undissociated molecule (product). As a matter of fact, there are very good reasons to believe that in HCl, molecules of hydrogen chloride ~~to~~ exist in infinitely dilute solution

9/8/2019 COMPLETE IONIZATION OF AQUEOUS SOLUTION OF STRONG ACIDS AND BASES

H_2O, H_3O^+, OH^-

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$2H_2O \rightleftharpoons H_3O^+ + OH$$

$$k = \left[\frac{[H_3O^+][OH]}{[H_2O]}\right]$$ At equilibrium this will occur.

If it is recognised that in any dilute water solution, the concentration of water molecules far exceed that of any other species and hence remains perpetually constant and dependent on hydroxyl ion and hydroxonium ion only

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]}$$

$$K \times [H_2O] = [H_3O^+][OH^-]$$

$$K_w = [H_3O^+][OH^-]$$

At 25°C K_w (Ionization constant of water) $= 10^{-14} mol/dm^3$.

This eqn shows that in H_2O solution, the concentration of H_3O^+ and OH^- are inversely proportional

This equation can be used to distinguish between neutral solution acid or base

Neutral solution is a solution when:-

i $[H_3O^+] = [OH^-]$ Neutral solution
ii $[H_3O^+] > [OH^-]$ Acid solution
iii $[H_3O^+] < [OH^-]$ Base solution

When $[H_3O^+] > [OH^-]$, considering the PH scale that $[H_3O^+] > 10^{-7} mol/dm^3$ Acidic

$[OH^-] > 10^{-7} moldm^{-3}$ Basic

$[OH^-] = [H_3O^+] = 10^{-7}$ Neutral

Example;-

Calculate H_3O^+ concentration and OH^- conc in 0.02mol/dm³ HCl.

Note;- Strong electrolyte ionises completely

Solution

$$[H_3O^+] = 0.02\,mol/dm^3$$

$$K_w = 10^{-14}\,mol/dm^3$$

$$[H_3O^+][OH^-] = 10^{-14}$$

$$[OH^-] = \frac{10^{-14}}{H_3O^+}$$

$$[OH^-] = \frac{10^{-14}\,mol/dm^3}{0.02\,mol/dm^{-3}}$$

$$[OH^-] = 0.0000000000005$$

$$[OH^-] = 5\times10^{-13}\,//$$

PH SCALE.

PH can be used to represent decimal numbers and this was propounded by Peter Launcts sorenger in the year.

PH scale is a numerical scale which extends from 0 to 14.

The number on the scale represent the relative acidic of the solution and can be compared to the actual hydrogen ion concentration.

The mid point is 7 at 25°C

A solution that has a PH of 7 is neutral, that less than 7 is acid and that which has a PH greater than 7 is basic

RELATIONSHIP B/W PH & MOLARITY OF ACID SOLN

The hydrogen ion of a solution is 10^{-PH} M

$$H_3O^+ = 10^{-PH} M$$

So, the H_3O^+ conc. of a solution with a PH of 3 is 10^{-3} Molar

For a neutral solution, the H_3O^+ concentration is 1.0×10^{-7} mol/dm^3

$$PH = -\log(10^{-7}) \text{ Neutral solution}$$

$$P = -(-7)$$

$$pH = 7$$

POH represent OH⁻. It is a relative basicity scale which is more convenient to refer to when working with alkaline solution.

It is called the negative logarithm of OH⁻.

$$pOH = -\log_{10}(OH^-)$$

$$[OH^-] = 10^{-POH} M$$

RELATIONSHIP BETWEEN PH & POH

PH + POH = 14 If hydrogen ion concentration multiply by OH^- concentration = 10^{-14}. Taking the logarithm of each specie and multiply all through by -1

That is :- $[H^+][OH^-] = 10^{-14}$

$-\log[H^+] - \log[OH^-] = -\log[10^{-14}]$

Example :-

Calculate the PH, POH and OH^- conc. of 0.001mol/dm³ HNO_3 solution assume that HNO_3 is completely dissociated

Step 1 :- Expressing the conc. HNO_3 in exponential form gives 1.0×10^{-4} since HNO_3 dissociate completely to give 1mole of H_3O^+ for each mole of HNO_3, the conc. of H_3O^+ equals the conc. of HNO_3 dissociate completely, therefore the $H_3O^+ = 1.0\times10^{-4}$

Step 2 :- Substitute the value of H_3O^+ in form PH

$$pH = -\log(H_3O^+)$$

$$pH = -\log(1.0\times10^{-4}) = -\log(1\times10^{-4})$$

$$pH + POH = 14$$

$$POH = \frac{14}{PH}$$

$$POH = \frac{14}{1\times10^{-4}}$$

$$POH = 0.0014$$

$$POH = 1.4 \times 10^{-3}$$

$$K_w = \frac{[H_3O^+][OH]}{[H_2O]}$$

21/8/2019.

MECHANIZATION OF COLOUR CHANGE.

All acid base indicators in common use are weak organic acid or base

$$\underset{\text{Acidic form of indicator (unionized)}}{HIn} \rightarrow H^+ + \underset{\text{Conjugate (ionized).}}{In}$$

Ionization constant of indicator.

$$K_a = \frac{[H^+][In^-]}{[HIn]} \quad \begin{matrix} \rightarrow \text{Basic form} \\ \rightarrow \text{Acidic Form} \end{matrix}$$

$$H^+ = \frac{[HIn]}{K_a + [In^-]}$$

It can be seen that the colour of the indicator depends on the ratio of the concentration of the ionized and unionized forms which is a direct function of the H^+ concentration.

In the presence of excess H^+, the equilibrium in $HIn \rightarrow (H^+)(In^-)$ will shift to the left ie the ionization will be suppressed and the conc. of In^- will be very small.

The colour will then be that of the unionized form which has it colour

In alkaline medium, there will be a decrease in H^+ concentration which will lead to further ionization of the indicator and so an increase in In^-. The colour of the ionized form will then be seen.

Indicators are used to determine where there is change in electronic potential in redox reaction.

BUFFER SOLUTION

According to Arrhenius acid base concept, Acid are compounds which yield H^+ or H_3O^+ when dissolved in water while Base is a compound which yields OH^- when dissolved in water.

NB A soluble base is called an alkaline.

STRONG ACID AND WEAK ACID

Strong acids are those acid which dissociate completely in dilute aqueous solution

The relative strength of acid is expressed quan-

The colour will then be that of the unionized form which has it colour
In alkaline medium, there will be a decrease in H^+ concentration which will lead to further ionization of the indicator and so an increase in In^-. The colour of the ionized form will then be seen.

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BUFFER SOLUTION

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NB A soluble base is called an alkaline.

STRONG ACID AND WEAK ACID

Strong acids are those acid which dissociate completely in dilute aqueous solution
The relative strength of acid is expressed quan-

titatively in terms of its dissociation constant known as Ka.

Ka is a measure of the tendency of acid to donate it proton in water

According to Bronsted Lowry theory, an acid is any substance which give the cation characteristics of the solvent.
The cation may originate either by the dissociation of the solute in the solvent or by the dissociation of the solvent in the solute.

A base is any substance which gives the anion feature of a solvent.
In neutralisation reaction, the rxn between acid and base yields solvent as one of it product when a Bronsted lowry acid and Bronsted lowry base reacts.

Bronsted lowry concept looked an acid as been non protonic.

SUMMARY OF ACID BASE THEORY

1 Arrhenius concept

(a) An acid is a substance that contains hydrogen and produced H^+ which is known as proton on dissociation in aqueous solution.

(b) A base is a substance that contains hydroxyl group and produces OH^- ion on dissociation in aqueous solution

(c) Neutralization is the combination of H^+ with OH^- to form water molecule.

2 Bronsted Lowry concept

(a) An acid is a proton donor

(b) A base is a proton acceptor

(c) Neutralization is the transfer of proton from an acid to a base.

3 Lewis concept

(a) An acid is an electron pair acceptor

(b) A base is an electron pair donor

(c) Neutralization is a rxn involving the formation of co-ordinate covalent bond between the electron pair donor and electron pair acceptor

NB Lewis concept is much more general.

Acid + Base → Salt (Neutralisation rxn)

SALTS

Salt is an ionic compound consisting of a positive ion (cation) derived from a base and a negative acid (anion) derived from an acid.

It is the product of neutralisation of a base with an acid

TYPES OF SALTS

1 Normal Salt

A salt which has no replaceable hydrogen atom or hydroxyl ion. Eg $NaCl$

2 Hydrogen Salt

This is a type of salt which have replaceable hydrogen atom Eg $NaHCO_3$

3 Hydroxyl Salt

These are salts which have replacable OH^- group.

Examples: $Ba(OH)Cl$, $Bi(OH)_2Cl$

$$Bi(OH)_2Cl \longrightarrow \underbrace{BiOCl}_{\text{oxyl salt}} + H_2O$$

Most of OH^- salt readily lose the element of one or more molecules of H_2O to become oxyl salt.

PROPERTIES OF SALT

1 Solutions of salt may be acidic, basic or neutral to acid-base indicators

2 Fused salt and aqueous solution of salt conduct electricity

3 Salt may taste salty, sour, sweet, bitter or tasteless.

HYDROLYSIS OF SALT

Hydrolysis of salt is the reaction of water and salt to give acid and base.

$$H_2O + NaCl \longrightarrow HCl + NaOH$$

Hydrolysis is the opposite of neutralisation

DEGREE OF HYDROLYSIS

The degree of hydrolysis of salt is the fraction or percentage of the salt that is hydrolised.

Since not all part of salt will be hydrolised, an hydrolysis of salt is dependent on the formation of the salt.

4 ways salt can be formed.

1 Rxn of Strong acid + weak Base

2 Rxn of strong acid + strong base
3 Rxn of strong base + weak acid
4 Rxn of weak acid + weak base

/8/2019.

THERMODYNAMICS

Thermodynamics is the study of energy changes that occurs in chemical & physical processes which does not contain time as a variable.

THERMODYNAMICS TERMS

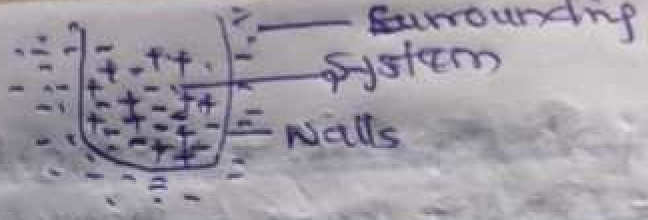
1 System; A thermodynamic system is the part of the physical universe in which the properties are under investigation

ii Surrounding; This is a region in the immediate vicinity of the system separated from the system by boundaries or walls.

iii Types of walls;-

a. Impermeable or diathermal; This is a wall that prevents the passage of matter but allows the passage of energy

Example;- Metal can with a liquid in it when heat, the liquid cannot pass through/escape from it but heat can pass through it



b. Permeable walls; It is a wall that allows the passage of matter and energy.

Example:- A porous ceramic material

c Adiabatic walls; This is a wall that prevents the passage of both matter and energy.

Example:- Thermoflasks

iv Types of systems:- This is determined by the type of walls or boundaries.

a Closed system: It is a system enclosed by impermeable walls. That is mass remains contant but energy may change.

Example:- A closed metal can containing a volatile liquid

b Open System; This is a system enclosed by permeable walls that is exchanges both matter and energy.

Example:- A beaker containing a volatile liquid or a beaker containing a volatile liquid

c Isolated system; This is a system enclosed by an adiabatic wall ie neither energy nor mass can be exchanged.

Example; A thermally insulated vessel containing a volatile liquid

5 Types of thermodynamic properties; - This is basically of two (2) types

a Extensive properties; These are properties that depends on the total amount of the substance of the system.

Example;- Mass, volume, heat capacity etc

b Intensive properties; these are properties that are based on the characteristics of the individual component of the system.

Example; Temperature, viscosity, specific heat capacity etc.

6 Thermodynamic process; This is a method of operation in which a change ~~of~~ in state is affected:-

Example;- Heating, Freezing and expansion

Thermodynamic processes can be carried out under various conditions

a Isothermal process; In this process, temperature is kept constant during operation which means $T=0$

b Adiabatic process; In this process, the heat of the system is constant ($dQ = 0$)

c Isobaric process: In this case, the pressure of the system remains constant ~~an~~ during the process ($P = 0$)

d Isochoric; In this process, the volume is constant ($V = 0$)

e Cyclic process: In this process, the system after undergoing a change returns again to it initial state of condition

28/8/2019.

FIRST LAW OF THERMODYNAMIC

The first law of thermodynamic states that the total energy of a system and ~~the~~ it surrounding must remain constant.

Mathematically, for a finite change, it is given as;- $\Delta E = q - W$. That is, the change in the internal energy of a system ΔE must be equal to the energy absorbed from the surrounding in the form of heat minus the energy loss to the surrounding in the form of external work done by the system.

The workdone by the system is given as;-

$$W = P\delta V$$

P = Pressure , δV = change in volume

In an isolated system, ΔE is equal to zero also for an isothermal condition, Δt is equal to zero and ΔE is equal to zero. The following equation was then derived from the first law.

$$q = w = nRT\ln\left(\frac{V_2}{V_1}\right)$$

Example i-

1 Calculate the energy in Joules required to increase the volume of a substance by $2\times10^{-6}m^3$ against a pressure of 0.5atm.

Solution

$P = 0.5atm$

$\Delta V = 2\times10^{-6}m^3$

$W = P\delta V$

Converting 0.5atm to Joules,

$1atm = 1.0135\times10^{5}Nm^{-2}$

$0.5atm = ?$

$P = 0.5\times1.0135\times10^{5}Nm^{-2}$

$P = 0.50675\times10^{5}Nm^{-2}$

$\therefore W = P\delta V$

$W = 0.50675\times10^{5}Nm^{-2}\times2\times10^{-6}m^3$

$W = 0.101Nm$

$W = 0.101J$ //

2 1 mole of an ideal gas is expanded isothermally and reversibly at 27°c from a volume of $3.0dm^3$ to $5.0dm^3$. calculate the workdone in kilojoules.

Solution

$W = nRT\ln(V_2/V_1)$

$n = 1mole$

$R = 8.314 J/mol/K$

$V_1 = 3.0dm^3$

$V_2 = 5.0dm^3$

$T = 27°C + 273 = 300K$

$W = 1 \times 8.314 J/mol/K \times 300K \ln\left(\frac{5.0dm^3}{3.0dm^3}\right)$

$W = 2494.2 \ln(1.6667)$

converting to kiloJoules

$= \frac{1274.15J}{1000}$

$= 1.274KJ$ //

THERMO CHEMISTRY

Thermochemistry is the study of calculation of heat changes that accompany chemical reactions and physical changes and it is based on the first law of thermodynamics to a great extent.

LAWS OF THERMOCHEMISTRY.

1 Lavioser and Laplace law

This law states that the heat of decomposition of a compound is numerically equal to it heat of formation but of opposite sign.

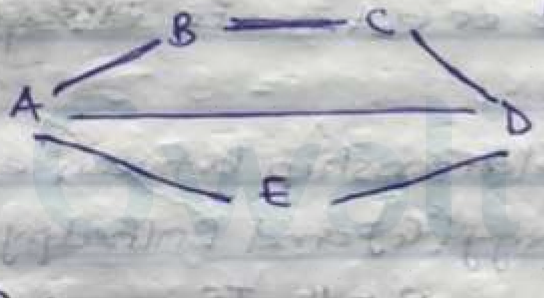
$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$, $\Delta H^\circ = -296.90 KJ/mol$

$SO_{2(g)} \longrightarrow S_{(s)} + O_{2(g)}$, $\Delta H^\circ = 296.90 KJ/mol$

2 Hess law

It state that the total enthalpy change in a chemical reaction is the same regardless of the route of the reaction provided the same conditions of temperature and pressure are maintained.

$\Delta H^\circ = -5 KJ/mol$



Example:-

1 Given the following thermochemical reactions

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H^\circ = -393.51 KJ/mol$

$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H^\circ = -282.99 KJ/mol$

calculate the enthalpy change of combustion of graphite to CO.

Solution

Required eqn :- $C + 1/2 O_2 \longrightarrow CO$ then,

*add eqn 1 & 11.

$$\left\{\begin{array}{ll} C + O_2 = CO_2 & \Delta H^\circ = -393.51 KJ/mol \; --- (1) \\ CO_2 = CO + 1/2 O_2 , & \Delta H^\circ = 282.99 KJ/mol \; --- (11) \end{array}\right.$$

*collect like terms.

$C + O_2 + CO_2 = CO_2 + CO + 1/2 O_2$ $\Delta H^\circ = -110.52 KJ/mol$

*make CO the subject of the formula.

$C + O_2 + \cancel{CO_2} - \cancel{CO_2} - 1/2 O_2 = CO$

$C + 1/2 O_2 = CO$ $\Delta H^\circ = -110.52 KJ/mol$

ENTROPY, FREE ENERGY & CHEMICAL EQUILIBRIU

ENTROPY (S) :- This is a measure of the degree of disorderliness or randomness in a system.

GIBB'S FREE ENERGY (G): This is used to describe or estimate the spontaneity of a process.

The relationship between entropy (S), Gibb's free energy (G) and Enthalpy (H) is given as

$$G = H - TS$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

A spontaneous process is one that occurs

On it own ($\Delta G^\circ = -ve$) while a non spontaneou
process cannot occur on it own ($\Delta G^\circ = +ve$)
If $\Delta G = 0$ then the process is said to be in
chemical equilibrium.

CHEMICAL EQUILIBRIUM: This is the state of a system in which there is no change in the concentration of the reactants or product with time.

The following equation was derived:-

$\Delta G^\circ = -RT\ln K_{eq}$.

Where:- K_{eq} = Equilibrium constant

R = Ideal gas constant ($8.314 Jmol^{-1}K^{-1}$)

T = Temperature in Kelvin

ΔG° = change in standard Gibb's free energ

Examples:-

1 The formation of Ammonia at 400°C has equilibrium constant of 1.64×10^{-4}. calculate the standard Gibb's energy change for the reaction

Solution

$T = 400°C + 273 = 673K$

$R = 8.314 Jmol^{-1}K^{-1}$

$\Delta G^\circ = ?$

$K_{eq} = 1.64 \times 10^{-4}$

$\Delta G^\circ = -RT\ln K_{eq}$

$\Delta G^\circ = -(8.314\,Jmol^{-1}K^{-1} \times 673K) \ln 1.64 \times 10^{-4}$

$\Delta G^\circ = -5595.322 \times -8.7156$

$\Delta G^\circ = 48766.84\,Jmol^{-1}$

$\Delta G^\circ = 48.77\,KJmol^{-1}$

11- Calculate the standard entropy change for a process at 25°C with ΔG° and ΔH° values of $-5.77\,KJmol^{-1}$ and $13.13\,KJmol^{-1}$ respectively.

Solution

$\Delta G^\circ = -5.77\,KJmol^{-1}$ $\quad \Delta S^\circ = ?$

$\Delta H^\circ = 13.13\,KJmol^{-1}$

$T = 25^\circ C + 273 = 298K$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$-5.77\,KJmol^{-1} = 13.13\,KJmol^{-1} - 298K\,\Delta S^\circ$

$298K\,\Delta S^\circ = 13.13\,KJmol^{-1} + 5.77\,KJmol^{-1}$

$$\Delta S^\circ = \frac{13.13\,KJmol^{-1} + 5.77\,KJmol^{-1}}{298K}$$

$$\Delta S^\circ = \frac{18.9\,KJmol^{-1}}{298K}$$

$\Delta S^\circ = 0.063\,KJmol^{-1}K^{-1}$

2/1/2019. EFFECTS OF TEMPERATURE ON REACTION RATE.

Kinetics provides information on the time a reaction takes place and how fast it occurs.

Collision is the ability of a reaction to collide with each other.

Note:- It isn't every collision that result in a reaction

There are 2 types of collision namely:-

a Effective collision
b ~~I~~Ineffective collision

EFFECTIVE COLLISION:- Here, there is high probability that a product will be formed.

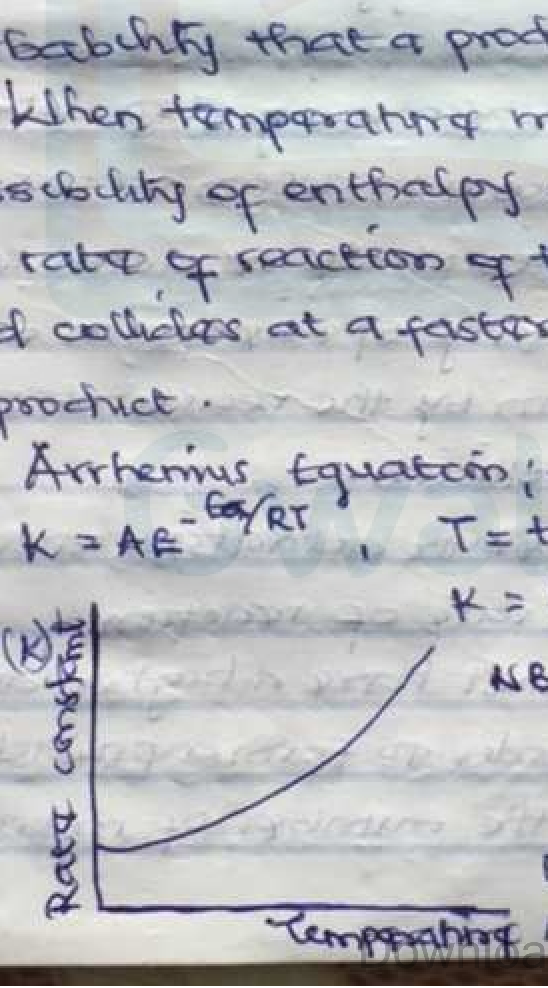
When temperature increases, there is possibility of enthalpy increasing and as such, the rate of reaction of the particle speeds up and collides at a faster rate thereby producing a product.

Arrhenius Equation:-

$K = AE^{-Ea/RT}$, T = temperature

K = Rate constant

$R \propto 1/T$



NB: With increase in temperature, Rate constant increases.

EA = Activation Energy

A = Preexponential Factor

- In collision theory, gases molecules frequently collides with one another.
- The rate of reaction is equivalent to the number of reaction.
- Reaction rate is dependent on temperature
- Concentration affects reaction rate and the more the concentration, the higher it collision vice versa

The minimum amount of energy required to initiate a chemical reaction is known as activation energy

Note:-

The rate determining step determines how fast or slow a reaction occurs.

Transition state or activation complex is a temporary specie form or intermediate product form by the reactant specie as the result of collision.

4/9/19 Note:- The smaller the activation energy (Ea) the faster the rate of reaction

Reactant must have a higher activation energy inorder to form a product.

The higher the number of molecules present the more

Frequency they collide

$$K = Ae^{-E_a/RT}$$

$$\ln K = \ln A - E_a/RT$$, where $\ln A$ is the intercept

The equation above is an equation of a linear graph.

NB The rate of reaction is directly proportional to temperature; - $\gamma \propto T$

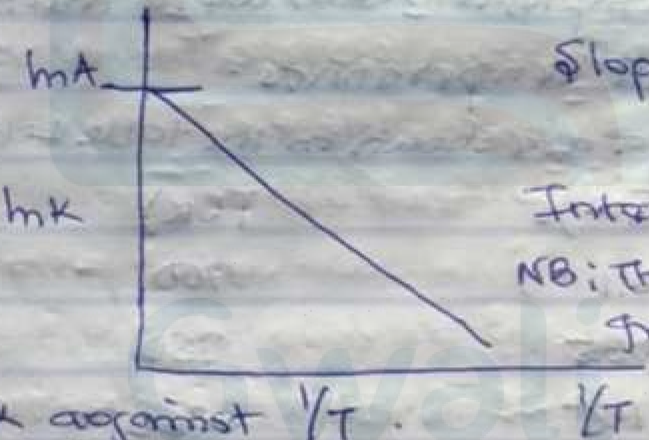
$$\gamma = KT$$

$$K = \gamma/T$$

γ = rate of reaction.

T = Temperature.

K = Arrhenius constant



Slope = $-\frac{E_a}{R}$

Intercept = lnA

NB; This is a straight line graph with a negative slope.

Graph of lnK against 1/T.

A rate ~~of~~ constant of any reaction when 1/T tends to zero is lnA. It is also the rate constant when the temperature tends to infinity

Assuming we are given T_1, K_1, T_2, K_2.

$\ln K = \ln A - E_a/RT$

Inputting the values; -

$\ln K_1 = \ln A - E_a/RT_1$ ---- eq(i)

$\ln K_2 = \ln A - E_a/RT_2$ ---- eqn ii

Subtracting equation ii from eqn(i)

$\ln K_2 - \ln K_1 = -E_a/RT_2 - (-E_a/RT_1)$

$\ln K_2 - \ln K_1 = -E_a/RT_2 + E_a/RT_1$

$\ln K_2 - \ln K_1 = E_a/RT_1 - E_a/RT_2$

$\ln K_2 - \ln K_1 = E_a/R\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

The rate constant for the decomposition of acetaldehydes (CH_3CHO) were measured at fiv

different temperatures.

The data are shown in the table below: -

$K\left(\frac{1}{M^{1/2}}\right)s$	T(K)
0.011	700
0.035	730
0.105	760
0.343	790
0.789	810

Take $R = 8.314\ J\,mol^{-1}K^{-1}$

Plot $\ln K$ versus $\frac{1}{T}$ and determine the activation energy (in KiloJoule per mole) of the reaction

Note that the reaction is 3/2 order in acetaldehyde

9/9/2019: To find the rate constant, you take the inverse of lnK ie lnK = e^{-}.

Note:- e^{-} means inverse of whatever lnK is

Assuming lnK is 20 then the inverse or rate constant is ;- $\ln K = e^{-20}$, $\ln K = \frac{1}{20}$.

Question:-

1 In terms of collision theory, to which of the following is the rate of a chemical reaction proportional.

a change in free energy per second

b change in temperature per second

c change in collision per second

d change in product of molecule

2 The variation of d rate constant with temperature for the decomposition of Hydrogen & Iodine is given as:-

$2HI(g) \longrightarrow H_2(g) + I_2(g)$

What is the activation energy for the reaction?

$Jmol^{-1}s^{-1}$

(Temperature) K	K (rate constant)
555	3.52×10^{-7}
575	1.22×10^{-6}
645	8.59×10^{-5}
700	1.16×10^{-3}
781	3.95×10^{-2}

$R = 8.314 Jmol^{-1}K^{-1}$

Steps:-

Find the value for the reciprocal of T and

Solution

T (K)	$\frac{1}{T}$ (K^{-1})	K	$\ln k^{-1}$
555	1.8×10^{-3}	3.52×10^{-7}	−14.86
575	1.74×10^{-3}	1.22×10^{-6}	−13.62
645	1.55×10^{-3}	8.59×10^{-5}	−9.36
700	1.43×10^{-3}	1.16×10^{-3}	−6.76
781	1.28×10^{-3}	3.95×10^{-2}	−3.23

11/09/2019. ELEMENTARY CHEMICAL KINETICS.

Direction of the reaction
Velocity of the reaction
Yield (product) of the reaction } Hints in chemical kinetic

In chemical kinetics, we look at the

reaction rate and the mechanism of the reaction.

Reaction mechanism describes the series of stepwise reaction by ~~which~~ that is involve before the overall product is gotten.

chemical reaction is a one step reaction.

$$\text{reaction rate} = \frac{\text{change in concentrate } \Delta(A)}{\text{change in time } \Delta(t)}$$

- Temperature
- Surface Area
- Concentration
- Catalyst

} Things that can affect chemical reaction

Reaction rate is usually expressed as change in concentration per unit time of a substance involved in that reaction. In other words, for a generalised chemical eqn, reaction rate can be expressed unambiguously in terms of any specie by dividing the conc. change of the selected specie by the stoichiometry co-efficient of that specie in a balanced equation.

$$aA + bB \longrightarrow cC + dD$$

$$-\frac{1}{a}\frac{d(A)}{d(t)} = -\frac{1}{b}\frac{d(B)}{d(t)} = +\frac{1}{c}\frac{d(C)}{dt} = +\frac{1}{d}\frac{d(D)}{dt}.$$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

$$-\frac{1}{2}\frac{d(H_2)}{dt} = -\frac{d(O_2)}{\delta t} = +\frac{1}{2}\frac{d(H_2O)}{dt}$$

RATE LAWS AND RATE CONSTANT

RATE LAW.

The rate of an elementary (one step) chemical rxn is proportional to the concentration of the reactant raised to a power equal to the number of molecules of that species participating in that reaction.

$$A \longrightarrow P$$

$r \propto (A)^1$ where; A = concentration of reactant

$r = K(A)^1$ --- eqn (i) P = Product

$A + A \longrightarrow P$ r = rate of chemical rxn

$$2A \longrightarrow P$$

$r = K(A)^2$ ------ eqn (ii)

For homogeneous reaction;- $A + B \longrightarrow P$

$$r = K[A][B]$$

$$A + 2B \longrightarrow P$$

$r = K(A)(B)^2$ --- eqn (iii)

In the rate law, the co-efficient K is called the rate constant which is independen on concentration but dependent on the nature of reactant, temperature and addition of catalyst

The power to which the concentration of a species the reactant is raised in a rate law is known as THE ORDER OF RXN
The overall order of reaction will be d sum of the individual order of the differen reactant

$$aA + bB + cC \longrightarrow \text{Product}$$

$$r = K(A)^a (B)^b (C)^c$$

$$a + b + c = \text{order} \quad (3 \text{ order of reaction})$$

From equation(1) (1st order)

$$r = K(A)^1$$

$$K = \frac{r}{(A)}$$

$$\text{rate of rxn} = \frac{\Delta(A)}{\Delta t} = \frac{mol/L}{s} = mol/Ls$$

$$\therefore K = \frac{r}{(A)} = \frac{mol/Ls}{mol/L}$$

$$= \frac{\cancel{mol}}{\cancel{L}s} \times \frac{\cancel{L}}{\cancel{mol}} = \frac{1}{s}$$

$$K_1 = s^{-1} \;//$$

From eqn (ii) (2nd order)

$$r = K(A)^2$$

$$K_2 = \frac{r}{(A)^2} = \frac{mol/s}{mol^2/L^2}$$

$$K_2 = \frac{mol}{\cancel{L}s} \times \frac{\cancel{L^2}}{mol^2} = \frac{L}{mol\,s}$$

$$\underline{\underline{K_2 = L/mol\,s}}$$

From eqn (iii) (3rd order)

$$r = K(A)(B)$$

$$K_3 = \frac{r}{(A)(B)^2} = \frac{mol/Ls}{Mol^3/L^3}$$

$$K_3 = \frac{Mol}{Ls} \times \frac{L^3}{Mol^3}$$

$$K_3 = \frac{L^2}{Mol^2 s} //$$

ZERO ORDER REACTION.

This are rxns in which the rate is not affected by changes in the concentration of one or more reactant because it is determined by some limiting factors oth than concentration such as amount of light absorbed in a photochemical rxn or the amount of catalyst in a catalytic reaction.

Question 1:-

$H_2 + I_2 \longrightarrow 2HI$. What is ~~order~~ rate of reaction?

a $r = K[H_2]^0[I_2]$

b $r = K[HI]^2$

[✓ c] $r = K[H_2][I_2]$

d $r = K[HI][I_2]$

Note:- In zero order reaction, rate ~~order~~ of rxn is equal to the rate constant of the reaction

$r = K$.

Zero order reaction is also known as a sudo first order reaction.

$r = K$ (ZERO ORDER)

$$-\frac{\delta(A)}{\delta t} = K$$

$$dA = -K\delta t$$

$$\int_0^t dA = \int_t -K\delta t$$

$$(A)_0^t = -K[t]_0^t$$

$$A_t - A_0 = -K(t-0)$$

$$A_t - A_0 = -Kt$$

$\therefore A_t - A_0 = -Kt$ (Integrated eqn 4 zero order rxn)

Question 2:

Which among these is incorrect?

a. $A_t - A_0 = -Kt$

b $A_t = A_0 - Kt$

c $A_t + Kt = A_0$

[✓ d] $A_t - Kt = A_0$

INTEGRATED HOMOGENOUS REACTION

$r = K_1(A)$ (1ST ORDER)

$$-\frac{\delta(A)}{\delta t} = K_1(A)$$

$$\int_0^t \frac{d(A)}{(A)} = \int_0^t -K_1 \delta t$$

$$[\ln(A)]_0^t = -K_1 t$$

$$\ln A_t - \ln A_0 = -K_1 t$$

Question 3:-

Which is incorrect?

a $\ln A_t - \ln A_0 = -K_1 t$

b $\ln \frac{A_t}{A_0} = -K_1 t$

c $\ln \frac{A_0}{A_t} = K_1 t$ {change in the sign brought about change in the variabl

[✓ d] $\ln \frac{A_t}{A_0} = K_1 t$

$r = k_2(A)^2$ (2ND ORDER)

$$-\frac{\delta(A)}{\delta t} = K_2(A)^2$$

$$\int_0^t \frac{d(A)}{(A)^2} = \int_0^t -K_2\delta t$$

$$\left[-\frac{1}{(A)}\right]_0^t = -Kt$$

$$\cancel{-}\left[\frac{1}{A_t} - \frac{1}{A_0}\right] = \cancel{-}Kt$$

$$\frac{1}{A_t} - \frac{1}{A_0} = Kt$$

HALF LIFE OF A FIRST ORDER .

This is the time taken or required for the concentration of A to reduce ~~to~~ half its initial value .

$$t_{1/2}[A] = \frac{[A_0]}{2}$$

$$\ln\frac{A_t}{A_0} = -Kt$$

$$\ln\frac{A_0/2}{A_0} = -Kt_{1/2}$$

$$\frac{\cancel{A_0}}{2} \times \frac{1}{\cancel{A_0}} = \ln\frac{1}{2} = -Kt_{1/2}$$

$$\ln 2 = Kt_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{K} = \frac{0.693}{K}$$

Question 4 :-

In a first order rxn, the half life of a radioactive substance is 5hours. calcul it rate constant.

Solution

$t_{1/2}$ = 5hours

$= 60 \times 60 \times 5$

$= 18,000s$.

$\therefore t_{1/2} = \frac{0.693}{K}$

$K = \frac{0.693}{t_{1/2}}$

$K = \frac{0.693}{18,000}$

$K = 0.0000385$ secs //

Question 5 :-

The half life for the 1st order decompositi of N_2O_5 is $2.05 \times 10^4 s$. How long will it take for a sample of N_2O_5 to decay t 60% of it initial value?

Solution

$K = \frac{0.693}{t_{1/2}\ 2.05 \times 10^4 s}$

$K = 3.38 \times 10^{-5} s^{-1}$

$$[N_2O_5] = \frac{60}{100}[N_2O_5]_0$$

$$= 0.6[N_2O_5]_0$$

$$\ln \frac{[N_2O_5]_0}{[N_2O_5]} = kt$$

$$\ln \frac{\cancel{[N_2O_5]_0}}{0.6\cancel{[N_2O_5]_0}} = 3.38\times10^{-5}s^{-1}\times t$$

$$\ln \frac{1}{0.6} = 3.38\times10^{-5}s^{-1}\times t$$

$$0.51 = 3.38\times10^{-5}s^{-1}\times t$$

$$t = \frac{0.51}{3.38\times10^{-5}}$$

$$t = 1511 \text{ secs} //$$

Question 5 :-

The reaction A to product is first order. If K is 1.75×10^{-5} at 350K, what percentage of K is left after 30 minutes ?.

Solution

let x represent the % of A left.

$t_{30minutes}$ $(A) = x\%(A)_0$

$$\ln \frac{A_0}{A_t} = kt$$

$$\ln \frac{\cancel{A_0}}{x\cancel{A_0}} = kt$$

$\ln\frac{1}{x} = 1.75\times10^{-5}\times t$

$\ln\frac{1}{x} = 1.75\times10^{-5}\times 30\times60\times60$

$\frac{1}{x} = e^{1.75\times10^{-5}\times30\times60\times60}$

$\frac{1}{x} = e^{0.0315}$

$\frac{1}{x} = 1.032$

$\frac{x}{100} = 969$

$x = 9.7\ \%$