ANTIDOTE TO A LEVEL PHYSICAL CHEMISTRY

FIRST EDITION

IT COVERS ALL THE ESSENTIAL TOPICS OF PHYSICAL CHEMISTRY

1. Mole concept
2. Matter
3. Structure and bonding
4. Chemical energetics
5. Physical Equilibria
6. Chemical Equilibria
7. Ionic Equilibria
8. Chemical kinetics
9. Electro chemistry
10. Atomic structure

RH BOOKS

PHYSICAL CHEMISTRY

Physical chemistry attempts to measure the influence of factors such as heat, light, pressure, concentration and others on both the reactants and the reaction itself. And to deduce from these measurements the fundamental laws governing chemical equilibrium. We shall cover about gas laws, mass spectrometer diffusion colligative properties, thermal chemistry, phase equilibrium, chemical kinetic chemical equilibrium and ionic equilibrium

MOLE CONCEPT

A mole is that amount of substance which contains as many elementary units as their atoms in carbon 12 where there are 6.02×10^{23} atoms, ions, molecules or electrons. The number of atoms (6.02×10^{23}) is called Avogadro's number or constant. And 1 mole of an element contains this number of atoms, **example**

12g of carbon, 24g of magnesium, 40g of calcium all contains $6.02\ 10^{23}$ atoms it is important to state the particles being used, **example** 1 mole of oxygen could mean 1 mole of oxygen atoms (16g) or 1 mole of oxygen molecules (32g).

The mass of an ion is taken to be the same as that of parent atoms example (Na and Na^+) since the loss or gain of an electron causes a negligible change in mass, **example** chlorine atom and chlorine ion each has a mass of 35.5g, Mg and Mg^{2+} each has a mass of 24g.

Molar mass is the mass of 1 mole of an atom.

Example

1. Calculate the weight of
   a) 0.4 moles of chlorine gas
   b) 0.2 moles of chloride ions

Solution

a) 1 mole of chlorine gas (Cl_2) contains 35.5g
0.4 moles of Cl_2 contain $4 \times 35.5 \times 2$
= 284g of chlorine gas

b) 1 mole of chlorine ion(Cl^-) contain 35.5g
0.2 mole of Cl contain $0.2 \times 35.5 \times 1$
= 7.1g of chlorine ions

2. The mass of 0.25moles of an element is 20g.
What is the atomic mass of the element?

Solution

0.25 mole of the element contain 20g of the element

1 mole of the element contain $\frac{1 \times 20}{0.25}$

= 80g

Therefore the atomic mass of the element is 80g

3. What is the weight of 12.04×10^{20} atoms of carbon?

Solution

6.02×10^{23} atoms of carbon contains 12g of carbon

12.04 × 1020 atoms contain $\dfrac{12 \times 12.04 \times 10^{20}}{6.02 \times 10^{23}}$

= 0.024g of carbon

CONCENTRATIONS AND MORALITY

The concentration of a substance is the amount of that substance per given volume of a solution. Concentration can be determined

i. As mass of the substance per given volume of a solution.

ii. As number of moles of a substance per given volume of a solution morality means the number of moles of a solute under consideration in a litre of a solution example

2 moles per litre /dm^3/1,000cm^3 is 2M

Recall that 1 litre of solution is the same as $1dm^3$ or $1,000cm^3$ of solution

Example

1. $25cm^3$ of an acidified solution of 0.02M potassium Maganate (vii) reacted exactly with $25cm^3$ of sodium nitrite. Potassium maganate (vii) reacts with sodium nitrite according to the following equation

$2MnO_4^-{}_{(aq)}, + 5NO_2^-{}_{(aq)} + 6H^+{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 5NO^{3-}{}_{(aq)},+3H_2O_{(1)},$

Calculate the concentration of the sodium nitrite

Solution

$1000cm^3$ of potassium maganate (vii) contains 0.02 moles

1 cm^3 of potassium maganate (vii) contains $\frac{0.02}{1000}$ moles

25cm3 of potassium maganate (vii) contains $\frac{0.02}{1000} \times 25$

= 0.0005 moles

But from the equation

2 moles of potassium maganate reacts with 5 moles of sodium nitrite

1 mole of potassium maganate reacts with $\frac{5}{2}$ moles of sodium nitrite

Therefore

0.0005 moles of potassium maganate reacts with $\frac{5}{2} \times 0.0005$

= 0.00125 moles of sodium nitrite

This means that;

$25cm^3$ of sodium nitrite contains 0.00125 moles

$1cm^3$ of sodium nitrite contains $\frac{0.00125}{25}$

$1,000cm^3$ of sodium nitrite contains $\frac{0.00125}{25} \times 1000$

= 0.05 Moles per litre

2. 0.9875g of an impure potassium manganate (vii) was dissolved in water to make $250cm^3$ of solution. When $20.0cm^3$ of this solution was acidified with dilute sulphuric acid, warmed and titrated against sodium ethanedioate (oxalate) solution made by dissolving 1.675g of anhydrous sodium ethanedioate to make $250cm^3$ of solution. $24.40cm^3$ of the sodium ethanedioate solution was used. ($Na_2C_2O_4$=134 and $KMnO_4$ = 158).

Potassium manganate (vii) reacts with sodium ethanedioate according to the following equation.

$2MnO^-_{4(aq)} + 16H^+_{(aq)} + 5C_2O_4{}^{2-}{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 10CO_{2(g)} + 8H_2O_4$

a) Determine the molar concentration of maganate (vii) ions

b) Calculate the percentage purity of potassium maganate (vii)

Solution

a) $Na_2C_2O_4$ = 134

$250cm^3$ of solution contains $\frac{1.675 \times 1000}{250}$

$= \mathbf{6.7gl^{-1}}$

134g of sodium ethanedioate contains 1 mole

6.7g of sodium ethanedioate contain $\frac{6.7 \times 1}{134}$

= 0.05M

Therefore, $1,000cm^3$ of sodium ethanedioate contains 0.05 moles,

$24.4cm^3$ of sodium ethanedioate contains $\frac{24.4 \times 0.05}{1000}$

= 0.00122 moles

But 5 moles of sodium ethanedioate reacts with 2 moles of manganate (vii) ions

1 mole of sodium ethanedioate reacts with $\frac{2}{5}$ moles of manganate (vii) ions

0.00122 moles of sodium ethanedioate reacts with $\frac{2}{5} \times 0.00122$

= 0.000488 moles

Therefore,

$20cm^3$ of manganate (vii) ions contains 0.000488 moles

$1000cm^3$ of manganate (vii) ions contains $\frac{0.000488}{20} \times 1,000$

= 0.0244 mole per litre

b) Also, 1 mole of manganate (vii) ions contain 158g

0.0244 moles of manganate (vii) ions contains 158 × 0.0244

= $3.8552gl^{-1}$

Percentage purity = $\frac{\text{mass of pure manganate (vii) ion}}{\text{Mass of impure manganate (vii) ion sample}}$

$= \frac{3.8552}{0.9875 \times 4} \times 100$

$= \frac{3.8552}{3.95} \times 100$

= 97.6%

3. 1.55g of an acid, $C_nH_{2n}(COOH)_2$ was dissolved in water and the solution made up to $250cm^3$. $25.0cm^3$ of the solution required $23.5cm^3$ of a 0.1M aqueous sodium hydroxide for complete neutralization calculate
   a) i). The molar concentration of the acid
      ii). The molecular mass of the acid

   b) Determine the value of n

Solution

a)

i. The acid is dibasic, therefore it reacts with sodium hydroxide according to the equation

$$C_nH_{2n}(COOH)_{2(aq)} + 2NaOH_{(aq)} \longrightarrow C_nH_{2n}(COONa^+)_{2(aq)} + 2H_2O_{(l)}$$

$1000cm^3$ of sodium hydroxide contains 0.1 moles

$23.5cm^3$ sodium hydroxide contains $\frac{0.1 \times 23.5}{1,000}$

= 0.00235 moles

But 2 moles of sodium hydroxide reacts with 1 moles of the acid

1 mole of sodium hydroxide reacts with ½ moles of the acid

0.00235 moles of sodium hydroxide reacts ½ × 0.00235

= 0.001175 moles of acid

Therefore,

25cm^3 of the acid contains 0.001175 moles
1000cm^3 of the acid contains $\frac{0.001175}{25} \times 1000$
= 0.047M

ii. 250cm^3 of solution contains 1.55g of the acid
1,000cm^3 of solution contains $\frac{1.55 \times 1000}{250}$
= 6.2gl^{-1}

Then 0.047 moles of the acid contains 6.2g of the acid
1 mole of the acid contain $\frac{6.2}{0.047} \times 1$
= 131.9g

b) $C_nH_{2n}(COOH)_2 = 131.9$
$12n + 2n + (12 + 16 + 16 + 1) \times 2 = 131.9$
$14n + 90 = 131.9$
$14n = 131.9 – 90$
$\frac{14n}{14} = \frac{41.7}{14}$
n = 2.99
Therefore, **n = 3**

DILUTION OF SOLUTIONS

A solution whose concentration is accurately known is called a **standard solution**

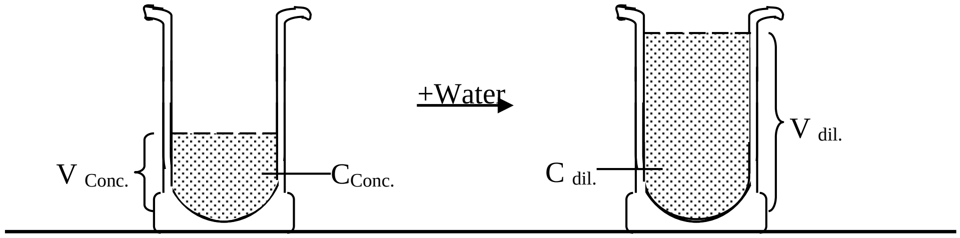
Standard solutions can be diluted to lower concentrations by addition of water. The process is called **dilution**.

NOTE:

It is only the volume of the solvent which increased the amount of substance in the final less concentrated solution remains the same. That is

n (concentrated solution) = n (diluted solution)
C (Conc.) × V (Conc.) = C (dil.) × V (dil.)
Or C (Conc.) × V (Conc.) = C (dil.) (V Conc. + VH_2O)

ILLUSTRATION OF THE DILUTION PROCESS



Then $C_{\text{Conc.}} \times V_{\text{Conc.}} = C_{\text{dil.}} \times V_{\text{dil.}}$

STOCK SOLUTIONS

The concentration of stock solution is calculated first and then adding known volume of the stock solution to get the desired lower concentration. The number of times the volume of the more concentrated solution is diluted to obtain the less concentrated solution is called the **dilution factor**

Example

a) Calculate the concentration of a stock solution of hydrochloric acid with the following label specification
   Density (mass per cm^3) = $1.18cm^{-3}$
   % purity (w/w) = 36%

b) Calculate the volume of the stock solution that should be taken to dilute it to $2dm^3$ of concentration $0.80\ moldm^{-3}$

Solution

a)

$1cm^3$ pure HCl contains 1.18g of HCl

$1000cm^3$ of pure HCl contain 1.18×1000g of HCl

Then

$100cm^3$ of stock contain 1.18×1000g of HCl

$36cm^3$ of stock contain $\frac{1.18 \times 1000 \times 36}{100}$

$\mathbf{= 11.8 \times 36g\ dm^{-3}}$

Therefore, mass concentration in g $dm^{-3} = 11.8 \times 36$

Hence molar mass of HCl = 1 + 35.5

= 36.5

And 36.5g of HCl contains 1 mol of HCl

11.8×36g of HCl contains $\frac{11.8 \times 36}{36.5}$

$= 11.6\ Moldm^{-3}$

$= 11.6M$

b) C(Conc.) = 11.6 mol dm^{-3}
C (dil.) = 0.80 Mol dm^{-3}
V (dil.) = 2 dm^3

Using $C\ Conc. = \frac{C\ dil. \times V\ dil.}{C\ Conc.}$

$= \frac{0.8 \times 2}{11.6}$

= 0.138 dm^3

= 138 cm^3

SELF TEST

1. 20.0 cm^3 of a 0.01M manganate (vii) ion solution required exactly 16.65 cm^3 of a solution containing 4.8gl^{-1} of an oxalate $(COO^- X^+)_2.2H_2O$. Calculate the atomic mass of X

2. 48.00 cm^3 of a solution containing 7.00g per litre of potassium hydroxide required 25.00 cm^3 of 0.12M Phosphoric acid for complete neutralization
   i) Calculate the molar ratio in which phosphoric acid reacts with potassium hydroxide.

ii) Write equation for the reaction.

3. 3.8g of solder containing tin was dissolved in excess hydrochloric acid. The solution was made up to 250 cm^3 25 cm^3 of this solution required 23.5cm^3 of a 0.01M potassium dichromate (vii) solution for complete reaction.
   Write the equation for the reaction that took place.

a). Calculate (i). The number of moles of potassium dichromate (vi)
(ii). The number of moles of tin in the 250 cm^3 of solution

b). Determine the percentage of tin in the solder by mass.

4. a). Concentrated nitric acid is 70% (W/W) and has a density of 1.42 gcm^{-3}. Calculate the morality of the concentrated nitric acid.

b). 12.68cm^3 of the acid in (a) was dissolved in water and the solution made up to 250cm^3 with distilled water. Calculate the volume of the solution and that would react completely with 25.0cm^3 of a 0.2M sodium carbonate solution.

5. 1.10g a dibasic acid $R\text{-}(COOH)_2\ nH_2O$ was boiled with 250 cm^3 of 0.1M sodium hydroxide for some time in cooling 25 $cm^3$of the residual solution required 9.0 cm^3 of sulphuric acid of concentration 0.05 $moldm^{-3}$ for complete reaction. Calculate the value of n in the formula (R=14, C=12, O=16, H=1).

6. A sample of divalent metal M contaminated with its oxide was dissolved in 50cm^3 of 0.1M hydrochloric acid. 30cm^3 of hydrogen gas measured at s.t.p was evolved 20cm^3 of 0.1M sodium hydroxide was required to neutralize the excess acid. Calculate the percentage of M in the sample.

7. In an experiment 3.15g of $BaCl_2.XH_2O$ was shaken with water and diluted to make 1 dm^3 of solution using distilled water. 20cm^3 of this solution were taken and excess potassium sulphate was added to it and then titrated with silver nitrate solution containing 11.45g of silver ions per litre. 4.9cm^3 of the silver nitrate solution were added to just precipitate the chloride ions completely. Calculate the value of X in $BaCl_2$. XH_2O

8. 5.2g of ammonium chloride contaminated with sodium chloride as impurity were boiled for some time with 100cm^3 of 2M sodium hydroxide the residual solution was made up to 250cm^3 of solution using distilled water 25 cm^3 of this solution required 21.8 cm^3 of 0.5M of hydrochloric acid for complete neutralization . Calculate the percentage purity of the ammonium chloride.

9. 25cm^3 of solution Q containing 9.6 l^{-1} of a mixture of ethanedioate acid and sodium ethanedioate was titrated with sodium hydroxide of concentration 0.1M, 19.80cm^3 of the sodium hydroxide solution was required for complete reaction. The resultant solution was acidified by adding 50 cm^3 of sulphuric acid of concentrated 1 mol dm-1 and warmed to 70°C. This solution required 35.4dm^{-3} of potassium manganate (vii) of concentration 0.02 moldm^{-3} for complete oxidation. Calculate the percentage of sodium ethanedioate in Q.

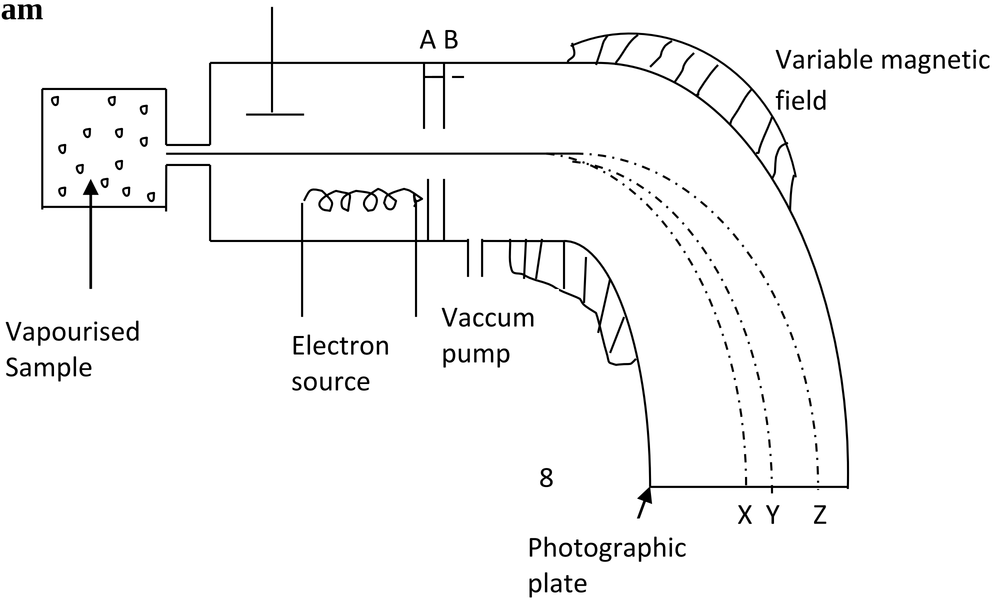
RELATIVE ATOMIC MASS (R.A.M)

The R.A.M of an element is the mass of an atom of the element relative to $^{1}/_{12}$ a mass of 1 atom of carbon -12 Isotopes.

Determination of R.A.M

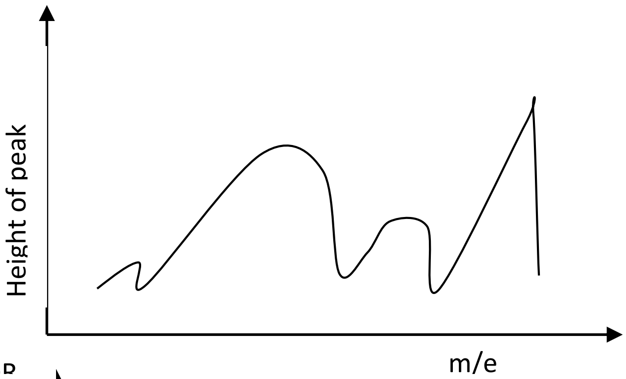
It is determined using a mass spectrometer

Diagram

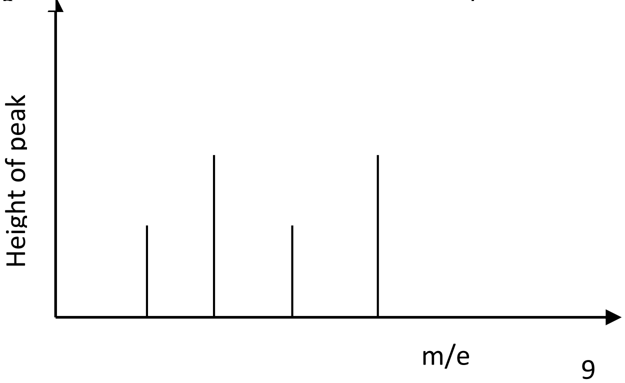


The vapourised sample is produced in the ionization chamber where the particles collide with electrons from electron source and produce a mixture of ions example Aluminum atoms may produce $A1^{+}$, $A1^{2+}$, $A1^{3+}$ ions. The mixture of positive ions is attracted by a charged plate which is maintained at a negative potential.

After immerging from slit B, the ions pass through a strong magnetic field which deflects the ions. The degree of curvature depends on several factors;
The stronger the magnetic field, the greater the extent of deflection.
The greater the accelerating voltage, the more rapidly the ions will be moving and the less by will be deflected.
A lighter ion is deflected more than a heavier one of the same charge.
The higher charged ion is deflected more than an ion with a simple charge but of the same mass because the higher the charge of a particle the more it is attracted or repelled by a charge body.
Thus the degree of curvature is based on mass charge ratio (m/e)
Ions with high m/e ratio are deflected less than those with lower m/e ratio
Example: X has a lower m/e and Z has a higher m/e ratio.
The ions fall on the photographic plate and produce a mass spectrum of a series of line at different places.
If the plate is calibrated the masses of the different particles can be deduced from the positions of the lines of the spectrum. In this case the instrument is called a mass spectrograph that is to say, when a photographic plate is used. For ions carry a unit charge m/e ratio is always a constant m and a single line will be obtained. In this case the photographic plate is replaced by an amplifier which amplifies charges and records them graphically as below and in this case the instrument is called a mass spectrometer.

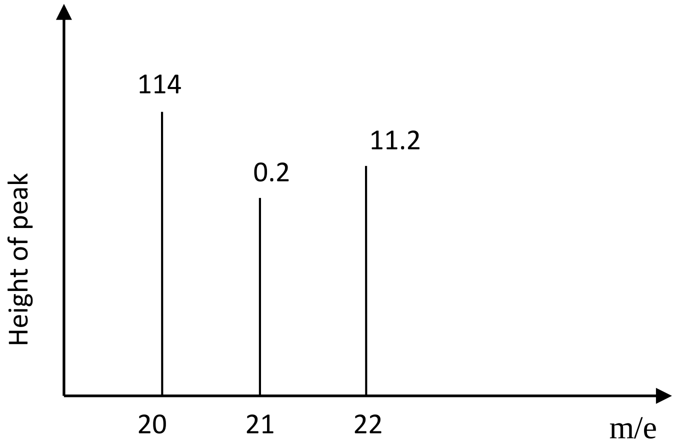


OR



Examples

1. **1.** The diagram below shows the mass spectrum of Neon find the relative atomic mass of Neon.



NOTE:

- Determine the masses of individual isotopes
- Determine the total abundance of the ions.
- Workout the total mass of each isotope

Solution

Isotopic mass	**abundance**	**Total mass isotope**	
20	114	20×114	= 2280
21	0.2	21×0.2	= 4.2
22	11.2	22×11.2	= 246.2
	125.4		**2530.6**

Average mass of Neon = $\frac{2530.6}{125.6}$

= 20.18 (no units) because it is a ratio or a percentage

2. The abundance of ^{37}Cl is 25% and that of ^{35}Cl is 75% in mass spectrometer. Determine the relative atomic mass of chlorine.

Solution

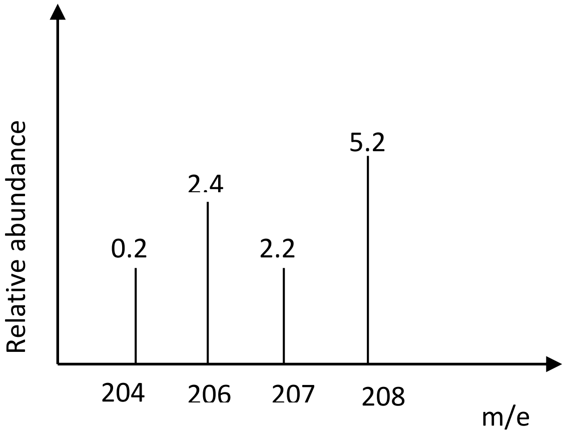
Isotopic mass	**Abundance (5)**	**Total % mass of isotope**
37	25	92.5
35	75	2625
	100	**3550**

Average mass of Cl = $\frac{3550}{100}$

= 35.5

SELF TEST

1. The diagram below shows the mass spectrum for naturally occurring isotopes of Lead. Find the relative atomic mass of Lead.



Ans. 207.22

2. The table below shows the information from a mass spectrum of a Lead sample.

Isotope	**detector current /MA**
204	0.16
206	2.72
207	2.50
208	5.92

Calculate

i). The relative abundance of the different isotopes of lead in the sample used.

ii). the relative atomic mass of lead

3. The mass spectrum of an element A contained four lines at mass/charge of 54, 56, 57 and 58 with relative intensities of 5.84, 91.68, 2.17 and 0.31 respectively.
   - i) Explain what the term relative intensities means
   - ii) Calculate the relative atomic mass of A
   - iii) Explain why the values of relative atomic masses have no units.

THE GAS LAWS

BOYLES' LAW

It states that 'at a given temperature the volume of a given mass of a gas is inversely proportional to the pressure i.e.

$V \propto \frac{1}{p}$

It deals with the effect of pressure on volume of a gas under constant temperature

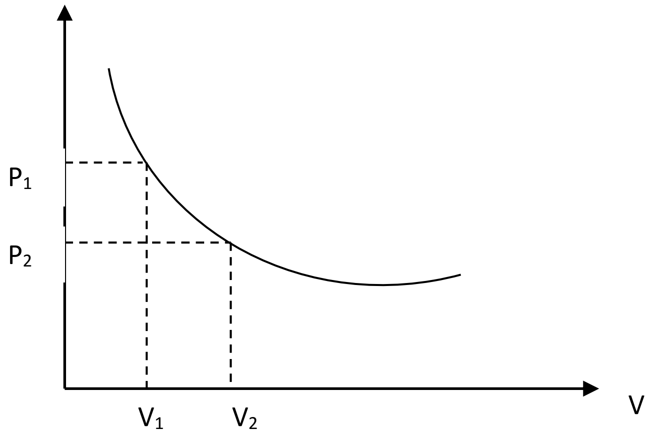
$V = \frac{k}{p}$

PV = K (a constant)

And for two conditions

$$P_1V_1 = P_2V_2$$

Graphically



CHARLES'S LAW

At a given pressure, the volume of a given mass of a gas is directly proportional to the absolute temperature.

$V \propto T$

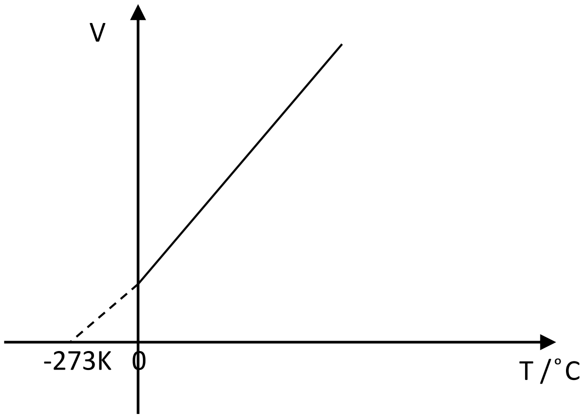
$V = KT$

And $\frac{V}{T} = K$ (a constant)

For two conditions

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

Graphically



The line cuts the temperature axis at -273.15^{0}C. It is the temperature at which the gas is expected to have zero volume. However, this is not true because the gas liquefies or solidifies before it reaches this temperature.

Any gas which obeys both Boyles and Charles laws is said to be an ideal gas or behaves ideally.

Ideal gas equation

At constant temperature

$$V \propto \frac{1}{P}$$

At constant pressure

$$V \propto T$$

From above two (combining the above two)

We obtain $V \propto \frac{T}{P}$

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

$$\frac{PV}{T} = K \text{ (a constant)}$$

For two conditions

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

This is called the equation of state for an ideal gas when a gas is 1 mole the constant is called the molar gas constant R and its value is 8.31Jmol^{-1}K^{-1}

Then PV = RT

For n moles of a gas

$$PV = nRT \text{ at s.t.p}$$

This is an ideal gas equation and it holds only for ideal or perfect gases.

Gas particles are very small compared with distances between them. We assume that the gas particles have no attraction for each other and that particles have no volume. They are called point masses.

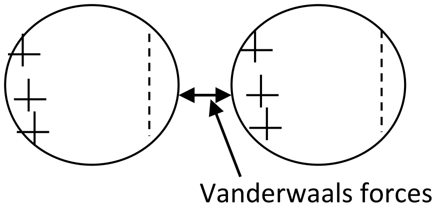
Such a gas does not exist, this imaginary gas which is composed of molecules with mass but no volume and no mutual attractions is known as an ideal or perfect gas.

Differences between real and ideal gas

- Real gases have a volume of their own while ideal gases are assumed to have no volume.
- Real gases have forces of attraction between them but ideal gases are assumed to have no forces of attraction between them.

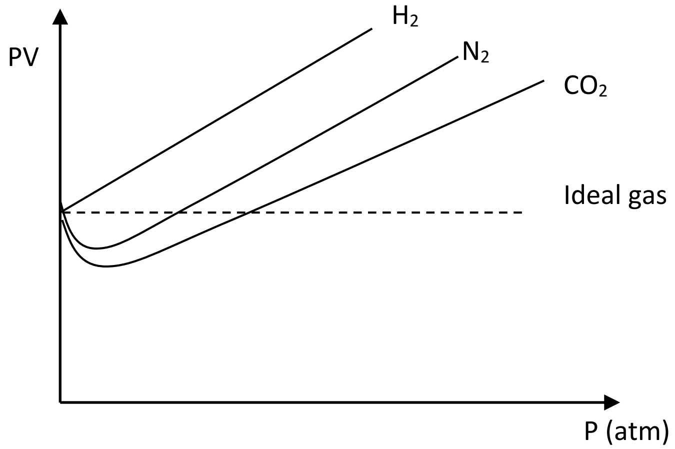
- Under particular conditions of temperature and pressure real gases liquefy while ideal gas does not.

For many gases at low pressures and high temperature, the molecules approach the behavior of ideal gas molecules because the molecules of ideal and real gases are far apart most of the total volume is empty space, at high pressure and low temperature, ideal gas molecules still remain far apart. But under these conditions the real gas molecules come close together and some electrons in one molecule repel those of another molecule. These molecules acquire charges and attract each other.

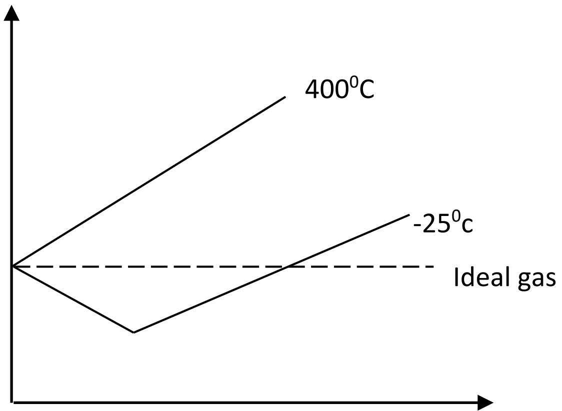


These attractive forces are called Vanderwaals forces .They operate when the molecules are very close to each other i.e. at high pressure and low temperature

Evaluation of a constant value of the product PV at all pressures is an attribute to an ideal gas.



The following curves show the value of PV for N_2 plotted against pressure for a number of temperatures

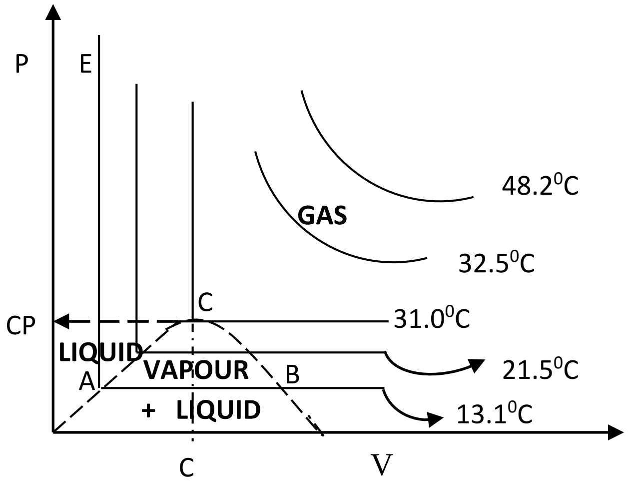


The curves have different shapes at different temperature N_2 approaches ideal behavior at 400^{0}C. At low temperature (at A) the gas behaves ideally.

ANDREW'S ISOTTHERY FOR CARBONDIOXIDE

An **Isotherm** is a curve which gives the variation of volume with pressure of a gas at constant temperature.

Andrew investigated the relationship of pressure and volume at high pressure and various temperatures



- Along AB, the volume of the gas decreases corresponding to an increase in pressure.
- Between B and A the volume decreases rapidly at constant pressure, along this line, the gas is liquefying and at A the carbondioxide is completely a liquid. The gas and liquid are present together along this region.
- The steepness of the curve AE indicates that the liquid is not easily compressed.
- The point C is called critical point for the gas and three critical quantities are defined.

Critical Temperature Tc	Is the temperature above which the gas fails to liquefy under compression
Critical pressure Pc	Is the pressure which is just sufficient to liquefy the gas at its critical temperature.
Critical volume Vc	Is the volume of 1 mole of a gas at the critical temperature and pressure.

Just above the TC, the isotherms, show marked deviations from that of an ideal gas. At higher temperature like 48.2^{0}C, the deviation from ideality is much less and the Isotherm approximates to that of ideal gas.

Formular mass

This is the sum of all the relative atomic masses of all the atoms in a formula of the compound.

The formula mass of a gas can be determined if its mass and volume are known. The given volumes are first converted to other volumes at S.T.P (standard temperature and pressure, T = 273K, P =760mmHg or 101300pa or N/m^2 or 1 atm, R = 8.31Jmol^{-1}K^{-1})

Examples

Solution

1. If the volume of a gas collected at 60^{0}C and pressure of 1.05×10^5Nm^{-2} is 60cm^3, what will be the volume at s.t.p

Solution

$P_1 = 1.05 \times 10^5 Nm^{-2}$ $\quad$ $T_1 = 60 + 273$

$V_1 = 60cm^3$ $\quad$ $= 333K$

$P_2 = 101300Nm^{-2}$

$T_2 = 273K$

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

$$\frac{1.05 \times 10^5 \times 60}{333} = \frac{101300 \times V_2}{273}$$

$$V_2 = \frac{1.05 \times 10^5 \times 60 \times 273}{333 \times 101300}$$

$= 51cm^3$

2. The volume of a gas weighing 3.5g at 20^{0}C and at a pressure of a 7640Nm^{-2} was 1500cm^3. What is the relative formula mass of the gas

$P_1 = 97640$ Nm^{-2} $\quad$ $P_2 = 101300$ Nm^{-2}

$V_1 = 1500cm^3$ $\quad$ $T_2 = 273K$

$T_1 = 293K$ $\quad$ $V_2 = ??$

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

$$V_2 = \frac{97640 \times 1500 \times 273}{101300 \times 293}$$

$= 1347.1cm^3$

Therefore

1347.1cm^3 contains 3.5g

$22400\ \text{cm}^3$ contains $\dfrac{22400 \times 3.5}{1347.1}$

$\mathbf{= 58.2}$

Hence the formula mass is **58**

SELF TEST

1. What mass of oxygen would be required to fill a 2dm^3 flask at 20^0C and $9 \times 10^4\text{Nm}^{-2}$ pressures?
   (Ans. 2.36g) take $R = 8.31\text{Jmol}^{-1}\text{K}^{-1}$

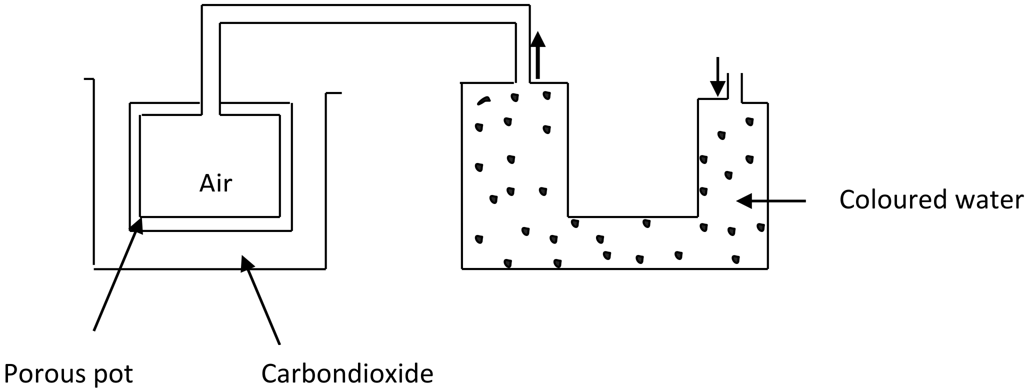
2. 202cm^3 of gas X at 13^0C and 770 mmHg weigh 0.262g. Calculate the formula mass of X
   (Ans. 30g)

GASEOUS DIFFUSION

It's defined as the spreading out of gaseous molecules from regions of high pressure to regions of low pressure. All gases spontaneously diffuse into one another to form a homogenous mixture

NB

Lighter gases diffuse more faster than heavier ones.



Observation

Water rises towards the porous pot

Explanation

Air molecules diffuse out of the porous pot faster than carbondioxide molecules diffusing in. Pressure inside the pot decreases hence the movement of water molecules towards the pot.

NB
If hydrogen was used instead of carbondioxide, the reverse process would occur.

Graham's law gaseous diffusion

It states that "At constant pressure and temperature the rate at which a gas diffuses at S.T.P is inversely proportional to the square root of its density".

Rate of diffusion $\propto \frac{1}{\sqrt{Density}}$

$$R \propto \frac{1}{\sqrt{P}}$$

Consider the rates of two gases A and B with densities ρ_A and ρ_B respectively.

$R_A \propto \frac{1}{\sqrt{\rho A}}$, $R_B \propto \frac{1}{\sqrt{\rho B}}$

$R_A = \frac{K}{\sqrt{\rho A}}$, $R_B = \frac{K}{\sqrt{\rho B}}$

Thus combining the two, we obtain

$$\frac{Ra}{Rb} = \frac{\sqrt{\rho B}}{\sqrt{\rho A}}$$

$$\frac{Ra}{Rb} = \sqrt{\frac{\rho B}{\rho A}}$$

The rate of diffusion of a gas is also inversely proportional to the square root of its molar mass

$R \propto \frac{1}{\sqrt{M}}$

Such that $R_A = \frac{K}{\sqrt{MA}}$ and $R_B = \frac{K}{\sqrt{MB}}$

$$\frac{RA}{RB} = \sqrt{\frac{MA}{MB}}$$

The relative or vapour density of a gas or vapour is the mass of any volume of a gas relative to the mass of an equal volume of hydrogen.

$$\text{Then Vapour density} = \frac{\text{Mass of a volume of gas}}{\text{Mass of an equal volume of hydrogen}}$$

Since equal volumes contain equal number of molecules

$$V.D = \frac{\text{Mass of n molecules of gas}}{\text{Mass of n molecules of hydrogen}}$$

If you take one molecule

$$V.D = \frac{\text{Mass of 1 molecule of gas}}{\text{Mass of 1 molecule of hydrogen}}$$

$$= \frac{\text{Mass of 1 mole of gas}}{\text{Mass of 1 mole of hydrogen}}$$

$$= \frac{\text{Molar mass of gas}}{\text{Molar mass of hydrogen}}$$

$$= \frac{\text{Molar mass of gas}}{2}$$

Such that $\boxed{\text{molecular mass} = 2 \text{ x } V.D}$

GASEOUS EFFUSION

This is the passage of a gas through a very small hole into a vacuum. It can be applied in the separation of Isotopes. The rates of effusion of diffusion gases under the same conditions are inversely proportional to the square roots of their densities and molar masses.

Examples

1. A gas B diffuses through a porous position at rate of 2.62 litres/second. Helium diffuses through the same partition at a rate of 8.49 l/s. What is the molecular mass of B. (He = 4)

Solution

$R_B = 2.62$ l/s

$R_{He} = 8.49$

$$\frac{R_B}{R_{He}} = \sqrt{\frac{M_{He}}{M_B}}$$

$$\frac{2.62}{8.49} = \sqrt{\frac{4}{M_B}}$$

$$\left(\frac{2.622}{8.49}\right) = \frac{4}{M_B}$$

$$M_B = 4 \times \left(\frac{8.49}{2.62}\right)^2$$

$$\mathbf{= 42g}$$

2. A gas X diffuses four times as rapidly as sulphurdioxide under the same conditions. If the density of sulphurdioxide at the given temperature and pressure is 2.88×10^3 gcm^{-3}.What is the density of X

Let $R_{so_2} = n$, $R_x = 4n$

$P_{SO_2} = 2.88 \times 10^3$, $P_x = ?$

$$\frac{n}{4n} = \sqrt{\frac{P_X}{2.88 \times 10^3}}$$

$$P_x = \left(¼\right)^2 \times 2.88 \times 10^3$$

$$= \underline{\mathbf{180gcm^{-3}}}$$

SELF TEST

1. It requires 45 seconds for a certain number of moles of unknown gas to pass through a small hole. Under the same conditions it requires 18 seconds for the same number of moles of oxygen to diffuse. Find the molecular mass of unknown gas ***(Ans. 200g)***
2. $6.3cm^3$ of gas X diffuse through a porous partition in 5 minutes if $7.4cm^3$ of oxygen diffuse through the same partition in the same time. Calculate the molecular of X ***(Ans. 44g)***

NOTE: The rate of Diffusion increases with increase in temperature

EMPIRICAL FORMULAE

Empirical formula of compound is the simplest formula which expresses the relative number of atoms of constituent element present in the molecule. It is calculated from the mass or percentage composition

Examples

1. A compound P contains carbon 66.7% and hydrogen 11.1% and the rest being oxygen.
   a) Determine the empirical formula of P
   b) If the vapour density of P is 36, determine the molecular of P (C=12, H=1,O =16)

Solution Percentage composition of oxygen = 100 – (66.7+1.1)
= 22.2%

	Carbon	**Hydrogen**	**Oxygen**
	C	H	O
%	66.7	11.1	22.2
	$\frac{66.7}{12}$	$\frac{11.1}{1}$	$\frac{22.2}{16}$
Divide by the smallest	$\frac{5.6}{1.39}$	$\frac{11.1}{1.39}$	$\frac{1.39}{1.39}$
	4	8	1

Therefore empirical formula is C_4H_8O

Molecular mass = 2 × vapour density
= 2 × 36
= 72 Molecular formula = C_4H_8O

Then $(C_4H_8O)n = 72$
$[(4 \times 12) + (8 \times 1) + 16]n = 72$
$72n = 72$
$n = 1$

2. 3.1g of an organic compound containing carbon, hydrogen and oxygen only produced 4.4g of carbondioxide and 2.7g of water on complete combination. Determine its empirical formula.

Solution

Molecular mass of carbondioxide = 44g
44g of carbondioxide contains 12g of carbon
1g of carbondioxide contains $\frac{12}{44}$g of carbon
4.4g of carbondioxide contains $\frac{12}{44} \times 44$
= 1.2g of carbon

And

18g of water contains 2g of hydrogen
1g of water contains $\frac{2g}{18}$
2.7g of water contains $\frac{2}{18} \times 2.7$g
= 0.3g of hydrogen

Then mass of oxygen = 3.1 – (0.3+1.2)
= 3.1 – 1.5
= 1.6g

Such that	**C**	**H**	**O**
	1.2	0.3	1.6
	$\frac{1.2}{12}$	$\frac{0.3}{1}$	$\frac{1.6}{16}$
	$\frac{0.1}{0.1}$	$\frac{0.3}{0.1}$	$\frac{0.1}{0.1}$
	1	**3**	**1**

Therefore, empirical formula is CH_3O

The composition of the element should be converted to percentage.

Carbon $= \frac{1.2}{3.1} \times 100$

= 38.71%

Hydrogen = $\frac{0.3}{3.1} \times 100$

= 9.677%

Oxygen = $\frac{1.6}{3.1} \times 100$

= 51.6%

Self test

1. a). 20g of a compound was found to contain 8g of carbon, 1.33g of hydrogen and the rest was oxygen.

   Calculate the empirical formula of the compound. The vapour density of a compound is 30. Determine its molecular formula ***(Ans.*** $C_2H_4O_2$***)***
2. Complete combination of 7.5g of an organic compound Y containing carbon, hydrogen and oxygen gave 17.8g of carbondioxide and 9.27g of water.
   - i) Calculate the empirical formula of y.
   - ii) When vapourised at 760mmHg and 400K, 0.225g of Y occupied 100cm^3. Calculate the molecular formula of Y ***(Ans.*** $C_4H_{10}O$ ***and*** $C_4H_{10}O$***).***

3. 0.236g of an organic compound Y on combustion gave 0.528g of carbondioxide and 0.324g of water. If 0.295g of Y at S.T.P gave 56 cm^3 of Nitrogen. Determine the molecular formula of Y. ***(Ans.*** C_3H_9N***)***

COLLIGATIVE PROPERTIES

Colligative property of solution is one which depends on the concentration (amount) of dissolved particles and not their nature.

An intensive property is one which does not depend on the quantity of matter. Example density, boiling point and others.

Colligative properties include;

- Depression of freezing point.
- The elevation of boiling point.
- Osmotic pressure.
- Vapour pressure lowering of the solvent

These properties are used to determine the molecular weight of a solute dissolved in the solvent.

Depression of freezing point (Cryoscopic method)

When a solid dissolves in a liquid, the freezing point of the liquid is lowered. If T_1 is the freezing point of the pure solvent and T_2 is that of the solution, then $(T_1 - T_2)$ is the depression of the freezing point. It's proportional to the mass of the solute dissolved in a given mass of a solvent and is inversely proportional to the relative formula mass of the solute

$\triangle T \propto \frac{m}{M}$, $\triangle T$ = depression of freezing point.

$\triangle T \propto n$

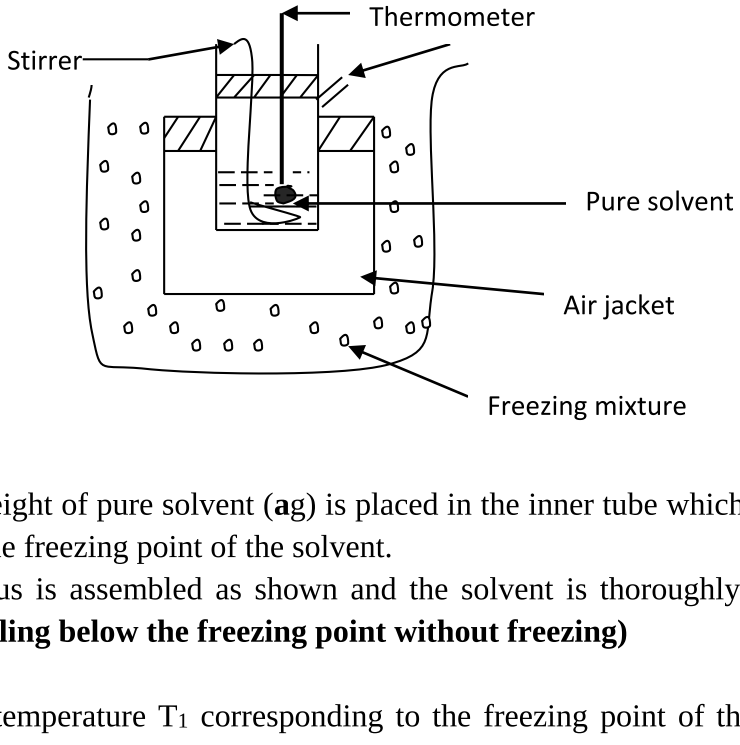
And $\triangle T = K_f \frac{m}{M}$

K_f is the <u>freezing point constant or Cryscopic constant</u>. It is the freezing point depression when one mole of a non-volatile solute is added to 1000g of solvent.

If the K_f of a solvent is known, the R.F.M of the solute can then be determined

<u>Measurement of the depression of freezing point (Beckman's method)</u>

This method is applicable when the freezing point depression is very small. It makes use of a special thermometer called Beckman's thermometer which is very sensitive to small changes in temperature



A known weight of pure solvent (**a**g) is placed in the inner tube which is cooled to a temperature just above the freezing point of the solvent.

The apparatus is assembled as shown and the solvent is thoroughly stirred to eliminate super cooling **(cooling below the freezing point without freezing)**

The steady temperature T_1 corresponding to the freezing point of the pure solvent is noted. If super cooling has taken place the temperature will fall initially below the freezing point of the pure solvent but will rise to assume the steady value of the freezing point as the solvent crystallizes.

A weighed quantity of solvent (**b**g) is added to the solvent through the side arm. The freezing point (T_2) of the solution is then determined. The difference between the two temperatures (T_1-T_2) is called the lowering of the freezing point of the solvent.

Treatment of results.

$T = (T_1\text{-}T_2)^0C$

ag of solvent dissolves **b**g of solute

1000g of solvent dissolve $(\frac{b}{a} \times 1000)$ g of solute

Then ΔT^oC is caused by $(\frac{b}{a} \times 1000)$ g

$$Kf \text{ is caused by } (\frac{b}{a} \times 1000) \times \frac{Kf}{\Delta T}$$

$$= \frac{Kf}{\Delta T} \times \frac{b}{a} \times 1000$$

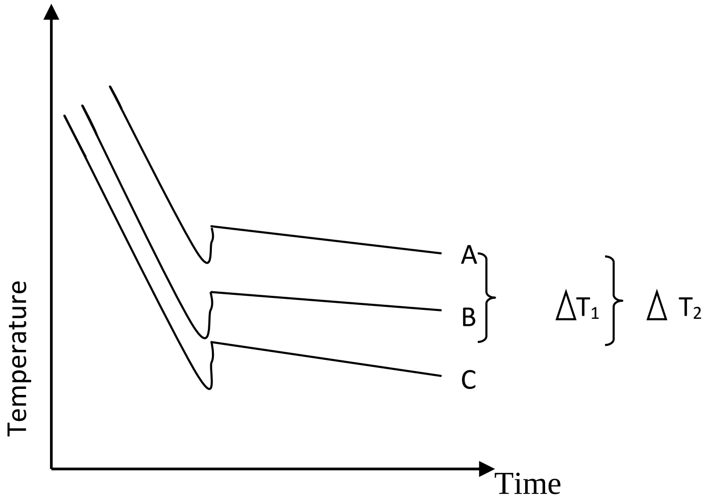
Hence molecular mass can be calculated from

$$\frac{Kf}{\Delta T} \times \frac{b}{a} \times 1000$$

NOTE:

- Freezing point constant (Kf) is the freezing point depression caused when 1 mole of a non-volatile solute is dissolved in 1000g of pure solvent.
- Freezing point.

THE COOLING CURVES FOR SOLVENT AND SOLUTIONS 1 AND 2 CONTAINING DIFFERENT AMOUNT OF SOLUTE ARE SHOWN BELOW



A = Cooling curve for solvent.
B = Cooling curve for solution 1
C = Cooling curve for solution 2

Example

1. 0.55g of nitrobenzene in 22g of ethanoic acid depresses the freezing point of ethanoic acid by 0.79ºC. Calculate the relative formula mass of nitrobenzene. (Kf for ethanoic acid is 3.9ºC $mol^{-1}Kg^{-1}$).

Solution

22g of ethanoic acid dissolves 0.55g of nitrobenzene

1000g of ethanoic acid dissolves $\frac{0.55 \times 1000g}{22}$ of nitrobenzene

= 25g of nitrobenzene

Also 0.79ºC is caused by 25g of nitrobenzene

3.9^0C is caused by $\frac{3.9 \times 25g}{0.79}$

= 123.4

Therefore the relative formula mass of nitrobenzene is 123

2. 1.5g of a compound P of molecular mass 89.9g on dissolving in 30g of water produce a freezing point at -1.04^0C at 760mmHg.. Calculate the freezing point constant per 1000g of water

Solution

$\Delta T = 0 - {}^-1.04 = 1.04^0C$

30g of water dissolves 1.5g of P

1000g water dissolve $\frac{1.5 \times 1000}{30}$

= 50g of P

Then 50g of P causes 1.04^0C

89.9g of P causes $\frac{1.04 \times 89.9}{50}$

= 1.87^0C

Therefore Kf = $+1.87^0C\ mol^{-1}Kg^{-1}$

3. A solution was prepared by dissolving 0.18g of naphthalene ($C_{10}H_8$) in 3g of camphor. The melting point of camphor is 177^0C. Calculate the melting point of the solution (Kf for camphor = $40^0C\ mol^{-1}kg^{-1}$)

Solution

3g of camphor dissolves 0.18g of napthaline

1000g of camphor dissolves $\frac{0.18 \times 1000}{3}$

= 60g of napthaline

But $C_{10}H_8 = 12 \times 10 + 8\times1$

= 128g

Then 128g of napthaline causes 40^0C

60g of napthaline causes $\frac{40 \times 60}{128}$

$=18.75^0C$

Therefore the melting point of solution

= 177-18.75

$= 158.25^0C$

Self test

1. The freezing point of a sample of pure benzene was found to be 5.481^0C. A solution of 0.321g of napthaline ($C_{10}H_8$) in 25g benzene began to freeze at 4.971^0C. A solution of 0.305g of benzoic acid is 25g of benzene began to freeze at 5.226^0C. Calculate

a) the K_f for 1000g of benzene

b) the R.F.M of benzoic acid in benzene

Ans. ($5.1^0Cmol^{-1}Kg^{-1}$, 244)

LIMITATION OF CRYOSCOPIC CONSTANT METHOD

- The solute should never dissociate nor associate, if it dissociates, it produces more particles and the depression of freezing point will be greater than expected.
- There must be no chemical reactions between the solute and solvent otherwise the formula mass includes that of the product example.

  $CaO_{(s)} + H_2O_{(1)} \xrightarrow{\qquad} Ca(OH)_{2\ (aq)}$
- The solution should be dilute so that the solute does not crystallize out on cooling.
- The R.F.M of the solute should not be very high otherwise the depression of the freezing point is not easily noticed.

ELEVATION OF BOILING POINT

The vapour pressure of a liquid is the pressure exerted by the vapour when it's in equilibrium, with the liquid. A liquid boils when its vapour pressure is equal to the atmospheric pressure.

The presence of a non-volatile solute in a liquid solvent lowers the vapour pressure of the solvent.

This is because the presence of a non-volatile solute at the surface of the solution reduces the escaping tendency of the solvent molecules.

Therefore the solution will at a higher temperature.

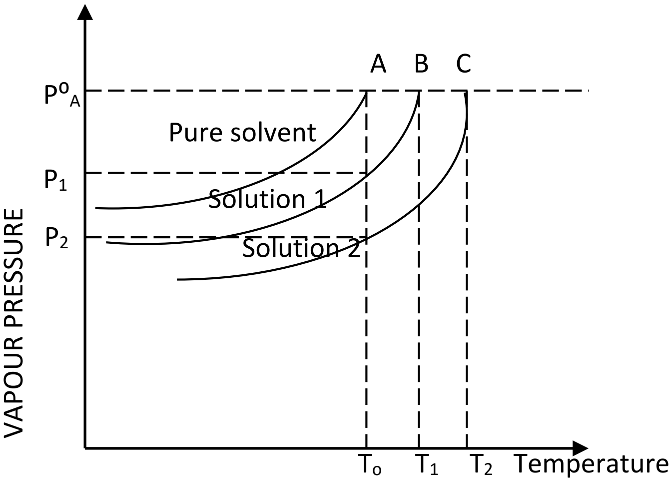
The extent of elevation is directly proportional to the molar concentration. Each solvent has a boiling point constant called **ebullioscopic constant**.

It's the elevation of the boiling point caused by dissolving 1 mole of a non-volatile solute in 1000g of solute.

NOTE:

The calculations for ebullioscopic constant, R.F.M of a dissolved solute are done in the same way as for cryoscopic constant.

Consider the variations of vapour pressure of a solvent and solution with temperature as shown below.



Curve A is for the pure solvent and B and C are the curves for solution of increasing concentrations. Solution 2 is more concentrated than solution 1. The curves B and C are below curve A at all temperature because the vapour pressure is always lower than that of solvents.

T_0, T_1 and T_2 are boiling points of pure solvent, solution 1 and solution 2 respectively, O and R are vapour pressure of solutions 1 and 2 respectively at temperature T_o and P_1 and P_2 are the vapour pressures corresponding to these points.

From the diagram $T_1 – T_0$ is the elevation of boiling point while $P^0_A – P_1$ is the lowering of the vapour pressure for solution 1.

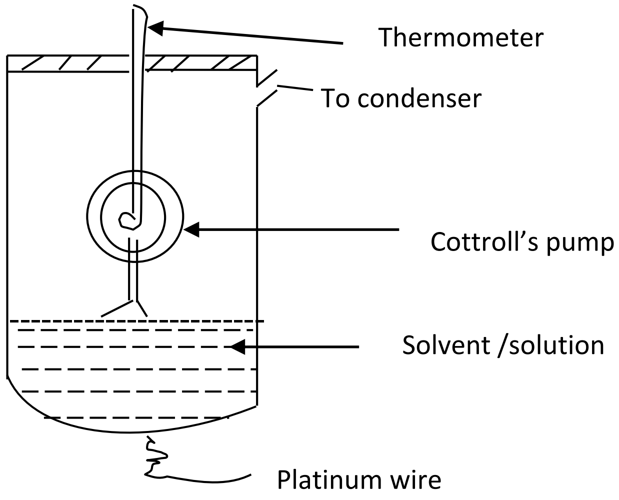
For dilute solutions the distances AB and BC are small and OB and RC can be regarded as straight lines so that AOB and ARC are regarded as similar triangles.

$$\frac{AB}{AC} = \frac{T_1-T_0}{T_2-T_0} = \frac{AO}{AR} = \frac{\text{Lowering of V.P of solution 1}}{\text{Lowering of V.P of solution 2}}$$

$$\frac{T_1 - T_o}{T_2 - T_o} = \frac{P^o_A - P_1}{P^o_A - P_2}$$

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

Determination of R.M.M by elevation of boiling point (by Cottroll's method)



- A known mass of pure solvent (**a** g) is put in tube A the solvent is heated and its boiling point(T_0° C) is recorded (when temperature remains constant)
  A known mass of solute (**b** g) is added through the side arm, The solution is heated and its boiling point (T_1°C) noted.

Treatment of result

Let the boiling point constant = K_b ^{0}C mol^{-1}Kg^{-1}

Elevation of boiling point constant AT= (T_1-T_o) °C

If **a** g of solvent dissolves **b** g of solute

1000g of solvent dissolves ($\frac{b}{a} \times 1000$) g of solute

If ΔT is caused by ($\frac{b}{a}$ 1000) g of solute

K_b is caused by $\left((\frac{b}{a} \times 1000) \times \frac{K_b}{\Delta T} \right)$ g of solute

Therefore R.F.M is given by $\frac{b}{a} \times 1000 \times \frac{K_b}{\Delta T}$

Example

1. Calculate the boiling point at atmosphere of a solution of 2.6g urea $CO(NH_2)_2$ in 50g of water
   (K_b = 0.52^{0}C mol^{-1}Kg^{-1}, H = 1, N = 14, O = 16)

Solution

50g of water dissolves 2.6g of area

1000g of water dissolves $\frac{2.6 \times 1000}{50}$

$= 52$g of Urea

Now RFM of $CO(NH_2)_2 = 12+16 + (14+2) \times 2$

$= 28+22$

$= 60$

60g of urea causes 0.52^{0}C

52 of urea causes $\frac{0.5 \times 52}{60}$

$= 0.451^{0}$C

Then boiling point $= 100 + 0.457$

$= 100.451^{0}$C

2. A solution of 1g of phenol in 50cm^3 of ether boiled at a temperature of 0.632^{0}C higher than that of pure ether. The K_b of ether is 2.12^{0}C mol^{-1}Kg^{-1}.The density of ether is 0.714g/cm^3. Calculate the relative formula mass of phenol.

Solution

Mass of ether $= 0.714 \times 50$

$= 35.7$g

35.7g of ether dissolve 1g of phenol

1000g of ether dissolves $\frac{1 \times 1000}{35.7}$

$= 28.011204$g of phenol

Now

0.632^{0}C is caused by 28.011204 g of phenol

2.12^{0}C is caused by $\frac{2.12 \times 28.011204}{0.632}$

$=93.96$

Therefore the R.F.M of phenol is 94

Self Test

1. Calculate the boiling point constant Kb of trichloromethane if 0.4g of camphor in 34.5g of trichloromethane rises the boiling point by 0.3^{0}C (Camphor = $C_{10}H_{16}O$)

   (Answer 3.9^{0}C)
2. The boiling point of a solution containing 0.3g of a hydrocarbon in 30g of ether is 0.17^{0}C higher than that of pure ether. If the K_b for ether per 100g is 21.6^{0}C mol^{-1}100g^{-1}. Calculate the R.M.M of the hydrocarbon

   (Ans. 127)

LIMITATIONS OF BOILING POINT ELEVATION METHOD

- The method is applicable of both the solvent and the solute doesn't react together.
- There should be no association or disassociation example strong acids and strong alkaline are dissociated in water.
  Ethanoic acid associates in benzene
- The solution should be dilute
- The R.F.M should not be very high.

Note: One advantage of freezing point depression method over boiling point elevation method in that freezing point method is not affected very much by pressure changes unlike boiling point which depends on the atmospheric pressure.

OSMOTIC PRESSURE

Osmosis is the diffusion of solvent molecules through a semi-permeable membrane from a dilute solution into a more concentrated one.

A semi-permeable membrane is a film of material which can be penetrated by a solvent but not by the solute example animal and plant cells.

Osmotic pressure is therefore the pressure which must be applied to stop solvent molecules from diffusing across a semi permeable membrane.

One mole of a solid A when vaporized occupies a volume of $22.4dm^3$ at 0^0C (273K) and exerts a pressure of $1.01325 \times 10^5 Nm^{-2}$ (Pa).

The osmotic pressure equation resembles that of ideal gas equation.

$$\Pi V = nRT$$

Where V = volume in m^3

Π = osmotic pressure

The osmotic pressure is used to determine the formula masses of organic compounds which cannot be determined by depression of freezing point or elevation of boiling point because they would show very little depression of freezing point or elevation of boiling point.

This is because the organic compounds such as starch and rubber have very high formula masses. Secondly the elevation of boiling point does not work because the compounds may decompose before the solution boils.

LIMITATIONS

- The solution should be dilute
- There must be no chemical reaction between solute and solvent.
- There must be no association or disassociation

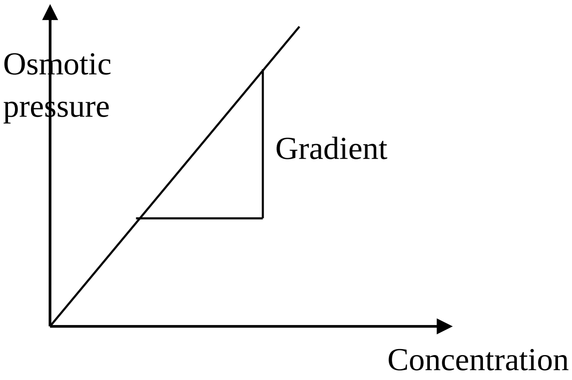
FACTORS THAT AFFECT OSMOTIC PRESSURE

1. **1.** Concentration: Osmotic pressure increases with concentration. This because when the concentrated, more solvent molecules will move to solution side and this increases the difference in solvent and solute side.
2. **2.** Temperature: Osmotic pressure increases with increase in temperature

   That is $PV = nRT$

   Then $\pi = nRT$ where n is concentration

   At constant temperature, a graph of osmotic pressure against concentration gives a straight line which passes through the origin.



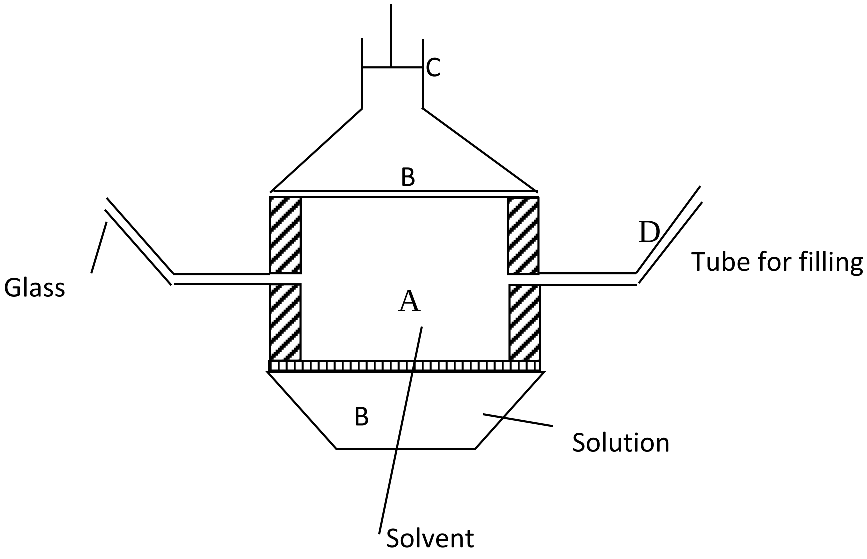
Then $\pi = RT.{}^{m}/_{v}$, but $({}^{m}/_{v})$ = concentration

$$\pi = RT.\frac{m}{M_r v}$$

Then $\pi = \frac{RT}{M_r}.\left(\frac{m}{v}\right)$

Hence the gradient (slope) = $\frac{RT}{M_r}$ and $M_r = \frac{RT}{gradient}$, for M_r = Molecular mass

Measurement of osmotic pressure



The solvent is placed in the horizontal porous cylinder A with a membrane. This cylinder is placed into the solution B that carries an attachment C through which pressure can be applied.

A is first filled with a solvent through D up to a definite point in the capillary. As a result of osmosis the level of liquid in the capillary will fall but applying pressure through C it's restored to its initial valve. This pressure is the osmotic pressure of the solution.

Example:

1. Calculate the molar mass of a compound Z given that a solution of 60g of Z in Idm^3 exerts an osmotic pressure of 431 x 10^5 NM^{-2} at 25^{0}C

Solution:

$V_1 = 1dm^3$ $\qquad$ $V_2 = ??$

$P_1 = 4.31 \times 105Nm^{-2}$ $\qquad$ $P_2 = 1.01 \times 10^5Nm^{-2}$

$T_1 = 25 + 273 = 298K$ $\qquad$ $T_2 = 273$

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

$$\frac{4.31 \times 10^5 \times 1}{298} = \frac{1.01 \times 10^5 \times V_2}{273}$$

$$V_2 = \frac{4.31 \times 10^5 \times 273}{1.01 \times 10^5 \times 298}$$

$$= \mathbf{3.9093295dm^3}$$

Now

3.9093295 dm^3 of Z contains 60g of Z

22.4dm^3 of Z contains $\frac{60 \times 22.4}{3.9083295}$

$$= \mathbf{343.79}$$

Hence the molecules of Z is **344g**

3. A polysaccharide has formula $(C_{12}H_{22}O_{11})n$. A solution containing 5g of the sugar per litre has an osmotic pressure of 5.34mmHg at 20^{0}C. Find the value of n. (H=1, C=12, O=16)

Solution

$V_1 = 1L$ $\qquad$ $V_2 = ??$

$P_1 = 5.34mmHg$ $\qquad$ $P_2 = 760mmHg$

$T_1 = 20+273 = 293K$ $\qquad$ $T_2 = 273K$

Using $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\frac{5.34 \times 1}{293} = \frac{760 \times V_2}{273}$$

$$V_2 = \frac{5.34 \times 1 \times 273}{293 \times 760}$$

$$\mathbf{= 0.0065467 litres}$$

Now this means that,

0.0065467litres of sugar contains 5g

litres 22.4sugar contains $\frac{22.4 \times 5}{0.0065467}$

$$\mathbf{= 17107.856}$$

Therefore the molar mass of sugar = 17108

Then $(C_{12}H_{22}O_{11})n = 17108$

$(12 \times 12 + 22 \times 1 + 11 \times 16)\ n = 17108$

$342n = 17108$

$$n = \frac{17108}{342}$$

$$\mathbf{= 50.02}$$

Hence the value of n is 50.

Self test

1. Calculate the R.F.M of sucrose if a solution containing 19.15g of sucrose per dm^3 has an osmotic pressure of 136300pa at room temperature
   (Ans. 347)

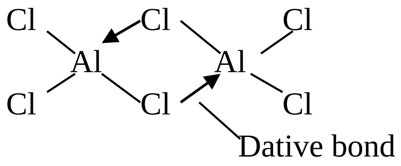
2. At 25^0C the osmotic pressure of the solution containing 1.35g of a protein per $100cm^3$ of solution was found to be 1216pa. Calculate the R.M.M of the protein if the molar volume at S.T.P is $22.4dm^3$
   (Ans. 27498.6)
3. Calculate the molecular mass of a solute y if 20g of solute in $100cm^3$ of solution has an osmotic pressure of $3 \times 10^6 N/m^2$ at 27^0C
   (Ans. 166.2g)

EFFECT OF DISSOCIATION AND ASSOCIATION ON COLLIGATIVE PROPERTY

Dissociation is the process by which a compound separates into free ions. Dissociation increases the number of particles in solution. The effect is that colligative property will increase.

Example; $KCl(s) \longrightarrow K^+_{(aq)} + Cl^-_{(aq)}$

KCl dissociates to give two ions thus the colligative property will be twice the value calculated in the absence of ionization. Association is the process where two or more molecules combine to form one molecule. The combination is either through dative bonding or hydrogen bonding. Example $AlCl_3$ associates in vapour form to form Al_2Cl_6.



Association decreases the number of particles in solution. The effect is that the value of colligative property will be lower than the true value without association.

CHEMICAL ENERGETICS

This deals with the heat changes which accompany chemical reactions. Chemical processes such as combustion, neutralization, dilution and atomization are associated with corresponding energy changes.

Types of Reactions

The heat content of a system is called enthalpy and it's symbolized by "H". The change in enthalpy is given by $\triangle H$ and the symbol $\triangle H$ is pronounced as "delta H" and $\triangle H = H_2 – H_1$ where

H_1- heat content of reactants

H_2-Heat content of products

There are two major types of reactions

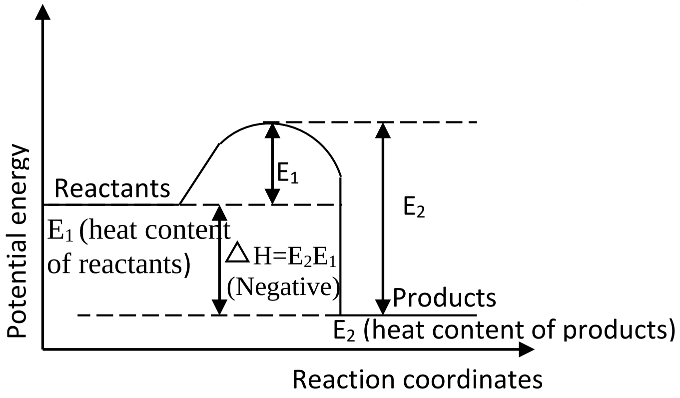
EXOTHERMIC REACTIONS

These proceed with evolution of heat energy to the surrounding .They are denoted - $\triangle H$ and with an arrow moving down because its vector quantity

Because the heat content of the products of an exothermic reaction is less that of the reactants.

The negative sign of the enthalpy change shows that the reacting system has lost heat energy to the surroundings **example.** Combustion reactions.

The diagram below shows the potential energy for an exothermic reaction.



E_1- activation energy for the forward reaction

E_2- activation energy for the backward reaction

$$\triangle H = E_2 – E_1$$

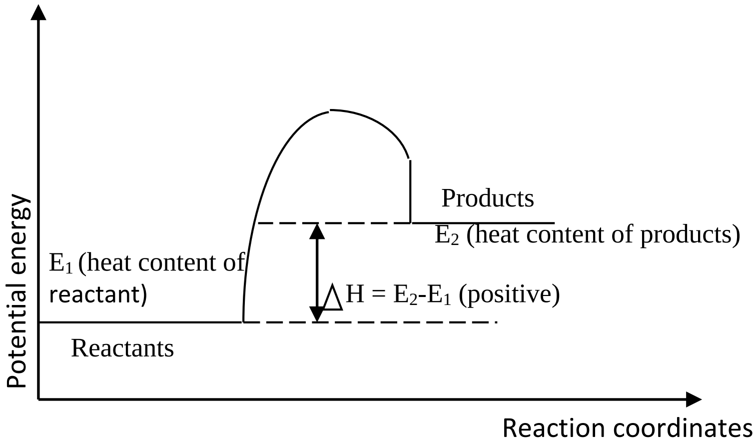
And $E_1 > E_2$, $\triangle H$ is negative and $\triangle H < O$

ENDOTHERMIC REACTIONS

These occur only if heat energy is absorbed by the system. They are represented by +△H and with arrow moving up because the heat content of the products is more than that of the reactants. The positive sign also shows that the reacting system has gained heat energy from the surroundings

Example; $H_2O_{(l)} \longrightarrow H_2O_{(g)}$

The diagram below shows the potential energy for an exothermic reaction



$E_2 > E_1$, and △H is positive then △H > O

NOTE:

- △H is measured in kilojoules, per mole and at constant pressure.
- △H is written at the end of a chemical equation.
- For a series, of reactions , the total enthalpy change is the sum of the enthalpy change of all the reactions
- △H varies slightly with temperature, that is, it is affected by temperature changes
- △H is directly proportional to the amount of substances involved in a reaction. The enthalpy change is doubled if the amount of material reacting is doubled.

HEAT OF REACTIONS

This is the amount of heat evolved or absorbed when the reaction occurs between molar quantities of the substances as represented by the equation and under standard conditions.

Standard conditions mean that the gases are at a pressure of one atmosphere, solutions are one molar and the substances are in their normal physical states at 25^0C

LAPLACE LAW

It states that the amount of heat needed to decompose a compound is equal but opposite in magnitude to the heat absorbed when that compound is formed.

That is if $A \longrightarrow B \quad \triangle H = -x \text{ KJmol}^{-1}$

$B \longrightarrow A \quad \triangle H = +x \text{ KJmol}^{-1}$

NOTE:

- When measurements are made on reacting systems only changes in enthalpy content are measured
- Elements in their standard states are assigned zero enthalpies.

Heat of formation

This is the enthalpy change when one mole of a substance is formed from its elements in their standard states. The enthalpy of formation of a substance is denoted by$\triangle H^0 f$. The superscript o means standard conditions and the subscript f indicates the formation reaction

Consider the following reactions

a). $\frac{1}{2} N_{2(g)} + \frac{1}{2} O_{2(g)}, \longrightarrow NO_{(g)} \quad \triangle H^o f = +90.2KJmol^{-1}$

b). $C \text{ (graphite)} + 2H_{2(g)} \longrightarrow CH_{4(g)} \triangle H^0 f = -74.8xJmol^{-1}$

c). $\frac{1}{2} N_{2(g)} + \frac{3}{2} H_{2(g)} \longrightarrow NH_{3(g)} \triangle H^0 f = -74.8KJmol^{-1}$

A boil at each of these thermo chemical an equation shows that one mole of each of the products (i.e. NO, CH_4, NH_3) is formed from its elements. The elements are in their standard states; recall that the enthalpy of each of the elements is zero.

Reactions a), b) and c) could also be written as

a) $\triangle H^0 f\ [NO_{(g)}] = +90.2KJmol^{-1}$
b) $\triangle H^0 f[CH_{4(g)}] = -74.8KJmol^{-1}$
c) $\triangle H^0 f[NH_{3(g)}] = - 46.1KJmol^{-1}$

The first statement for example means that 1 mole of nitrogen monoxide had been formed from half a mole each of nitrogen and oxygen with 90.2KJ of heat being absorbed in the process

The enthalpy of a compound is equal to its heat of formation.

Example

Calculate the heat of formation of benzene from the reaction below.

$C_6H_6 + {}^{15}/_{2}O_{2\ (g)} \longrightarrow 6CO_{2\ (g)} + 3H_2O_{\ (l)} \quad \triangle H = -3164KJ$

Given

(Heat of formation of $CO_2 = -392KJmol^{-1}$)

(Heat of formation of $H_2O = -286KJmol^{-1}$)

Solution

$C_6H_6 + {}^{15}/_{2}O_{2\ (g)} \longrightarrow 6CO_{2\ (g)} + 3H_2O$

$X \quad + \quad 0 \qquad\qquad 6(-392) + 3(-286)$

$\triangle Hr = \triangle H \text{ products} - \triangle H \text{ reactants}$

$-3164 = (-2354 + -858) - X$

$-3164 = -3210 - X$

$X = -46\ KJmol^{-1}$

Alternatively

You need

$6C_{(s)} + 3H_{2(g)} \longrightarrow C_6H_{6(s)}$

You have

Eqn. (1) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}\quad \triangle Hf = -392$

Eqn. (2) $H_{2(g)} + {}^{1}/_{2}O_{2(g)} \longrightarrow H_2O_{(l)}\quad \triangle Hf = -286$

NOW

6 × eqn. (1) + 3 × eqn. (2)

Because you need 6 cations and 3 hydrogen molecules to form C_6H_6

Gives

$$6C_{(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} \quad = -392 \times 6$$

$$+ 3H_{2(g)} + \frac{3}{2}O_{2(g)} \longrightarrow 3H_2O_{(l)} \quad = -256 \times 3$$

Eqn. (3) $6C_{(s)} + 3H_{2(g)} + \frac{15}{2}O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)} \quad = -3210$

Then the eqn. (3) + the reverse of combustion of benzene

$$6C_{(s)} + 3H_{2(g)} + \frac{15}{2}O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)} \quad = -3210$$

$$+ 6CO_{2(g)} + 3H_2O_{(l)} \longrightarrow C_6H_{6(s)} + \frac{15}{2}O_{2(g)} \quad = +3164$$

$$6C_{(s)} + 3H_{2(g)} \longrightarrow C_6H_6(s) \quad = -46KJmol^{-1}$$

Example 2

1. Calculate using Hess' law the standard enthalpy of formation of carbon monoxide from the following data.

a) $C(graphite) + O_{2(g)} \longrightarrow CO_{2(g)}\ \triangle H^0f = -313.5KJmol^{-1}$

b) $CO_{(g)} + ½\ O_{2(g)} \longrightarrow CO_{2(g)}\ \triangle H^0C = -283.0KJmol^{-1}$

(Ans. -110.5KJmol^{-1})

2. Calculate the enthalpy of formation of carbon disulphide using Hess's law from the following data.

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}\quad \triangle H = -394KJmol^{-1}$

$S_{(g)} + O_{(g)} \longrightarrow SO_{2(g)}\quad \triangle H = -297KJmol^{-1}$

$CS_{2(S)} + 3O_{2(g)} \longrightarrow 2SO_{2(g)} + CO_{2(g)}\quad \triangle H = -1075KJmol^{-1}$

(Ans. +87KJmol^{-1})

3. Use the following data below to calculate the standard enthalpy of formation of potassium chloride.

$KOH_{(aq)} + HCl_{(aq)} \longrightarrow KCl_{(aq)} + H_2O_{(l)}$ H = 573KJmol^{-1}

$K_{(s)} + \frac{1}{2}O_{2(g)} + \frac{1}{2}H_{2(g)} + (aq) \longrightarrow KOH_{(aq)}$ H = 487KJmol^{-1}

$KCl_{(s)} + (aq) \longrightarrow KCl$ H = +18KJmol^{-1}

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ H = 286KJmol^{-1}

$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{(g)} + (aq) \longrightarrow HCl_{(l)}$ H = -164KJmol^{-1}

(Ans. 440.3KJmol^{-1})

NOTE: The more negative the enthalpy of formation of a compound the more stable it is. The more positive the heat of formation the less stable is the compound

Example

Compound	**H^0f**
NaCl	- 418
HBr	-36
HI	+26
NCl_3	+230

The order of stability is

$NaCl > HBr > HI > NCl_3$

Self check

1. Given the following data below

   $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ H = - 394KJmol^{-1}

   $S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$ H = - 297KJmol^{-1}

   $CS_{2(s)} + 3O_{2(g)} \longrightarrow 2SO_{2(g)} + CO_{2(g)}$ H = - 1075KJmol^{-1}

   Calculate the enthalpy of formation of carbon disulphide.

   (Ans. 87KJmol^{-1})

2. Use the following information to calculate the enthalpy of formation of carbon hydroxide.

   $Ca(s) + \frac{1}{2}O_2(aq) \longrightarrow CaO(s)$ H = - 637.56KJmol-1

   $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ H = -286.78KJmol-1

   $CaO + H_2O \longrightarrow Ca(OH)_2$

Dissociation energy

The heat of dissociation energy is the heat necessary to break up 1 mole of a molecule into its constituent gaseous atoms **example**

$N_{2\,(g)} \longrightarrow 2N_{(g)}$

The heat of sublimation is the heat necessary to convert 1 mole of a solid element into a gaseous state.

A reaction can be endothermic at one temperature and exothermic at another temperature due to the difference in the physical states of substances at the two temperatures.

The combination of hydrogen and iodine is endothermic at low temperature and exothermic at high temperature. This is due to the heat absorbed to sublimate the iodine.

Consider the reaction

$S_{(s)} + O_{2\,(g)} \longrightarrow SO_{2\,(g)}$

During combustion the processes occurring are

a) $S_{(s)} \longrightarrow O_{2\,(g)}$, Sublimation
b) $O_{2(g)} \longrightarrow 2O_{(g)}$, Dissociation

The energy in (b) is the bond dissociation energy

Example

Nitrogen (N_2) can be written as N ≡ N. Therefore the inertness of nitrogen at room temperature is due to its high bond dissociation energy. The heats of formation of many compounds of nitrogen are endothermic because of the difficulty in breaking the tripple bond in nitrogen and the double bond in oxygen also.

The standard enthalpy of combustion ($\triangle H^0C$)

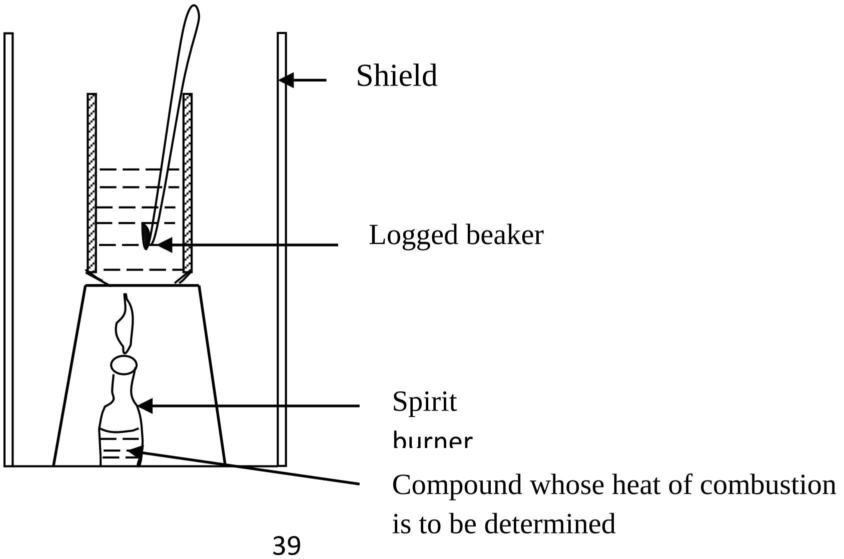
This is the enthalpy change when one mole of a substance is completely burnt in oxygen under standard conditions.

Organic compounds containing carbon, hydrogen and oxygen only burn in oxygen to give carbondioxide and water. All combustion reactions are exothermic

Example

C (graphite) + $O_{s\,(g)} \longrightarrow CO_{2\,(g)}$ $\triangle H = -393KJmol^{-1}$
C (diamond) + $O_{2\,(g)} \longrightarrow CO_{2\,(g)}$ $\triangle H = -395KJmol^{-1}$
From the two equations diamond is less stable than graphite (it spontaneously burns in air)
At s.t.p diamond is unstable and is converted to graphite by the reactions
C (diamond) $\longrightarrow$ C (graphite) $\triangle H = -2KJmol^{-1}$

Determination of enthalpy of combustion



- A known volume (Vcm^3) of cold water is put in a lagged beaker and to initial temperature (T_o) recorded.
- Some compound (such as ethanol) is added into the burner and the mass of the burner containing this compound before burning is determined (**a** g)
- The burner is lit and the flame kept steady under the water which is constantly stirred using a thermometer.
- After a reasonable rise in temperature of the water, the flame is extinguished and the highest attained temperature (T_1) recorded
- The mass of burner and the remaining compound after burning is determined (**b** g).

Treatment of results

Rise in temperature $\Delta T = (T_1 - T_0)^0C$

Mass of compound burnt M = (a – b) g

Mass of water = $V \times 1$

$= V_g$ because density of water is $1gcm^{-3}$

Heat evolved = heat gained by water

$= VC\theta$

$= V \times 4.2 \times \Delta T$ Joules

But M_g of the compound burn to give $V \times 4.2 \times \Delta T$ joules

M_R of compound burn to give $\frac{4.2\ V\Delta T}{m} M_R$ Joules

Where M_R is the molar mass of the compound

Hence

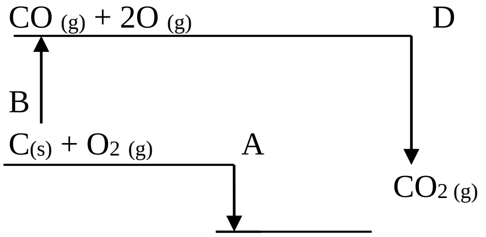
$$\Delta H^0C = \frac{4.2\ V\ \Delta T\ M_R}{m} \text{ Joules mole}^{-1}$$

$$= \frac{4.2V\Delta TM_R}{1000m} \text{ KJmol}^{-1}$$

HESS'S LAW

It states that the enthalpy change of a chemical reaction is the same irrespective to the number of stages passed through but it depends the final states of the reactants and products

Consider the formation of carbondioxide from carbon that is,



Example

Solution

Write the equations using standard heats of reactions throughout in KJmol-1

$C + O_2 \longrightarrow CO_2$ -393.5 −−−−−− (1)

$CO + ½\ O_2 \longrightarrow CO_2$ -283.0 −−−−−− (2)

Write the equation you want

$C + ½\ O_2 \rightarrow CO$ −−−———------------- (x)

Because both sides of the equation are equal, equations can be added or subtracted from one another

Reverse (2) and add to (1)

$CO_2 \longrightarrow CO + ½O_2$ + 283.0

$+ C + O_2 \longrightarrow CO_2$ - 393.5

$C + CO_2 + O_2 \rightarrow CO + CO_2 + ½\ O_2$ -110.5

We obtain

$C_{(s)} + ½O_{\ (g)} \longrightarrow CO_{\ (g)}$ -11.5

So $\triangle H^0 f$ for CO is $-110.5KJmol^{-4}$

Self check

1. Calculate the heat of formation of ethane given that the heats of the combustion of carbon, hydrogen and ethane are $-393KJmol^{-1}$, $-285KJmol^{-1}$ and $-1393KJmol^{-1}$ respectively
   (Ans. = 37KJmol^{-1})
2. The heats of combustion of carbon, hydrogen and ethanol are -393, -286, -1371 $KJmol^{-1}$ respectively. Calculate the heat of formation of ethanol
   (Ans. -273KJmol^{-1})

BOND ENERGIES

It's the amount of energy required to break 1 mole of a particular bond in a molecule producing free gaseous atom or radicals. It's numerically equal but opposite to the heat of formation of that bond from gaseous atoms.

It can be calculated if the heat of formation of a compound is known. The heats of dissociation are always endothermic

Methane gas can be formed from one mole of solid carbon and 2 moles of gaseous hydrogen. This can be done in two ways.

a) The carbon and hydrogen are changed from their normal states into gaseous atoms which then combine to give methane.

$C_{\ (g)} \longrightarrow C_{(g)}$ $\triangle H = 720KJ$

$2H_{2\ (g)} \longrightarrow 4H_{(g)}$ $\triangle H = 862KJ$

$C_{(g)} + 4H_{(g)} \rightarrow CH_{4(g)}$ $\Delta H = x$

X is the heat of formation of methane from gaseous atoms. Adding the 3 equations
$C_{(g)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ $\Delta H = (720 + 562 + x)$ KJ

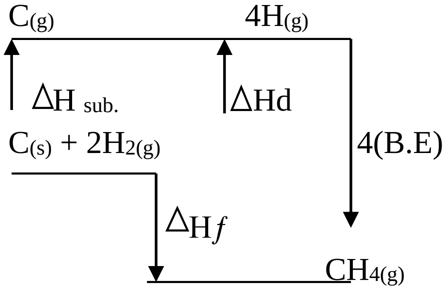
b) 1 mole of carbon and 2 moles of hydrogen molecule are directly combined to form methane

$C_{(g)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ $\Delta H = -74KJmol^{-1}$ from Hess's law

$$720 + 862 + x = -74$$
$$x = -1656$$

This is the energy change when 4C-H bonds in methane are formed. Thus the energy of formation of 1C-H bond $= \frac{-1656}{4} = -414KJmol^{-1}$

Alternative method



ΔH_f – enthalpy of formation of methane
ΔH sub. - Enthalpy of sublimation of carbon
ΔHd – Dissociation energy of hydrogen
$\Delta B.E$ – bond energy for formation of methane

Given that

$\Delta H_{sub.} = 720KJmol^{-1}$
$\Delta H_d = 215.5$KJ/mole of hydrogen atom
$\Delta H_f = .74KJmol^{-1}$

Then from Hess's law

$$H_f = Hsub. + Hd + B.E$$

And $-74 = 720 + 4(215.5) + B.E$

$$74 = 720 + 862 + B.E$$

And B.E = -1656 for 4 C-H

And the bond energy for C-H bond

$$= \frac{-1656}{4}$$
$$= -414KJmol^{-1}$$

When the standard enthalpy change of a reaction cannot be measured, an approximate value can be obtained using average standard bond enthalpy.

And

Heat of reaction = Σ bond energy of reactants - Σ bond energy of products

Example

Calculate the enthalpy change of reaction for the reaction

$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$, given standard bond enthalpies in $KJmol^{-1}$

H – H = 436, Cl – Cl = 242, H – Cl = 431

Solution

Bond energy for reactants,	**products**
H – H = 436	= 2(431)
Cl – Cl = $\underline{242}$	= 862
678	

Heat of reaction = 678 – 862

= $-184KJmol^{-1}$

Self Check

1. Some bond energies are given below:

Bond	**Energy** $\mathbf{1KJMol^{-1}}$
Cl – Cl	242
C – H	435
Cl – H	431
C – Cl	339

Determine the enthalpy change for the reaction in methane reacts with chlorine in the presence of sunlight to form chloromethane.

2. Find the enthalpy change for the reaction

   $C_2H_{6(g)} \longrightarrow C_2H_{2(g)} + 2H_{2\,(g)}$ given bond energies

   H – H = 436 C – H = 414

   C – C = 346 C ≡ C = 610

   (Ans. 520 $\mathbf{KJmol^{-1}}$***)***

3. Using a diagram, calculate the standard enthalpy of formation of propane

   $3C\ (graphite) + 4H_{2(g)} = C_3H_{8(g)}$ from the following data

a) $C_3H_{8(g)} + 50_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(l)} \quad \Delta H_3 = -2220KJmol^{-1}$

b) $C(graphite) + O_{2(g)} \rightarrow CO_{2(g)}, \quad \Delta H_1 = -393.5KJmol^{-1}$

c) $H_{2(g),} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)} \quad \Delta H_2 = -285.8KJmol^{-1}$

(Ans. -103.6KJmol^{-1})

NOTE:

Bond-breaking is an endothermic process and bond-making is an exothermic process.

For diatomic molecules in the gaseous sate, bond dissociation enthalpy is twice the enthalpy of atomization

Use of bond energies

The information allows, among other things the

- Strengths of bonds to be compared
- Understanding of the structure and bonding of covalent compounds
- Understanding of the mechanism of chemical reactions
- Calculations of enthalpy changes in reactions

NOTE:

Examination of the mean bond energy values for N – N, N =N, N≡N, C-C, C=C, C ≡ C and C–O , C = O, C ≡ O

Show that bond enthalpies increases as the number of bonds increases.

Factors affecting bond energy

1. Electro negativity difference between atoms, the greater the electro negativity difference, the bigger the bond energies since the atoms will be strongly attracted to each other
2. The number of bonds holding the atoms in covalent molecules a single bond is weaker than a double bond which is in turn weaker than a tripple bond
3. The atomic radius-small atoms like hydrogen form a much stronger bond with other atoms since it can be attracted very closely towards the nucleus of the other atom. This gives rise to relatively bigger bond energy.

Check

The bond energies and the atomic numbers of the element in group (vii) in the periodic table are given in the table below

Element	**F**	**Cl**	**Br**	**I**
Bond energy (KJmol-1)	158	242	193	151
Atomic number	9	17	35	53

Explanation

Bond energy rises sharply from F to Cl and then from Cl to I it decrease with increase in atomic number it is expected that the bond energy in group (vii) would decrease with increase in atomic size since increased size results in less effective overlap of orbital .
The abnormally low bond energy of F than expected is due to the small atomic size of F. Therefore small F-F distance hence inter-nuclear repulsion and also the large electron-electron repulsions between the ion pairs of two F atoms weaken the bond.

Heat of Atomization (sublimation)

This is the amount of energy required to form one mole of gaseous atom from its molecule or solid element in a standard state. It is always an endothermic change.
$\frac{1}{2} H_{2(g)} \rightarrow H_{(g)} \quad \Delta H$ atm
$C_{(s)} \longrightarrow C_{(g)}, \quad \Delta H_{sub.}$

Heat of hydrogenation

This is the enthalpy change when 1 mole of unsaturated compound reacts with hydrogen gas

Self check

Find the enthalpy of hydrogenation of Ethyne to ethane from the following data.

a) $C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(l)}, \quad \Delta H = -1393KJmol^{-1}$

a) $C_2H_{2(g)} + \frac{5}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + H_2O_{(l)} \quad \Delta H = -1310KJmol^{-1}$

b) $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}, \quad \Delta H = -285KJmol^{-1}$

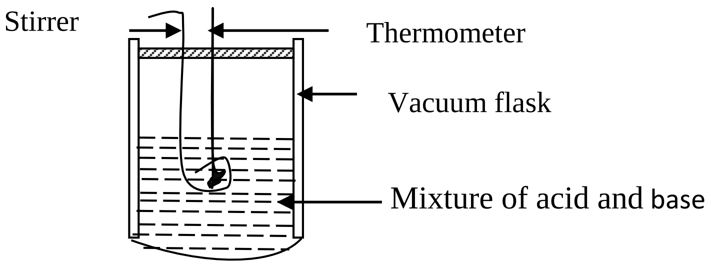
(Ans. -202KJmol^{-1})

Standard enthalpy of neutralization

Is the enthalpy change which occurs when one mole of hydrogen ions (H^+) from an acid reacts with one mole of hydroxyl ions ($\bar{O}H$) from an alkali under standard conditions.
That is $H^+_{(aq)}, + \bar{O}H_{(aq)} \longrightarrow H_2O_{(l)}$
The amount of heat of neutralization for a strong acid reacted with a strong base is always constant and quite high because a strong acid and a strong base are fully ionized in solution giving many free hydrogen ions and hydroxyl ions which then react readily to release a lot of heat.

Weak acid by a strong base or vice versa or both can be weak produces a smaller and inconsistent value of enthalpy of neutralization because energy is initially used up to practically dissociate the weak electrolyte.

Measurement of heat neutralization



Pour Vcm^3 of 2M hydrochloric acid into the flask and record its temperature ($T_1{}^0C$)
Vcm^3 of 2M sodium hydroxide is measured and its initial temperature recorded ($T_2{}^0C$)
Sodium hydroxide is then carefully added to the acid with constant stirring and the highest temperature attained is recorded ($T_3{}^0C$)

Treatment of results

Initial average temperature = $\frac{T_1 + T_2}{2}$

Final temperature of mixture T_3

$$\Delta T = T_3 \left(\frac{T_1 + T_2}{2}\right)$$

Total volume = V + V

= 2V cm^3

Mass of mixture = 2Vg (assume density of solution = 1g dm-3)

Heat evolved = $MC\theta$

$= 2V \times 4.2\Delta T$

$= 8.4V\Delta T$

Equation $H^+_{(aq)} + \bar{o}H_{(aq)} \rightarrow H_2O_{(aq)}$

Moles of water formed = moles of acid used

$= \frac{2 \times V}{1000}$

$= \frac{2V}{1000}$ moles

Then $2V/_{1000}$ moles of water evolve $8.4V\Delta T$ joules

1 mole of water evolve $\frac{8.4V \times \Delta T \times 1000}{2V}$ joules

$= \frac{8.4V\Delta T \times 1000}{2V \times 1000}$ KJ

$= 4.2V\Delta T$ KJ mol^{-1}

Hence $H^o_n = 4.2V\Delta T$ KJmol^{-1}

Enthalpy of solution

This is the enthalpy change when 1 mole of a solute is dissolved in a specified amount of solvent to form an infinitely dilute solution without change in PH

NOTE: Hydrated salts dissolve with absorption of heat in order to dislodge water of crystallization. The heat absorbed sets free the water of crystallization before the ions of the salt can be separated by the water at high temperature than the corresponding anhydrous forms. When anhydrous copper (ii) sulphate dissolves the reaction is exothermic.

Lattice energy (L.E or U_L)

This is the energy required to break don 1 mole of a solid ionic crystals into its gaseous ions example

$NaCl_{(s)} \longrightarrow Na^+_{(g),} + Cl^-_{(g)}$

Alternatively

Lattice energy to the energy given out when 1 mole of a solid ionic crystal is formed from its gaseous ions example

$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)}$

Factors affecting Lattice energy

1. Electro negatively difference between the bonded atoms, if the electro negativity difference is big, then the molecule becomes polar with a strong attraction between the atoms. This gives a big value of lattice energy.
2. Ionic radius large cations have less attraction for anions because of the reduced effective nuclear attraction and U_L becomes less.
3. The product of ionic charges. the larger the charges , the stronger will be the attraction and therefore the bigger the lattice energy example Magnesium Chloride because of the greater charge on the magnesium (Mg^{2+}) which strongly attracts the Chloride ion(Cl^{-1})

Effects of Lattice energy

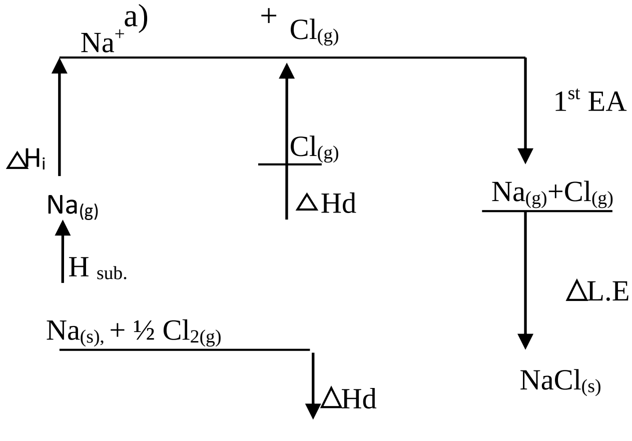
i) It affects the solubility of ionic compounds in that the smaller the lattice energy of the salt, the higher its solubility since that salt will have a reactively weaker attraction between its ions which can be easily overcome by the polar water molecules.

ii) It affects the volume of the melting point of an ionic compound, the higher the lattice energy the higher the melting point.

Determination of Lattice energy

Lattice energy cannot be easily determined experimentary but can be calculated by the help of a born Haber cycle. Except for the lattice energy or lattice enthalpy term, all other enthalpy terms shown in the cycle are obtained from experiments. Thus the lattice enthalpy change can be calculated since all other enthalpy terms in the cycle are known.

The diagram shows how the born-Haber cycle can be used to determine the lattice enthalpy of sodium chloride.



$Na_{(s)} + \frac{1}{2} Cl_{2(g)} \longrightarrow NaCl_{(s)}$

$\triangle H_{sub.}$ = Enthalpy of sublimation

$\triangle HE$ = first ionization energy of sodium

$\triangle Hd$ = Bond dissociation energy

$\triangle E.A$ = First electron affinity of chlorine

$\triangle L.E$ = Lattice energy

$\triangle Hf$= enthalpy of formation of sodium chloride

Then by applying Hess's law lattice enthalpy can be calculated from.

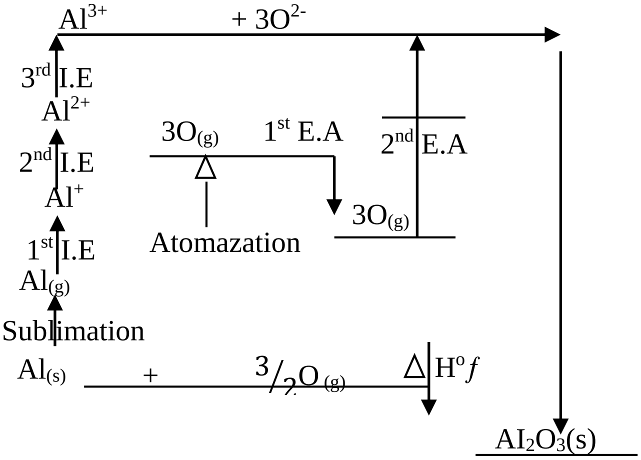
$\triangle H_{sub.} + \triangle H_i + \triangle H_d + E.A + L.E = \triangle Hf$

NOTE:

Lattice energy values are always exothermic since they relate to formation of bonds . The values are considered as experimental values since they are obtained from enthalpy terms that are obtained from experiments

Example

b).



SELF CHECK

1. Calculate the electron affinity of chlorine .Use the following data

Lattice energy of rubidium chloride = 665KJmol^{-1}

Association energy of chlorine = 226 KJmol^{-1}

Heat of atomization of rubidium = 84 KJmol^{-1}

Ionization energy of rubidium = 397KJmol^{-1}

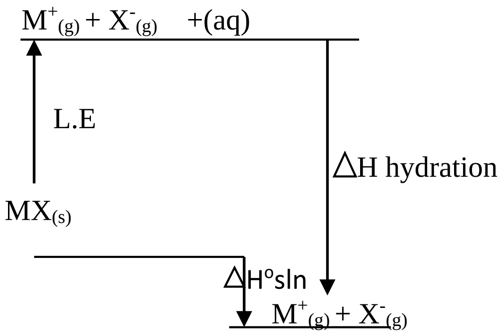
Enthalpy of formation of rubidium, chloride = - 439 KJmol^{-1}

(Ans. -368KJmol^{-1})

Enthalpy of hydration

This is the energy evolved when one mole of a gaseous ion dissolves in water to give an infinitely dilute solution. It's a measure of how strong an ion is attracted to water molecules. Therefore the smaller the ionic radius, the greater is the hydration energy since the ion will have higher polarizing water. Hydration energy is always negative because it involves attraction between gaseous ions and water molecules. Whether a compound dissolves or not depends on the lattice energy and hydration energy. Hydration energy of a compound is equal to the sum of hydration energy and its constituent ions which dissolve exothermically (with heat of a solution negative)

Relationship between lattice energy, enthalpy of solution and enthalpy of hydration of a salt MX



Key

ΔHsoln. = enthalpy of solution

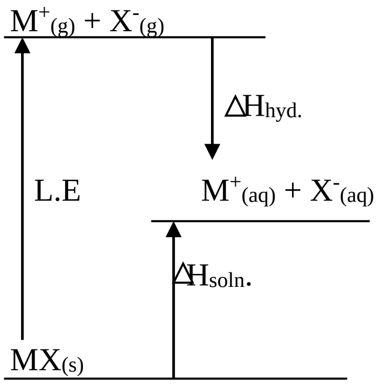
I.E = lattice energy

ΔH_{hyd}. = enthalpy of hydration

Then ΔHs = L.E + $\Delta H_{hyd.}$ But H_{hyd} (MX) = $H_{hyd.}(M^+) + H_{hyd.}(X^-)$

For an ionic compound to dissolve in water the lattice energy should be overcome by hydration energy that is hydration energy should be numerically greater than lattice energy. Hence the more negative the enthalpy of solution, the more soluble is the salt at room temperatures. If heat of solution is negative, it means that hydration energy is bigger than lattice energy.

Energy diagram for salts which dissolve endothermically (heat of solution is positive)



Hence lattice energy is bigger than hydration energy

Self check

1. Using sodium chloride, draw an energy diagram to show how lattice energy, hydration and enthalpy of solution are related.
2. The lattice energy of salt AB and MX are 966 and 843KJmol^{-1} respectively and their hydration energies are -963 and -883KJmol^{-1} respectively. Draw the energy level diagram (born Haber cycle) for each salt and use it to calculate the heat of a solution of each salt. ***(Ans. AB = +3KJmol^{-1}, MX = -40KJmol^{-1})***

Factors which favour solubility of salts in water.

1. Lattice energy, a very soluble salt should have a small lattice energy showing a weak attraction between the opposite ions in the solid state.
2. Hydration energy, a very soluble salt should be larger and more negative hydration energy indicating a strong attraction of the opposite ions by the polar water molecules.
3. Ionic radius of the ions, a small cation with a high charge density increases the solubility of salt by causing high polarization of water molecules that result in high hydration energy.

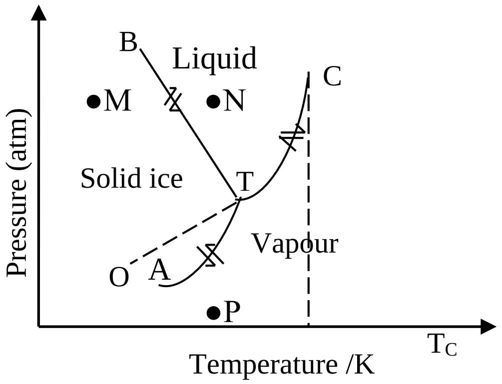
PHASE EQUILIBRIUM

It's about phases and the factor affecting phases

A phase is a homogenous part of a system that is physically separated from the rest by physical a boundary. Phase equilibrium is affected by three factors i.e. vapour pressure, temperature and composition. Two liquid layers in contact represent two phases because there is a surface of separation between them.

A mixture of gases always makes one phase (single phase) because the system is homogenous. A saturated solution in the presence of excess solute is a two phase system.

Phase diagram for water



Curve AT

It’s called the sublimation curve and separates the solid form vapour. It shows a variation of vapour pressure of ice with temperature. The vapour pressure of this solid increase with temperature until a temperature corresponding to point T is reached when the solid begins to melt.

Line TB

This shows the variation of the melting point of ice with pressure. It’s called freezing or fusion curve and separates solid phase from liquid phase. The line slopes to the left indicating that the melting point of ice decreases with increase in vapour pressure.

Curve TC

This shows the variation of boiling point of liquid water with vapour pressure. It’s called boiling or vapourisation curve.

Point T

This is where all the curves meet and it’s called the tripple point of water. It’s a point where all the three phases of water co-exist in equilibrium.

Point C

It’s the critical point corresponding to the critical temperature T_C. Above the critical temperature T_C the liquid phase and the vapour phase of a component cannot be distinguished. The critical temperature T_C is the temperature above which water exists as vapour only.

Curve TO

This is obtained if water is cooled below its freezing point without freezing (super cooling). The phases present a long T_O be liquid and vapour and they are very unstable with respect to ice. The curve T_O is hence called metastable curve.

Qn. What happens to M if temperature increases at constant pressure?

Solution

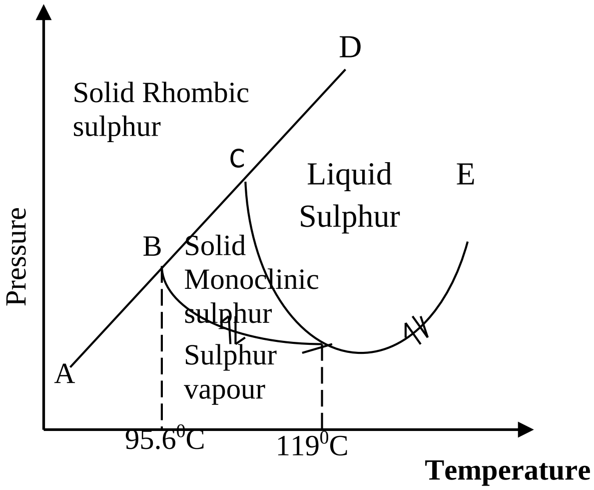
M will remain in solid form until it reaches curve TB where it begins to melt at constant temperature. The temperature remains constant until it has completely turned to liquid. It then remains in liquid form until it reaches curve TC when it begins to evaporate and temperature remains constant until it has completely turned to vapour and any increase in temperature will move the system through vapour forms.

Self check

What happens to substance N when pressure is decreased at constant temperature and to P when the pressure is increased at constant temperature?

Phase diagram for sulphur

Sulplur has two crystalline forms (allotropes) namely rhombic and monoclinic sulphur. It’s also plotted by pressure against temperature at a constant composition.



Curve AB

This is the sublimation curve along which solid rhombic sulphur is in equilibrium with sulphur vapour at various temperatures and pressure.

Point B

It’s a tripple point at which solid Rhombic and solid monoclinic sulphur are in equilibrium with sulphur vapour

Line BC

This shows various temperatures and pressure along which the monoclinic and rhombic sulphur are in equilibrium.

Point C

It’s a tripple point at which solid rhombic, solid monoclinic and liquid sulphur are in equilibrium.

Line CD

This is the melting point or fusion curve for rhombic sulphur showing various temperature and pressure at which rhombic sulphur is in equilibrium with liquid sulphur.

Curve BT

This is sublimation curve along which solid monoclinic sulphur is in equilibrium with sulphur vapour.

Curve TE

This is vapourisation curve along which liquid sulphur is in equilibrium with sulphur vapour at various temperature and pressure.

Point E

This is the critical point beyond which liquid sulphur and sulphur vapour cannot be distinguished.

NOTE:

95.6^0C is the transition temperature below which rhombic sulphur is the most stable and above which monoclinic sulphur is the most stable.

BINARY SYSTEMS

Pressure is kept constant; we plot temperature against composition the phase that is most affected by pressure changes in ignored.

Miscible Liquids

These are liquids which dissolve in each other completely to form homogenous mixture example ethanol and water, Benzene and methyl benzene

For a binary solution containing a volatile solute in a suitable solvent, the vapour above the miscible solution will contain molecules of both the solute and the solvent in different proportions

RAOULT’S LAW

It states that the partial vapour pressure of any volatile component of an ideal solution is proportional to the mole fraction of that component in the solution at that temperature.

That is for a solution containing components A and B.

$P_A = X_A P^o_A \qquad , P_B = X_B P^o_B$

Where P_A= partial pressure of component A.

X_A= mole fraction of A

i.e. $X_A = \frac{n_A}{n_A + n_B}$

P^o_A = vapour pressure of A

From Raoult’s law of partial pressure, the total vapour pressure above the solution is equal to the sum of the partial pressures of the components

That is $P_{total.} = P_A + P_B$

Raoult’s law can also be stated as the fractional lowering of the vapour pressure of a solvent is equal to the mole fraction of the solute in a solution.

That is $\frac{P^o - P}{P^o} = \frac{n}{n + N}$

n – Moles of the solute
n + N – moles of the solution
P_o – vapour pressure of a solvent
P – Vapour pressure of solution
N – Moles of solvent

This holds true only for the dilute solutions when the solute is neither dissociated nor associated. Since the solution is dilute.

$\frac{P^o - P}{P^o} = \frac{n}{N}$, since n is very small compared to N. If M_1 is the mass of solute of formula mass M_1 dissolved in a mass M_2 of solvent of formula mass M_2 then

$\frac{P^o - P}{P^o} = \frac{m_1 / M_1}{m_2 / M_2}$

But for a given quantity of a solvent, P^o and N are constants so that $P^o - P \propto n$.

AN IDEAL SOLUTION

This is a solution which obeys Raoult's law over the whole composition range. This can be achieved when

a) The molecules of the components in the ideal solution have similar sizes, molarities and interactions (cohesive and adhesive forces are the same).
b) There is no absorption or evolution of heat on mixing components.
c) When there is no change in the final expected volume on mixing.

Examples of liquids which can form ideal solutions are

- Propan-1-ol and propan-2-ol
- Hexane and heptanes
- Benzene and methyl benzene

Example

1. a). Calculate the composition of a mixture A,B which at 760mmHg boils at 88^0C (the saturated vapour pressure of A and B are 957 and 378mmHg respectively)
   b) Calculate the composition of the vapour obtained when the liquid mixture in (a) above boils.

Solution

a) Using Raoult's law

$P_A = X_A P^o_A$

$P_B = X_B\ P^o_B$

But $P_A = 957X_A$

$P_B = 378X_B$

And $X_A + X_B = 1$

$X_B = 1 - X_A$

Then $P_B = 378\ (1 - X_A)$

But solution boils when $P_A + P_B = 760$

$957X_A + 378(1-X_A) = 760$

$957X_A + 378 - 378X_A = 760$

$579X_A = 760-378$

$579X_A = 382$

$$X_A = \frac{382}{579}$$

$= 0.6598$ or 66%

But $X_B = 1-X_A$

$= 1 - 0.6598$

= 0.3402 or 34%

NOTE: The partial pressures of the vapour in equilibrium with the mixture of two liquids are obtained from the measurements of the total vapour pressure P and the composition of the vapour. That is,

$P_A - X_A^1P$ where P- total pressure

X_A^1 = composition of A in the vapour

Thus $P_A = X_A^1P$

$$X_A^1 = \frac{P_A}{P}$$

(P =760mmHg at boiling)

$$X_A^1 = \frac{X_A P^o_A}{P}$$

$$= \frac{0.66 \times 957}{760}$$

= 0.83 83%

$$X^1_B = \frac{X_B\ P^o_B}{P}$$

$$= \frac{0.34 \times 378}{760}$$

= 0.169 → 17%

NOTE:

The higher the vapour pressure of a liquid component, the lower is its boiling point and vice versa.

2. 10g of a solid paraffin wax were dissolved in 80g of ethoxyethane at 25^0C. The vapour pressure of the solution was 499mmHg that of ethoxyethane at 25^0C is 510mmHg. Find the molecular mass of the paraffin wax.

Solution

Ethoxyethane $C_2H_5OC_2H_5 = 74$

Using $\frac{P^o - P}{P^o} = \frac{M_1/M_1}{M_2/M_2}$

$$\frac{510 - 499}{570} = \frac{10/M_1}{80/74}$$

$$\frac{11}{570} = \frac{10 \times 74}{80M_1}$$

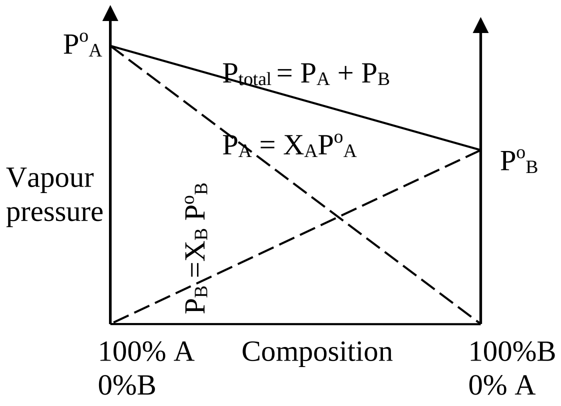
$$M_1 = \frac{10 \times 74 \times 510}{11 \times 80}$$

= 429g

Self check

1. A solution containing 80% A and 20% B forms an ideal solution. If the vapour pressure of pure components A and B are respectively 100 and 500atm. Calculate the total vapour pressure of the solution and the composition of the vapour.
   (Ans. 180atm, X_A = 44%, X^1_B = 56%)
2. ***(a)*** Heptane and octane form an ideal solution. Calculate the vapour pressure of a solution containing 50g of heptane and 28.5g of octane at 20°C. The vapour pressure of pure heptane and octane at 20°C are 420Pa and 150Pa. Calculate the composition of vapour above the mixture. ***(Ans. 330, and 84.85% for heptane and 15.15% octane).***
   (b) If the vapour above the mixture is cooled, the liquid mixture of the same composition is obtained. Calculate the mole fraction of each component in vapour if the liquid mixture obtained is heated. ***(Ans. 0.94 heptane, 0.06 – octane)***

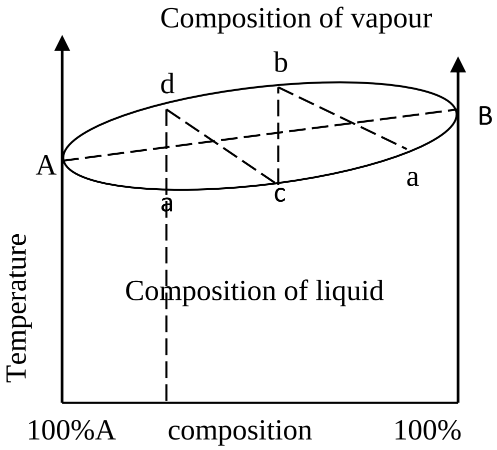
Variation of vapour pressure with composition or an ideal solution of components A and B



Fractional distillation of an ideal solution

The components of an ideal solution can be completely separated by fractional distillation. This is a process used to separate components with different close boiling point from a solution.

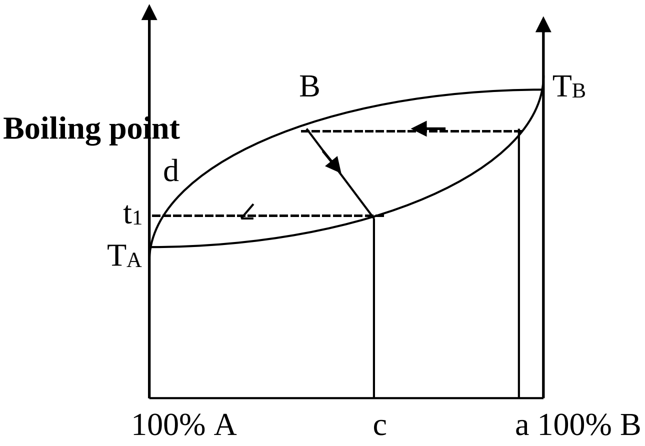
It can be described using a boiling point composition diagram. For components A and B where vapour pressure of pure A is higher than that of pure B, it implies that the boiling point of A will be lower than that of B.



- A- Boiling point of A
- B- Boiling point of B

The lower curve shows variation of the boiling point of the liquid with composition of the liquid while the upper curve shows variation of the composition of the vapour with the boiling point of the liquid mixture during distillation.

Description of separation by fractional distillation.



When the liquid mixture of composition **a** is heated it boils at a temperature to give out vapour **b** which is in equilibrium with the boiling liquid but richer in component A. When this vapour **b** condenses it forms liquid mixture of composition **c** of the same composition that will be heated by the rising hot vapour within the column.

Liquid **c** then boils at a temperature t_1 to form vapour **d** which is in equilibrium with it but more richer in component A. repeated condensation and vaporization within the column finally gives out more volatile component A of lower boiling point (higher vapour pressure) as the distillate while the less volatile component B with higher boiling point (lower vapour pressure) will be the main liquid residue.

NOTE:

This technique is important in industries example in separation of nitrogen and oxygen from liquid air, separation of constituents of petroleum, preparation of organic compounds etc.

NON IDEAL SOLUTIONS (Real Solutions)

They can be divided into three

a) nearly ideal solutions
b) negatively
c) positively

These are solutions which do not obey Raoult's law. These solutions deviate from Raoult's law either by due to very strong intermolecular attraction or very strong intermolecular repulsion between the molecules of one pure component and those of other pure component.

This interaction results form a big difference in the molecular structure of the molecules of the two components.

These interactions may lead to the vapour pressure above the solution being higher or lower than expected from Raoult's law

Types of deviation from Raoult's law

1. Negative deviation

Cause

This is caused by a strong intermolecular attraction between the molecules of the two different molecules in the solution. That is, for a solution of components A and B, the attraction between A and B is much stronger than between B and B

That is, A – B > A –A, B – B

Effects

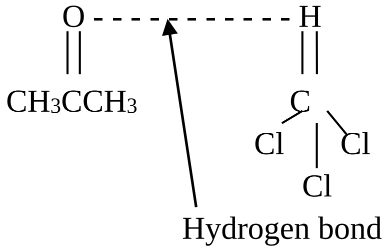
This attraction between molecules of different components leads to

- A decrease in the escaping tendency of the molecules into the vapour state.
- Lowering the total vapour pressure above the mixture
- Evolution of heat on mixing.

- Increase in boiling point of a mixture
- Decrease in the volume of the mixture than expected.

NB:

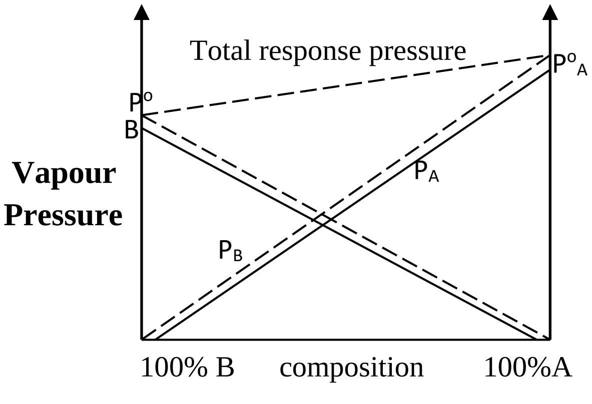
There must be formation of hydrogen bonds e.g. propanone and chloroform, hence less vapour will escape.



Examples

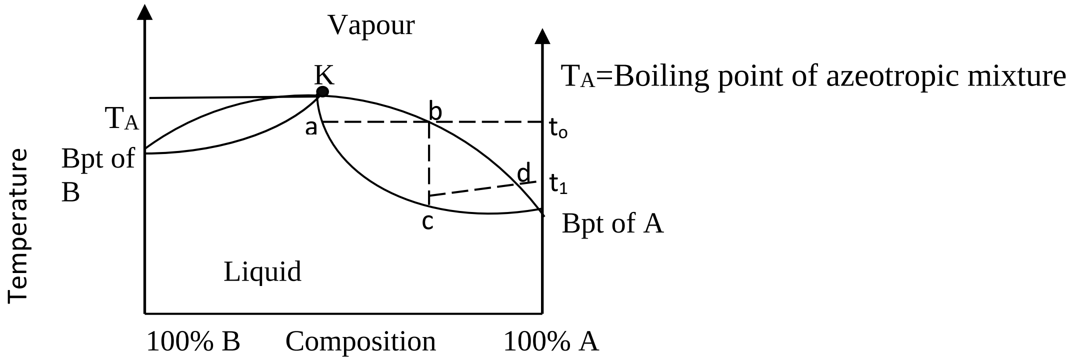
- Sulphuric acid and water
- Nitric acid and water.
- Hydrochloric acid and water
- Propanal and trichloromethane

Vapour pressure composition diagram for negative deviation



……… expected vapour pressure of A and B if the solution was ideal.

Boiling point composition diagram for negative deviation



Fractional distillation of a mixture showing negative deviation

When a liquid mixture **a** is heated, it boils at temperature to give vapour **b** which is richer in component A. This vapour condenses in the column to give liquid C of the same composition. As liquid C descends down the column it will meet hot rising vapour which makes it boil at temperature t_1 to give vapour **d** which is even more richer in **A**. Repeated condensation and evapourisation within the column produces a pure sample of component A as the distillate while the residue will be a liquid mixture of composition K that is azeotropic mixture.

When a liquid mixture of composition K is heated, it will eventually distil at constant temperature to give the vapour of the same composition as liquid K. This liquid is referred to as an azeotropic mixture.

This is a mixture which behaves like a pure substance by distilling at constant temperature with constant composition.

However, it differs from a pure substance by having its composition changing with pressure.

A mixture showing negative deviation has minimum vapour pressure but maximum boiling point as azeotropic mixture.

Positive deviation

This is caused by weaker attractive forces between the molecules in solution than between those in each pure liquid or by stronger intermolecular repulsion between the molecules of the different components in solution that

A – A B – B > A – B

Effects

- Increased escaping tendency of molecules to the vapour state.
- Increase in the total vapour pressure above the mixture
- Lowering the boiling point of the mixture.
- Absorption of heat on mixing.
- Increase in the volume of the mixture.

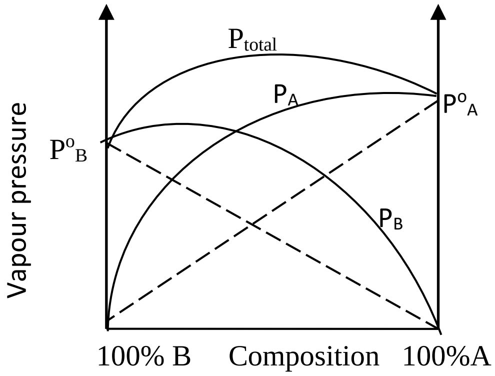
Examples

Ethanol and water; ethanol has hydrogen bonds and water has also hydrogen bonds between molecules but on mixing these bonds are broken and it is an endothermic change

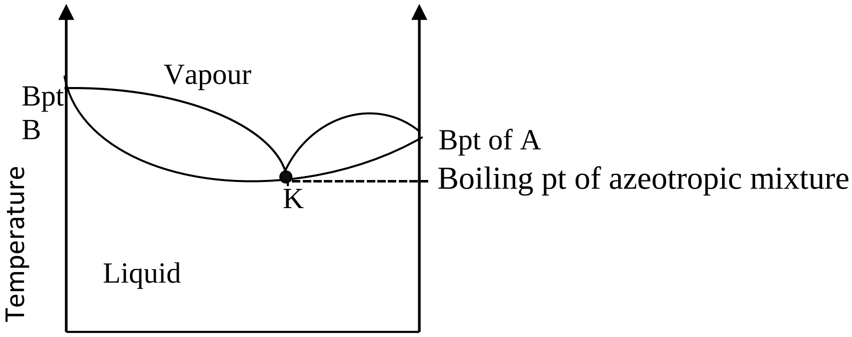
Propanol and water

Ethanol and tetra chloromethane and liquid hydrocarbon e.g. benzene (ethanol has hydrogen bonds and tetra chloride methane has Vanderwaal's forces and on mixing, hydrogen bonds are broken and vanderwaal forces are weakened.

Vapour pressure composition diagram for positive deviation



Boiling point diagram for a mixture showing positive deviation



For a mixture showing positive deviation, the azeotropic mixture (constant boiling mixture) has the lowest boiling point but a maximum vapour pressure

On distillation, azeotropic mixture is always a distillate.

Example

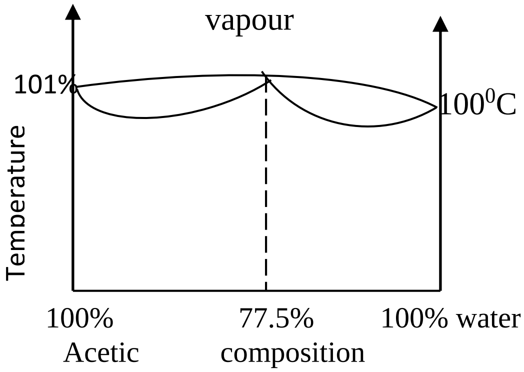
Acetic acid and water form a maximum boiling mixture containing 77.5% of acetic acid which boils at 108^0C. The boiling point of acetic acid is 101^0C.

a) Sketch a labeled diagram of a mixture of acetic acid with water showing variation of boiling point with composition.
b) Briefly describe what happens when a mixture containing 50% acetic acid is distilled.
c) Explain what happens if a mixture of 77.5% acetic acid is heated.

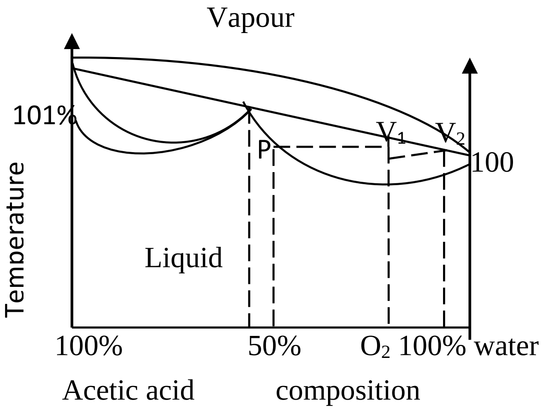
d) A constant boiling point mixture of acetic in (b) has density 1.05gdm^{-3}. Calculate the volume of acid needed to prepare one litre of 0.2M acetic solution.

Solution

a)



b)



When a mixture containing 50% acetic acid is heated, it's vapour pressure increases up to a point P where it boils off to give a vapour of composition V$_1$, Vapour V$_1$ is condensed to form liquid **a$_2$** richer in the more volatile component (water). When **a$_2$** is distilled vapour V$_2$ is given off which condenses to liquid **a$_3$** much richer in water. Repeated distillation produces a pure sample of water as the distillate while the residue liquid in the flask will be an azeotropic mixture of 77.5% acetic acid.

c) When an azeotropic mixture of 77.5% acetic acid is heated, it boils at a constant temperature to give a distillate whose composition is the same as that of mixture (77.5% acetic acid)

d) 50% acetic acid means,

100cm^3 of solution contains 50cm^3 of acetic acid

$$1000\text{cm}^3 \text{ of solution contains } \frac{50 \times 1000}{100}$$

$$= 500\text{cm}^3$$

Mass of acetic acid = 2.05 × 500

= 525g

Molar mass of acetic acid

(CH_3COOH) = 60g

Then 60g of acetic acid contains 1 mole

525g of acetic acid contain $\frac{1 \times 525}{60}$

= 8.75

Hence the morality of solution is 8.75

So, 8.75 moles are in 1000cm^3 of solution

0.2 moles are in $\frac{0.2 \times 1000}{8.75}$

= 22.857cm^3

SEPARATION OF AN A ZEOTROPIC MIXTURE

This can be done by

- Distilling the mixture in the presence of quick lime (Calcium Oxide) to absorb water.
- Solvent extraction, when an azeotropic mixture is shaken with a suitable solvent in which one of the components from the mixture is more soluble.
- Distilling the azeotropic mixture in the presence of a third component.
- By absorption of one of the components using charcoal.

IMMISCIBLE LIQUIDS

These are liquids which are not soluble in each other. Mixing these liquids leads to formation of two difference layers with a less dense liquid floating on top.

In a liquid mixture of immiscible liquids, there is no inter molecular attraction or repulsion between the molecules of the components. Due to this each liquid component will exert its own vapour pressure above the mixture consequently the total vapour pressure above the mixture of immiscible liquids is the sum of the vapour pressure of the pure components at that given temperature. Example for liquids A and B that are immiscible

$P_{total} = P^o_A + P^o_B$

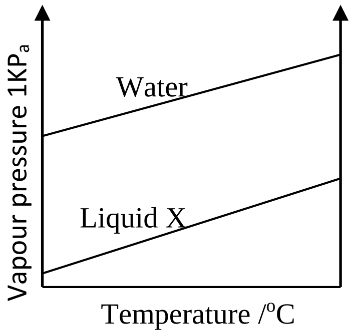
P^o_A – vapour pressure of pure A

P^o_B – vapour pressure of pure B

The boiling point of this mixture would be much lower than the boiling point of each component in the mixture that is, P_{total} = external pressure = $P^o_A + P^o_B$

Composition of vapour boiling point

The vapour pressure of water an immiscible liquid X at different temperature



For an immiscible mixture

$$X_i = \frac{P_i^o}{P_{total}}$$

That is, for A in vapour

$$X^1_A = \frac{P^o_A}{P_{total}} = \frac{n_A}{n_t}$$

For B in vapour

$$X^1_B = \frac{P^o_B}{P_{total}} = \frac{n^1_B}{n_t}$$

From above

$$P^o_A = X_A^1\ P_{total} \text{ ---------------------- (i)}$$

$$P^o_B = X_B^1\ P_{total}$$

Dividing $\frac{P^o_A}{P^o_B} = \frac{X_A^1}{X_B^1}$

$$\frac{P^o_A}{P^o_B} = n_A/n_t / n_B/n_t$$

$$\frac{P^o_A}{P^o_B} = \frac{n_A}{n_B}$$

$$= W_A/M_A / W_B/M_A$$

$$\boxed{\frac{P^o_A}{P^o_B} = \frac{W_A M_B}{W_B\ M_A}}$$

STEAM DISTILLATION

It's the removal of a component which is immiscible with water from a mixture by passing steam through the mixture.

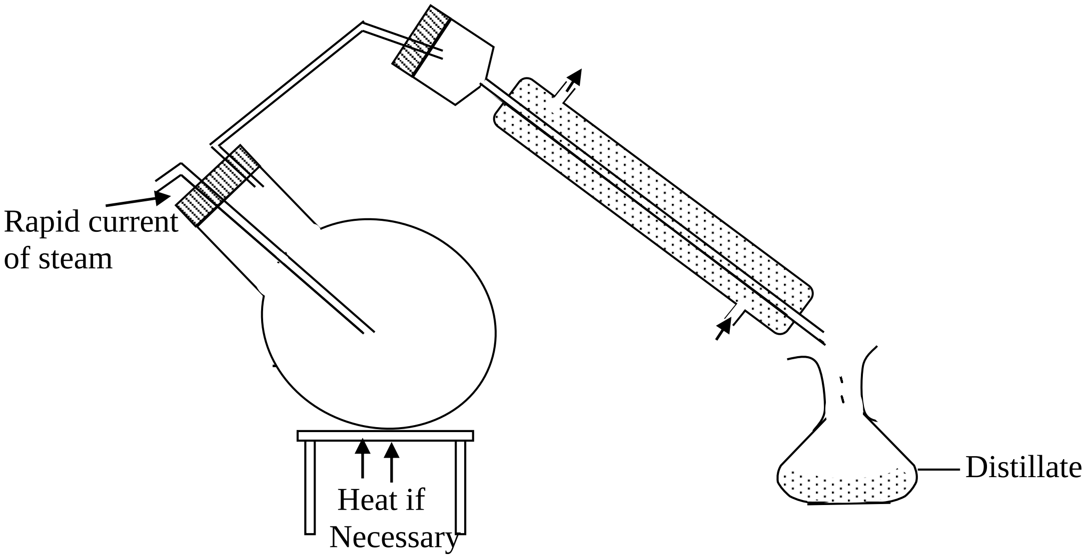
PROCESS OF STEAM DISTILLATION

Since the component and water are immiscible, at any given temperature each component will contribute its own vapour pressure to the total vapour pressure of the mixture. Therefore the total vapour pressure above the mixture is equal to the sum of the separate vapour pressures. However, for a liquid mixture to boil the total vapour pressure above it should be equal to the atmospheric pressure. Therefore, when the mixture is heated its vapour pressure increases and reaches the atmospheric pressure at a lower temperature so that the boiling point of the mixture is lower than that of either liquid.

Direct heating of this mixture is avoided because these substances have very high boiling points at which they tend to decompose when heated directly. Components that can be isolated by steam distillation include;

- Amino benzene
- Chloro benzene
- Nitrobenzene etc

Apparatus for steam distillation



PRINCIPLE OF STEAM DISTILLATION

The following are principles, behind steam distillation. The substance to be steam distilled is immiscible with water; the two substances contribute to vapour pressure independent of each other. The vapour pressure above the mixture is the sum of the two vapour pressure.

On heating, the vapour pressure increases till the sum equals the atmospheric pressure such that the mixture boils at a temperature lower than the boiling point of either liquid.

Advantages of steam distillation

- It prevents thermo decomposition of organic substances which have very high boiling points.
- It helps in the purification or isolation of a substance of high boiling point by allowing it to boil at a much lower temperature.
- It helps in determining relative molecular mass (R.M.M) of substances immiscible with water provided the composition of the vapour and the vapour pressure of the substances are known. That is,

$$\frac{W_A}{W_B} = \frac{P^o_A M_A}{P^o_B M_B}$$

$$\boxed{\frac{P^o_A}{P^o_B} = \frac{W_A M_B}{W_B M_A}}$$

Disadvantage

- It produces a distillate which is a mixture of water and an immiscible organic liquid.

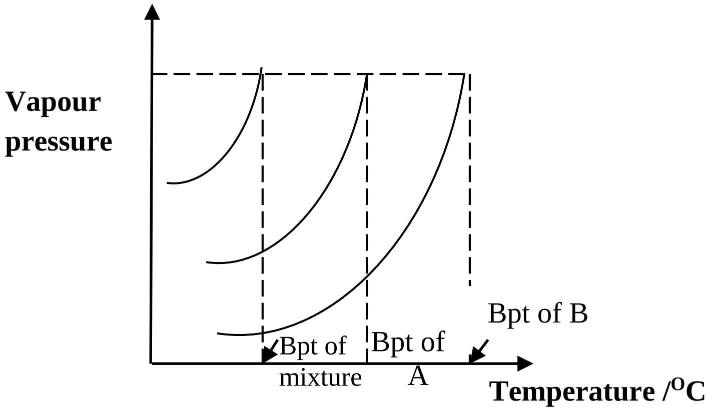
Separation of the distillate

1. Solvent extraction

The distillate is shaken with an organic solvent in which the organic liquid from the distillate dissolves leaving the water as separate layer. Finally the organic solvent can be distilled off.

2. By adding a drying agent like an hydrous sodium sulphate to remove the water

Variation of P^o_A, P^o_B and their immiscible mixture with temperature



Examples

1. When a compound Y is steam distilled at standard atmospheric pressure the distillation temperature was 86^{0}C. The vapour pressure of water at 86^{0}C is 740mmHg, the distillate contained 85% by mass of water. Calculate the relative mass of Y

Solution

$$\frac{M_1}{V_2} = \frac{P^o{}_1 M_1}{P^o{}_2 M_2}$$

Mixture boils at 760mmHg

V.P $_{water}$ = $P^o{}_1$ = 740mmHg

V.P$_4$ = $P^o{}_2$ = 760 -740

= 20mmHg

$$\frac{W_{water}}{W_y} = \frac{P_{water}\ M_{water}}{P^o{}_Y\ M_y}$$

$$\frac{85}{15} = \frac{740 \times 18}{20 \times M_y}$$

$$M_y = \frac{740 \times 18 \times 15}{20 \times 85}$$

$$\underline{\underline{\mathbf{= 117.53}}}$$

2. When a substance Y was distilled at 93^0C and 750mmHg the distillate contained 55% of Y by mass. Calculate the relative molecular mass of Y (The partial pressure of water at 93^0C is 654mmHg)

Solution

$$\frac{W_{water}}{W_Y} = \frac{P^o{}_{H2O}\ M_{water}}{P^o{}_Y\ M_Y}$$

$P_{total} = P^o{}_Y + P^o{}_{water}$

$750 = P^o{}_Y + 654$

$P^o{}_Y$ = 96mmHg

And $\frac{45}{55} = \frac{18 \times 654}{96 \times M_Y}$

$$M_Y = \frac{18 \times 654 \times 55}{45 \times 96}$$

= 149.9

Self check

1. A mixture of water and Chlorobenzene is distilled at an external pressure of 740.2mmHg and the liquid boils at 90.3^{0}C. The vapour pressure of pure water at 90.3^{o}C is 530.1mmHg. Calculate

i) The vapour pressure of Chlorobenzene (C_6H_5Cl)

ii) The percentage composition of Chlorobenzene in the distillate (C = 12, H=1, O=16, Cl=35.5)

(Ans. (i) 210.1mmHg (ii). 71.3%)

2. Chlorobenzene which is immiscible with water is steam distilled at 91^{0}C under atmospheric pressure of 752mmHg. A sample of the distillate contains 23.7g of Chlorobenzene for every 10g of water. Calculate the vapour pressure for water and Chlorobenzene at 91^{0}C (C=12, H=1, O=16, Cl =35.5)
   (Ans. P_{water} = 545.2mmHg $P^o_{Chlorobenzene}$ = 206.8mmHg)
3. a). When 4.90g of an organic compound X containing carbon and hydrogen only was burnt in oxygen, 15.78g of carbondioxide and 5.38g of water were formed.
   Calculate the empirical formula of X.

b). X was steam distilled at 80^{0}C and 760mmHg and the distillate was found to contain 90.8% by mass of X. The vapour pressure of water at 80^{0}C and 760mmhg and the distillate water found to contain 90.8% by mass of X. (The vapour pressure of water at 80^{0}C is 240mmHg)

i) Calculate the formula mass of X

ii) Deduce the molecular formula of X

NOTE:

The following are conditions of steam distillation.

- The substance to be separated must be immiscible with water.
- The substance should be able to exert a very high vapour pressure at around 100^{0}C for it to distill at such a low temperature.
- It should have a high molecular weight so that it constitutes a high proportion of the distillate.

DISTRIBUTION OF SOLUTES BETWEEN IMMISCIBLE LIQUIDS

This is explained by the distribution or partition law which states that

When two immiscible liquids are in contact and the solute soluble in both is added to the mixture in varying amount. This solid will distribute itself in such a way that at equilibrium, the ratio of its concentration in the two immiscible liquids is constant provided the temperature is constant and the solute being in the same molecular state.

That is; Concentration of solute in solvent A = K_D

Concentration of solute in solvent B

Where K_D is the partition (distribution) coefficient .This distribution coefficient is the ratio of the concentration of a solute in one of the solvent to the concentration both of the same solute in the second solvent when solvents are present in one system and are immiscible.

Limitations of distribution Law

- The solute should not associate or dissociate in either solvent.
- The solute is soluble in both solvent but more soluble in one of the solvents than the other.
- The temperature is kept constant.
- The two solvents are immiscible

Application of distribution law

Solvent extraction

This is the isolation of a solute from one solvent in which it's less soluble by extracting with another solvent which is immiscible but in which the solute is more soluble. This isolation helps to determine the concentration of a solute in each solvent after the equilibrium is formed and also its K_D between the two solvents.

Procedure

A known weight of solute is dissolved in a known volume of one solvent A in a separating funnel. A known volume of another solvent B which is immiscible with solvent A is added to the same funnel. The mixture is shaken properly and left to stand for the solute to form equilibrium between the immiscible solvents A and B and also for the two solvents to form two separate layers. A known volume of each layer is pipetted and the solute is titrated with a suitable standard solution. The moles of the solute on the total volume of each layer are then calculated
Hence

$$\boxed{K_D = \frac{\text{Concentration of solute in A}}{\text{Concentration of solute in B}}}$$

Examples

1. Suppose the partition coefficient of a solute A between ether and water is 4. Suppose we have a solution containing 15g of A in 50cm^3 of water and 50cm^3 of ether are available for extraction.

Let xg be the amount of A extracted by ether.
The amount of A remaining in water is $(15 - x)$ g

That is

$$K_D = \frac{[A]_{ether}}{[A]_{water}}$$

But $[A]_{ether} = \frac{x}{50}$, $[A]_{water} = \frac{15-x}{50}$

And $$\frac{x/50}{\frac{15-x}{50}} = 4$$

$$\frac{x}{15-x} = 4$$

$$x = 60 - 4x$$
$$5x = 60$$
$$x = \frac{60}{5}$$
$$= 12g$$

Then amount remaining in water = 15 – 12
= 3g

Hence 12g of A were extracted and 3g remained in water.
If the available ether is used in two equal portions. Then let y be amount of A extracted

And $[A]_{ether} = \frac{y}{25}$

$$[A]_{water} = \frac{15 - y}{50}$$

$$K_D = \frac{y/25}{\frac{15-y}{50}}$$

$$4 = \frac{2y}{15-y}$$

$$2y = 60 - 4y$$
$$6y = 60/6$$
$$=10g$$

Hence 10g of A were extracted and 5g remained in water if Z is the amount of A extracted in the second extraction then,

$$4 = \frac{z/25}{\frac{5-z}{50}}$$

$$4 = \frac{2z}{5-z}$$

And $$2z = 20 - 4z$$

$$6z = 20$$

$$z = {}^{20}/_{6}$$

$$\mathbf{= 3.33g}$$

The total amount of A extracted using two equal portions is (10 + 3.33) = 13.33g
Leaving 1.67g

Conclusion

Extracting a solute with small volume of the extracting solvent is more efficient since it gives a bigger amount of the solute extracted.

Example

When 100cm^{3}of aqueous solution containing 30g of ethanoic acid was shaken with 50cm^3 of butan-1-ol, 12g of ethanoic acid remained in aqueous layer.
Calculate,

a) The distribution coefficient of ethanoic acid between water and butan-1- ol.
b) The aqueous solution of ethanoic acid in (a) was shaken twice with 25cm^3 portions of butan-1-ol. Calculate the mass of ethanoic acid extracted.

Solution

a). Mass of ethanoic acid in aqueous layer = 12g
Mass of ethanoic acid in butan-1-ol = 18g that is, (30-12)
Then

$[CH_3COOH]$in $_{aq}$ = ${}^{12}/_{100}$

And $[CH_3COOH]_{organic}$ = ${}^{18}/_{50}$

$$K_D = \frac{[CH_3COOH]_{organic}}{[CH_3COOH]_{aq}} = \frac{{}^{18}/_{50}}{{}^{12}/_{100}}$$

$$= {}^{18}/_{50} \times \frac{100}{12}$$

$$\mathbf{= 3}$$

b). Let Xg be the mass extracted by 25cm^3 of butan-1-ol

$$[CH_3COOH]_{organic} = {}^{x}/_{25}$$

And

$$[CH_3COOH]_{aq} = \frac{30-x}{100}$$

Then $K_D = 3 = \dfrac{x/25}{(30-x)/100}$

$$3 = \frac{x}{25} \times \frac{100}{(30-x)}$$

$$3 = \frac{4x}{(30-x)}$$

$4x = 90 - 3x$

$7x = 90$

$x = 90/7$

$x = 12.86\text{g}$

Mass remaining in aqueous layer = 30 -12.86

= 17.14g

If yg are extracted in the second extraction

Then $3 = \dfrac{y/25}{\dfrac{17.14 - y}{100}}$

$$= 3 = \frac{y}{25} \times \frac{100}{(17.6 - y)}$$

$$3 = \frac{4y}{17.14 - y}$$

And $4y = 57.43 - 3y$

$7y = 57.43$

$y = 51.43/7$

= 7.35g

And

Total mass extracted = (1286+7.35)

= 20.21g

NOTE:

The K_D is supposed to remain constant at constant temperature if the solute is in the same molecular state in the two solvents.

Self check

1. 1 litre of water containing 15g of dissolved amino benzene is shaken with
   a) $100cm^3$ of benzene
   b) Two successive volume of benzene of $50cm^3$.

The partition coefficient of amino benzene between benzene and water is 10. Calculate the amount of amino- benzene extracted in (a) and (b)

(Ans. (a) 7.5g (b) 8.33g)

2. 50cm^3 of 0.1M ammonia solution was shaken to equilibrium with 50cm^3 trichloromethane in a stoppered bottle at 25^{0}C. 25cm^3 of the aqueous layer reacted completely with 24cm^3 of 0.1M HCl

a) What is the concentration of ammonia in the aqueous layer at equilibrium

b) What is the concentration of ammonia in trichloromethane layer

c) Calculate the distribution coefficient between water and trichloromethane at 25^{0}C

d) If 50cm^3 of trichloromethane were used instead of 50cm^3 what would be the K_D

(Ans. (a) 0.096M (b) 0.004M (c) 24)

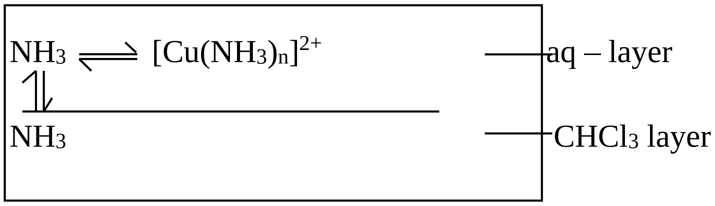
3. Describe how the K_D for butan-1-4, dioic acid (succinic acid) between water and ethoxyethane can be determined. ***(Ans. Standard solution is sodium hydroxide).***
4. Describe how the K_D for iodine between water and trichloromethane can be determined ***(Ans. standard solution is sodium bisulphate)*** using starch indicator.

Determining the composition of a complex formed by a solute and a solvent

Example; NH_3 and $Cu^{2+}_{(aq)}$

The K_D of NH_3 between water and an organic solvent like trichloromethane ($CHCl_3$) or tetrachloromethane (CCl_4) can help in determining the composition of the complex formed between Cu^{2+} and NH_3 or an amine. This complex is formed when excess aqueous ammonia or amine is added to an aqueous solution of Cu^{2+} giving a deep blue solution. The deep blue aqueous solution contains both free ammonia and the fixed complexed ammonia molecules.

When this solution is shaken with an organic solvent like $CHCl_3$ the free NH_3 in the aqueous layer will distribute itself and form equilibrium with free NH_3 in the $CHCl_3$ layer. Therefore for n molecules of NH_3 complexing with one Cu^{2+} in aqueous layer the equilibrium will be



Determining the value of n in the complex

The concentration of free NH_3 in the organic layer is determined by titrating a known volume of that layer with a standard hydrochloric acid

If K_D = $[NH_3]$ free in aq – layer

$[NH_3]$ in organic layer

Then

a) $[NH_3]$free in aq – layer = $K_D \times [NH_3]$ in organic layer

b) $[NH_3]$ complexed = total $[NH_3]$ – $[NH_3]$ free both in aq and in organic
c) $[Cu^{2+}]$ in the complex = moles of CU^{2+} in the total volume of aq- layer.

The value of n is obtained from the ratio

$$\begin{array}{ccc} [Cu^{2+}] \text{ in complex} & : & [NH_3] \text{ in complex} \\ 1 & : & n \end{array}$$

Example

A solution of 25cm^3 of 0.1M copper (ii) sulphate was shaken with 25cm^3 of ammonia solution and the resulting solution shaken with trichloromethane ($CHCl_3$) and the mixture allowed to settle. 20cm^3 of the $CHCl_3$ layer required 10.2cm^3 of 0.05M hydrochloric acid and 10cm^3 of the aq-layer required 16.5cm^3 of 0.5M hydrochloric acid if the partition coefficient of NH_3 between water and $CHCl_3$ is 25. Calculate the value of n in the complex $[Cu(NH_3)_n]^{2+}$

Solution

$CHCl_3$-layer

Moles of HCl that reacted = $\frac{0.05 \times 10.2}{1000}$

= 0.00051 moles

But $HCl_{(aq)} + NH_4OH_{(aq)} \longrightarrow NH_4Cl_{(aq)} + H_{2(l)}$

From reaction ratio

20cm^3 of organic layer contain 0.00051 moles

1000cm^3 of organic layer contain $\frac{0.00051 \times 1000}{20}$

=0.0255M

And $K_D = \frac{[NH_3]_{\text{free in aq.}}}{[NH_3]_{CHCl_3}}$

$25 = \frac{[NH_3]_{free}}{0.0255}$

$[NH_3]_{free} = 25 \times 0.0255$

$= 0.6375$ (UnComplexed)

Moles of HCl in 16.5cm^3 = $\frac{16.5 \times 0.5}{1000}$

= 0.00825 moles

From reaction ratio,

10cm^3 of aq – layer contain 0.00825moles of NH_3

1000cm^3 of aq-layer contain $\frac{0.00825 \times 1000}{10}$

= 0.825M

But

0.825 moles ≡ total concentration of NH3 in aq-layer that is both complexed and free

Then,

$[NH_3]_{complex}$ = Total $[NH_3]_{aq} - [NH_3]_{free}$
= 0.825 – 0.6375
= 0.1875 moles

Also

Moles of Cu^{2+} in $25cm^3 = \frac{25 \times 0.1}{1000}$
= 0.0025 moles

From reaction ratio

$50cm^3$ (of total solution) contain 0.0025 moles
$1000cm^3$ (of total solution) contain $\frac{0.0025 \times 1000}{50}$
= 0.05M

That is, $[Cu^{2+}]$ = 0.05M

Then

$[Cu^{2+}]_{complexed}$: $[NH_3]_{complexed}$
0.05 : 0.1875
1 : 3.75
1 : 4

Hence → n = 4

And formula of complexed then is

$[Cu(NH_3)_4]^{2+}$

Self check

Excess NH_3 was shaken with equal volume of $CHCl_3$ and 0.05M aq. Solution is copper (ii) sulphate and allowed to stand. Some NH_3 reacted with Cu^{2+} to form a complex $[Cu(NH_3)_n]^{2+.}$ At equilibrium the concentration of NH_3 in the $CHCl_3$ and in the aq layer were 0.021 moles per litre and 0.725 moles per litre respectively.

(K_D of NH_3 between water and $CHCl_3$ is 25)

a) Calculate the concentration of free NH_3 in aq-layer
b) The concentration of NH_3 that formed the complex with copper.
c) Calculate the value of n in the complex

(Ans. a) 0.525 b). 0.2 c) 4)

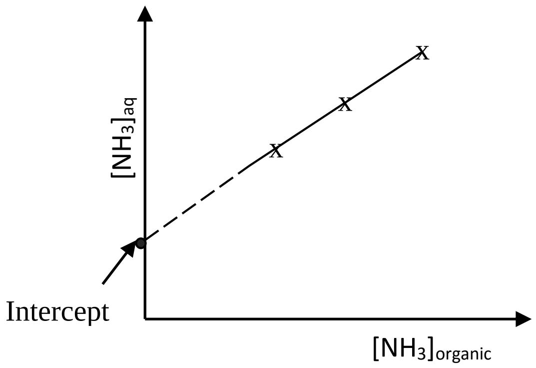
NOTE:

A graph of $[NH_3]_{free}$ in aq Vs $[NH_3]_{organic}$, is a straight line, whose slope = K_D

Interpretation

a) Slope = K_D
b) The intercept on the vertical axis represents minimum concentration of NH_3 that can form a complex with $Cu^{2+.}$ The intercept equals $[NH_3]$in complex
c) The value of n in the complex = $\frac{\text{intercept}}{[Cu^{2+}]}$

That is



Experiment

Determination K_D of iodine between water and trichloromethane

Iodine added to a mixture of water and $CHCl_3$. The mixture is shaken until all iodine has dissolved and is left to stand until equilibrium is attained the temperature is noted.

A known volume of each layer is pipette and titrated with standard sodium thiosulphate solution using starch indicator.

The concentration of iodine in each layer is calculated using the reaction ratio below

$2S_2O_3^{2-}{}_{(aq)}, + I_{2(aq)} \longrightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-{}_{(aq)}$

The ratio of the concentration of iodine in the two layers is a constant and it is the distribution coefficient.

A BINARY MIXTURE

There are two main phase diagrams that has to be drawn

1. We plot temperature against composition and ignore the vapour. When a pure solid is melted and cooled it will begin to crystallize at its freezing or melting point. Addition of another solid to a molten pure substance would lower the freezing point of pure substance.

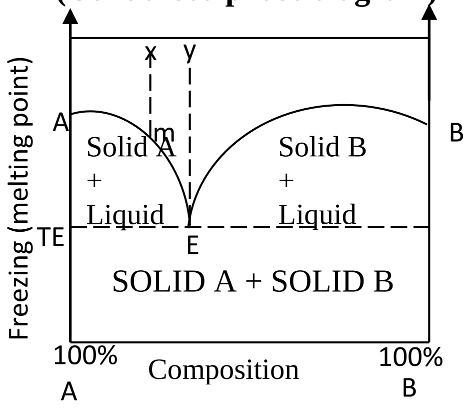
NB: We shall look at cooling waves

2. Vapour pressure against composition at a constant temperature (liquid in liquid mixtures)

Variation of freezing or melting point with composition of liquid.

a) Mixture with components A and B

(Condensed phase diagram)



Point A
This is the freezing or melting point of pure A.

Point B
This is the freezing or melting point of pure B

Point E
This the eutectic point, it's the lowest point below which pure solid A and B are in equilibrium with the liquid mixture.

Effective Temperature (TE)
This is the lowest temperature below which only solid A and solid B exist. At this temperature a mixture whose composition corresponds to that of the eutectic would have the two pure solid components in equilibrium with the liquid.

Eutectic mixture (Point E)
This is a mixture at which the eutectic point and eutectic temperature would have the pure solid components in equilibrium with the liquid mixture of the same composition

Curve AE
This is the freezing point curve of component A along which solid A is in equilibrium with the liquid mixture. It shows the lowering of freezing point of A as component is added to it.

Curve BE

It's a freezing point curve of B a long which solid B is in equilibrium with the liquid mixture. It also shows the lowering of freezing point of B as more components A is added to it.

NOTE:

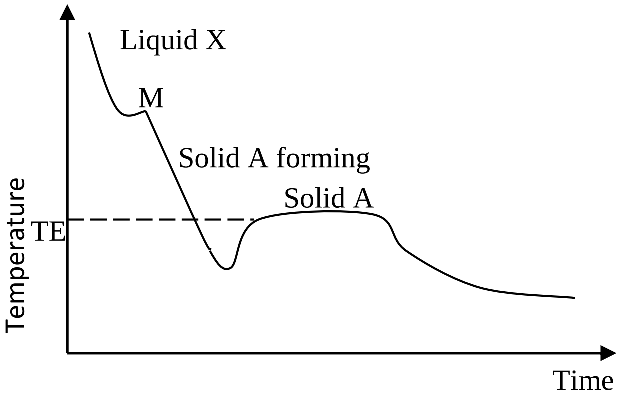
Any liquid mixture whose freezing point and composition fall on curve AE will always separate out into pure solid A while those whose freezing point and composition fall on curve BE will separate out into pure solid B.

Cooling a liquid mixture

a) If a liquid X is cooled, its temperature would drop with a decrease in volume, when the temperature drops up to a value corresponding to point M on curve AE, pure solid A will begin separating out with evolution of heat. With further lowering of temperature more solid A precipitates out leaving a liquid mixture which is richer in component B. The composition of the liquid mixture will tend towards E until it becomes equal to the composition of the eutectic mixture when the temperature remains constant hence solid B begins precipitating in addition to solid A.

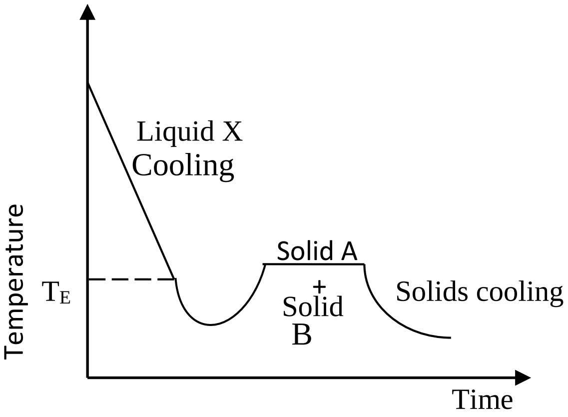
After total solidification of this eutectic temperature the two solids can then cool further.

Cooling curves of liquid mixture X and Y



b) For liquid mixture Y corresponding to the eutectic mixture, its temperature would drop until the eutectic temperature is reached when pure solid A and solid B begin to solidify simultaneously. The temperature remains constant until total solidification has occurred. The solid formed will have the same composition as the original liquid mixture Y

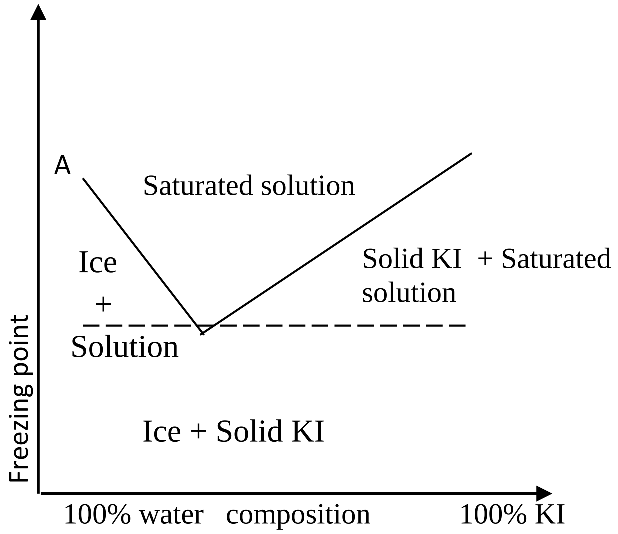
Cooling curve for mixture Y



Examples of substances which give this phase diagram

- Zinc and Cadmium
- Aluminum and silicon
- Lead and Antimony
- Ice and sodium chloride.
- Silver chloride and Potassium chloride
- Any salt and water.

Consider variation of freezing point with composition of potassium iodide – water system



Point A

Freezing po

int or melting point of ice.

Curve AP

Freezing point curve of water along which ice is in equilibrium with the solution of KI. It indicates the lowering of the freezing point of water with addition of more KI to it.

Point P

This is the eutectic point where pure solid KI, ice and the saturated solution are all in equilibrium at the eutectic temperature.

Characteristics of eutectic

- It has a sharp melting point just like a pure substance.
- It has a cooling curve just like a pure substances
- Eutectics are not compounds

NOTE: An eutectic is considered to be a mixture and not a compound because;

a) It’s seen to be consisting of two kinds of crystals under a microscope.
b) The composition and melting point of an eutectic can change with pressure.
c) The composition of an eutectic rarely corresponds to a simple chemical formula like that of a compound.

SOLIDIFICATION OF SOLIDS

Solubility is defined as the mass of the substance in grammes at a particular temperature dissolved in 100g of solvent in the presence of excess of the solid.

A saturated solution is one in which the solution is in equilibrium with excess solute. This is a dynamic process with some particles in the solution returning to the solid and some particles of the solid dissolving in the solution.

Consider the solubility of potassium nitrate

$KNO_{3(s)} + H_2O_{(l)} \rightleftharpoons$ saturated solution $\Delta H = +$

Since the process is endothermic, Lachatelier’s principle suggests that increasing the temperature increases the solubility of Potassium nitrate in order to absorb the added heat by shifting the equilibrium to the right

If the solubility process is exothermic, then increase in temperature decreases the solubility of the salt.

Example

1. The solubility of a salt at 75^0C is 40g/100g of water. When 280g of its saturated solution at 75^0C was cooled to 20^0C, 30g of crystals were formed. Calculate the solubility in grammes/100g of water at 20^0C.

Solution

140g of solution contain 40g of salt

280g of solution contain $\frac{40 \times 280}{140}$

= 80g of salt

Mass of water = 280 – 80 = 200g of water

At 20^0C crystals formed 30g

The mass of solute dissolved at 20^0C = 80 – 30

= 50g

And then

200g of water at 20^0C contain 50g of salt

100g of water contain $\frac{50 \times 100}{200}$

= 25g

Hence solubility of a salt at 20^0C is 25g/100g of water

2. A solution contains 25g of solute X in 100g of water at 50^0C. What mass of the solid X must be added to this solution to make it saturated (Solubility of solute X is 33g/100g of saturated solution at 50^0C).

Solution

100g of saturated solution contain 33g of X

Mass of salt = 33g

Mass of water = 100 – 33 = 67g

Then 67g of water contain 33g of X

100g of water contain $\frac{33 \times 100}{67}$

= 49.25g/100g of water

And extra mass of solid X = 49.25 – 25

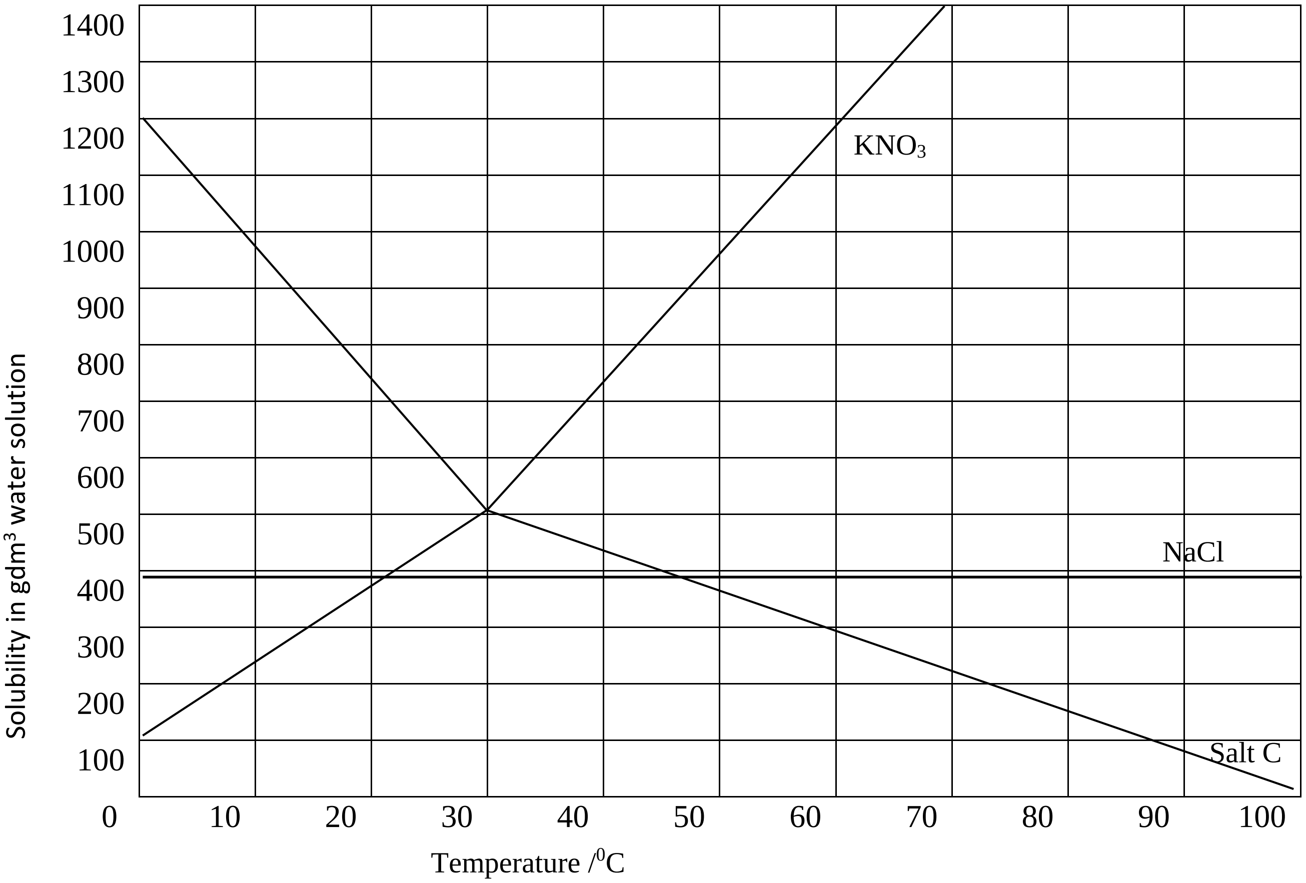
= 24.25g

Hence 24.25g of solid X must be added to this solution to make it saturated.

FRACTIONAL CRYSTALLIZATION

This is a process used to separate two or more solutes by making use of their different changes in the solubilities with temperature in the same solvent.

Example; The graph below shows how the solubility of sodium chloride (NaCl), potassium nitrate (KNO_3) and salt C changes with temperature.



Check; Sodium chloride increases in solubility very little as the temperature rises for a similar rise in temperature, the solubility of potassium nitrate increases for more than sodium chloride. The solubility of salt C decreases as temperature increases. Increasing the temperature of a saturated solution would result in the formation of crystals.

Separation of two salts of different solubilities

Look at the graph. Consider what would happen if a solution containing 350g of sodium chloride and 1100g of potassium nitrate at 70^0C was allowed to cool. At 58^0C crystals of potassium nitrate start to crystallize out. At room temperature of about 28^0C the solubility of the potassium nitrate is 450g. Therefore (1100 – 450) = 650g of potassium will have crystallized out.

At 28^0C the sodium chloride is an unsaturated solution thus no sodium chloride crystallizes out. This means a mixture of two salts with different solubilities can be separated by crystallization. A proportion of the more soluble salt crystallizes out and the less soluble salt stays in the solution.

This technique is known as **fractional crystallization**. In some cases it may be necessary to repeat the process several times to obtain pure products.

This indicates that the salt with lower solubility at lower temperature (less soluble salt) crystallizes out first leaving behind the salt with higher solubility (more soluble salt).

Example

Sodium chloride is obtained from lakes like L. Katwe in this way. The lake water is collected and allowed to evaporate slowly by the heat from the sun. This leaves a strong solution of salts. Sodium chloride is more soluble and it remains in solution. The solution is evaporated a little more by heat from the sun or by heating and on cooling sodium chloride crystallizes out and it's about 90% pure. The water left behind contains Magnesium salts which are so soluble that they do not crystallize out in sodium chloride.

NOTE: A suitable solvent for re-crystallization is one in which the solute.

1) Is sparingly soluble or insoluble at low temperature
2) Is soluble at a higher temperature without decomposing.

Re-crystallization is used in purifying both organic and inorganic solutes in which there are small amount of impurities.

HOW PURE POTASSIUM NITRATE CAN BE OBTAINED FROM A MIXTURE CONTAINING POTASSIUM NITRATE AND SODIUM CHLORIDE

Explanation

This can be done by fractional crystallization method which utilizes the difference in solubilities of the salts at different temperatures. From the graph potassium nitrate is observed to have a higher solubility at higher temperatures above 30^0C where as sodium chloride is more soluble at lower temperatures below 30^0C.

During this process potassium nitrate and sodium chloride are dissolved in water heated to higher temperatures above 60^0C. When the solution is concentrated and cooled potassium nitrate will crystallize out first since it has a lower solubility at lower temperatures. The first drop of crystals formed will thus contain potassium nitrate possibly mixed with a small amount of sodium chloride.

By dissolving these crystals in hot water and then repeating the process of crystallization, pure crystals of potassium nitrate will be obtained free from sodium chloride.

Whereas the molten liquor remaining in the flask will relatively be richer in the sodium chloride.

Therefore separating pure samples of potassium nitrate from the mixture

The purity of the separated sample can be tested by determining their melting points and then comparing with the standard values from the thermodynamic data.

Self check

The solubilities of salts A and B and different temperatures are shown in the table below.

Temperature		0	10	30	40	50	60
Solubility/100g of water	A	13	20	45	63	85	110
	B	32.5	34	36	37	38	39

a) (i). Plot a graph of solubility against temperature for salt A and B using the same axes.
   (ii). A saturated solution of A was cooled from 45^0C to 25^0C determine the mass of salt deposited
   (Ans. 34g)

b) Explain how a pure sample of A can be obtained from a mixture containing salts A and B Name one method that can be used to test for purity of the separated sample.

c) The melting point of pure cadmium and pure bismuth are 321^0C and 271^0C respectively. The table below shows the melting points of various mixtures of the two metals.

Percentage of Cd	20	35	50	65	80	95
Melting points	226	190	156	184	242	300

i) Draw a fully labeled phase diagram for Cd – Bi system and explain the shape of the graph.

ii) Using the diagram explain what would happen if a liquid mixture containing 25% Cd at 350^0C was gradually cooled

CHEMICAL KINETICS

The rate of a chemical reaction and the factors affecting the rate of the reaction can be expressed as i)The rate of increase of concentration of the products.

iii) The rate of decrease of concentration of the reactants

Experimentally the rate of reaction can be determined by physical or chemical methods.

Physical methods

a) A change in gas volume can be measured after various time intervals example the reaction of a metal with an acid and the decomposition of hydrogen peroxide. The volume of hydrogen gas and oxygen gas produced respectively can be measured at intervals.
b) An increase or decrease in gaseous pressure can be used to follow many gaseous reactions.
c) Electrical properties. A change in conductance indicates a change in the concentration of ions.
d) Thermal conductivity. A gaseous reaction can be followed by measuring a thermal conductivity of the gaseous mixture of reaction gases.
e) Observing colour changes, as in the case of thiosulphate and an acid.

CHEMICAL METHODS

Titration can be used to follow the change in the concentration of the reactants of the products. A sample of the reaction mixture is withdrawn with a pipette and the reaction stopped. This may be done by removing one of the reactants by chemical reaction. A titration is then performed to find the concentration of one of the reactants or one of the products examples. The cause of an alkaline hydrolysis is an ester is followed by measuring the concentration of an alkali at various times after the start of the reaction.

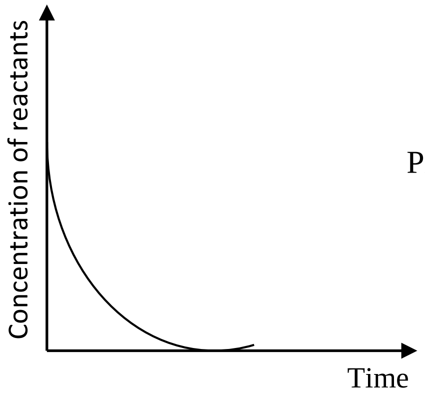
$CH_3COOCH_2CH_3 + NaOH \rightleftharpoons CH_3COONa + CH_3CH_2OH$

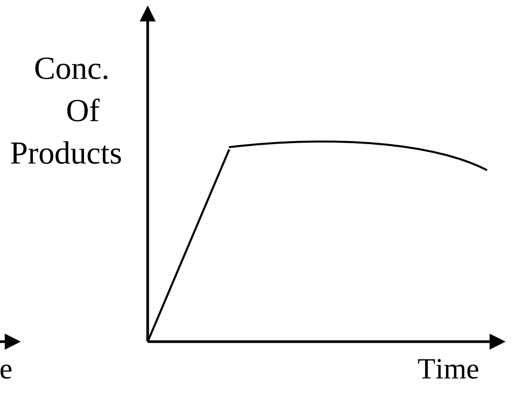
<u>Factors which affect the rate of chemical reactions</u>

a) **Concentration.** The higher the concentration of reactants the faster the rate of reaction. This is because at high concentration the molecules are near to each other and this therefore increases the rate of collision resulting into faster reaction. Therefore, the rate of reaction is directly proportional to the initial concentration of reactants. In reactions the reactants are in solution where the solution may be liquid or gaseous. In a liquid solution the concentration can be changed either by adding or removing the reactants or by changing the volume of the system as by adding or removing the solvent.

Hence,

When the progress of a reaction is followed by determining the concentration of a product or reactant at regular time intervals, a graph of concentration time is shown below





Thus Rate of chemical reaction is the speed at which the reactants or concentrations of reactants are decreasing or concentration of products is increasing. That is to say the amount of reactants used per unit time or the amount of products per unit time. Then the rate of reaction at a particular time is determined by drawing a tangent to the curve at that time and then finding its gradient.

NOTE: Then determining the effect of each factor on the reaction rate, all other factors must be kept constant.
Now consider a reaction for A and B
$mA + nB \longrightarrow$ products
Then Rate = $K[A]^m [B]^n$ where
K is the proportionality constant called the rate constant whose value depends upon temperature but not upon concentration.
m and n are the order of reactions with respect to reactant A and reactant B
(m + n) is called the overall order of the reaction.

NOTE:
For the kinds of reactions studied in A-level courses, the orders may be 0, 1 or 2 but m + n will not exceed 2.

Order of a reaction

Is the sum of powers to which the concentration terms are raised to in the rate equation, example for $x A + yB \longrightarrow$ product.
The rate = $K[A]^x \times [B]^y$
Such that the order = x +y

Rate constant

Is the ratio of the rate of a reaction to the functions of the concentration terms whose value depends upon temperature but not upon concentration example

Rate = $K[A]^x [B]^y$
Then K = ${Rate}/{[A]^x[B]^y}$

Molecularity
Is the number of molecules or ions involved in a particular reaction, that is total number of species taking part in the rate determining step of the reaction.
For a reaction which occurs in stages the reaction is determined by the slowest step.

Consider the reactions below.

a). $X \longrightarrow Y$ (Unimolecular reaction)

b). $A + B \rightarrow C$ (Molecularity is 2 since two species A and b are involved.

NOTE: Order is experimentally determined while molecularity of a reaction is determined from the stochiometric equation example for the reaction 2x + y = products, molecularity = 3
The order of a reaction may be fractional but molecularity is always an integer. (whole number).

Consider the rate equation below.

Rate = $K[A]^x[B]^y$ the reaction is of order x with respect A and of order y with respect to B. The overall order is $(x + y)$

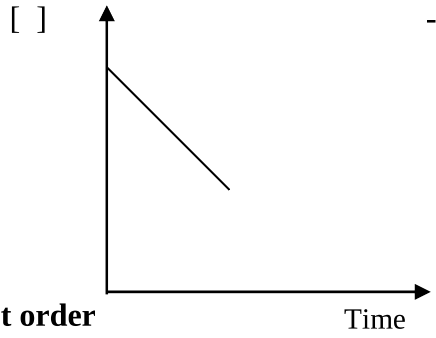
Rate determining step

Is the slowest step in the reaction mechanism .It controls the overall rate of the reaction

Graphs of specific orders

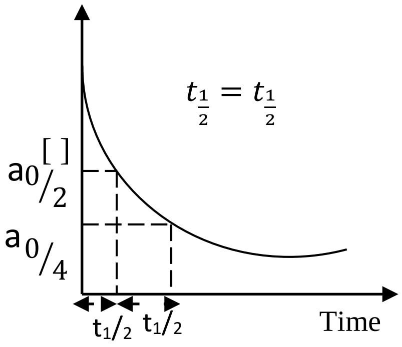
(Let concentration be [ ]

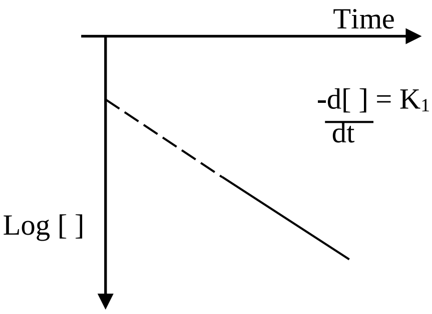
a) **Zero order**



$$\frac{-d[\ ]}{dt} = K_o[\ ]^0$$

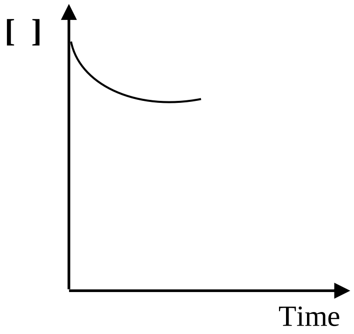
b) **First order**

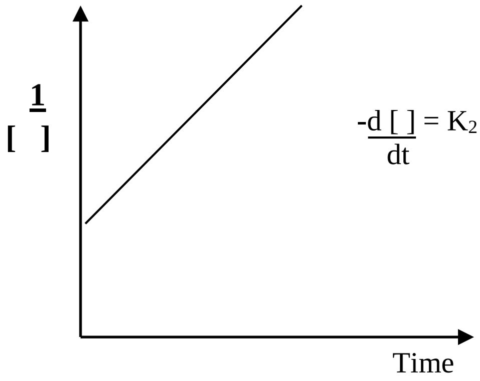




$$\frac{-d[\ ]}{dt} = K_1[\ ]^1$$

c). Second order





$$-\frac{d[\ ]}{dt} = K_2[\ \ ]^2$$

Summary of straight line graphs

Y-axis	**X-axis**	**Order**
Concentration	Time	Zero
Rate	Concentration	first
Log concentration	Time	Time first
Rate	Square of concentration	second
Reciprocal of concentration	Time	second

NOTE: The coefficients in the balanced equation are not necessarily the process in the rate expression

Self check

1. Study the kinetic data for the decomposition of a compound X

Time /minutes	**Concentration of Y /mol dm^{-3}/x10^{-4}**
0.0	2.90
18.0	2.30
30.0	2.00
54.0	1.60
80.0	1.30
120.0	1.00

a) Plot a graph of concentration of Y against time
b) Determine the rate f a reaction at 100 minutes
c) Show how the rate at 10 minutes compares with that at 100 minutes. Explain your answer

2. Given 2A ⟶ products

Time /hrs	0	1.3	2.0	4.0	5.3
Log_{10}[A]	-0.07	-0.24	-0.33	-0.57	-0.74

a) Plot a graph of log[A] against time

b) From your graph determine the order of the reaction.
c) Calculate (i). The rate constant for the reaction
(ii). The half life of the reaction.

Determining Orders

When determining the order of reaction with respect to a reactant, the concentration of the other reactants involved is kept constant. The table below shows some kinetics data for the iodination of propanone cataylsed by hydrochloric acid.

Experiment	**[iodine]**	**[propanone]**	**[HCl]**	**rate**
A	0.001	0.5	1.25	1.1
B	0.002	0.5	1.25	1.1
C	0.002	1.0	1.25	2.2
D	0.002	1.0	2.50	4.4

- Experiment A and B rate does not depend upon [iodine] because varying [iodine] that double it when the rest are constant to the rate remains the same.
  And – rate $\propto$ $[\text{iodine}]^0$ and reaction is zero order with respect to iodine.
- Experiment B and C, rate doubles when [propone] doubles, - Rate $\propto$ $[\text{propanone}]^1$ and reaction is first order with respect to propanone
- Experiment C and D, rate doubles, when [HCl] doubles and – rate $\propto$ $[\text{HCl}]^1$ and reaction is first order with respect to HCl. Hence

$$= \text{rate} \propto [\text{iodine}]^0 [\text{propanone}]^1 [\text{HCl}]^1$$

But any number to power zero is one, and 1 is omitted.

So the differential rate equations is then

$$\text{Rate} = K[CH_3COCH_3][H_3O^+]$$

And the iodination of propanone is a second reaction overall.

Example

The following kinetic data were obtained for reactions

$A + 2B \longrightarrow \text{product}$

Experiment	**[A]mol^{-1}**	**[B]mol^{-1}**	**rate mol^{-1}s^{-1}**
1	3×10^{-2}	3×10^{-2}	2.7×10^{-5}
2	3×10^{-2}	6×10^{-2}	5.4×10^{-5}
3	6×10^{-2}	3×10^{-2}	10.8×10^{-5}
4	6×10^{-2}	6×10^{-2}	21.6×10^{-5}

1.
a) What is the order of reaction with respect to
(i) A (ii) B
b) What are the units of the rate constant

c) Using results in experiment 1 above, calculate the rate constant.
d) What happens to the rate when the concentration of A and B are both doubled.

Solution

a)

i) In 1 and 3, doubling the concentration of A quadruples the rate thus the reaction is 2nd order with respect to A.

iii) In 1 and 2, doubling the concentration of B, doubles the rate therefore the reaction is 1st order with respect to B.

b) from rate = K $[A]^2[B]$

$$K = \frac{Rate}{[A]^2[B]} = \frac{mol^{-1}s^{-1}}{mol^2l^{-2}\,mol^{-1}}$$

$$= \mathbf{mol^{-2}l^2S^{-1}}$$

Units of rate constant are $mol^{-2}l^2s^{-1}$

c) $K = {Rate}/{[A]\ ^2[B]}$

$$= \frac{2.7 \times 10^{-5}}{(3 \times 10^{-2})^2(3\times10^{-2})}$$

$$= \mathbf{1\ mol^{-2}l^2s^{-1}}$$

d) In experiment 1 and 4, doubling the concentration of A, quadruples the rate (increases the rate 4 times) and doubling the concentration of B doubles the rate (increases the rate 2 times). This means that the rate increases (4 × 2) times and the rate is $(2.7 \times 10^{-5}\times8)moll^{-1}s^{-1}$

2. The rate equation for certain reaction is

Rate = K [P] $[Q]^2$[R]

a) State what would happen to the rate of reaction if
i) The concentration of P and Q are kept constant but that of R doubled.
ii) Concentration of all the species is halved.
iii) The concentrations of all the species are doubled.

b) The following results were obtained in the study of a reaction between peroxodisulphate and iodide ions

Experiment no.	**$[S_2O_8^{2-}]$ $moldm^{-3}$**	**[I] $moldm^3$**	**initial rate $moldm^{-3}S^{-1}$**
1	0.024	0.024	9.6×10^{-6}
2	0.048	0.024	1.92×10^{-5}
3	0.048	0.012	9.6×10^{-6}

i) Write the rate equation
ii) Calculate the rate constant for the reaction and state its units

Solution

a) (i). the rate also doubles or becomes twice the original rate.

ii). Rate becomes 1/16 times the original rate. Or reduces 16 times.

iii). Rate becomes 16 times the original rate

b) (i). Rate = $K[S_2O_8^{2-}][I^-]$

(ii). Rate = $K[S_2O_8^{2-}][I^-]$

$9.6 \times 10^{-6} = K\,(0.024)\,(0.024)$

$K = 0.0167$

$\mathbf{= 1.67 \times 10^{-2} mol^{-1} dm^3 s^{-1}}$

And units are $mol^{-1}dm^3s^{-1}$

Self check

1. For the reaction A + B $\rightarrow$ C, the following data was obtained.

Exp't	**[A]moll^{-1}**	**[B]mol^{-1}**	**Rate moll^{-1}mm^{-1}**
1	0.1	0.1	2×10^{-3}
2	0.2	0.2	8×10^{-3}
3	0.1	0.2	8×10^{-3}

a) Write the rate experiment for the reaction and calculate the value of K and give its units.

b) What would be the initial rate of formation of C if the initial concentration of A was 0.6M and that of B was 0.3M

(Ans. R =$K[B]^2[A]^0$, K=0.2mol^{-1}lmin^{-1}, R= 0.018moll^{-1}Min^{-1})

NOTE:

If A $\longrightarrow$ products, if the starting concentration of A is **a** and after time **t** the concentration of x has 'disappeared'.

	A	**product**
Initially	a	0
After t	$a - x$	x

The rate of formation of products

$$\frac{dx}{dt} = k(a - x)$$

$$\frac{dx}{dt} = k(a - x)$$

$$\int \frac{dx}{a-x} = \int kdt$$

$$-In(a - x) = kt + C$$

When $t = 0,\ x = 0$

$$-Ina = C$$

Then $Ina - In(a-x) = Kt$

$In\left(\frac{a}{a-x}\right) = kt$

$t = t_{1/2}\ , x = {}^{a}/_{2}$

Then $Kt_{1/2} = In\left(\frac{a}{a-a/2}\right)$

$Kt_{1/2} = In\,2$

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

The half life of a reaction $t_{1/2}$, Is the time interval required for the concentration of a reactant to decrease to half its original value. It is independent of the original amount and it's always constant for a given reaction.

NOTE: The half-life of a first order reaction is a constant {½ InK_1} independent of the concentration of reactant whose value is decreasing by half.

Examples

Decays of radioactive isotopes such as

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{1}e$$

Self Check

The half life of a first order reaction is 100s

a) Calculate the rate constant
b) Determine the percentage of the reactant that reacted after 250^0C
(*Ans. a). 0.693* × *$10^{-2}s^{-1}$ b).*

<u>Determination of the order of reaction with respect to iodine</u>

(Introduction of propanone catalysed by sulphuric acid)

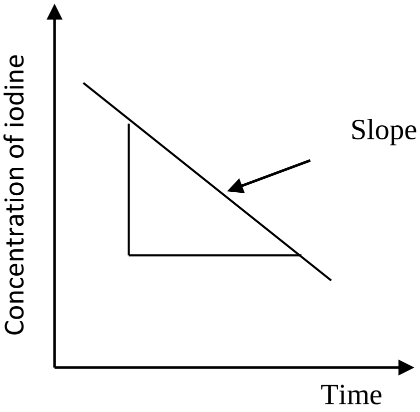
a) A fixed volume of propanone and dilute sulphuric acid is pipette into a conical flask. Then a known volume of iodine solution is added into the flask and a stop clock is started simultaneously.

Stopper the flask and stir the liquid so as to mix it. At known time intervals, portions of the reaction mixture are withdrawn and run into conical flasks containing a known volume of sodium bicarbonate.

This stops the reaction by removing the H^+ ions which act as a catalyst to the above reaction. Now, the concentration of iodine left after a given time intervals, it can be determined by titrating the mixture with a standard solution of sodiumthiosulphate required to reach the endpoint is directly proportional to the iodine present.

$$I_{2(aq)} + 2S_2O_3{}^{2-}{}_{(aq)} \longrightarrow S_4O_6{}^{2-}{}_{(aq)} + 2I_{(aq)}$$

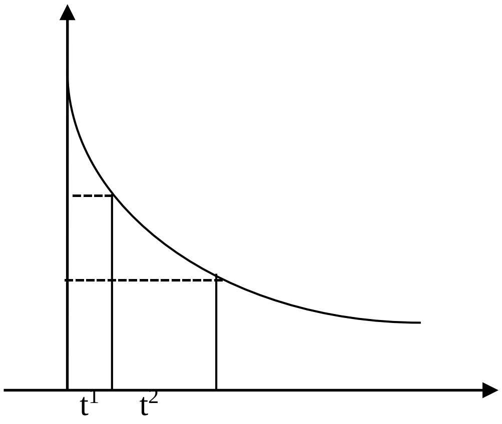
A graph of concentration of I_2 against time is plotted



The graph obtained will be a straight line with a negative gradient, indicating that the rate of reaction is independent of the concentration of iodine. That is, the order of reaction with respect of iodine is zero.

Determination of order of reaction with respect to hydrogenperoxide

Pipette a known volume of hydrogen peroxide (say 10cm^3) into a conical flask and add 1cm^3 of about 0.2M sodium hydroxide solution followed by 1M Iron(iii)chloride solution. Shake the flask and leave to stand for 3 minutes. Add 20cm^3 of 1M sulphuric acid to stop the reaction and find the remaining hydrogen peroxide by titrating with a standard solution of potassium permanganate from the burette until the solution turns pink. Repeat the procedure above for 6, 9, 12 and 15 minutes before adding sulphuric acid. Plot a graph of volume of potassium permanganate against time and used it to determine the order of the reaction.



It is found that $t_1 = t_2$ hence the reaction is a first order with respect to hydrogen peroxide.

b) Temperature

Increase in temperature increases the rate of reaction. This is because increase in temperature increases the kinetic energy of the reacting species which increases their chance of colliding with one another to form products. Hence the higher the temperature the greater the chance of reactants to gain energy greater than activation energy.

The higher the temperature the faster the reaction, that is, a role of thumb, a ten degree rise in temperature doubles a rate of a reaction.

The temperature of any reaction is related to rate constant by the equation

K = A$e^{-\left(\frac{\varepsilon a}{RT}\right)}$ where A is a constant, K is rate constant, ε_a = activation energy

T = temperature in Kelvin and R is gas constant

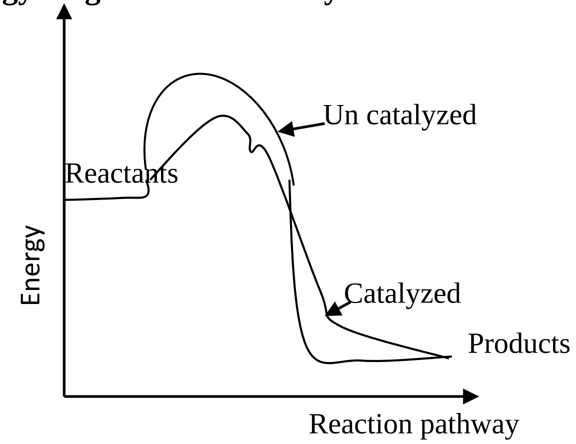
c) Activation energy

Is the minimum energy with which the reactant molecules must collide for a reaction to occur. The lower the activation energy, the faster the reaction.

d) Catalysts

A catalysts speed up reactions but are not consumed by reactants and therefore do not appear as reactants in the overall equations. They provide alternative reactions path way with activation energies lower than those of the un-catalyzed reactions. Thus they speed up the rate of attainment of equilibrium for a reversible reaction without altering its composition at equilibrium. Hence catalysts lower by the same amount the activation energies of the forward and reverse reactions of a reversible reaction.

Energy diagram with a catalyst in the reaction



e). Surface area

The larger the surface area of reactants, the faster the reaction. This is because the area in contact with other reactants has increased and therefore the number of particles per volume increases thereby increasing the number of particles colliding per unit time. Hence increasing the rate of reactants for example powdered surfaces in solid lumps have larger area than their corresponding lumps of solid like magnetism ribbon marble chips etc. this is because the surface area in contact with other reactants is increased in powdered form

f). Pressure

Pressure only affects gaseous reactions depending on whether the reaction occurs with an increase in volume or occurs with a decrease in volume. For reactions which occur with a

$\rightleftharpoons$

$\rightleftharpoons$

decrease in volume (example $N_{2(g)} + 3H_{2(g)}$ $2NH_3$), the rate of reaction is increased by an increase in pressure. This is because an increase in pressure increases the number molecules per unit volume and this increases the rate at which molecules collide with each other hence increasing the rate of the reaction. The reverse is true for reactions which occur with an increase in volume (example $2NO_{2(g)}$ $2NO_{(g)} + O_{2(g)}$)

Self check

a) The following data were obtained experimentally on the rates of the reaction under different conditions at 300K

[A]moll^{-1}	**[B]moll^{-1}**	**Rate moll^{-1}s^{-1}**
2.0×10^{-2}	1.0×10^{-2}	1.0×10^{2}
2.0×10^{2}	2.0×10^{-2}	2.0×10^{2}
4.0×10^{-2}	2.0×10^{-2}	4.0×10^{2}

(1). Write down an expression for experimental rate equations using these data and show your reasoning

ii). What is the activation energy for the backward reactions.

c). How would you expect the

i). equilibrium constant for the reaction to change if the temperature was raised.

ii). Rate of reaction to change if the temperature was raised. Explain your answer.

d). Sketch on one diagram the variation of concentration C with time during the reaction after A and B are mixed for two temperature T_1 and T_2 where $T_2 > T_1$

(Ans. A (i) 150KJ)

2. The following results were obtained in the study of temperature and rate constant

Temperature/K	293	305	318
Rate constant	1.76×19^{-5}	1.35×10^{-4}	4.98×10^{-4}

Plot a graph of log K against $\frac{1}{T}$. Use your graph to determine activation energy.

CHEMICAL EQUILIBRIA

Are concerned with reversible reactions and the factors affecting a reversed reaction. All reversible reactions reach a stage of chemical equilibrium or balance.

A reversible reaction is one that does not go to completion. Not all the reactants are converted to products and the reaction proceeds in two directions

Example

$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

Activation energy

This is the energy which the molecules must acquire before they react. When oxygen and hydrogen are kept together in a container there is no reaction although the molecules collide. If the mixture is heated to 800^0C, the gases react evidently. This is because the heat provides the activation energy. Two different collide together either producing two new molecules or combining to give one type of molecule example

$$2HBr_{(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} + Br_{(g)}$$

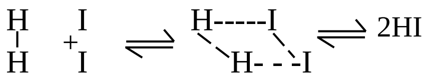
$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

The bonds are broken and new ones are formed only when two molecules collide with enough energy.

Bond breaking and bond making occur simultaneously

Bonds begin to form between hydrogen and iodine atoms while the H – H and I – I bonds stretch and become weaker. The molecules approach closer and an activated complex is formed.

This is an unstable species which reacting molecules form in order to be converted to products. All the four atoms are joined together by weak bonds of abnormal length. That is,

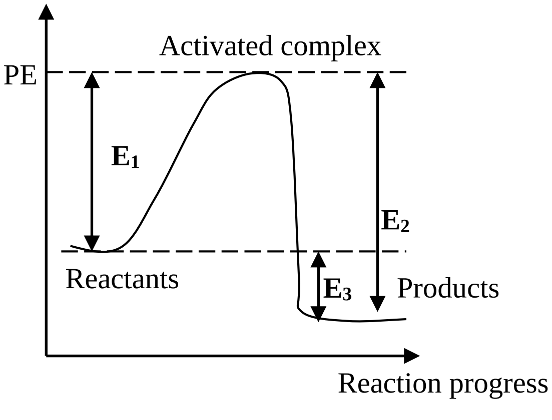


$$\begin{matrix}H & & I\\ | & + & \\ H & & I\end{matrix} \rightleftharpoons \begin{matrix}H\text{-----}I\\ H\text{- - -}I\end{matrix} \rightleftharpoons 2HI$$

Activated complex

The new bonds decrease top the normal H-I bond length while the other bonds break. The formation of the activated complex is accompanied by an increase in the potential energy of the system because the stretching of bonds absorbs energy. Activation energy is the difference in energy of activated complex and the reactants.

The energy changes for an exothermic reaction



E_1 is the activated energy of the forward reaction. If the reacting particles have got enough amount of energy to form the activated complex. It may decompose into either the reactants or products. If the supplied energy is greater, the complex loses energy **E_2** as the new H – I bonds shortened. The difference between E_2 and **E_1 (E_3)** is the heat evolved in the forward reaction.

NOTE: The complex can be reached from opposite direction. **E_2** will be activation energy of the reverse reaction. This reverse reaction would be endothermic since the heat absorbed would be greater than that given out.

EQUILIBRIUM CONSTANT K_c

Consider a reversible reaction $A + B \rightleftharpoons C + D$. The forward and backward reaction proceeds until a point is reached where their rates become equal. At this point an equilibrium is attained if K_1 and K_2 are the rate constants for forward and backward reactions respectively

The rate of forward reaction = $K_1[A]\,[B]$

Rate of backward reaction = $K_2[C]\,[D]$

At equilibrium the rate of forward reaction equals rate of backward reaction.

$K_1[A]\,[B] = K_2[C][D]$

And $$\frac{K_1}{K_2} = \frac{[C]\,[D]}{[A]\,[B]}$$

But $\frac{K_1}{K_2}$ constant K_c (equilibrium constant)

$$\Rightarrow K_c = \frac{[C]\,[D]}{[A]\,[B]}$$

It's the ratio of products of concentration of the products to the product of concentrations of reactants

The bracket [ ] imply molar concentration. The K_c express $\frac{[C]\,[D]}{[A]\,[B]}$ is called the law of mass action

Which states that "At a given temperature there is a fixed relationship between the molar concentration of the products and reactants in the equilibrium mixture of a reversible reaction".

Examples

1. Write equilibrium constant expression for the following
   a) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$
   b) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

Solution

a). $K_c = [NO]^2 / [N_2]\,[O_2]$ moldm^{-3}

b). $K_c = \frac{[PCl3][Cl_2]}{[PCl5]}$ moldm^{-3}

Generally for; $xA_{(g)} + yB_{(g)} \rightleftharpoons zC_{(g)} + wD_{(g)}$

Then $K_c = \frac{[C]^z\ [D]^w}{[A]^x\ [B]^y}$

And for reactions involving solids the concentration of solids is assumed to be constant and does not appear in the expression Example

$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

Then

$K_c = \frac{[H_2]^+}{[H_2O]^+}$ $moldm^{-3}$

Factors which affect equilibrium reactions

Effect of temperature

The effect of temperature on any equilibrium reaction depends on whether the reaction is exothermic or endothermic. If the reaction is endothermic, increasing the temperature favours it but if it's exothermic then it's favoured by lowering the temperature.

a) Consider the reaction below.

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $\triangle H = {}^{+}180 KJmol^{-1}$ at 25^0C

The forward reaction is endothermic and thus is favoured by high temperature.

If the reaction is carried out at a lower temperature (example 10^0C) the backward reaction is favoured, and then K_c decrease, and the equilibrium position shifts to the left.

b). For $3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_3$ $\triangle H = -92KJmol^{-1}$ at 20^0C.

The reaction is exothermic and the forward reaction is favoured by low temperature .Therefore carrying out the reaction at a low temperature for example 20^oC. The forward reaction would be favoured and more H_2 and N_2 combine to form NH_3. Thus the concentration of NH_3 increase, while the concentration of H_2 and N_2 decrease.

Since $K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]}$ then K_c increases

Carrying out the reaction at a high temperature (example 30^0C) the backward reaction would be favoured. More of NH_3 decomposes to give N_2 and H_2 thus increasing their concentration. K_c decreases and the equilibrium shifts to the left.

NOTE: It's only temperature and not any other factor that affects the magnitude of K_c.

Effect of concentration

The effect of concentration on equilibrium occurs in accordance with Lechatehier's principle. The principle states that **"if a system is n stable equilibrium and one of the conditions like temperature, pressure or concentration is changed, the equilibrium shifts so as to restore the original conditions".**

Consider the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

If O_2 is added, the equilibrium system adjusts itself so as to restore the original conditions by some SO_2 reacting with some O_2 to form SO_3.

This means that the concentration of SO_3 increases and that of SO_2 decreases. Similarly by removing SO_3 the equilibrium shifts to the right. But addition of excess SO_3 would cause equilibrium to move to the left.

If the concentration of SO_2 was reduced by removing some, then SO_3 would decompose to give SO_2 and O_2 thus increase the concentration of oxygen and decreasing the concentration of SO_3 causing equilibrium to shift to the left.

All the changes in concentration of reactants and products occur so as to maintain K_c constant since it's only affected by temperature.

Consider

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

In this reaction addition of concentrated H_2SO_4, shifts the equilibrium to the right because it removes the water (H_2O). Addition of sodium hydroxide (NaOH) reverses the reaction because it reacts with CH_3COOH to form sodium ethanoate (CH_3COONa^+) and H_2O. In both cases the value of K_c remains constant.

Qn. For the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$. State the effect of increasing hydrogen on equilibrium position and explain what happens when a substance that can remove nitrogen is introduced in the system at equilibrium.

Effects of pressure

Pressure has almost no effect on the concentration of liquids and solids. It affects mainly gases and an increase of pressure on a gaseous system is equivalent to an increase in concentration of the reacting substance.

The rate of reaction is greater at higher pressure which can be caused by decreasing the volume of the container or applying external pressure or adding another gas taking part or not taking part in the reaction.

The position of the equilibrium is only changed by pressure when there is a change in volume of the reaction.

a) <u>Reactions which occur with decrease in volume</u>

Example

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Ratio 1_{vol} 3vol $\rightleftharpoons$ 2vol

Total 4vol $\rightleftharpoons$ 2vol

$4 \longrightarrow 2$ (decrease)

$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$

And etc

Any reaction which occurs with a decrease in volume is favoured by high pressure. In the above reactions the equilibrium shifts to the right. K_c remains constant. This s because increase in pressure decreases the volume and the concentration of all the species increases, but changes in the concentration does not affect the equilibrium constant. Decrease in pressure for such reactions favours a backward reaction.

b) Reactions which occur with increase in volume

$2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$

Ratio $2_{vol} \rightleftharpoons 2_{vol} + 1_{vol}$

Total $2_{vol} \rightleftharpoons 3_{vol}$

$2 \longrightarrow 3$ (increase)

Decrease in pressure shifts the equilibrium to the right to produce more moles and restore the original pressure. Meanwhile high pressure favours the backward reaction; however, the equilibrium constant does not change.

c) Reactions with no change in volume

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Ration 1vol: 1vol $\rightleftharpoons$ 2vol

Total 2vol $\rightleftharpoons$ 2vol

$2 \longrightarrow 2$ (no change)

These reactions are not affected by pressure. The equilibrium and the equilibrium constant are not affected.

NOTE:

1. A homogenous system is one in which the reactants and the products are of the same phase.
2. A heterogeneous system is one in which the substances are not all in same phase example

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

$K_c = [CO_2]$

This means that the concentration or pressure of CO_2 is constant at any particular temperature. At fixed temperature, adding more CO_2 will keep its concentration or pressure constant by reacting with CaO to form $CaCO_3$ whose concentration is constant.

K_p is the equilibrium constant in terms of pressure. It's the ratio of the product of the partial pressures of the products to the product of the partial pressure of the reactants.

If $A_{(s)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$

Then $K_p = \dfrac{P_C \times P_D}{P_B^2}$

Effect of a catalyst

A catalyst increases the rate of both the forward and backward reactions but does not affect the equilibrium position and value of K_c. The same quantity of product is got but in a shorter time. A catalyst only increases the rate at which the equilibrium is reached. It doesn't affect equilibrium position since it does not take part in chemical reaction but it just lowers activation energy.

Experimental determination of K_c

Example (Esterification)

Reaction between ethanol and ethanoic acid

$CH_3CH_2OH_{(1)} + CH_3COOH_{(aq)} \rightleftharpoons CH_3COOCH_2CH_{3(aq)} + H_2O_{(l)}$

Known amounts of both acid and alcohol are mixed in the flask to keep the temperature constant. The mixture is allowed to stand for a short time, and at intervals fixed volumes of the mixture are titrated with a standard solution of sodium hydroxide using phenolphthalein indicator. This determines the amount of acid left and this is found to fall with time, finally reaching a constant minimum which is taken as the amount present at equilibrium

Results

Let $V dm^3$ be the volume of solution and x moles be amount of acid that has reacted (determined) at equilibrium

Let a and b be the initial amount of acid and alcohol respectively.

$$CH_3CH_2OH_{(l)} + CH_3COOH_{(aq)} \rightleftharpoons CH_3COOCH_{2(aq)} + H_2O_{(l)}$$

Initially before equilibrium	b	a	0	0
At equilibrium	$b-x$	$a-x$	x	x
Equilibrium concentration	$\frac{(b-x)}{V}$	$\frac{a-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

But $K_c = \frac{[CH_3COOCH_2CH_3]\,[H_2O]}{[CH_3CH_2OH]\,[CH_3COOH]}$

$$= \frac{{}^{x}/_{V} \cdot {}^{x}/_{V}}{\left(\frac{b-x}{V}\right)\left(\frac{a-x}{V}\right)}$$

$$K_c = \frac{x^2}{(b-x)\,(a-x)}$$

And K_c can be determined

Qn. If 12g of ethanoic acid were mixed with 13.8g of ethanol, calculate the mass of ethyl ethanoate present at equilibrium given Kc = 0.348. ***(Ans. 7.92g)***

Decomposition of hydrogen iodide (HI)

A fixed amount of HI in a fixed volume (example in bulb is heated and when equilibrium is attained, the bulb is rapidly cooled and broken under potassium iodide solution. The iodine formed is then titrated with a standard solution of sodium thiosulphate using starch indicator.

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

Let 2n = number of moles of HI heated.
X = degree of dissociation of HI at equilibrium
Vdm^3 = total volume of the bulb

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

Initial	2n	0	0
Equilibrium, amounts	$2n(1-x)$	nx	nx
Equilibrium concentration	$\frac{2n(1-x)}{V}$	$\frac{nx}{V}$	$\frac{nx}{V}$

Then
$$K_c = \frac{[H_2]\,[I_2]}{[HI]^2} = \frac{\frac{nx}{V}\cdot\frac{nx}{V}}{\frac{(2n(1-x))^2}{V}}$$

$$= \frac{n^2x^2}{4n^2(1-x)^2}$$

$$= \frac{x^2}{4(1-x)^2}$$

Examples

1. When equilibrium portions of H_2 and I_2 were heated together at a certain temperature the system at equilibrium was found to contain $0.0017moldm^{-3}$ of H_2 and $0.0118mol\ dm^{-3}$ of HI. Calculate the equilibrium constant for the reaction at this temperature

Solution

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(aq)}$$

Aq concentration	0.0017	0.0017	0.0118

$$K_c = \frac{[HI]^2}{[A_2][I_2]} = \frac{(0.0118)^2}{0.0017 \times 0.0017}$$

$$\mathbf{= 48.2}$$

2. At 500^0C the value of K_c for the reaction

$H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$ is 1.6

In an experiment the gases were mixed with initial concentration of 0.5M each of the H_2, CO_2, steam and CO. Calculate the final equilibrium concentration of each component at 500^0C.

Solution

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$$

Initially 0.5 0.5 0.5 0.5

NOTE: when K_c is greater than one
Equilibrium lies more to the right
Let x be the amount of H_2 that reacts at equilibrium

At equilibrium $0.5 - x$ $0.5 - x$ $0.5 + x$ $0.5 + x$

And $K_c = \frac{[CO]\,[H_2O]}{[H_2]\,[CO_2]} = 1.6$

$$\Rightarrow \quad \frac{(0.5 + x)\,(0.5 + x)}{(0.5 - x)\,(0.5 - x)} = 1.6$$

$$\Rightarrow \quad \frac{0.25 + x + x^2}{25 - x + x^2} = 1.6$$

$$0.25 + x + x^2 = 0.4 - 1.6x + 1.6x^2$$

$$0.6x^2 - 2.6x + 0.15 = 0$$

Take $x = 0.06$

Then $[CO_2] \equiv [H_2] = 0.5 - 0.06$

= 0.44M

And $[CO]\,[H_2O] = 0.5 + 0.06$

= 0.56M

3. 1 mole of H_2 and 1 mole of I_2 were introduced into a one litre container at 470^0C. What will be the final concentration in the container when equilibrium has been established ($K_c = 45.9$ at 470^0C)

Solution

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

If x moles have reacted at equilibrium

At equilibrium

$1 - x$ $1 - x$ $2x$

$$K_c = \frac{(2x)^2}{(1-x)(1-x)}$$

$$45.9 = \frac{4x^2}{(1-x)(1-x)}$$

$$45.9(1 - 2x + x^2) = 4x^2$$

$$45.9 - 91.8x + 45.9x^2 = 4x^2$$

$$41.9x^2 - 91.8x + 45.9 = 0$$

Take x = 0.772.

Then [HI] = 2 × (0.772) and $[H_2] \equiv [I_2]$ = 1 – 0.772

= 1.544 = 0.228

4. 0.3 moles of hydrogen and 0.14moles of iodine were heated at 630K if 0.2 moles of hydrogen iodine were formed. Calculate the equilibrium constant at the same temperature.

   Solution;

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

	H_2	I_2	$2HI$
Before	0.3	0.14	0
At eqm.	$0.3 - x$	$0.14 - x$	$2x$

But $2x$ = 0.2

$x = 0.1$

Therefore $[H_2]$ = 0.3 – 0.1

$[I_2]$ = 0.14 – 0.1

= 0.04

[HI] = 2 × 0.1

= 0.2

$$\text{Then } K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{(0.2)^2}{0.2 \times 0.04}$$

= 5

Self check

1. Consider the equilibrium $A_{(g)} + B_{(g)} \rightleftharpoons AB_{(g).}$

   Calculate the concentration of AB in a two litre container into which 0.5moles of A and 0.6 moles of b have been injected ($K_c = 4 \times 10^{-2}$)

   (Ans. 2.9 x 10^{-3})

2. H_2 and I_2 react according to the equation

   $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

At a certain temperature partial pressure of $H_2 = 2.5\times10^{-1}$ atm and that of $I_2 = 1.6 \times 10^{-1}$atm.

a) Calculate the equilibrium constant for the reaction. PAI = 4×10^{-1} atm.

b) In a second experiment at the same temperature, I_2 and HI were mixed together with each gas at a partial pressure of 3×10^{-1}atm. What are the partial pressures of H_2 and HI at equilibrium?

c) In a third experiment pure HI was injected into a flask at a partial pressure of 6×10^{-1} atm. What are the partial pressures of H_2, I_2 and I_I at equilibrium

(Ans. (a) 4, (b) p_{H_2} = 0.0375atm P_{HI} = 0.255atm c) P_{H_2} = 0.15 atm P_{I_2}= 0.15atm P_{HI}=0.3atm)

3. The stoichiometric amount of nitrogen and hydrogen were reacted at 50 atm. At equilibrium 0.8 moles of NH_3 were formed. Calculate

a) Amount of hydrogen and Nitrogen at equilibrium

b) Value of equilibrium constant for the reaction

(Ans. N_2 = 0.6, H_2 = 1.8, $K_p = 7.51 \times 10^{-4}$ atm^{-2})

4. At a given temperature 2 moles of phosphorus pentachloride decomposed and at equilibrium was found to contain 35% chloride. Calculate the equilibrium constant K_P at the same temperature if the total pressure is 50 atmospheres. ***(Ans. K_p = 20.42atm)***

5. 3.0g of ethanoic acid and 2.3g of ethanol were mixed and left to react at 100oC for one hour until equilibrium was reached. 50cm3 of 1.0M hydrochloric acid. 33.3cm3 of acid was required for complete nuetralisation. Calculate the value of Kc.

(Ans. K_c = 3.976)

Applications of equilibrium reactions

Equilibrium reactions are applied in the following industrial pressures.

a) The manufacture of sulphuric acid in which the raw materials sulphurdioxide and oxygen are passed over vanadium (v) oxide catalyst at an optimum pressure of between 1 to 3 atmospheres and temperature of about 450^{0}C.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \; \Delta H = -188KJmol^{-1}$$

The yield of SO_3 is increased by

i) Use of low temperature since the forward reaction is exothermic.

ii) Use of high pressure since the forward reaction occurs with a decrease in volume.

iii) Increasing the concentration of either SO_2 or O_2 but excess O_2 is preferred since its cheaply obtained from air.

iv) Decreasing concentration of SO_3 by constantly removing it as soon as it's formed.

b) Manufacture of Ammonia (NH_3) by harber process.

The raw materials are hydrogen and nitrogen.

Iron is used as a catalyst at a temperature of about 550^{0}C, pressure of about 200-1000 atmosphere.

$$2N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \; \Delta H = - 92KJmol^{-1}$$

The yield of NH_3 is increased by

1. i) Increasing pressure.
2. ii) Decreasing temperature
3. iii) Removing NH_3 as soon as its formed
4. iv) Increasing concentration of N_2

ELECTRO CHEMISTRY

Electrolytes conduct electricity because they contain ions. The current flowing through a given solution is proportional to the reciprocal of the resistance of the solution and this quantity is known as conductance of the solution.

If R is the resistance, $1/_{R}$ is the conductance expressed in per Ohm (Ω^{-1}). To compare the resistances of difference substances the idea of resistivity is used.

In the same way for conductance conductivity is used. Electrolytic conductivity is the relative ease with which a sample can transmit electricity.
The resistance of an electrolyte is given by

$$R = \rho \frac{L}{A} \ , \quad \rho \ \frac{RA}{L}$$

Where ρ - is resistivity in Ω cm
L – Length of electrolyte in cm
A- Cross sectional area in cm^2

The recipirical of resistivity $\frac{1}{\rho}$ is called conductivity or electrolytic conductivity or specific conductivity

It's symbolized by K (kappa) = $\frac{1}{\rho}$ ($\Omega^{-1}cm^{-1}$)

$$R = \frac{1}{K} \cdot \frac{L}{A}$$

DILUTION

The concentration of a solution is the number of moles of solute in $1000cm^3$ of solution. The reciprocal of concentration gives the dilution which is the volume in cm^3 of solution that contains 1 mole of solute i.e. $\frac{1}{C}$ = V_m (dilution)

Therefore concentration of $0.1moldm^{-3}$ means that in one dm^3 we have 0.1 mole of the solute.
Dilution (V_m) = $\frac{1}{C} = \frac{1}{0.1}$ = $10mol^{-1}dm^3$ which means that in $10dm^3$ of solution there is one mole of electrolyte or a 0.1M solution has dilution of $V_m = \frac{1000}{C}$

$$= \frac{1000}{0.1}$$

$$= 10{,}000\,\text{cm}^3\text{mol}^{-1}$$

MOLAR CONDUCTIVITY

This is defined as the conductance of a volume of solution containing 1 mole of solute with the solution placed between two electrodes 1cm apart.

It was introduced so as to remove the effect of water on conductivity. Comparison of the conductivities of 1M and 0.1M solution is not fair because the 1M acid contains 1 mole of acid per dm^3 where as a 0.1M contains 0.1 moles per dm^3.

To compare them an equal terms volume of solutions containing equal amounts of solute must be considered. This is done by comparing molar conductivity instead of conductivity
Molar conductivity is denoted by Λ and

$$\Lambda = KV_m \qquad \Omega^{-1}\text{mol}^{-1}\text{cm}^2$$
$$= K\cdot \frac{1}{C}$$
$$= \frac{K}{C} \quad \Omega^{-1}\text{mol}^{-1}\text{cm}^2$$

If the concentration is in moldm^{-3} or molm^{-3} then

$$\Lambda = \frac{K}{C} \quad \Omega^{-1}\text{mol}^{-1}\text{m}^{-1}\text{m}^3$$
$$= \frac{K}{C} \quad \Omega^{-1}\text{mol}^{-1}\text{m}^2$$

Example

Calculate the molar conductivity of 0.1M hydrochloric acid given that it's electrolytic conductivity is $3.91\Omega^{-1}\text{m}^{-1}$

Solution

Molar conductivity $\Lambda = \frac{K}{C}$

$0.1\text{M} = 0.1\,\text{moldm}^{-3}$

$C = 0.1\times1000\,\text{molm}^{-3}$

$= 100\ \text{molm}^{-3}$

And $\Lambda = \frac{K}{C}$

$$= {}^{3.91}/_{100}$$

$$\mathbf{= 0.0391\Omega^{-1}mol^{-1}m^2}$$

Factors which affect electrolytic conductivity of solution

a) **Temperature:** At a fixed temperature, K of an electrolyte weak or strong depends on.

- The number of ions present per unit volume
- The speed at which the ions move.

b) **Concentration of electrolyte:** The higher the concentration the decrease in the degree of ionization thus decrease in the number of the ions per unit volume hence increase in conductivity.

NOTE:

The reciprocal of concentration is called dilution which expresses the number of m^3 containing one mole of an electrolyte

i.e. $V = \frac{1}{c}$

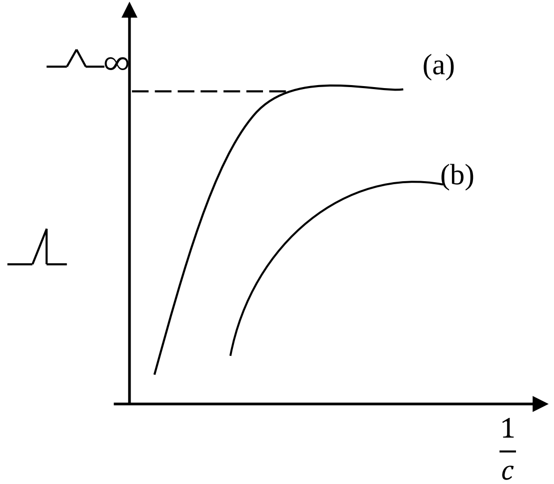
Factors affecting molar conductivity

a) **Concentration of solution**. This decreases with increase in concentration of electrolyte, for both weak and strong electrolyte.

b) **The charge an ion**. The greater the ionic charge, the more strongly attached is the ion, the greater its mobility and the greater the molar conductivity.

c) **The radius of the ion**. The smaller the radius of an ion the greater the charge density and hence the greater the shell of water molecules attracted, the lower is the mobility and the lower the molar conductivity.

The graph of against dilution



Graph (a) shows the variation of molar conductivity of a strong electrolyte with dilution. The molar conductivity increases with dilution. This is because as dilution increases the ions become far apart from one another and thus ionic interference is very little.

The increase in molar conductivity with dilution continues until a maximum point beyond which it remains constant. The molar conductivity at this point is called molar conductivity at zero concentration or molar conductivity at infinite dilution .That is,

Λ_o Or Λ_∞

Graph (b) shows the conductivity of a weak electrolyte with dilution. The increase in molar conductivity with increasing dilution is due to the ionization of a weak electrolyte (degree of ionization)

Example

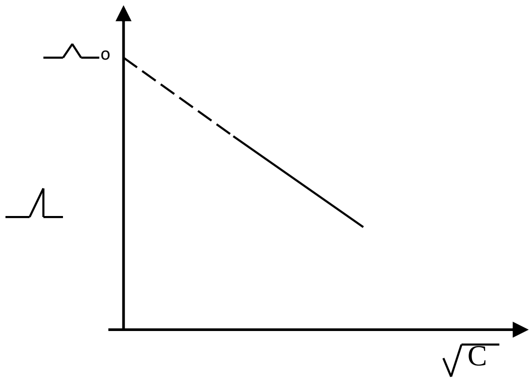
$CH_3COOH \rightleftharpoons CH_3CO\bar{O} + H^+$ —— (i)

$H^+ + H_2O \rightleftharpoons H_3O^+$ ––– (ii)

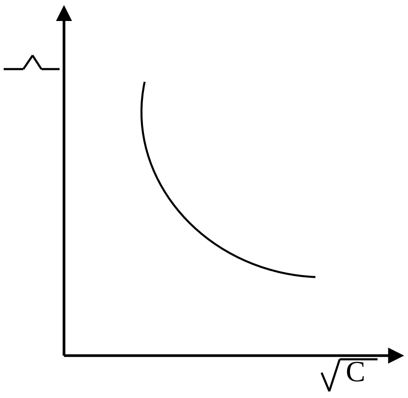
The removal of H^+ ions in equation (i) shifts the equilibrium, to the right in order to restore the equilibrium constant and more ions are produced. The number of ions produced depends on the amount of water added. This number increases continuously and the molar conductivity does not have a limit.

The corresponding curves for molar conductivity against square root of concentration are shown below.

a) Strong electrolyte



b) Weak electrolyte



THE INTERIONIC ATTRACTION THEORY

The conductance of a solution of a given solute depends on two factors.

- i) The number of ions.
- ii) Their velocity

Strong electrolytes such as sodium chloride are completely ionized at all reasonable concentrations. The variation of molar conductivity with concentration for a strong electrolyte cannot be due to a change in the number of ions because this is constant. The increase in molar conductivity is due to the increase in ionic mobility (ionic velocity with decreasing concentration.

This is the basis of the interionic attraction theory of electrolytic conductivity. The theory is that in a dilute solution the ions are relatively far apart and they exert little attraction on one another.

As the concentration increases the ions come closer together and the attraction between them results in a decrease in their velocity and hence decrease in the molar conductivity.

Explanation

a) For strong electrolyte, molar conductivity decreases with concentration because at higher concentration, the number of ions per unit volume increases so that ionic interferences also increase.
b) For weak electrolyte, molar conductivity decreases with concentration because it depends on the degree of ionization. At higher concentration, the degree of ionization is small hence decrease in conductivity

Kohlravsch's law of independent ionic migration

State that "The molar conductivity of an electrolyte (strong) at infinite dilution is the sum of the molar conductivities of its ions. That is, at infinite dilution the ions conduct independent of each other

Example

Λ NaCl = Λ Na$^+$ + Λ Cl$^-$

This law can be applied to indirectly determine the molar conductivity of a weak electrolyte at infinite dilution

NOTE Λ O = Λ o$^+$ + Λ ö

Example

The molar conductivities at infinite dilution and at 25°C of hydrochloric acid, sodium ethanoate and sodium chloride are 426, 91 and 126.5$\Omega^{-1}cm^2mol^{-1}$ respectively. Calculate the value of ethanoic acid

Solution

Λ H$^+$ + Λ Cl$^-$ = 426 —— (i)
Λ $CH_3CO\bar{O}$ + Λ Na$^+$ = 91 —— (ii)
Λ Na$^+$ + Λ Cl$^-$ = 126.5 —— (iii)

Equation (i) + (ii) – (iii)

⇒ Λ $CH_3CO\bar{O}$ + Λ H$^+$ = 426 + 91 – 126.5
= 390.5$\Omega^{-1}cm^2mol^{-1}$

Alternatively

$CH_3COONa + HCl \rightleftharpoons CH_3COOH + NaCl$

Then Λ CH_3COONa + Λ HCl = Λ CH_3COOH + Λ NaCl
= 91 + 426 – 126.5

$= 390.5\Omega^{-1}cm^{2}mol^{-1}$

Self check

1. The molar conductivities of potassium nitrate, potassium cylimide and nitric acid at infinite dilution are respectively 145, 156 and 421 $\Omega^{-1}cm^{2}mol^{-1}$. Calculate the molar conductivity of hydrocyanic acid at infinite dilution
   (Ans. 432 $\Omega^{-1}cm^{2}mol^{-1}$)

2. Calculate the molar conductivity of ammonia solution given that the molar conductivities at infinite dilution of sodium chloride, ammonia chloride and sodium hydroxide are respectively 113, 134.1 and 225.2 $\Omega^{-1}cm^{2}mol^{-1}$.
   (Ans. 246.3Ω^{-1} $cm^{2}mol^{-1}$)

Some molar conductivities of ions at infinite dilution

Ion	**$\Omega^{-1}cm^{2}mol^{-1}$**
H^{+}	349.8
$\bar{O}H$	198.6
Li^{+}	38.69
Na^{+}	50.1
K^{+}	73.5
Cl^{-}	37.35
SO_4^{2-}	160.04
Mg^{2+}	106
Ba^{2+}	127.3

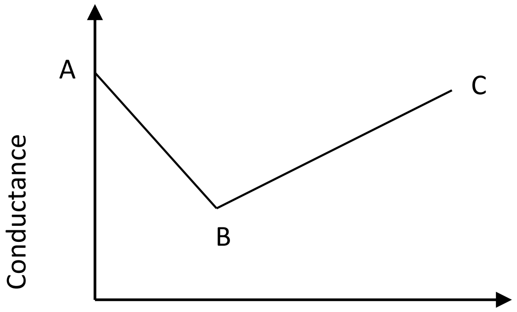
Because of small ionic radius of Li^{+} ion it's heavily hydrated and the hydrated ion is so large that its ionic mobility is low (its velocity) and it conducts less than the hydrated Na^{+} ion.
For the same reason Mg^{2+} has a low conductivity compared to Ba^{2+}, H^{+} ion has one proton and is not heavy hydrated hence its molar conductivity is very high.

Ba^{2+} ion is larger than the hydrated Na^{+} but the former has a double charge and conducts more than the latter. The higher the charge, the higher the molar conductivity. This explains why the molar conductivity of SO_4^{2-} is higher compared to that of the Cl^{-} ion.

Application of conductance

1. The measurement of conductance can be used to determine the concentration of an acid or alkali (conductirmetric titration).

Example



Volume of NaOH added to 25cm^3 of HCl

Usually there is a significant difference between the conductivity of the original solution and that of the resultant mixture when the titrate is added. At the end point there is a sharp change in conductivity.

25cm^3 of 0.1MHCl are pipette into a conductivity cell and the conductance of the solution is measured.

NaOH solution is added slowly and the conductance of the mixture is measured at intervals.
A graph of conductance against volume of NaOH added is plotted. A minimum point B gives the end point and the volume of NaOH added up to that point is noted.

Trend

There is a decrease from A to B because H^+ ions are being removed by $\bar{O}H$ ions form the alkali to form H2O.That is, $\bar{O}H_{(aq)} + H^+_{(aq)} \longrightarrow H_2O_{(l)}$ and they are replaced by Na^+ ions of low conductivity
Generally,
$H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + \bar{O}H_{(aq)} \longrightarrow Na^+_{(aq)} + Cl_{(aq)} + H_2O_{(l)}$

At B (minimum point) only NaCl and H_2O are present. The conductance increases a long BC because the concentration of Na^+ and $\bar{O}H$ ions increases
BC is less steep than AB because $\bar{O}H$ and Na^+ ions have lower conductivity than H^+ ions.

2. **Study of complexes**

Suppose A and B react in solution to form a complex AB, then the formation of the complex can be followed by conductivity measurements. If a larger complex ion is formed then conductivity decreases because its velocity is less than that of the original species.
Example $[Cu(NH_3)_4]^{2+}$ has lower conductivity than Cu^{2+} cation.

Conductivity is used to determine the ratio in which a given ion reacts with a given ligand hence it can be used to determine the coordination number.

3. **Determination of the solubility of a sparingly solute salt**

The electrolytic conductivity of a solute is equal to the conductivity of the solution less that of water.

$K_{solute} = K_{solution} - K_{water}$

Molar conductivity of a saturated solution of a salt

$$\Lambda_s = K/C = KV$$

But if the salt is saturated

$$\Lambda_s = \Lambda_\infty$$

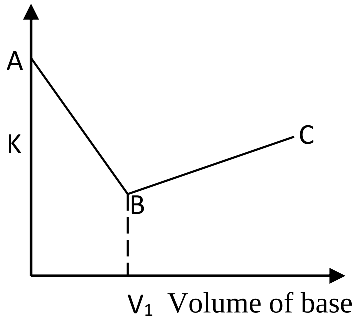
and $\Lambda = K/C = K/S$

$$\Rightarrow S = \frac{K}{\Lambda_\infty} \quad \text{where s = solubility of the salt}$$

Conductrimetric Titrations

a) **A strong acid against a strong base**

(That is HCl and NaOH)



Explanation

Conductivity decreases along AB, B is the end point, then it rises along BC. Because, Along AB conductivity fall due to the fast moving H^+ ions being removed and replaced by the less conductivity Na^+. That is,

$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$

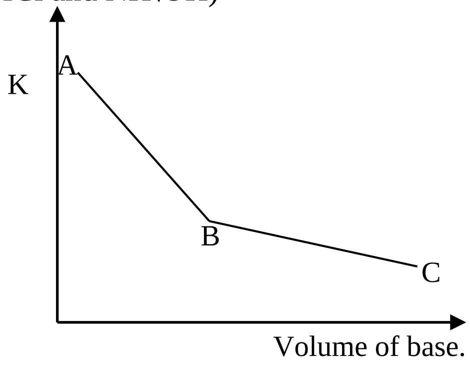
Conductivity rises a long BC due to excess fast conducting $\bar{O}H$ ions from the base. That is,

$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + \bar{O}H_{(aq)}$

V_1 is the volume of the base required for complete neutralization.

b) **Strong acid against weak base**

(That is HCl and NH_4OH)



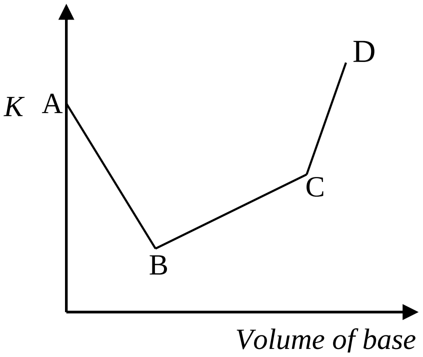
Conductivity decreases, along AB and more less levels off along BC, because along AB the fast mobile H^+ ions of the acid are being removed and replaced by the less mobile NH_4^+ ions of the weak base. That is,

$HCl_{(aq)} + NH_4OH_{(aq)} \longrightarrow NH_4Cl_{(aq)} + H_2O_{(l)}$

And along BC it is due to the excess base added. That is, the ionization of the weak base $NH_4OH_{(aq)} \longrightarrow NH_4^+{}_{(aq)} + \bar{O}H_{(aq)}$ which produces NH_4^+ and $\bar{O}H_{(aq)}$ ions is suppressed by its salt NH_4Cl which produces more NH_4^+, shifting the equilibrium to the left and the conductivity remains constant along BC

c) **Weak and against strong base**

(That is C_6H_5 COOH and NaOH)



Conductivity initially decreases along AB because $C_6H_5\text{-}CO\bar{O}$ ions formed by the reaction of benzoic acid and sodium hydroxide suppress ionization of weak acid.

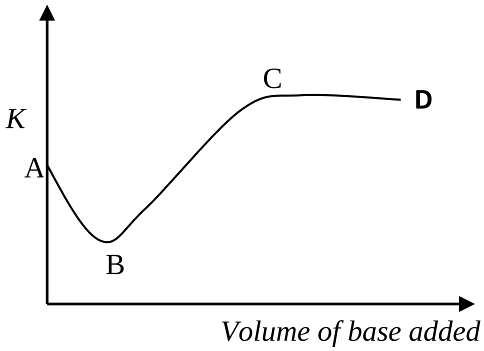
$C_6H_5COOH \rightleftharpoons C_6H_5CO\bar{O} + H^+$ ‒ ‒ ‒ ‒ ‒ ‒ (1)

$C_6H_5COONa \rightarrow C_5H_5CO\bar{O} + Na^+$ ‒ ‒ ‒ ‒ ‒ ‒(2)

The benzoate ions produced by reaction (2) suppress ionization of benzoic acid in reaction (1)

The rise in conductivity along BC is due to the formation of C_6H_5COO and Na^+ ions. The sharp rise along CD is due to excess $\bar{O}H$ ions from the base added.

d) **Weak acid and weak base**
(That is, CH_3COOH and NH_4OH)



At **A** conductivity is low because ethanoic acid is a weak electrolyte. A long AB conductivity decrease due to neutralization of H^+ by NH_3. The fast moving H+ ions are replaced by slow moving NH_4^+ ions. Conductivity also decreases due to the suppressions of the dissociation of ethanoic acid by ethanoate ions ($CH_3CO\bar{O}$). Along BC conductivity increases, due to the formation of ammonium ethanoate which is a strong electrolyte. C is the end point and the conductivity hence is high due to the strong electrolyte formed compared to the reactants which are weak electrolytes. Along CD conductivity is constant. This is due to the suppressions of dissociation of NH_3 by the NH_4^+ ions already present.

ELECTROLYTES AND DISSOCIATION

Weak electrolytes are those which are not completely ionized at ordinary dilution example ethanoic acid, carbonic acid. They ionise or dissociate as the dilution is increased. The degree of dissociation or ionization is the fraction or percentage of the molecules that dissociate. If Λ is the molar conductivity at a certain dilution and alpha ($\propto$) the degree of dissociation then

$$\Lambda \propto \alpha$$

Meaning that, $\Lambda = K\alpha$ at infinite dilution all the electrolyte is dissociated or ionized and $\alpha = 1$

$$\Rightarrow \Lambda_\infty = K$$

Then $\dfrac{\Lambda}{\Lambda_\infty} = \dfrac{K\alpha}{K}$

And $\dfrac{\Lambda}{\Lambda_\infty} = \alpha$

The value $\dfrac{\Lambda}{\Lambda_\infty}$ for a strong electrolyte is called the apparent degree of dissociation.

Suppose an electrolyte has a degree of dissociation α in a solution and each molecule of the electrolyte gives n ions. At equilibrium the number of particles is $(1-\alpha) + n\alpha$

Example

$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^{-}$$
$$1-\alpha \qquad\qquad \alpha \qquad 2\alpha$$

Total number of particles at equilibrium = $(1-\alpha) + 3\alpha$

As a result the osmotic pressure of the solution and other related properties, such as freezing point depression, boiling point elevation and lowering of vapour pressure are greater than would be.

The relationship below holds.

$$\frac{(1-\alpha) + \cap\,\alpha}{1} \equiv \frac{\text{observed freezing point depression}}{\text{calculated freezing point depression}} \equiv \frac{\text{observed boiling point elevation}}{\text{calculate boiling point elevation}}$$

Example

1. A solution containing 6.66g of CH_3COOH per litre has an electrolytic conductivity of $5.21 \times 10^{-4}\Omega^{-1}cm^{-1}$ at 25^0C. The molar conductivity of the acid at infinite dilution at 25^0C is $391\Omega^{-1}cm^2mol^{-4}$ .Calculate the degree of dissociation (molar mass of CH_3COOH= 60g)

Solution

From $\alpha = \dfrac{\Lambda}{\Lambda_{\infty}}$

$$\text{Conc. in mol}^{-1} = {}^{6.66}/_{60}$$
$$= 0.111mol^{-1}$$
$$\Lambda = \frac{1000K}{C}$$
$$= \frac{1000 \times 5.21\times10^{-4}}{0.111}$$
$$= 4.69\Omega^{-1}cm^2mol^{-1}$$
$$\text{And } \propto = \frac{4.69}{391}$$
$$\mathbf{= 0.012 \text{ or } 12\%}$$

2. The electrolytic conductivity of 0.016M CH_3COOH at 18^0C is $0.0196\Omega m^{-1}$. The molar conductivities at infinite dilution of H^+ and CH_3COO^- at 18^0C are 3.15×10^{-2} and $0.35\times10^{-2}\Omega m^{-1}$ respectively. Calculate the degree of ionization of ethanoic acid.

Solution

$$C = \mathbf{0}.016mol^{-1} = 0.016 \times 10^3 \ molm^{-3}$$
$$\Lambda = {}^{K}/_{C} \qquad = \frac{0.096}{16} = \frac{\Omega m\text{-}1}{m\cap m^{-3}}$$
$$\mathbf{= 1.225 \times10^{-3}\ \Omega mol^{-1}m^2}$$

$$\Lambda_{\infty}(CH_3COOH) = \Lambda_{\infty}CH_3CO\bar{O} + \Lambda\ \infty\ H^+$$
$$= 0.35 \times 10^{-2} + 3.15 \times 10^{-2}$$

$$= 3.5 \times 10^{-2}$$

$$\alpha = \frac{\Lambda_{\propto}}{\Lambda_{\infty}} = \frac{1.225 \times 10^{-3}}{3.5 \times 10^{-2}}$$

$$= 0.035$$

$$= \underline{\mathbf{3.5 \times 10^{-2}}}$$

3. A solution containing 2.4g of strontium chloride in 112g of H_2O gives a freezing point of -0.654^0C. Calculate the apparent degree of dissociation of the salt under these conditions. (Strontium = 88, Cl= 35.5, K_f for water = $1.86^0C\ mol^{-1}kg^{-1}$)

Solution

112g of water contain 2.4g of $srCl_2$

1000g of water contain $\frac{2.4 \times 1000}{112}$

= 21.43g

And observed f.p depression

$$\mathbf{= 0 - {}^{-}0.654 = 0.654}$$

But $SrCl_2 = 88 + (35.5) \times 2$

=159

Then 159 of $SrCl_2$ depresses 1.86

21.43g of $SrCl_2$ depresses $\frac{1.86 \times 21.43}{159}$

$$\mathbf{= 0.251^0C}$$

Also $SrCl_2 \longrightarrow Sr^{2+} + 2Cl^-$

And n = 3

Using $(1-\alpha) + n(\alpha) = \frac{\text{observed } f\text{.p depression}}{\text{Calculated } f\text{.p depression}}$

$$1 - \alpha + 3\alpha = \frac{0.654}{0.251}$$

$$1 + 2\alpha = 2.6056$$

And

$$\boldsymbol{\alpha} \mathbf{= 0.80 \text{ or } 80\%}$$

Self check

1. Calculate the freezing point of a solution containing 5.85g of NaCl in 100g of water if its degree of dissociation is 0.83 (Kf for water = $1.86^0C\ mol^{-1}kg^{-1)}$

Ans. (-3.4^oC)

2. 0.01M HCl was titrated with 1M NaOH. The conductivity of the resultant solution was measured during the titration. Assuming water does not conduct; calculate the values of the conductivities in the following cases.

a) Before the titration started.
b) When the acid was neutralized
c) When twice as much NaOH as that required for complete neutralization has been added.

The ionic conductivities in $\Omega^{-1}cm^2\ mol^{-1}$ are $H^+ = 350$, $Na^+ = 50$, $\bar{O}H = 200$, $Cl^- = 76$

(Ans. a=4.26 ×$10^{-3}\Omega^{1}cm^{-1}$ b=1.26 ×$10^{-3}\Omega^{1}cm^{-1}$ c = 3.76 x$10^{-3}\Omega^{1}cm^{-1}$)

SOLUBILITY PRODUCT

When a sparingly soluble salt such as silver chloride is shaken with water, a saturated solution is formed. Since AgCl is a strong electrolyte, the dissolved part is completely ionized and there liquid contains a low concentration of ions limited by the low solubility of AgCl. Consider the following equation

$AB_{(s)} \rightleftharpoons A^+_{(aq)} + B^-_{(aq)}$ ——(1)

The equilibrium constant $K_c = \frac{[A^+]\ [B^-]}{[AB]}$

But the concentration of solid is constant.

Then $[A^+]\ [B^-]$ = a constant Ksp

$Ksp = [A^+]\ [B^-]$ ——— (2)

Equation (1) is called the solubility equation for saturated solution of the salt AB.

Equation (2) is called the solubility product expression for the salt AB

The solubility product is the product of the concentration of the ions in a saturated solution of a sparingly soluble ion is compound raised to the corresponding powers.

NOTE:

1. If a solution AB is unsaturated then

   $Ksp >> [A^+]\ [B^-]$
2. If a solution of AB is saturated then

   $Ksp = [A^+][B^-]$

   This solution does not dissolve any more solute (AB)
3. If $Ksp << [A^+][B^-]$ then salt AB will be precipitated
4. The concentration of the ions in solution can be increased by evaporation This will deposit AB

When an electrolyte gives more than one of a certain kind of ion, the concentration of that ion is raised to the corresponding number

Example $PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$

$Ksp = [Pb^{2+}]\ [Cl^-]^2$

In general if $A_yB_{x(s)} \rightleftharpoons yA^+_{(aq)} + xB^-_{(aq)}$

Then $K_{sp} = [A^+]^y[B^-]^x$

The solubility of a sparingly soluble salt such as AgCl is determined by conductivity methods. By measuring the electrolytic conductivity the solubility of a salt can be determined. The molar conductivity at infinite dilution can be calculated from the molar conductivities of ions example

$$\Lambda AgCl = \Lambda\ Ag^+ + \Lambda\ Cl^-$$

Then using $\Lambda = K/C$

C can be determined.

Example

1. The electrolytic conductivity of a saturated solution of compound XCl at 25^0C is $2.4 \times 10^{-4}\ \Omega m^{-1}$. If the molar conductivity at infinite dilution of XCl is $1.51\times10^{-2}\ \Omega^{-1}m^2mol^{-1}$, find the solubility of XCl in $moldm^{-3}$ at 25^0C.

Solution

Using $\Lambda = K/C$ and $C = K/\Lambda$

$$= \frac{2.4 \times 10^{-4}}{1.51 \times 10^{-2}}$$

$$= 1.6 \times 10^{-2} molm^{-3}$$

$$= \frac{1.6 \times 10^{-2} mol}{\dfrac{(m^3 \times 10^6)\ cm^3}{10^3 dm^3}}$$

$$= \frac{1.6 \times 10^{-2}}{10^3}$$

$$= 1.6 \times 10^{-2} \times 10^{-3}$$

$$\mathbf{= 1.6 \times 10^{-5}\ moldm^{-3}}$$

2. $400cm^3$ of 0.02M Na_2SO_4 is added to $800cm^3$ of hard water containing 0.01M Ca^{2+} ions. Find out whether a precipitate of $CaSO_4$ will be formed.
   (K_{sp} of $CaSO_4 = 3 \times 10^{-3}\ mol^2\ l^{-1}$)

Solution

The precipitate is formed if $K_{sp} << [Ca_2]\ [SO_4^{2-}]$

Total volume = 400 + 800

= **$1200cm^3$**.

If x is new molarity of Ca^{2+} ions.

New number of moles of $Ca^{2+} = \frac{1200x}{1000}$

Since on dilution, number of moles does not change.

$$\frac{1200x}{1000} = \frac{800 \times 0.01}{1000}$$

$$x = \frac{800 \times 0.01 \times 1000}{1200 \times 1000}$$

$$\mathbf{= 6.67 \times 10^{-3}M}$$

Moles of Na_2SO_4

$1000cm^3$ contain 0.02

$$400cm^3 \text{ contain } \frac{0.02 \times 400}{1000}$$

$$\mathbf{= 8 \times 10^{-3} moles}$$

But $1200cm^3$ contain 8×10^{-3} moles

(Total volume)

$$\text{Then } 1000cm^3 \text{ contain } \frac{8 \times 10^{-3} \times 1000}{1200}$$

$$\mathbf{= 6.67 \text{ x } 10^{-3}M}$$

$\Rightarrow$ $[Ca^{2+}] = 6.67 \times 10^{-3}$

$[SO_4^{2-}]= 6.6 \times 10^{-3}$

And

$$Ksp = [Ca^{2+}] [SO_4^{2-}]$$

$$= 6.67 \times 10^{-3} \times 6.67 \times 10^{-3}$$

$$\mathbf{= 4.45 \times 10^{-5} mol^2 l^{-2}}$$

Since $Ksp << [Ca^{2+}][SO_4^{2-}]$

Then a precipitate of $CaSO_4$ is formed

3. The Ksp of $Ca^3(PO_4)^2$ at 25^0C is 6.0×10^{-29} mol^5dm^{-5}. Calculate the solubility of $Ca_3(PO_4)_2$ at 25^0C

Solution

$$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO_4^{3-}{}_{(aq)}$$

$$x \qquad 3x \qquad 2x$$

Let x be solubility of $Ca_3(PO_4)^2$

Then

$$Ksp = [Ca^{2+}]^3 [PO_4^{3-}]^2$$

$$6.0 \times 10^{-29} = (3x)^3 (2x)^2$$

$$6.0 \times 10^{-29} = (27x^3) (4x^2)$$

$$6.0 \times 10^{-29} = 108x^5$$

And

$$x^5 = \frac{6.0 \times 10^{-29}}{108}$$

$$x = \sqrt[5]{\left(\frac{6.0 \times 10^{-29}}{108}\right)}$$

$$\mathbf{= 8.89 \times 10^{-7} moldm^{-3}}$$

CHECK

a) When NaOH solution added to $CaCl_2$ solution a white precipitate is formed but when NH_3 solution is added to the same solution no precipitate is formed

Explanation

NaOH is a strong electrolyte and when added to Ca^{2+} ions, the Ksp of $Ca(OH)_2$ is easily exceeded That is, Ksp << $[Ca^{2+}] [\bar{O}H]^{-2}$ and the precipitate forms. On the other hand, ammonia solution being a weak electrolyte when added to Ca^{2+} ions, the concentration of $\bar{O}H$ ions is so low that the Ksp of $Ca(OH)^2$ is not exceeded. That is,

Ksp > $[Ca^{2+}] [\bar{O}H]^2$ and no precipitate forms

b) Distinguishing Ca^{2+} and Mg^{2+}

Solution

Since Mg^{2+} is smaller than $Ca^{2+}Mg(OH)^2$ has a higher lattice energy than $Ca(OH)^2$, thus $Ca(OH)_2$ is more soluble and a higher solubility product. As a result $Mg(OH)_2$ is easily precipitated. Therefore NH_3 solution is used to distinguish between Ca^{2+} and Mg^{2+} ions

Addition of NH_3 solution to Ca^{2+} ions, does not precipitate $Ca(OH)_2$ but when added to Mg^{2+} ions while precipitate of $Mg(OH)_2$ is formed

Experiment

Determination of solubility product of lead (ii) hydroxide in water

A fixed volume of a saturated solution of the lead (ii) hydroxide is pipette and then titrated with a standard solution of hydrochloric acid using methyl orange indicator to determine the concentration of hydroxyl ions. The number of moles of hydroxyl in volume pipetted is then calculated. The total number of moles in $100cm^3$ of the saturated solution is then determined from the solubility equation.

$Pb(OH)_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2\bar{O}H_{(aq)}$

The concentration of Pb^{2+} in $1000cm^3$ of the saturated solution will be half that of $\bar{O}H$

From the Ksp expression

Ksp = $[Pb^{2+}] [\bar{O}H]^2$ the value of Ksp can then be determined.

THE COMMON ION EFFECT

Consider the equilibrium of sparingly soluble salt $BaSO_{4(s)} \rightleftharpoons Ba^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$
Addition of the H_2SO_4 to the above produces $SO_3{}^{2-}$ and H^+ ions. The $SO_4{}^{2-}$ ions from the H_2SO_4 is said to be a common ion to $SO_4{}^{2-}$ from $BaSO_4$. Similarly addition of $Ba(NO_3)_2$ produces Ba^{2+} and NO^{-3} ions.
The Ba^{2+} of $Ba(NO_3)_2$ is said to be a common ion to the Ba^{2+} of the saturated solution of $BaSO_4$

Addition of a soluble salt containing a common ion decreases solubility of any sparingly soluble salt example; consider a saturated solution of $PbSO_4$.

$PbSO_{4(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + SO_4{}^{2-}$
Addition of a solution of Na_2SO_4 produces $SO_4{}^{2-}$ which is a common ion to the above equilibrium. This increases concentration of $SO_4{}^{2-}$ ion in the equilibrium so that to maintain Ksp constant, the excess $SO_4{}^{2-}$ ions from Na_2SO_4 react with Pb^{2+} to precipitate more $PbSO_4$. This reduces the solubility of $PbSO_4$. And addition of $Pb(NO_3)_2$ has a similar effect.

Example

1. $BaSO_4$ is sparingly soluble in water.
   a) Write an equation for the solubility of $BaSO_4$ in water.
   b) Write an expression for the solubility product of $BaSO_4$.
   c) A saturated solution of $BaSO_4$ contains $0.002563gl^{-1}$ of salt. Calculate the solubility product of $BaSO_4$.
   d) Calculate the solubility of $BaSO_4$ in $1dm^3$ of 0.1M $BaCl_2$ solution.

Solution

a) $BaSO_{4(s)} \rightleftharpoons Ba^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$

b) $Ksp = [Ba^{2+}][SO_4{}^{2-}]$

c) Solubility of $BaSO_4 = \frac{0.002563}{233}$

$$\mathbf{= 1.1 \times 10^{-5}\ mol^{-1}l^{-1}}$$

And $Ksp = 1.1 \times 10^{-5} \times 1.1 \times 10^{-5}$

$$\mathbf{= 1.21 \times 10^{-10}\ mol^2l^{-2}}$$

d) $[Ba^{2+}]$ in water $= 1.1 \times 10^{-5}\ moldm^{-3}$

And $[Ba^{2+}]$ in 0.1M $BaCl_2 = 0.1moldm^{-3}$

The concentration of Ba^{2+} in $BaSO_4$ in negligible
Therefore

New $[Ba^{2+}] = 0.1\ moldm^{-3}$ (in $BaCl_2$)

If the solubility of $BaSO_4$ in $BaCl_2$ is x $moldm^{-3}$
Then

$[Ba^{2+}] = 0.1moldm^{-3}$

$[SO_4^{2-}] = x$ moldm^{-3}

And Ksp = $[Ba^{2+}][SO_4^{2-}]$

$1.21 \times 10^{-10} = 0.1 \times x$

$$x = \frac{1.21 \times 10^{-10}}{0.1}$$

$$\mathbf{= 1.21 \times 10^{-9} moldm^{-3}}$$

Therefore solubility of $BaSO_4$ is 1.21×10^{-9} moldm^{-3} in 1dm^3 of 0.1M $BaCl_2$

NOTE:

Mass of $BaSO_4$ precipitated = Solubility in water – Solubility in $BaCl_2$

$= 0.002563 - 2.829 \times 10^{-1}$

$\mathbf{= 2.56 \times 10^{-3} gdm^{-3}}$

2. If the solubility of AgCl in water is 1.3×10^{-5}mol^{-1} what will it be in litre of 0.1M NaCl

Solution

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^{-1}_{(aq)}$$

$$Ksp = [Ag^+][Cl^-]$$

$$= 1.3 \times 10^{-5} \times 1.3 \times 10^{-5}$$

$$= 1.69 \times 10^{-10} mol^2 l^{-2}$$

But $[Cl^-]$ in water = 1.3×10^{-5} mol^{-1}

New $[Cl^-]$ in NaCl = 0.1 mol l^{-1}

If the solubility of AgCl is NaCl is x mol l^{-1}

Then

$$[Ag^+] = x \text{ mol } l^{-1}$$

$$[Cl^-] = 0.1 \text{ mol } l^{-1}$$

From Ksp = $[Ag^+][Cl^-]$

$$1.69 \times 10^{-10} = x \times 0.1$$

And $$x = \frac{1.69 \times 10^{-10}}{0.1}$$

$$\mathbf{= 1.69 \times 10^{-9} mol\ l^{-1}}$$

Hence the solubility of AgCl in NaCl is 1.69×10^{-9}mol l^{-1}

SELF CHECK

1. The Ksp of $Mg(OH)_2$ at 19^0C is 4.2×10^{-12} mol^{3}l^{-3}. What mass of $Mg(OH)_2$ can dissolve in

a) One litre of 0.01M NaOH at this temperature

b) One litre of 0.1M $Mg(NO_3)_2$ at this temperature

(N=14, O =16, Na=23, Mg =24)

(Ans. a=2.44 ×10^{-6} gl^{-1} b= 1.88×10^{-4} gl^{-1})

2. The solubility product of $PbCl_2$ is 1.6×10^{-5} $mol^{-1}l^{-3}$ at 25^0C

a) Write an expression for the solubility of $PbCl_2$

b) Calculate

i) The concentration of the Cl^- in mol l^{-1} in a saturated solution of $PbCl_2$ at 25^0C

ii) The solubility of $PbCl_2$ in gl^- at 25^0C

c)

i) State what would be observed if a saturated solution of Lead (ii) ethanoate was added to a solution of $PbCl_2$ at 25^0C

ii) Give a reason for your answer in c(i)

(Ans. b(i) 3.17×10^{-2} mol l^{-1} (ii) $4.41gl^{-1}$)

i) A white precipitate

ii) $(CH_3COO)_2Pb$ increases the concentration of Pb^{2+} ions which react with Cl^- ions to form a white precipitate $PbCl_2$

COMPLEX IONS

Consider the solubility of AgCl in water

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

Addition of NH_3 solution to the above equilibrium leads to the formation of a complex ion. $Ag(NH_3)_2^+$ the concentration of Ag^+ in the equilibrium decreases and in order to restore Ksp more AgCl dissolves. This the solubility of AgCl decreases.

Similarly

i). $PbCl_2$ is more soluble in concentrated HCl than in dilute HCl. This is due to the formation of the complex ion That is,

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}.$$

Addition of concentrated HCl increases the Cl^- ions concentration which will combine with Pb^{2+} to form a complex

$$Pb^{2+}_{(aq)}) + 3Cl^-_{(aq)} \rightleftharpoons [PbCl_4]^{2-}_{(aq)}$$

ii). Copper (ii) Chloride is more soluble in a solution of NH_3 than in water due to the formation of $CU(NH_3)_4^{2+}$

APPLICATION OF COMMON ION EFFECT

- Purification of common salt
- Salting out of soap

- Precipitation of hydroxides

Hydroxides of Al^{3+}, Fe^{3+}, and Cr^{3+} are precipitated by NH_3 solution in presence of solid NH_4Cl.

While $Mg(OH)_2$ and $Zn(OH)_2$ are not precipitated

In solution the following equilibrium occurs

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + \bar{O}H_{(aq)} \text{ ——— } (2)$$

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}{}_{(aq)} + 2\bar{O}H_{(aq)} \text{ ——— } (1)$$

$$NH_4Cl_{(s)} \rightleftharpoons NH_4^+{}_{(aq)} + Cl^-{}_{(aq)} \text{ ——— } (3)$$

In equilibrium (3) NH_4Cl increases the concentration of NH_4^+ which in turn shift equilibrium (2) to the left. This reduces $\bar{O}H$ ions in equilibrium (1) and more $Mg(OH)_2$ dissolves to restore the value of Ksp. As a result precipitation of $Mg(OH)_2$ is prevented.

The precipitation of $Al(OH)_3$, $Fe(OH)_3$ and $Cr(OH)_3$ is also hindered but not prevented because their solubility products are lower than those of $Zn(OH)_2$ and $Mg(OH)_2$

CHECK

When NH_3 solution is added to a solution containing Al^{3+} a white precipitate is formed. In presence of NH_4Cl, Al^{3+} do not form a precipitate with NH_3 solution

Explanation

When NH_3 solution is added to a solution of AI^{3+} ,the $\bar{O}H$ ions from the weak base combine with AI^{3+} to form a white precipitate which is $Al(OH)_3$. On adding NH_4Cl the NH_4^+ combine with $\bar{O}H$ ions so that Ksp exceeds $[Al^{3+}][\bar{O}H]^3$ and a white precipitate does not form.

Application of solubility product

- Determination of R.F.M of complexes
- Prediction of precipitation
- Selective precipitation

IONIC EQUILIBRIA

Acid base and salts theory

An acid is defined as a substance which denotes a proton

$$H_2SO_4 \rightleftharpoons SO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)}$$

The SO_4^{2-} is the conjugate base and H_2SO_4 is the conjugate acid.

A base is a substance that accepts a proton

$Base + H^+{}_{(aq)} \longrightarrow acid$

$H_2O_{(l)} + H^+{}_{(aq)} \longrightarrow H_3O^+{}_{(aq)}$

$NH_{3(aq)} + H^+_{(aq)} \rightarrow NH_4^+{}_{(aq)}$

The strength of an acid is measured by the ease with which it donates a proton while that of a base is measured by the ease with which it accepts protons

THE IONIC PRODUCT OF WATER

Pure H_2O has a very slight conductivity due to its slight dissociation

$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + \bar{O}H_{(aq)}$

Applying the equilibrium law

$$K = \frac{[H^+][\bar{O}H]}{[H_2O]}$$

Since the degree of dissociation of H_2O molecules is very small, concentration of water is taken to be a constant so that

$$K_w = [H^+][\bar{O}H]$$

K_w is called ionic product of water.

It's equal to 1×10^{-14} mol^{2}l^{-2} or mol^{2}dm^{-6} at 25^0C

$[H^+] = [OH] = 1 \times 10^{-7}$ mol l^{-1}

$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + \bar{O}H_{(aq)} \quad \triangle H = +ve$

Increase in temperature shifts equilibrium to the right in order to absorb the added heat and restore the original equilibrium. The concentration of $\bar{O}H$ and H^+ increases and the K_w increases. Thus K_w increases with increase in temperature.

Hydrogen ion concentration and PH

The PH of a solution is the logarithm to base ten of the reciprocal of the H^+ concentration

$$PH = \log_{10}\frac{1}{[H^+]}$$

$$PH = -\log_{10}[H^+]$$

It is a measure of the $[H^+]$

Consider the ionization of water

$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + \bar{O}H_{(aq)}$

Pure water can be considered as an acid at 25^0C

It contains 1×10^{-7} moll^{-1} of H^+ ions

$\Rightarrow [H^+] = 1 \times 10^{-7}$

Therefore PH $= -\log_{10}[H^+]$

$= -\log_{10}(1\times10^{-7})$

= 7

At 50^0C, $K_w = 5.47 \times 10^{-14}$ mol^{2}l^{-2}

$K_w = [H^+] [OH]$

$[H^+] = 2.34 \times 10^{-7}$ mol l^{-1}

$\Rightarrow$ PH= - log (2.34×10^{-7})

= 6.63

Thus as temperature increase, the PH of H_2O decreases and its acidity increases.

NOTE

i) The PH of H_2O also decreases when left standing in air. This is because it absorbs CO_2 from the atmosphere to form weak carbonic acid.

$$H_2O_{(l)} + CO_{2(g)} \rightleftharpoons H_2CO_{3(aq)} \rightleftharpoons 2H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

PH OF ACIDS

Calculate the PH of 0.01M HCl solution since the acid is completely ionized $[H^+] = [HCl]$

$= 0.01$

Therefore PH = - log (0.01)

= 2

With a more concentrated solution, the PH can be calculated if the concentration and degree of ionization of the acid are known. The degree of ionization of a 4M solution if HCl is 0.45. Thus of the 4 moles the number of moles dissociated is 4 × 0.45 = 1.8 moles

$[H^+] = 0.45 \times 4$

= 1.8

PH = - log (1.8)

= - 0.255

Thus for an incompletely dissociated acid

$[H^+] = C\alpha$

Where C is concentration

α is the degree of dissociation

For weak acids the $[H^+]$ can also be determined, from the concentration and dissociation constant K_a.

Consider the ionization of a weak acid HA. If C is the initial concentration of the acid and alpha is the degree of dissociation.

$$HA_{(aq)} \rightleftharpoons H^+_{(g)} + A^-_{(aq)}$$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

Since $[H^+] = [A^-]$ $K_a = \frac{[H^+]^2}{[HA]}$

$$K_a = \frac{[H^+]^2}{C}$$

$$[H^+]^2 = K_aC$$

$\Rightarrow$ [H$^+$] = $\sqrt{K_aC}$ …………………………….. (1)

But [H$^+$] = Cα

$\Rightarrow$ Cα = $\sqrt{K_aC}$

And $C^2\alpha^2 = K_aC$

$\alpha^2 = \frac{K_a C}{C^2}$

$\alpha = \sqrt{\frac{K_a}{C}}$ …………………………………… (2)

Then

(1)^2 · (2)^2

[H$^+$]^2.$\alpha^2 = K_aC.\left(\frac{K_a}{C}\right)$

[H$^+$]$^2 = \frac{{K_a}^2}{\alpha^2}$

And [H$^+$] = $\frac{K_a}{\alpha}$

NOTE

C = $\frac{1}{v}$

Example

1. A 0.01M solution of chloromethanoic acid is 18% ionized. Calculate the PH of the solution and Ka of the acid

Solution

α = 18%

= 0.18

C = 0.01M

$\alpha = \sqrt{\frac{K_a}{C}}$

$\alpha^2C = K_a,\ K_a = \alpha^2C$

= 0.182 × 0.01

= 3.24 × 10^{-4} moldm^{-3}

[H$^+$] = $\sqrt{K_aC}$

= $\sqrt{3.24 \times 10^{-4} \times 0.01}$

= 1.8 × 10^{-3}

And PH = - log (1.8 × 10^{-3})

= 2.745

2. The PH of a 0.001M solution of an acid is 3.59
   Calculate
   i) Dissociation constant
   ii) Degree of dissociation

Solution

i) PH= - log [H$^+$]

3.59 = - log [H$^+$]

And [H$^+$] = $10^{-3.59}$

$= 2.57 \times 10^{-4}$

But [H$^+$] = $\sqrt{K_a C}$

$(2.57 \times 10^{-4})^2 = K_a \times 0.001$

$K_a = 6.61 \times 10^{-5}$ mol l^{-1}

ii) $\propto = \sqrt{\frac{Ka}{C}}$

$= \sqrt{\frac{6.61 \times 10^{-5}}{0.001}}$

$= 0.257$

$= 2.57 \times 10^{-1}$

Self check

1. Calculate the PH of 0.02M H_2SO_4
   (Ans. 1.3979)
2. Calculate the molarity of a solution of H_2SO_4whose PH is 4.35
   (Ans. 2.23 × 10^{-5})
3. The PH of 0.001M methanoic acid is 3.63 calculate
   a) Dissociation constant Ka of the acid
   b) The PK$_a$ of the acid
   c) The degree of dissociation of the acid
   (Ans. a = 5.48 × 10^{-5}mol l^{-1} b = 4.26 α = 0.234)

THE PH OF ALKALIS

Consider

$$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + \bar{O}H_{(aq)}$$

$$[OH] = [NaOH]$$

From $K_w = [H^+]\,[\bar{O}H]$

$$[H^+] = \frac{K_w}{[\bar{O}H]}$$

$$PH = -\log[H^+]$$

$$= -\log\left(\frac{K_w}{\bar{O}H}\right)$$

$$PH = -\log K_w + \log[OH]$$

$$PH = \log[\bar{O}H] - \log K_w$$

Or

$$PH = -\log K_w - (-\log[\bar{O}H]$$

$$= -\log K_w - P(-OH)$$

$$\Rightarrow PH = 14 - POH$$

As in the case of acids, $[\bar{O}H]$ can be got from $[\bar{O}H] = K_bC$ where K_b is the base dissociation constant of a weak base.

Example

1. Calculate the PH of a solution of 0.0M NaOH solution

Solution

$[\bar{O}H] = 0.02$

$PH = 14 - POH$

$= 14 + \log(0.02)$

$= 12.301$

2. The Ksp of $Mg(OH)_2$ is 8.8×10^{-12} mol^3l^{-3}, what is the PH of a saturated solution at equilibrium
   ($K_w = 1 \times 10^{-14}$)

Solution

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2\bar{O}H_{(aq)}$$

Let x be $[Mg^{2+}]$

Then $[\bar{O}H] = 2x$

$$Ksp = [Mg^{2+}]\,[\bar{O}H]^2$$

$$8.8 \times 10^{-12} = x.4x^2$$

$$\frac{4x^3}{4} = \frac{8.8 \times 10^{-12}}{4}$$

$$x^3 = 2.2 \times 10^{-12}$$

$x = \sqrt[3]{2.2 \times 10^{-12}}$

$= 1.3 \times 10^{-4}$mol l^{-1}

Therefore $[\bar{O}H] = 2 \times 1.3 \times 10^{-4}$

$=$ **2.6×10^{-4}mol l^{-1}**.

PH = - logK_w – POH

PH = 14 – POH

PH = 14 – (-log 2.6×10^{-4})

= 10.4

Self Check

1. Calculate the concentration in mol l^{-1} of Mg^{2+} in a solution of $Mg(OH)_2$ whose PH is 10.61
   (Ans. 2.037×10^{-4} mol l^{-1})
2. A solution of 0.4M XOH of 1.4×10^{-5}
   a) Calculate the dissociation constant of the weak base XOH
   b) What is the $[H^+]$ of 0.4M XOH
   c) Calculate the PH of the solution
   d) What is the concentration of $\bar{O}H$ in a solution of 0.1M XOH ($K_w = 1 \times 10^{-14}$)

(Ans. a) $K_b = 4.9 \times 10^{-10}$mol l^{-1} b). 7.143×10^{-10}mol l^{-1}) c). PH= 9.146 d). 7.0×10^{-6}mol l^{-1})

3. A 0.01M solution of phenylamine is 8% ionized calculate
   a) The base dissociation constant
   b) PH of solution

(Ans. a) Kb= 6.4×10^{-5} mol dm^{-3} b). PH= 10.9)

Example

The molar conductivity of 0.05M solution of benzoic acid at 25^0C is $9.46 \times 10^{-4}\Omega^{-1}cm^2mol^{-1}$.If the molar conductivities at zero concentration of H^+ and $C_6H_3CO\bar{O}$ are 2.8×10^{-2} and 6×10^{-2}'$\Omega^{-1}cm^2mol^{-1}$ respectively.

Calculate a). The degree of dissociation of the acid

b). The dissociation constant of the acid

c). PH of solution

Solution

a) Using $\alpha = \frac{\Lambda \propto}{\Lambda \infty}$

$\Lambda_{\infty} C_6C_5OOH = \Lambda_{\infty} H^+ + \Lambda_{\infty} C_6H_5CO\bar{O}$

$= 2.8 \times 10^{-2} + 6 \times 10^{-2}$

$= 8.8 \times 10^{-2}\Omega cm^2mol^{-1}$

And $\alpha = \frac{9.46 \times 10^{-4}}{8.8 \times 10^{-2}}$

$= \mathbf{1.075 \times 10^{-2}}$

b) $\alpha = \sqrt{K_a/c}$ and $\alpha^2 C = Ka$

$\Rightarrow (1.075 \times 10^{-2})^2 \times 0.05 = Ka$

$\Rightarrow K_a = 5.778 \times 10^{-6}$ mol l^{-1}

c) PH= - log $[H^+]$

= - log (5.375×10^{-4})

= 3.27

NOTE

1. PK values are defined as

P_{Ka}= - logK_a

P_{Kb}= - logK_b

The higher the value of K_a or K_b the stronger is the acid or base.

2. For conjugate acid – base pairs.

$P_{Ka} + P_{Kb} = P_{Kw}$ example,

a) Given that P_{Ka} of NH_4^+ at 25^0C is 9.25, calculate the PH of an aqueous solution of 0.1M NH_3 solution

Solution

From $P_{Ka} + P_{Kb} = P_{Kw}$

$P_{Kb} = P_{Kw} - P_{Ka}$

= 14 – 9.25

= 4.75

And P_{Kb} = - logK_b

4.75 = - logK_b

$K_b = 1.778 \times 10^{-5}$ mol l^{-1}

Then $[\bar{O}H] = \sqrt{K_b c}$

$= \sqrt{1.778 \times 10^{-5} \times 0.1}$

$= \mathbf{1.33 \times 10^{-3}}$ **mol l^{-1}**

Thus PH= 14 – POH

= 14 – (-log 1.33×10^{-3})

=11.12

Self check

1. Calculate the PH of a 0.003M ethanoic acid whose P_{Ks} is 9.24 ($K_w = 10^{-14}$)
   (Ans. PH = 5.88)

SALT HYDROLYSIS

Hydrolysis is a reaction between H_2O and another species to form an associated species plus H^+ or $\bar{O}H$.

Salts of strong acids and weak bases and those of strong bases and weak acids undergo hydrolysis in aqueous solutions.

Consider the equilibrium of water (H_2O)

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + \bar{O}H_{(aq)}$$

If any species is added which associates with either $\bar{O}H$ or H^+ ions. The H_2O equilibrium shifts to the right to produce excess H^+ or $\bar{O}H$ ions.

If NaCl is added to H_2O, there is no hydrolysis; the Na^+ and Cl- do not affect the H_2O equilibrium because there is no possibility of forming associated species. The Na^+ and $\bar{O}H$ do not associate because NaOH is a strong electrolyte and so is HCl acid. But if sodium ethanoate ($CH_3CO\bar{O}Na^+$) is added to H_2O hydrolysis occurs because $CH_3CO\bar{O}$ ions associate with H^+ ions to form ethanoic acid (CH_3COOH) species

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + \bar{O}H_{(aq)} \text{———} (1)$$

$$CH_3COO_{(aq)} + H^+ \rightleftharpoons CH_3COOH_{(aq)} \text{———} (2)$$

The $CH_3CO\bar{O}$ in (2) combine with H^+ from (1) and this disturbs the equilibrium of H_2O. To restore K_w more H_2O ionizes. This puts $\bar{O}H$ concentration in excess and solution would have a PH greater than 7. Thus an aqueous solution of a salt from a weak acid and strong base is alkaline. The net effect is the sum of the two equations above.

$$CH_3CO\bar{O}_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + \bar{O}H_{(aq)}$$

A salt from a strong acid and weak base forms an acidic solution in H_2O example hydrolysis of phenyl ammonium chloride.

$$CH_5NH_3Cl \longrightarrow C_6H_5N^+H_3 + Cl^-$$

In solution

$$C_6H_5{}^+NH_3 + H_2O \rightleftharpoons C_6H_5NH_3OH + H^+$$

Since phenyl ammonium hydroxide is a weak base the solution is acidic due to excess H^+ formed.

Consider the following hydrolysis

$$A^- + H_2O \rightleftharpoons HA + \bar{O}H$$

The hydrolysis constant is give by;

$$K_h = \frac{[HA]\,[\bar{O}H]}{[A^-]}$$

In solution the following equilibrium exist

$$H_2O \rightleftharpoons H^+ + \bar{O}H$$

$$HA \rightleftharpoons H^+ + A^-$$

$$K_w = [\bar{O}H]\,[H^+]$$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

From above, eliminating $[H^+]$

$$\frac{K_w}{K_a} = \frac{[\bar{O}H]\,[HA]}{[A^-]} = K_h$$

Therefore, $K_h = \dfrac{K_w}{K_a}$

Example

1. Calculate the PH of a solution of CH_3COONa made by dissolving 8.4g in $1dm^3$ of H_2O if the hydrolysis Constant is 5.5×10^{-10} $moldm^{-3}$

Solution

$CH_3COONa_{(s)} \longrightarrow CH_3CO\bar{O}_{(aq)} + Na^+_{(aq)}$

$CH_3CO\bar{O}_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH + \bar{O}H$

$$K_h = \frac{[CH_3COOH]\,[\bar{O}H]}{[CH_3CO\bar{O}]}$$

$$K_h = \frac{[\bar{O}H]^2}{[CH_3CO\bar{O}]}$$

And $[CH_3CO\bar{O}] = C = [salt]$

$$K_h = \frac{[\bar{O}H]^2}{C}$$

$$[OH] = \sqrt{CK_h}$$

$$= \sqrt{\frac{8.4}{82} \times 5.5 \times 10^{-10}}$$

$$\mathbf{= 7.51 \times 10^{-6} moldm^{-3}}$$

$PH = 14 - (-\log[\bar{O}H])$

$= 14 + \log[7.51 \times 10^{-6}]$

$\mathbf{= 8.88}$

2. Calculate the PH of 0.1m CH_3COONa if it's K_h is 5.6×10^{-10}

Solution

$CH_3COONa_{(s)} \longrightarrow CH_3CO\bar{O}_{(aq)} + Na^+_{(aq)}$

$K_h = 5.6 \times 10^{-10}$

$\mathbf{C = 0.1}$

$CH_3CO\bar{O}Na_{(s)} \longrightarrow CH_3CO\bar{O}_{(aq)} + Na^+_{(aq)}$

$CH_3CO\bar{O}_{(aq)} + H_2O \longrightarrow CH_3COOH_{(aq)} + \bar{O}H_{(aq)}$

$K_h = \underline{[CH_3COOH]\,[\bar{O}H]}$

$[CH_3CO\bar{O}]$

$$= \frac{[CH_3COOH]\,[\bar{O}H]}{C}$$

$$K_h = \frac{[\bar{O}H]^2}{C}$$

$$[\bar{O}H] = \sqrt{CK_h}$$

$$= \sqrt{0.1 \times 5.6 \times 10^{-10}}$$

$$= 7.48 \times 10^{-6} \text{mol l}^{-1}$$

And PH =14 – (- log$[\bar{O}H]$)

=14 – (- log 7.48×10^{-6})

= 8.87

3. (a)(i). Ammonia undergoes the following reaction in H_2O

$$NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + \bar{O}H_{(aq)}$$

Write the expression for base dissociation constant K_b for NH_3

ii). Water ionizes according to the equation

$$H_2O + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + \bar{O}H_{(aq)}$$

Write an expression for ionization constant K_w of H_2O

iv). The hydrolysis of NH_4Cl is given by the equation

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+{}_{(aq)})$$

Express the hydrolysis constant K_h for NH_4Cl in terms of K_b and K_w

b) Calculate

i). The hydrolysis constant K_h for ammonium chloride given $K_w = 10^{-14}$ and $K_b = 1.8 \times 10^{-5}$

ii). The $[H^+]$ of a 0.01M NH_4Cl solution

iii). The PH of the solution

Solution

a(i). $K_b = \frac{[NH_4^+]\,[\bar{O}H]}{[NH_3]}$ assume H_2O is in excess and its concentration remain constant

ii). $K_w = [H_3O^+]\,[\bar{O}H]$

$$K_h = \frac{[NH_3]\,[H_3O^+]}{[NH_4^+]}$$

(ii) ÷ (i)

$$\frac{K_w}{K_b} = \frac{[H_3O^+]\,[\bar{O}H]\,[NH_3]}{[NH_4^+]\,[\bar{O}H]}$$

$$= \frac{[H_3O^+]\,[NH_3]}{[NH_4^+]}$$

$$= \mathbf{K_h}$$

Then $K_h = \frac{10^{-4}}{1.8 \times 10^{-5}}$

$= 5.56 \times 10^{-10}$ mol l^{-1}

ii).from $K_h = \dfrac{[NH_3]\,[H_3O^+]}{[NH_4^+]}$

$$K_h = \frac{[H_3O^+]^2}{[NH_4^+]}$$

$$K_h = \frac{[H_3O^+]^2}{C}$$

$$[H_3O^+] = \sqrt{CK_h}$$

$$= \sqrt{5.56 \times 10^{-10} \times 0.01}$$

$$= 2.36 \times 10^{-6} \text{ moldm}^{-3}$$

And $[H_3O^+] = [H^+] = 2.36 \times 10^{-6}$ mol l^{-1}

iii). PH $= -\log[H^+]$

$= -\log 2.36 \times 10^{-6}$

= 5.63

NOTE:

a) Salts formed from strong acids and strong bases example NaCl does not undergo hydrolysis. This is because both the strong acid and strong base do not disturb the ionic equilibrium of H_2O. The PH of such solution is 7.

b) Salts formed from weak solutions are neutral example CH_3COONH_4 In solution.

$CH_3COONH_4 \longrightarrow CH_3CO\bar{O}_{(aq)} + NH_4^+{}_{(aq)}$ ——(1)

$CH_3CO\bar{O}_{(aq)} + H_2O_{(l)} \longrightarrow CH_3COOH_{(aq)} + \bar{O}H_{(aq)}$ ——(2)

$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H^+$ ——(3)

Both $CH_3CO\bar{O}$ and NH_4^+ from (1) react with H^+ and $\bar{O}H$ from H_2O. This upsets the H_2O equilibrium causing H_2O molecules to ionize but since H^+ and $\bar{O}H$ are equally removed and CH_3COOH and NH_4OH are both weak, the H^+ and $\bar{O}H$ concentrations remains the same. Hence the solution remains neutral.

Self check

1. $Fe(OH)_3$ and phenyl amine react with water according to the following equations.

   $Fe(OH)_{3(s)} \rightleftharpoons Fe^{3+}{}_{(aq)} + 3\bar{O}H_{(aq)}$, ($K_{sp} = 1 \times 10^{-38}$)

   $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + \bar{O}H$ ($K_b = 4.3 \times 10^{-10}$)

a) Write the expressions for solubility product Ksp for $Fe(OH)_3$ and base dissociation constant K_b for phenyl amine

b) The equation for reaction between phenyl amine and Fe^{3+} is given below.

$Fe^{3+} + 3C_6H_5NH_2{}^+{}_{(aq)}\ 3H_2O_{(l)} \rightleftharpoons Fe(OH)_{3(s)} + 3C_6H_5NH_3{}^+{}_{(aq)}$

i) Write an expression for the equilibrium constant for the reaction.
ii) Express the equilibrium constant in terms of Ksp and K_b
iii) Calculate the value of the equilibrium constant
iv) What does the value of this constant signify

***(Ans. Kc =** $K_b{}^3/K_{sp}$, **K= 7.95 x** 10^9 **l** mol^{-1}**, (**By value of K_c means that the equilibrium lies very much to the right)*

BUFFER SOLUTIONS

A buffer solution is a mixture of a weak acid and its salt formed when it reacts with a strong base or a weak base and its salt formed when it reacts with a strong acid. Such a mixture maintains a constant PH when a small amount of alkali or acid is added. There are two types of buffers i.e.

a) Acidic buffers.
b) Basic buffers.

ACIDIC BUFFER

An acidic buffer consists of a weak acid and its salt from a strong base example
CH_3COOH / CH_3COONa, H_2CO_3 /$NaHCO_3$

Action of an acidic buffer

Consider a mixture of CH_3COOH and CH_3COONa.
CH_3CooH is slightly dissociated and CH_3COONa is highly dissociated.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3CO\bar{O}_{(aq)} + H^+{}_{(aq)} \text{ ——— } (1)$$
$$CH_3COONa_{(aq)} \rightleftharpoons CH_3CO\bar{O}_{(aq)} + Na^+{}_{(aq)} \text{ ——— } (2)$$

This solution will contain excess $CH_3CO\bar{O}$ and a larger reservoir of an ionized CH_3COOH molecules and small amount of H^+ ions .If a small amount of H+ ions added combines with $CH_3CO\bar{O}$ to form un ionized CH_3COOH . Therefore the PH will remain unchanged. Addition of $\bar{O}H$ from NaOH, KOH, the $\bar{O}H$ will react with H^+ ions from (1) to form H_2O and the PH remains constant. Thus addition of $\bar{O}H$ or H^+ does not change PH.

BASIC BUFFERS

A basic buffer consists of a weak base present together with its salt from a strong acid example
NH_4OH/NH_4Cl

Action of a basic buffer

In solution the base is slightly ionized while the salt is fully ionized

$$NH_4OH \rightleftharpoons NH_4{}^+{}_{(aq)} + \bar{O}H_{(aq)} \text{ ——— } (1)$$
$$NH_4Cl_{(aq)} \longrightarrow NH_4{}^+{}_{(aq)} + Cl_{(aq)} \text{ ——— } (2)$$

The solution has excess NH_4^+, large reservoir of NH_4OH and small amount of $\bar{O}H$.
Additions of H^+ ions react with $\bar{O}H$ from (1) to form H_2O and the PH remains constant.
Addition of $\bar{O}H$ react with NH_4^+ (excess) from (2) to form unionized NH_4OH and the PH remains constant.

PH OF BUFFER SOLUTIONS

The PH of a buffer solution can be calculated from the dissociation constant of the weak acid or base and the concentration of the salt present in the mixture.

Acidic Buffers

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3CO\bar{O}_{(aq)} + H^+_{(aq)}$$

$$K_a = \frac{[CH]_3CO\bar{O}]\,[H^+]}{[CH_3COOH]}$$

$$[H^+] = \frac{K_a\,[CH_3COOH]}{[CH_3CO\bar{O}]}$$

The acid is slightly dissociated and its concentration is regarded as being constant. The salt is highly dissociated and the concentration of $CH_3CO\ddot{O}$ is regarded as derived entirely from CH_3COONa. Therefore,

$$[H^+] = Ka\,\frac{[acid]}{[Salt]}$$

$$PH = -\log[H^+]$$

$$= -\log K_a\,\frac{[acid]}{[Salt]}$$

$$= -\left(\log K_a + \log\frac{[acid]}{[Salt]}\right)$$

$$= Pk_a + \log\frac{[salt]}{[acid]}$$

If [salt] = [acid]
Then $PH = P^{Ka}$

Basic Buffer

NH_4OH/NH_4Cl

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + \bar{O}H_{(aq)}$$

$$NH_4Cl_{(aq)} \longrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

$$K_b = \frac{[NH_4^+]\,[\bar{O}H]}{[NH_4OH]}$$

$$[\bar{O}H] = K_b\,\frac{[NH_4OH]}{[NH_4^+]}$$

Since NH_4Cl is fully ionized

$[NH_4^+]$ = [salt] and NH_4OH is slightly dissociated so that

$[NH_4OH]$ = base

$$\text{Therefore } [\bar{O}H] = K_b \frac{[\text{base}]}{[\text{Salt}]}$$

$$\text{And PH} = -\log K_b \frac{[\text{base}]}{[\text{Salt}]}$$

$$= -\log_{Kb} + \log \frac{[\text{salt}]}{[\text{Base}]}$$

$$= P^{Ka} + \log \frac{[\text{salt}]}{[\text{Acid}]}$$

NOTE:

PH = 14 – POH

Examples;

1. Calculate the PH of a buffer which consists of 4.1g of CH_3COONa per litre of solution. And 0.01M CH_3COOH whose $K_a = 1.7 \times 10^{-5} moldm^{-3}$

Solution

RFM of CH_3COONa = 82

[Acid] = 0.01M

$$[\text{Salt}] = \frac{4.1}{82}$$

$$\mathbf{= 0.05m}$$

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3CO\bar{O}_{(aq)} + H^+_{(aq)}$$

$$Ka = \frac{[CH_3CO\bar{O}]\,[H^+]}{[CH_3COONa]}$$

$$[H^+] = K_a \frac{[\text{acid}]}{[\text{Salt}]}$$

$$= \frac{1.7 \times 10^{-5} \times 0.01}{0.05}$$

$$\mathbf{= 3.4 \times 10^{-6}\ moldm^{-3}}$$

$$PH = -\log [H^+]$$

$$= -\log 3.4 \times 10^{-6}$$

= 5.469

2. a). 3.2g of CH_3COONa are added to litre of a 0.01M solution of CH_3COOH. Calculate the PH of the mixture

b) If $1cm^3$ of 1M HCl is added to one litre of the above mixture, calculate the new PH.

c). Calculate the change in PH when $1cm^3$ of 1M NaOH is added to one litre of the above mixture in (a)

($Ka = 1.84 \times 10^{-5}$), Na=23, O=16, C =12, H=1)

Solution

R.F.M of CH_3COONa = 82

$$[\text{Salt}] = {}^{3.28}/_{82}$$

$$= 0.04M$$

$$[\text{Acid}] = 0.01M$$

$$[H^+] = K_a \frac{[\text{acid}]}{[\text{Salt}]}$$

$$= \frac{1.84 \times 10^{-5} \times 0.01}{0.04}$$

$$[H^+] = 4.6 \times 10^{-6}\ \text{moldm}^{-3}$$

$$PH_2 = -\log(4.6 \times 10^{-6})$$

$$\mathbf{= 5.34}$$

b). Addition of $1cm^3$ of 1M HCl to one litre of H_2O would give a solution of $[H^+] = 0.001\text{mol } l^{-1}$ (approximately)

$$0.01 + 0.001$$

$$CH_3COOH \rightleftharpoons CH_3CO\bar{O} + H^+$$

$$CH_3COONa \longrightarrow CH_3CO\bar{O} + Na^+$$

$$0.04 - 0.001$$

The combination of H^+ and $CH_3CO\bar{O}$ of the salt increases the concentration of CH_3COOH molecules from 0.01 to 0.011M and this reduces the concentration of $CH_3CO\bar{O}$ from 0.04 to 0.039M

Therefore,

New concentration of acid = 0.011M

$$[\text{Salt}] = 0.039M$$

$$[H^+] = Ka \frac{[\text{acid}]}{[\text{Salt}]}$$

$$= \frac{1.84 \times 10^{-8} \times 0.011}{0.039}$$

$$\mathbf{= 5.19 \times 10^{-6} mol\ l^{-1}}$$

$$PH = -\log[H^+]$$

$$= -\log(5.19 \times 10^{-6})$$

$$= 5.28$$

c) When NaOH is added to the solution it reacts with ethanoic acid, this causes concentration of ethanoic to fall while concentration of salt increases.

$1cm^3$ of 1M NaOH = $^1/_{1000}$ moles (approximate)

= 0.001

New [acid] = 0.01 – 0.001

= 0.009M

[Salt] = 0.04 + 0.001

= 0.041

$$[H^+] = Ka \frac{[acid]}{[Salt]}$$

$$= \frac{1.84 \times 10^{-5} \times 0.009}{0.041}$$

$$\mathbf{= 4.04 \times 10^{-6}\ mol\ l^{-1}}$$

Then PH = - log 4.04×10^{-6}

= 5.39

Change in PH = 5.39 – 5.34

= 0.05

3. $20cm^3$ of 0.1M NaOH solution was added to $100cm^3$ of 0.1M solution of CH_3COOH, calculate the PH their resulting solution ($Ka = 1.7 \times 10^{-5}$)

Solution

$CH_3COOH_{(aq)} + NaOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$

Moles of NaOH in $20cm^3$ = $\frac{20 \times 0.1}{1000}$

= 0.002 moles

Moles of acid = $\frac{100 \times 0.1}{1000}$

= 0.01 moles

Moles of acid left = 0.01 – 0.002

= 0.008 moles

Total volume of solution = 20 + 100

= $120cm^3$

$120cm^3$ of solution contain 0.002 moles of salt

$1000cm^3$ of solution contain $\frac{0.002 \times 1000}{120}$

= 0.0167M

Then [salt] = 0.0167M

Similarly, [acid] = $\frac{0.008 \times 1000}{120}$

$= \mathbf{0.067M}$

$[H^+] = K_a \frac{[acid]}{[salt]}$

$= \frac{1.7 \times 10^{-5} \times 0.067}{0.0167}$

$= \mathbf{6.82 \times 10^{-5} mol\ l^{-1}}$

PH = - log 6.82×10^{-5}

= 417

Self Check

1. 0.03 moles of NH_4Cl are added to one litre of 0.01M NH_3 solution. Calculate.
   a) Concentration of $\bar{O}H$ in solution
   b) PH of the solution ($K_b = 2 \times 10^{-5}$, $K_w = 10^{-14}$)
   (Ans. a = 6.67×10^{-6} mol l^{-1} b = 8.82)

2. Calculate the PH of a solution which was made by adding $30cm^3$ of 0.1M HCl to $80cm^3$ of 0.1M NH_3 solution ($K_b = 1.8 \times 10^{-5}$ $moldm^{-3}$)
   (Ans. 9.477)

3. Calculate the mass of CH_3COONa that should be added to one litre of 0.1M CH_3COOH in order to give a solution whose PH is 4. State any assumptions made. ($K_a = 1.8 \times 10^{-5}$)
   (Ans. 1.476gl^{-1})

<u>Assumptions</u>

- There is no volume change of the solution on addition of CH_4COONa.
- The concentration of acid does not change because the added $CH_3Co\bar{o}$ should increase the concentration of acid by shifting equilibrium to the left.

$$CH_3COOH \rightleftharpoons CH_3CO\bar{O} + H^+$$

<u>Applications of buffer solutions</u>

- ✓ In medicine and agriculture to prepare standard solutions since PH of living cells must be maintained
- ✓ A buffer solution is used by the body in maintaining the PH of its fluids.
- ✓ In fermentation process. Most fermentation processes must be carefully buffered because any change in PH would cause death of the fermenting organisms.

THEORY OF INDICATORS

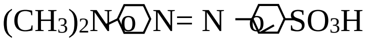
Indicators are substances which vary in colour according to $[H^+]$ of the solution which they are added. They are either weak acids or weak bases.

Most indicators used in acid alkali titrations are weak acids and their degree of dissociation is greatly affected by the PH of the solution.

Different indicators change colour over different ranges of $[H^+]$ example

Indicator	PH range	Acid	Alkali
Methyl orange	3.0 – 5.0	Red	yellow
Phenolphthalein	8.3 - 10.0	colourless	Pink
Litmus	5.0 - 8.0	Red	Blue

Action of an indicator

1. **Methyl Orange**  that is, HA

When dissolved in water H_2O an equation is set up. That is,

$$\underset{\text{Red}}{HA} \rightleftharpoons \underset{\text{yellow}}{A^- + H^+}$$

The red colour is due to undissociated HA and the yellow colour is due to dissociated A^- ions. Addition of $\bar{O}H$ ions increases the number of A- ions enough to show their yellow colour.

Addition of an acid provides H^+ ions which reduce A^- ions and form more HA which is red

2. Phenolphthalein indicator (P_hH)

In solution it ionizes as

$$\underset{\text{Colourless}}{HPh} \rightleftharpoons \underset{\text{pink}}{H^+ + Ph}$$

Addition of $\bar{O}H$ removes H^+ to form H_2O. This decreases $[H^+]$ and hence to restore the equilibrium more HPh dissociates and increases $[Ph^-]$ hence the indicator shows the colour of the dissociated ion which is pink

END POINT

At the end point the number of HPh molecules and Ph^- ions present are equal because the two colours of the indicator will be shown t an equal extent.

This occurs at different Ph of each indicator.

If K_a is the dissociation constant of the indicator then

$$K_a = \frac{[H^+]\,[Ph^-]}{[HPh]}$$

$$[H^+]\,K_a = \frac{[HPh]}{[Ph^-]}$$

Since at the end point [HPh] = [Ph$^-$] then,

$[H^+] = K_a$

And $PH = -\log [H^+]$

$= -\log K_a$

For the case of phenol indicator

$K_a = 7 \times 10^{-10} moll^{-1}$ and the corresponding PH is 9.1

For methyl orange

$K_a = 2 \times 10^{-4} moll^{-1}$ and the corresponding PH is 3.7

PH Change during titration

During titration the PH of the solution changes as acid or base is added. The change depends on the strength of the acid or alkali used.

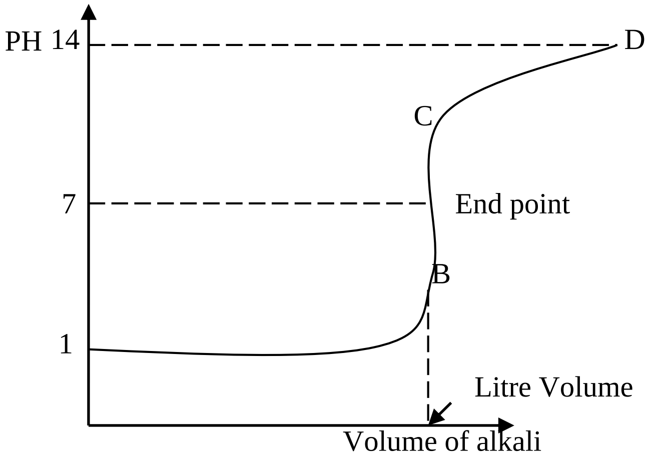
It's important to use an indicator which changes colour around the range in which a marked PH change during the reaction occurs.

Example

Titration	**Marked PH change**	**indicator**
Strong/strong base	4 -10	Most indicator
Weak acid/strong base	7.5 - 10.5	Phenolphthalein
Weak acid /weak base	No marked range	No indicator

TITRATION CURVES

Titration of a strong acid against a strong alkali



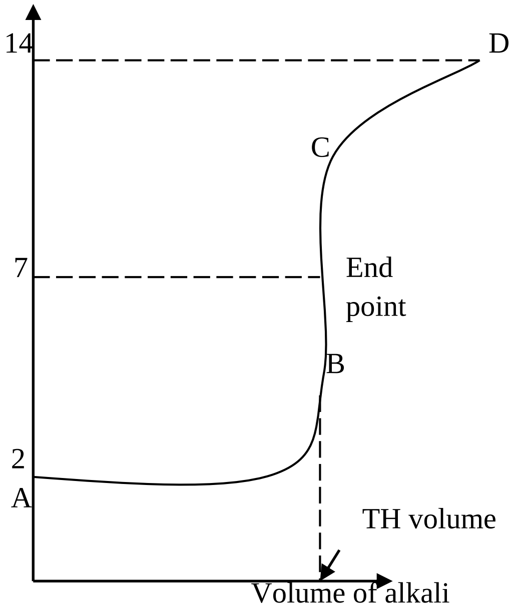
Explanation

PH at A is due to strong acid which is completely ionized. A gradual rise in PH a long AB is due to removal of H$^+$ (hydrogen ions) from solution. At the end point the PH sharply rises and it is at 7 because no hydrolysis of the salt. The rise PH along CD is due to excess alkali after the end-point.

NB

Methyl orange, litmus paper and phenolphthalein indicators can be used under this titration because they have a range of PH between 3.5 and 9.5

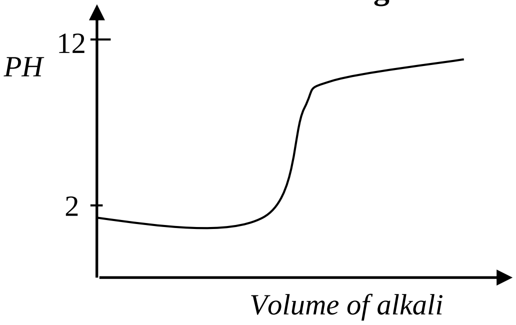
Titration of weak acid against strong base



At A the PH is due to weak acid, but gradually increases along AB due to removal of H^+(hydrogen ions) from the solution. At the end point it rapidly rises and the resultant solution has a PH greater than 7 due to hydrolysis of the salt and along the CD, the PH rises due to excess alkali.

NB Phenolphthalein is the only suitable indicator because it has PH range between 7.5 and 10.5

Titration of weak base against strong acid



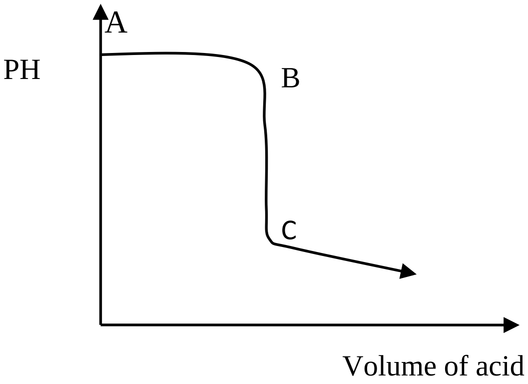
At the beginning the PH is low because the acid is completely ionized. There is a gradual increase in PH as the base is added because neutralization, takes place forming salt and water

The remaining acid is diluted by the increased volume of water so concentration of hydrogen ions decreases and PH increases. Towards the end-point the remaining acid is neutralized and is highly diluted .there is a rapid increase in PH as the acid is completely neutralized. The PH at the equivalent point is below seven due to hydrolysis of the salt. There is a gradual increase in PH as the base is added because there is no acid for the weak base to react with. But because the base is weak and exists mainly as molecule, PH rises only towards 10 and not 14.

NB

Phenolphthalein and thymolblue are unsuitable indicators

Titration of strong acid with a weak base



PH at A is due to the weak base. But gradually decreases along AB as the acid is added because of increase in concentration I hydrogen ions and decrease in concentration of hydroxyl ions. At the end-point there is a rapid decrease in PH along BC

The PH at the end-point is below due to the hydrolysis of the salt formed. The rapid decrease in PH along CD is due to excess acid added.

Self check

1. a) Draw diagrams to show the change in PH when a 0.1M sodium hydroxide solution is added in portions to

  i) $20cm^3$ of a 0.1M hydrochloric acid.

  ii) $20cm^3$ of a 0.1M ethanoic acid explain the shapes of the curves.

    a. Sketch a graph to show the variation of PH during the titration of hydrochloric acid with ammonia solution and explain the shape of the graph.

2. Sodium hydroxide solution was added to $25cm^3$ of 0.1M ethanoic acid and the PH of the solution was measured at intervals the results are given in the table below.

Volume of NaOH/Cm^3	0	4	8	12	16	20	22	22.5	23	24	28
PH of mixture	2.8	3.5	4	4.5	5.1	5.8	7	9	10.5	11.4	12.3

  i) Plot a graph of PH against volume of sodium hydroxide

  ii) Explain the shape of the curve.

  iii) Determine the PH at the end point

  iv) Calculate the morality of sodium hydroxide solution

b). Determine the dissociation constant ka of ethanoic acid

c). Describe how sodium hydroxide can be prepared on a large scale

(Ans. a) iii) 9 =0.2   iv) 0.11M   b). K_a= 2.5 x 10^{-5})

ELECTRO - CHEMISTRY

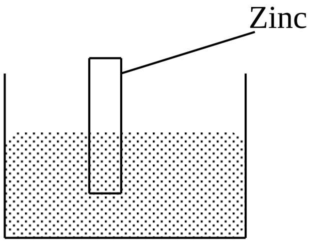
When a metal is placed in water r in a solution of one of its salts, the metal may dissolve leaving a buildup of electrons on the metal. That is;

Example

$$\begin{array}{lll} & M_{(s)} \longrightarrow & M^{2+}_{(g)} + 2e^- \\ & Zn_{(s)} \longrightarrow & Zn_{(g)} \\ & Zn_{(g)} \longrightarrow & Zn^{2+}_{(g)} + 2e^- \\ + & Zn^{2+}_{(g)} \longrightarrow & Zn^{2+}_{(aq)} \\ \hline & Zn_{(s)} \longrightarrow & Zn^{2+}_{(aq)} + 2e^- \end{array}$$

The energies involved in form in forming ions are sublimation, ionization and hydration.

To change one mole of metallic zinc to hydrated Zn^{2+} ions, energy is absorbed. An excess of electrons is left behind on the surface of the metal which acquires a negative charge. This negative charge builds up and makes it more and more difficult for the loss of Zn^{2+} ions as the Zn rod will increasingly attract Zn^{2+} ions rather than release them. This results in an electric double layer of the zinc rod.



Eventually an equation is set up

$$Zn_{(s)} \rightleftharpoons Zn^{2+}_{(g)} + 2e^-$$

The formation of the electric double layer is accompanied by potential difference called the electrode or redox potential between the surface of the metal and the liquid. This depends on the type of the metal, concentration of metal ion already present in the liquid. The further to the left the position of the equilibrium and the smaller the electrode potential.

Reduction : Is the gain of electrons by an oxidant

Oxidation : Is the loss of electrons by a reductant.

Redox : Is the transfer of electrons from a reductant to an oxidant

Metal displacement reaction

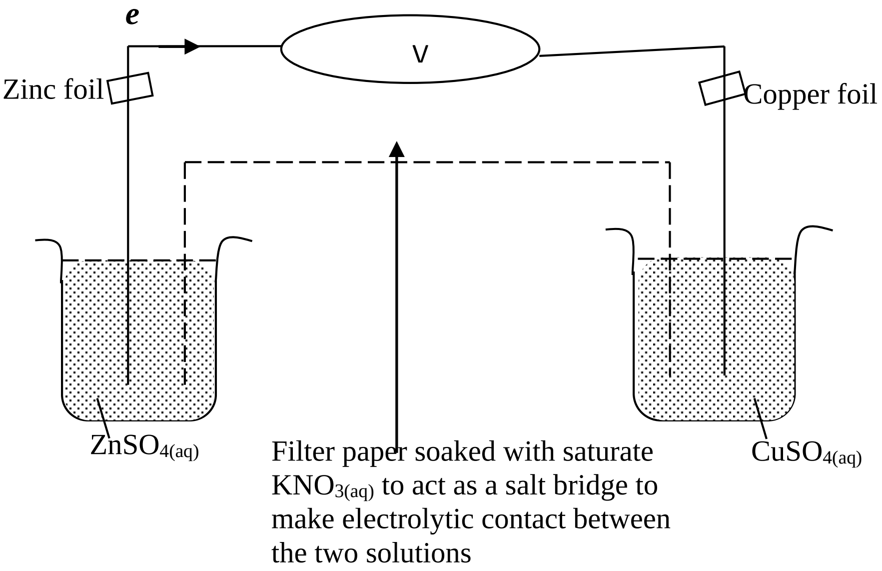
$$Fe_{(s)} + \underset{\text{Blue solution}}{Cu^{2+}_{(aq)}} \longrightarrow \underset{\text{green solution}}{Fe^{2+}_{(aq)}} + Cu_{(s)}$$

This is a redox because two moles of electrons are transferred from one mole of iron atom to one mole of copper (ii) ions. That is

Fe is the reductant by losing electrons and
Cu^{2+} is the oxidant by gaining electrons.

Note: Electrons flow from a metal that displaces the other and the one displaces is on the right hand side. So Electrons travel from zinc atom to aqueous copper(i) ions.

Diagram for Zn/Cu^{2+}



Reaction: $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

That is, $Zn_{(s)} / Zn^{2+}_{(aq)}, // \ Cu^{2+}_{(aq)} / Cu_{(s)}$

But if we interchange the diagram, That is,

$Cu_{(s)} + Zn^{2+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + Zn_{(s)} \quad E^{\theta} = -ve$

And the cell notation becomes

$Cu_{(s)}/Cu^{2+}_{(aq)} \ // \ Zn^{2+}_{(aq)} / Zn_{(s)}$

Self check

Draw a fully labeled diagram to show the arrangement of the apparatus you would use to measure the electromotive force (e.m.f) of a cell consisting of

a) Fe and Zn
b) Iron and copper
c) Ag and Cu electrodes, indicating the flow of electrons in each case write the cell notation, half equations and overall equations.

e.m.f. (electromotive force) of an electrochemical cell: Is the maximum potential difference (voltage) between the electrodes.

The standard e.m.f of an electrochemical cell: Is the maximum voltage at temperature of 25^0C, a pressure of one atmosphere and with solution of concentration equal to 1 $moldm^{-3}$

Electrolytic cells differs from an e.m.f cell in that

a) In e.m.f cells, oxidation occurs at the negative electrode while in electrolytic cells, oxidation occurs at the positive electrode.
b) In electrolytic cells, power is supplied externally while e.m.f. cells generate power.

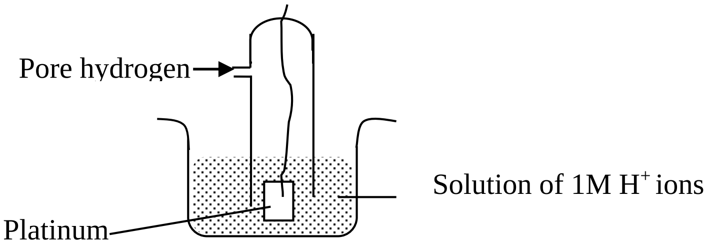
Standard hydrogen electrode

Is the half cell consisting of pure hydrogen gas at 25^0C and one atmospheric pressure, bubbling past a platinised platinum electrode dipping into a 1 $moldm^{-3}$ solution of hydroxonium ion of H_3O^+.

Platinum is used as the electrical contact the half cell electron transfer reaction occurs between the hydrogen gas and the aqueous hydrogen ions, That is;

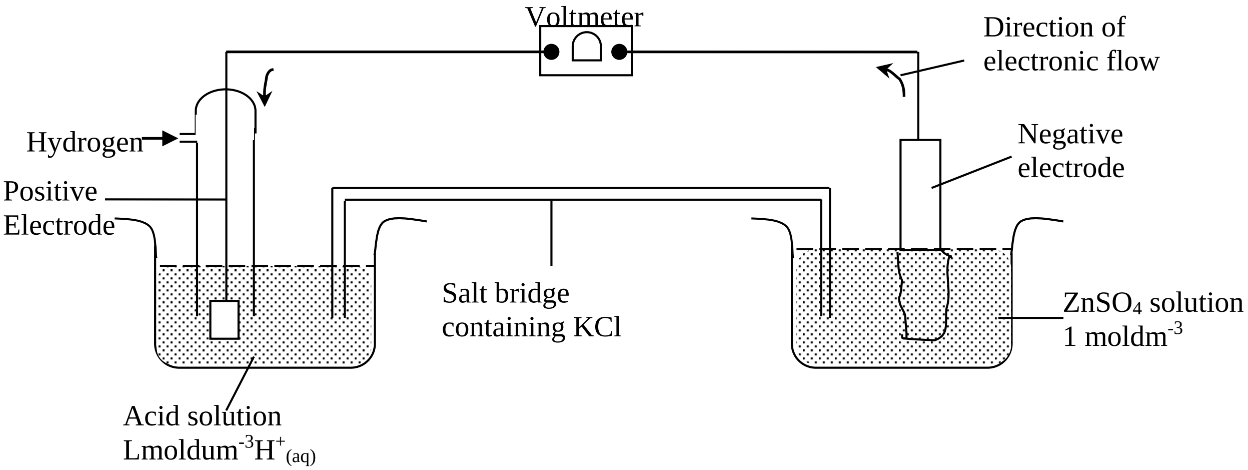
$$H_{2(g)} \rightleftharpoons 2H^+_{(aq)} + 2e^-$$

Diagram



NB: Platinum is too inert to act as a reductant that is why is used as the electrical contact.

The standard electrode potentials for other metals are found by combining them with a standard hydrogen electrode and measuring the e.m.f. of the cell formed



The electrode potential of the standard hydrogen electrode (S.H.E.) is assigned a valve of 0 volts, when an electrode is used in conjunction with a metal electrode placed in the molar solution of the ion the e.m.f obtained is called **Standard electrode potential (E^o)** of the metal measured by the potentiometer.

Standard electrode potential is the reduction electrode potential of electrode which is the e.m.f of the cell reaction with respect to the standard hydrogen electrode under standard conditions.

The standard electrode potential (E^o); Is the e.m.f of an electro chemical cell represented by a cell diagram in which a standard hydrogen is shown as the half - hand half - cell.

The standard electrode potential for the hydrogen electrode must be zero because the e.m.f of $H_{2(g)}/2H^+_{(aq)} // 2H^+_{(aq)}/H_{2(g)}$ will be zero under standard conditions.

Self check

Draw a well labeled diagram to show how the standard electrode potential of zinc can be determined.

Combining standard electrode potential

The number of electrons lost in the ion electron half equation for one electrode reaction must match the number of electrons gained in the ion-electron half equation for the other electrode reaction before the two half equation can be combined to obtain the equation for the overall cell reaction.

Say: $Zn^{2+}_{(aq)} /Zn_{(s)}$ – 0.76
$Cu^{2+}_{(aq)} /Cu_{(s)}$ + 0.34

The zinc electrode system is above copper electrode system. Zinc will therefore be the negative electrode and copper will be the positive, so I write the copper electrode system as the right hand half cell $Cu^{2+}_{(aq)}$ /$Cu_{(s)}$ and the zinc electrode system as the left hand half cell. $Zn^{2+}_{(g)}/Zn_{(s)}$. But must turn the zinc electrode system around so that the zinc metal is on the extreme left. This $Zn_{(s)}/Zn^{2+}_{(aq)}$ and the complete cell then becomes

$Zn_{(s)}/Zn^{2+}_{(aq)} // Cu^{2+}_{(aq)}/Cu_{(s)}$ $\quad$ E^0 cell $= +0.34 - (-0.76)$
$= + 0.34 + 0.76$
$= + 1.1V$

Example:

$Fe^{2+}_{(aq),} + 2e^- \longrightarrow Fe_{(s)}$ $\quad$ –0.44V
$Cu^{2+}_{(aq)} + 2e- \longrightarrow Cu_{(s)}$ $\quad$ +0.34V

Then $\quad$ $Fe_{(s)}/Fe^{2+}_{(aq)} // Cu^{2+}_{(aq)}/Cu_{(s)}$ $\quad$ E^o cell $= +0.34 - (^-0.44)$
$= + 0.78V$

<u>Self Check</u>

The standard electrode potential of copper and silver are given below.

$Cu^{2+}_{(aq)} + 2e- \longrightarrow Cu_{(s)}$ $\quad$ $E^0 = +0.34V$
$Ag^+_{(aq)} + e- \longrightarrow Ag_{(s)}$ $\quad$ $E^0 = +0.80$

(Ans. +0.46V)

Note:

- A stronger oxidizing agent is the one that has a higher electrode potential
- If the two electrodes potential have opposite signs (one positive and the other negative ignore the signs and find the sum of the number)
- If the two electrodes potential have the same sign (both positive and both negative) find the difference between the numbers. That is:-

$$E^0\text{cell} = E^0\text{right hand half cell} - E^0\text{left hand half cell}$$
$$= E^0_{RHE} - E^0_{LHE}$$

- A metal higher up in the series is a better reducing agent in aqueous solution that one that lies below it. That is, from most to least.
  Li^+, K^+, Ba^{2+}, Ca^{2+}, Na^+, Mg^{2+}, Al^{3+}, Mn^{2+} , Zn^{2+} , Cn^{3+} FE^{2+}, Co^{2+}, N_1^{2+}, Sn^{2+}, Pb^{2+}, H^+, Cu^{2+}, Ag^+, Au^{3+}, $_{(aq)}$
- A metal high least negative/ high positive E^o is the best oxidizing agent because it has least tendency to gain electrons. And that with least positive / high negative Eo is the best reducing agent because it has greatest tendency to lose electrons.

Self Check

1. The equations below show the standard electrode potentials of some half reactions.

$Cu^{+}_{(aq)} + e \longrightarrow Cu_{(s)}$ $E^{o} = +0.52V$

$Cu^{2+}_{(aq)} + e \longrightarrow Cu^{+}_{(aq)}$ $E^{o} = +0.67V$

Which of the two ions, Cu^{+} and Cu^{2+} is a stronger oxidizing agent? Give reasons for your answer.

2. Given $Fe^{2+}_{(aq)} + 2e \longrightarrow Fe_{(s)}$ $E_{o} = +0.44V$

$Al^{3+}_{(aq)} + 3e \longrightarrow Al_{(s)}$ $E_{o} = -1.66V$

Calculate the initial e.m.f of the cell under standard conditions, What practical application is made of this cell system.

(Ans. -1.22V)

NB. Determination of standard electrode potential of an electrode requires the introduction of a second electrode. However, this second electrode also produces its own e.m.f. thus making such measurements relative rather than absolute.

Example: Consider the half reactions

$MnO_4^{-}{}_{(aq)} + 8H^{+}_{(aq)} + 5e \rightleftharpoons Mn^{2+}_{(aq)} + 4H_2O_{(s)}$ – $E^{o} = +1.51V$ –①

$2H^{+}_{(aq)} + O_{2(g)} + 2e \rightleftharpoons H_2O_{2(aq)}$ $E^{o} = +0.68V$ –②

The voltage given applies to the forward reaction for the backward reaction the sign of the voltage must be changed. The forward reaction is a reduction in which the oxidizing agent shown on the left is reduced by gaining electrons. The overall electrode potential is given by

$$E^{o}{}_{cell} = E^{o}{}_{oxidant} - E^{o}{}_{reductants}$$
$$= {}^{+}1.51 - {}^{+}0.68$$
$$= {}^{+}0.83V$$

NOTE

When the electrodes combine to form a cell the valve of E^{o} for the cell must be positive if the cell reaction is to happen spontaneously. The overall reaction for the above electrodes is obtained as follows.

2①– 5②

$2MnO_4^{-}{}_{(aq)} + 16H^{+}_{(aq)} \rightleftharpoons 2Mn^{2+}_{(aq)} + 8H_2O_{(aq)}$

$10H^{+}_{(aq)} + 5O_{2(aq)} \rightleftharpoons 5H_2O_{2(aq)}$

$2MnO_4^{-}{}_{(aq)} + 16H^{+}_{(aq)} + 5H_2O_{2(s)} \rightleftharpoons 2Mn^{2+}_{(aq)} + SO_{2(aq)} + 8H_2O_{(1)}$

$E^{o} = 0.83V$

Since the overall potential is positive, the permanganate should oxidize H_2O_2. In equalizing the number of electrons the electrode potential is not affected because the electrode potential is independent of the quantity of material in the cell.

NOTE: the reaction is possible/feasible if standard electrode potential of cell is positive or the free energy of cell is negative. The free energy of a cell is given by

$$\triangle G^{\theta} = -nE^{\theta}F$$

Where n is number of electrons involved, E^{θ} is standard electrode potential of the cell and F is faraday.

Self check

1. Consider the Fe^{3+}/Fe^{2+} system. The electrode potentials for Fe^{3+}/Fe^{2+} and Fe^{2+}/Fe and +0.77V and –0.44V respectively. Find out whether the following disproportionation is possible

(Ans. E^o = -1.21V then does not occur)

2. Given below are standard electrode potentials at 298K

$Ca^{2+}_{(aq)} + 2e \rightleftharpoons Ca_{(s)}$ E^o = -2.87V
$Cu^{2+}_{(aq)} + 2e \rightleftharpoons Cu_{(s)}$ E^o = +0.34V
$MnO_{2(aq)} + 4H^{+}_{(aq)} + 2e \rightleftharpoons Mn^{2+}_{(aq)} + 2H_2O_4$ E^o = 1.23V
$Ag^{+}_{(aq)} + e \rightleftharpoons Ag_{(s)}$ E^o = +0.8V
$Fe^{3+}_{(aq)} + e \rightleftharpoons Fe^{2+}_{(aq)}$ E^o = +0.77V

   a. Arrange the above species in order of their reducing power starting with the most reducing
   b. A cell was made up of MnO_2/H^+ and Fe^{3+} / Fe^{2+} electrodes
      i) Write the equation for the reaction
      ii) Calculate the e.m.f of the above cell
      iii) What does the sign of the answer in b (ii) above signify
   c. (i) Construct a cell diagram for the reaction between copper and iron half cells.
      (ii) Write the overall equation for the reaction

(Ans. Ca^{2+}, Cu^{2+}, Fe^{3+} and MnO_2/H^+ because the more negative the electrode potential is the more reducing it is) E^o_{cell} = +0.46V)

3. The standard electrode potential for some half cells is shown below.

$Fe^{3+}_{(aq)} / Fe^{2+}_{(aq)}$ +0.76V
$I_{2(aq)} / I^{-}_{(aq)}$ +0.54V

   a) Write
      i. The convetion for the combined cell
      ii. The equation for the overall reaction
   b) Calculate the overall electrode potential for the cell.
   c) (i) State whether the reaction is feasible or not.
      (ii) Give a reason for your answer in c (i) above

(Answer. E^o = +0.22V, feasible because e.m.f is positive)

4. Given $Ca^{2+}_{(aq)} + 2e \longrightarrow Ca_{(s)}$, $E^o = -2.57V$
$Mg^{2+}_{(aq)} + 2e \longrightarrow Mg_{(s)}$ $E^o = -2.32V$

A cell was set up as below

$Mg_{(s)} / Mg^{2+}_{(aq)} // Ca^{2+}_{(aq)} / Ca_{(s)}$

i. Calculate e.m.f of the cell
ii. What conclusion can you draw from your e.m.f values

(Ans. $E^o = -0.55V$ not feasible because E^o is negative)

Factors which affect the value of standard electrode potentials

Atomization energy

The higher the atomization energy the lower is the value of standard electrode potential because it becomes difficult to convert the gaseous atoms into gaseous ions.

Ionization energy

The higher the ionization energy, the lower is the value of standard electrode potential because it becomes difficult to convert the solid metal into its gaseous atoms into gaseous ions.

Hydration energy

The higher the hydration energy, the higher the value because the gaseous ions are easily hydrated in aqueous solutions

Concentration of the solution and temperature etc.

Application of E° value

- To determine the equilibrium constant Kc. That is $E_{cell} = E^{\theta} - \frac{RT}{nF} K_c$
- Top predict the feasibility of a reaction
- To determine solubility of sparingly soluble salt. That is $E = E^{\theta} + \frac{RT}{nF} \log[M^{n+}]$
- To find free energy of the cell.

FARADAY’S LAWS

NOTE: The amount of an element liberated during electrolysis depends on

- The time for which the current is passed
- The amount of the current passed
- The change on the ions of the element

And Quantity of electricity $\varphi = \underset{(\text{Amperes})}{I}\underset{(\text{Seconds})}{t}$

In Coulombs

Faraday's first law

States that the amount of element liberated at the electrode is proportional to the quantity of electricity passed. That is;-

1 mole of electrons has a charge of one faraday (F) or 96500 coulombs. So,

1 electron = 1F = 1 × 96500C

2 electrons = 2F = 2 × 96500C etc

Faraday's second law

States that when the same quantity of electricity is passed through solutions of different electrolytes, the relative number of moles of the elements deposited are inversely proportional to the charges on the ions of each element respectively

Electrolysis of dilute H_2SO_4

At anode $4OH^-_{(aq)} - 4e^- \longrightarrow 2H_2O_{(s)} + O_{2(g)}$

At cathode $4H^+_{(aq)} + 4e^- \longrightarrow 2H_{2(g)}$

Overall equation $4OH^-_{(aq)} + 4H^+_{(aq)} \longrightarrow 2H_2O_{(l)} + 2H_{2(g)} + O_{2(g)}$

Example

During the electrolysis of dilute sulphuric acid using platinum electrodes, a current of 2 amperes was passed for 6.7 minutes at room temperature. Calculate the volume of the gas evolved at the anode and the cathode.

Solution

Number of coulombs passed = 2 × 6.7 × 60

= 804C

At the anode $4\bar{O}H_{(aq)} \longrightarrow 2H_2O_{(1)} + O_{2(g)} + 4e$

1 mole of oxygen at the anode is liberated by 4 electrons

= 4 × 96500

$= 3.56 \times 10^5 C$

Then moles of oxygen liberated

$$= \frac{804}{4 \times 96500}$$

$= 2.08 \times 10^{-3}$

But 1 mole of a gas occupies $24dm^3$ at room temperature

Then volume of oxygen at anode

$= 24 \times 2.08 \times 10^{-3}$

$= 0.05dm^3$

$= 50cm^3$

But for each volume of oxygen formed at anode, two volumes of hydrogen form at cathode

Therefore

Volume of hydrogen = 2 volume of oxygen

$= 2 \times 0.05$

$= 0.1dm^3$

$= 100cm^3$

Self check

A current of 5 amperes is passed for 32 minutes and 10 seconds between graphite electrodes through $CuSO_4$ solution.

Calculate the mass of copper deposited at the cathode and the volume of oxygen gas liberated at the anode.

(Ans. 3.2g, 600cm^3)

Application of electrolysis

- Electroplating
- The purification of metals
- Attention of metals
- Manufacture of chlorine and sodium hydrochloride

LET US REVISE

1. The energy changes that take place during the formation of barium chloride are shown in the table below.

Process	$\Delta H\theta$/ $KJmol^{-1}$
$Ba_{(s)} \xrightarrow{A} Ba_{(g)}$	+176
$Ba_{(g)} \xrightarrow{B} Ba^{2+}_{(g)} + 2e^-$	+1480
$Cl_{2(g)} \xrightarrow{C} 2Cl_{(g)}$	+242
$Cl_{(g)} + e^- \xrightarrow{D} Cl^-_{(g)}$	-364
$Ba^{2+}_{(g)} + 2Cl^-_{(g)} \xrightarrow{E} BaCl_{2(s)}$	-2018

a) Name the energy change for the processes

Solution

A: Atomisation energy of barium

B: Ionisation of barium

C: Bond dissociation energy of chlorine

D: Electron affinity of chlorine

E: Lattice energy of barium chloride

b) Calculate the standard enthalpy of formation of barium chloride.

Solution

$\Delta Hf^\theta = A + B + C + 2D + E$

$= 176 + 1480 + 242 + 2(-364) + (-2018)$

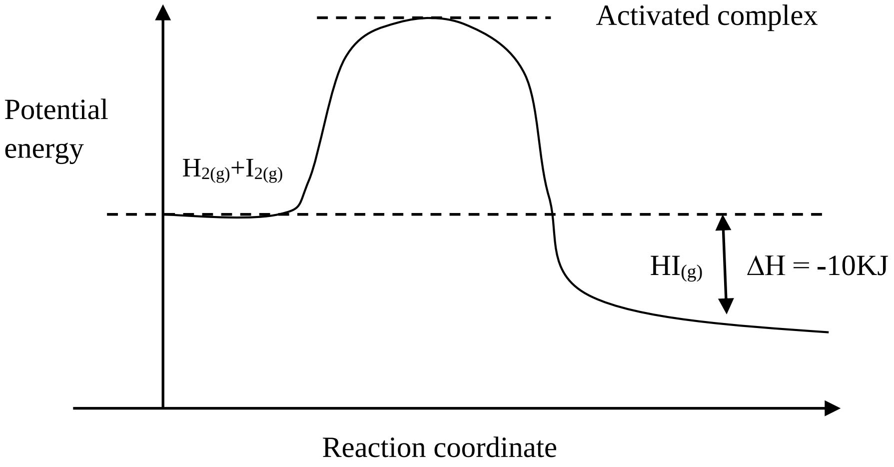
$= -848KJmol^{-1}$

2. Hydrogen reacts with iodine according to the following equation.

$H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$, $\Delta H = -10KJ$

a) Draw a labeled diagram for potential energy versus reaction coordinates for the reaction.

Solution



b) The rate of the reaction is given by

Rate = $K[H_2]\ [I_2]$

Determine the overall order of the reaction

Solution

1 + 1 = 2

c) When 0.1 mole of hydrogen and 0.2 moles of Iodine were mixed in a 500cm3 vessel at 400^0C the initial rate of formation of hydrogen iodide was 4.6×10^{-5} mol $dm^{-3}s^{-1}$

Calculate the value of k and give its units.

Solution

$$[I_2] = \frac{0.2 \times 1000}{500} = 0.4M, \qquad [H_2] = \frac{0.1 \times 100}{500} = 0.2M$$

$$K = \frac{4.6 \times 10^{-5}}{0.2 \times 0.4}$$

= 5.75×10^{-4} mol^{-1} dm^3s^{-1}

3.a) One of the limitations of the method of determining relative molecular mass by freezing point method is that the solute should not associate or dissociate in solution.

i) State three other limitations of determining molecular mass by freezing point method.

Solution

- The solution should be dilute
- The solute should be non-volatile
- The solute should not react with the solvent
- On freezing only the solvent solidifies

ii) Explain how association of a solute in solution affects the molecular mass determined by freezing point method.

Solution

Association of molecules of solute reduces mass of solute particles in solution. This results into a decrease in the value of freezing point depression. Since freezing point depression is inversely proportional to the relative molecular mass of the solute, the relative molecular mass will be higher than expected.

b) A solution containing 0.142g of naphthaline in 20.25g of benzene caused a lowering of freezing point of 0.284^{0}C. Calculate the molar mass of naphthaline (Cryoscopic constant, K_f of benzene is 5.12^{0}C mol^{-1}Kg^{-1})

Solution

20.25g of benzene dissolves 0.142g of naphthaline.

1000g of benzene dissolves $\frac{0.142 \times 1000}{20.25}$g of naphthaline

Then 0.284^{0}C is caused by $\frac{0.142 \times 1000}{20.25}$g of naphthaline

5.12^{0}C is caused by $\frac{0.142 \times 1000 \times 5.12}{20.25 \times 0.284}$

= 126.4g

Hence molar mass of napthaline is 126.4g

4. The equations for some redox reactions are shown below.

$2H^+_{(aq)} + 2Fe^{2+}_{(aq)} \rightleftharpoons H_{2(g)} + 2Fe^{3+}_{(aq)}$

$3Zn_{(s)} + 6\bar{O}H_{(aq)} + BrO_{3(aq)} + 3H_2O_{(l)} \qquad 3Zn(OH)_4^{2-}{}_{(aq)} + Br^-_{(aq)}$

a) For each reaction, write the half-cell reactions taking place at

(i) the anode

Solution

$Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e$

$Zn_{(s)} + 4\bar{O}H_{(aq)} \longrightarrow Zn(OH)_4^{2-}{}_{(aq)} + 2e$

(ii) the cathode

Solution

$2H^{+}_{(aq)} + 2e \longrightarrow H_{2(g)}$

$BrO_3^{-}{}_{(aq)} + 3H_2O_{(l)} + 6e \longrightarrow Br^{-}_{(aq)} + 6\bar{O}H_{(aq)}$

b)(i) For each reaction, write the cell notation of the cell made by combining the electrodes of each half-cell.

Solution

$Pt/Fe^{2+}_{(aq)}, Fe^{3+}_{(aq)}// H^{+}_{(aq)}\ H_{2(g)}/ Pt$

$Zn_{(s)}/\ \bar{O}H_{(aq)}, Zn(OH)_4^{2-}{}_{(aq)}// BrP_3^{-}{}_{(aq)}, H_2O(l), Br^{-}_{(aq)}, \bar{O}H_{(aq)}/Pt$

ii) State what each symbol used in (b)(i) stands for

Solution

/ - shows separation of phases

// - shows a salt bridge

, - shows separation of species in same phase

Pt – platinium electrode

5.(a)(i) Write the equation for the ionization of phenol in water.

Solution

$C_6H_5OH_{(aq)} + H_2O_{(l)} \rightleftharpoons C_6H_5\bar{O}_{(aq)} + H_3O^{+}_{(aq)}$

Or

$C_6H_5OH_{(aq)} \qquad C_6H_5\bar{O}_{(aq)} + H^{+}_{(aq)}$

(ii) If the pH of a 1.0 x 10^{-2} mol dm^{-3} solution of phenol is 5.95, Calculate the dissociation constant, Ka of phenol.

Solution

$$Ka = \frac{[H_3O^+][C_6H_5\bar{O}]}{[C_6H_5OH]}$$

But $[H_3O^+] = [C_6H_5\bar{O}]$

$$Ka = \frac{[H_3O^+]^2}{[C_2H_5OH]}$$

From pH = -log[H_3O^+]

[H^+] = $10^{-5.95}$

= 1.12 x 10^{-6} mol dm^{-3}

And

$$Ka = \frac{(1.12 \times 10^{-6})^2}{1.0 \times 10^{-2}}$$

= 1.26 x 10^{-6} mol dm^{-3}

b) 10 litres of aqueous solution of trichloroethanoic acid was completely neutralized by $10cm^3$ of a 0.01M sodium hydroxide. Calculate the pH of the solution of trichloroethanoic acid.

Solution

Number of moles of sodium hydroxide = $\frac{10 \times 0.01}{1000}$

= 1.0 x 10^{-4} moles

$$Cl_3CCOOH_{(aq)} + NaOH_{(aq)} \longrightarrow Cl_3CCOONa_{(aq)} + H_2O_{(l)}$$

1 mole of acid reacts with 1 mole of base.

Then, 10 litres of acid contain 1NO^{-4} moles

1 litre of acid contains $\frac{1 \times 10^{-4}}{10}$ x 1

= 1 x 10^{-5} moles

pH = -log[H^+]

= -log[1 x 10^{-5}]

= 5.0

c) The solution of trichloroethanoic acid in (b) was added to a 0.1M sodium trichloroethanoate. Calculate the pH of the resultant solution (Ka of trichloroethanoic acid is 0.224 mol dm^{-3} at 25^0C

Solution

$$pH = PKa + \log_{10}\frac{[salt]}{[acid]}$$

$$= -\log 0.224 + \log\frac{0.1}{1 \times 10^{-5}}$$

= 4.65

Alternatively

$$[H^+] = Ka = \frac{[Cl_3CCOOH]}{[Cl_3CCO\bar{O}]}$$

$$= \frac{0.224 \times 10^{-5}}{0.1}$$

$= 2.24 \text{ x } 10^{-5}$

And pH = $-\log[H^+]$

$= -\log 2.24 \text{ x } 10^{-5}$

= 4.65

6. Electrode potentials for some half cells are given below

Half cell	E^θ(v)
$Fe^{2+}_{(aq)}$, $Fe^{3+}_{(aq)}$/ Pt	-0.771
$Cr^{3+}_{(aq)}$, $Cr_2O_7^{2-}{}_{(aq)}$, $H^+_{(aq)}$/ Pt	-1.33

a) Write the cell notation for the cell formed when the two half cells are connected.

Solution

Pt/ $Fe^{2+}_{(aq)}$, $Fe^{3+}_{(aq)}$// $Cr_2O_7^{2-}{}_{(aq)}$, $Cr^{3+}_{(aq)}$, $H^+_{(aq)}$/ Pt

b) Write

i) equations for the half reactions

Solution

$Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e$

$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e \qquad 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

ii) equation for the overall reaction

Solution

$6Fe^{2+}_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} \qquad 6Fe^{3+}_{(aq)} + 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

c(i) Calculate the e.m.f of the cell

Solution

Cell = 1.33 – 0.771

= +0.559V

(ii) State whether the reaction is feasible or not

Give a reason for your answer

Solution

Reaction is feasible because the e.m.f of the cell is positive.

7.a) Silver ethanedioate is sparingly soluble in water. Write

(i) equation for the solubility of silver ethanedioate in water.

Solution

$Ag_2C_2O_{4(s)}$ + (aq) $2Ag^+_{(aq)} + C_2O_4^{2-}{}_{(aq)}$

(ii) the expression for solubility product, Ksp of silver ethanedioate

Solution

$Ksp = [Ag^+]^2[C_2O_4^{2-}]$

b) The solubility product, Ksp of silver ethanedioate is $5.3 \text{ x } 10^{-2}$ mol^3l-3 at 25^0C. Calculate the concentration of the following ions in a saturated solution of silver ethanedioate.

(i) Silver ions

Solution

Let $[Ag^+] = 2x$ and $[C_2O_4^{2-}] = x$

Then

$Ksp = [Ag^+]^2[C_2O_4^{2-}]$

$= (2x)^2(x)$

$= 4x^3$

But $\frac{4x^3}{4} = \frac{5.3 \text{ x } 10-2}{4}$

$$\sqrt[3]{x^3} = \sqrt[3]{\frac{5.3 \times 10^{-2}}{4}}$$

Hence, x = 0.2366M

Therefore $[Ag^+] = 2 \text{ x } 0.2366$

$= 0.4732M$

(ii) Ethanedioate ions

Solution

$[C_2O_4^{2-}] = 0.2366M$

c) Calculate the mass of silver nitrate that should be added to the saturated solution in (b) in order to reduce the concentration of the ethanedioate ions to a fifth of its original value.

Solution

New $[C_2O_4^{2-}] = \frac{1}{5}(0.2366)$

$= 0.0473M$

Then $5.3 \times 10^{-2} = [Ag^+]^2 \times 0.0473$, using Ksp expression

and

$$[Ag^+] = \sqrt[2]{\frac{5.3 \times 10^{-2}}{0.0473}}$$

$= 1.058M$

Therefore $[Ag^+]$ added $= 1.058 – 0.4732$

$= 0.5848M$

But R + M of $AgNO_3 = 108 + 14 + 16x3$

$= 170$

And mass of $AgNO_3 = 0.5848 \times 170$

$= 99.416g$

7. Phosphorus (V) chloride decomposes at high temperatures according to the following equation.

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

When 40.2g of phosphorous (V) chloride was placed in 4.5 litre vessel and heated at a certain pressure, 4.2g chlorine was formed at equilibrium.

a) Calculate the

(i) Amount of phosphorous (V) chloride and phosphorous (III) chloride at equilibrium in moles per litre

Solution

Rfm of $PCl_5 = 3l + 35.575$

$= 208.5$

Now $PCl_{5(g)} \longrightarrow PCl_{3(g)} + Cl_{2(g)}$

At equilibrium

40.2 – x x x
208.5

Moles of Cl_2 in 4.5 litres = $^{4.2}/_{71}$

Moles of Cl_2 in 1 litre = $\frac{4.2}{71} \times \frac{1}{45}$

= 0.013M

Moles of PCl_3 = 0.013M

Moles of PCl_5 in 4.5 litres = $\frac{40.2}{2088}$

= 0.1933M

Moles of PCl_5 in litres = $\frac{0.1933}{4.5}$

= 0.0429M

Moles of PCl_5 at equilibrium is 0.0429 – 0.013

= 0.0299M

ii) Equilibrium constant, Kc, for the reaction and state its units.

Solution

$$Kc = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{(0.013)^2}{0.0299} = 5.65 \times 10^{-3} mol\ l^{-1}$$

b) State how the value of the equilibrium constant would be affected and in each case give a reason for your answer if;

i) The pressure was increased

Solution

The value of the equilibrium constant remains the same increasing pressure shifts equilibrium from right to left due to decrease in volume, implying that chlorine reacts with phosphorous (III) chloride to give phosphorous (V) chloride thus concentration of chlorine and phosphorous (III) chloride decreases while that of phosphorous (V) chloride increase but individual concentrations of reactants and products re-adjust to keep the value of Kc constant.

ii) Some chlorine was removed at equilibrium

Solution

Removal of chlorine reduces its concentration, equilibrium shifts from left to right as phosphorous (V) chloride decompose to give more phosphorous (III) chloride and chlorine hence the value of equilibrium constant remains the same.

8. Dimethyl ammonium chloride undergoes hydrolysis in water according to the following equation

$(CH_3)_2NH^+{}_2(aq) + H2O(l) \rightleftharpoons (CH_3)_2NH_{(aq)} + H_3O^+{}_{(aq)}$

a) Write the expression for the hydrolysis constant Kn of dimethly ammonium chloride.

Solution

$$Kh = \frac{\left[(CH_3)_2NH_{(aq)}\right]\left[H_3O^+_{(aq)}\right]}{\left[(CH_3)_2N^+H_{2(aq)}\right]}$$

b) When 4.0 mol dm^{-3} of dimethyl ammonium chloride was hydrolysed 25.0cm^3 of the resulting solution required 75cm^3 of 0.01 mol dm^{-3} of sodium hydroxide for complete neutralization. Calculate the;

i) pH of the solution

Solution

Moles of H_3O^+ in 25cm^3 = moles of $\bar{O}H$ required for complete neutralization = $\frac{0.01\times7.5}{1000}$ moles

Moles of H_3O^+ in 1000cm^3 = $\frac{7.5\times10^{-5}\times1000}{25} = 3\times10^{-3}M$

pH = -log[H_3O^+]

= -log(3 x 10^{-3})

= 2.52

ii) Hydrolysis constant, Kh and state any assumptions made.

Solution

[H_3O^+] = [$(CH_3)_2NH$], [$(CH_3)_2N^+H_2$] = [Salt] = 4 mol dm^{-3}

$$Kh = \frac{[H_3O^+]^2}{[(CH_3)_2N^+H_2]} = \frac{(3\times10^{-3})^2}{4}$$

= 2.25 x 10^{-6} mol dm^{-3}

9.(i) State the effect on the vapour pressure of water and the total vapour pressure of the system when small amounts of the following substances are separately added to water at 25^{0}C

Substance added to water	Effect on	
	Vapour pressure of water	Total vapour pressure of the system
i) Sodium chloride	Decreases	Decreases
ii) Propanone	Increases	Increases
iii) Tetracloromethane	Remains constant	Increases

b) Explain your answer(s) in a(iii) above.

Solution

In a(ii) – the hydrogen bonds in water are stronger than intermolecular forces between water and propanone hence escaping tendency of molecules of each component into vapour phase increases causing increased vapour pressure of both water and proponone system.

In a(iii) – tetrachloromethane is immiscible with water each component exerts pressure independently, therefore vapour pressure remains constant. Also each component contributes its vapour pressure to the system thus vapour pressure increases.

c) An organic compound X was steam distilled at 95^{0}C at 760mmHg pressure. If the distillate contained 0.8g of water by mass, calculate the relative molecular mass of X.

(The saturated vapour pressure of water at 95^{0}C is 732.7mmHg)

Solution

$$\frac{Mass\ of\ X}{Mass\ of\ H_2O} = \frac{V.P_x.M_x}{V.P_{H_2O}.M_{H_2O}}$$

Mass of x = 1 – 0.8 = 0.2, VP$_x$ = 760 – 732.7 = 27.3mmHg

Then

$$\frac{0.2}{0.8} = \frac{27.3 \times M_x}{732.7 \times 18}$$

Rmm of x = 120.77 or 120.8

(Rmm of x should not have units since it’s a ratio).

10. Hydrogen and iodine react to form hydrogen iodide according to the following equation.

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

a(i) Write the expression for the equilibrium constant Kc, for the reaction.

Solution

$$Kc = \frac{[HI]^2}{[H_2][I_2]}$$

(ii) 1 mole of hydrogen and 1/3 mole of iodine were heated together at 450^{0}C until equilibrium was attained. Calculate the number of moles of hydrogen iodide present in the equilibrium mixture at 450^{0}C. (The equilibrium constant Kc for the reaction between hydrogen and iodine is 50).

Solution

$$H_{2(g)} \quad + \quad I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

At equilibrium (1-x)mole   (1/3-x) mole   2x mole

Where x = number of moles that reacted.

$$50 = \frac{(2x)^2}{(1-x)\left(\frac{1}{3}-x\right)}$$

Giving $69x^2 - 100x + 25 = 0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-100 \pm \sqrt{(-100)^2 - 4(69 \times 25)}}{2 \times 69}$$

Giving x = 1.12 or 0.32

The appropriate value of x = 0.32 mole

At equilibrium, moles of HI = 2 x 0.32

= 0.64 moles

b) Briefly describe how the concentration of iodine in the equilibrium mixture can be determined.

Solution

The iodine liberated is dissolved in aqueous potassium iodide and then titrated against standard sodium thiosulphate solution using starch indicator. The concentration of iodine can then be calculated.

Equation for the reaction is $I_{2(aq)} + 2S_2O_3{}^{2-}{}_{(aq)} \qquad S_4O_6{}^{2-}{}_{(aq)} + 2I^-{}_{(aq)}$

Self-check

1(a) The enthalpies of some reactions are given below

$\Delta Hf^\theta/KJmol^{-1}$

(i) $NaO_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(s)}$ $\quad \Delta H_1{}^\theta = -205$

(ii) $NaOH_{(s)} + (aq) \longrightarrow NaOH_{(aq)}$ $\quad \Delta H_2{}^\theta = -56.5$

(iii) $Na_{(s)} + H_2O_{(l)} + (aq) \longrightarrow NaOH_{(aq)} + \frac{1}{2} H_{2(g)}$ $\quad \Delta H_3{}^\theta = -410$

(iv) $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)}$ $\quad \Delta H_4{}^\theta = -285.8$

Calculate the standard enthalpy of formation of sodium oxide from its element.

b(i) from you answer in (a), state whether sodium oxide is a stable compound or not.

(ii) Give a reason for your answer in b(i) above.

(Ans (a) -787.8$KJmol^{-1}$)

2.a) Write

(i) equation for the hydrolysis of sodium benzoate in water.

(ii) the expression for the hydrolysis constant K_h of sodium benzoate.

b) A solution contains 0.2 moles of sodium benzoate per litre ay 25^0C.

(i) Calculate the pH of the solution

(The hydrolysis constant of sodium benzoate is $1.6x10^{-10}$ $moldm^{-3}$, K_h is 1.0 $x10^{-10}$ $moldm^{-3}$ at 25^0C).

(ii) State the assumptions you have made in b(i) above.

(Ans pH = 8.75)

3. Strontium hydroxide is sparing soluble in water.

a) Write

(i) equation for the solubility of strontium hydroxide in water.

(ii) an expression for the solubility product, Ksp of strontium hydroxide.

b) The solubility of strontium hydroxide is 0.524g per $100cm^3$ of water at 20^0C. Calculate the;

(i) Solubility product of strontium hydroxide at 20^0C and state its units.

(ii) Volume of a 0.01M potassium chromate (VI) solution that must be added to $1dm^3$ of a saturated solution of strontium hydroxide to precipitate strontium chromate (VI).

(Ksp of strontium chromate (VI) is $3.6x10^{-5}mol^2dm^{-6}$ at 20^0C)

c) Sodium hydroxide was added to a saturated solution of strontium hydroxide.

(i) State what happened to the solubility of strontium hydroxide.

(ii) Give a reason for your answer in a(i) above.

(Ans. B(i) 3.18 x10^{-4}mol^{3}dm^{-9}, b(ii) 83.7cm^3)

4. The table below shows kinetic data for the following reaction.

$5Br^-_{(aq)} + BrO^-_{3(aq)} + 6H^+_{(aq)} \qquad 3Br_{2(aq)} + 3H_2O_{(l)}$

Volume of BrO^-_3/cm^3	3.0	4.0	5.0	6.0	8.0	10.0
Time(t)/s	69.0	45.0	35.0	31.0	24.0	18.5

i) Plot a graph of $\frac{1}{t}$ against volume of bromated (V), BrO^-_3.

ii) Determine the order of the reaction with respect to bromated (V) and give a reason for your answer.

iii) Determine the rate constant for the reaction and state its units.

iv) Write equation for the rate of the reaction in terms of concentration of BrO^-_3.

(Ans. b(ii) First order – graph straight line, b(iii) 5.37x10^{-3}S^{-1}cm^{-3}, b(iv) rate = 5.3x10^{-3} [BrO^-_3]

5. Equations for some half-cell reactions are given below.

$SO_4^{2-}{}_{(aq)} + H_2O_{(l)} + 2e^- \longrightarrow SO_3^{2-}{}_{(aq)} + 2\overline{O}H_{(aq)}$ -0.90

$Cu^{2+}{}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ +0.34

a) Write equation for the overall reaction that would take place if the half cells are combined.

b) Calculate the e.m.f of the cell in (a)

c) State whether the cell reaction would be feasible or not. Give a reason for your answer.

(Ans. (b) +1.24V)

6.a) 25.0cm^3 of 0.30M sodium hydroxide was added to 225cm^3 of water. Calculate the pH of the resultant solution.

b) Calculate the mass of sodium ethanoate that should be added to 1dm^3 of a 0.1M ethanoic acid at 25^{0}C to give a solution whose pH is 5.5. State any assumptions made. (The acid dissociation constant for ethanoic acid, Ka = 1.8x10^{-5} moldm^{-3} at 25^{0}C)

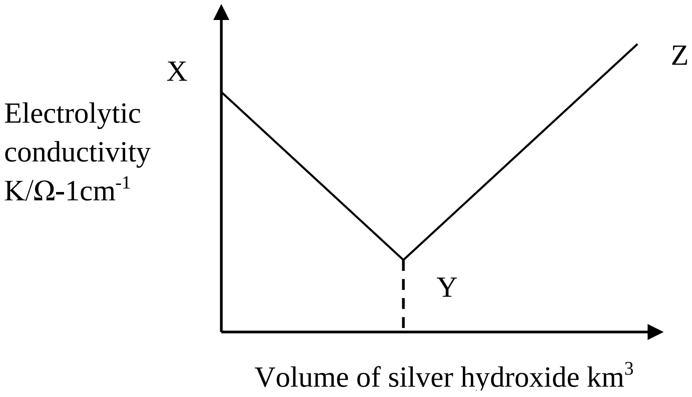
c) Few drops of dilute hydrochloric acid were added to the solution in (b).

(i) State what happened to the PA of the solution.

(ii) Give a reason for your answer in (c)(i)

(Ans. (a) pH = 12.48, (b) 46.65g (c) constant)

7.a) The conductimentric curve for the titration of hydrochloric acid and silver hydroxide is given below.



Explain the shape of the curve (XYZ)

b.(i) The molar conductivities of silver nitrate, potassium nitrate and potassium chloride are 134.0, 143.2 and $140.8\Omega^{-1}cm^2mol^{-1}$ respectively at infinite dilution at 25^0C. Calculate the;

(i) Molar conductivity of silver chloride at infinite dilution at 25^0C.

(ii) Solubility product, Ksp of silver chloride at 25^0C. (The electrolytic conductivity of water and that of a saturated solution of silver chloride are $5.5x10^{-8}$ and $1.934\Omega^{-1}cm^2$ respectively)

(Ans. (b)(i) 131.6 $\Omega^{-1}cm^2mol^{-1}$, b(i)$2.039x10^{-10}mol^2dm^{-6}$)

8.a) Define the term “azeotropic mixture.”

b) Use the data in the following table to draw a well labeled boiling point-composition diagram for the solution(s) of cyclohexane in methanol.

(Boiling point of pure cyclohetane and methanol are 81^0C and 65^0C respectively).

Mole fraction of methanol in		Boiling point of the mixture (Q)
Liquid mixture	Vapour above the mixture	
0.12	0.27	70
0.31	0.47	60
0.50	0.56	55
0.82	0.69	57
0.94	0.83	61

(i) Determine the boiling point and composition of the azeotropic mixture.

(ii) Explain why the azeotropic mixture cannot be separated into pure components by fractional distillation.

(iii) Describe what happens when a liquid containing 2 moles of cyclohexane and 8 moles of methanol is fractionally distilled.

c) Explain why the solution in which a non-volatile solute is dissolved in methanol boils above 65^0C.

9.a) Draw sketch graph to show the change in pH when a 0.1M solution of sodium hydroxide is added in portions to.

(i) $20cm^3$ of 0.1M hydrochloric acid

(ii) $20cm^3$ of 0.1M ethanoic acid

b) Explain the shapes of the curves in (a).

c) $20cm^3$ of 0.1M sodium hydroxide solution was added to $100cm^3$ of 0.1M ethanoic acid. Calculate the pH of the resultant solution.

(Ka for ethanoic acid is $1.75x10^{-5}moldm^{-3}$)

10.a) The label on a bottle of hydrochloric acid reads as follows;

Hydrochloric acid, Relative mass (mass of 1 mole) 36.45
Density $1.18gcm^{-3}$, M/V, 35%

Calculate (i) the morality of acid solution

(ii) The volume of the acid needed to make 0.04M HCl

c) A mixture of sodiumdihydrogen phosphate and disodium hydrogen phosphate acts as a buffer solution. Explain

Reference
Philip Mathew advanced chemistry
Essentials of physical chemistry by B.S Bahl
Advanced chemistry by ramsden

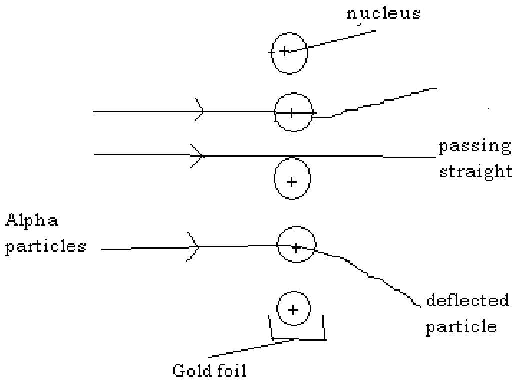
Atomic structure.

An atom is the smallest particle of matter that can take part in chemical reaction. Atoms consist of the fundamental particles and these include, protons, electrons and neutrons. The protons and neutrons are found in the nucleus of an atom while the electrons are found in energy levels.

Distribution of fundamental particles of an atom.

Protons

When alpha particles were subject to a gold foil most passed through an affected but a few were deflected in various directions. Alpha particles were thought to be highly energetic with a high penetrating power and could penetrate several mm thick of a concrete. Their deflection led to a conc that since Alpha P. are truly charged they were coming close to the centre of the atom which is also truly charge. Since only the small fraction war deflected them the centre of the atoms is very small compared to the entire size of the atom. Since protons are positively charged, they should be in the centre or nucleus of an atom. Since most of the alpha p passed through then the space outside the nucleus is occupied by the negatively charged electrons rotating with in orbitals.



(b) Neutrons

Mostly conducted series of experiments by weighing different atoms of different elements and found out that atomic masses are greater than the mass of protons and electron. To make up for exerted mass, the existence of masses was to prostitulate because since the proton mass that is concentrated in the nucleus and they have the same mass as protons with few variations. The nucleus was therefore found to contain protons and neutrons. The number of protons is called proton number/ neutron combine and make up the nucleon number or atomic mass / mass number.

Comparison in properties between protons, Neutrons and Electrons.

Properties	**Protons**	**Electrons**	**Neutrons**
Mass	1	$\frac{1}{1840}$	1
Charge	Positive	Negative	No charge.
Deflection by Electric field.	by negative plate.	by positive plate.	No deflection.

Nuclides and isotopes.

A nuclide is any atom with a specific number of neutron and protons e.g $^{24}_{12}\text{Mg}$, $^{23}_{11}\text{Na}$.

Isotopes there are different atoms of the same element with the same atomic number but if this mass number. Or are atoms of the same number of electrons and protons but of different electrons e.g

$^{35}_{17}Cl$ $^{37}_{17}Cl$ $^{12}_{6}C$

Since the chemical properties are determined by the number of electrons which are the same of in all isotopes. Therefore isotopes have got the same chemical properties. In order to evidence the existence of isotopes in atoms a mass spectrometer is used to detect the various isotopes on a mass spectrometer shown on a screen of recorder.

Radioactivity and nuclear structure.

Radioactivity is the spontaneous disintegration of unstable atoms of an element by giving new stable and fresh nuclides with emission of either alpha particles, Beta or Gamma rays. The element which disintegrates is said to be a radioactive element.

Properties of a radioactive elements

They are very unstable and disintegrate to give new nuclides. They emit rays or particles on disintegration such particles are alpha and Beta particles while the rays are Gram. Radioactivity substances affect photographic materials due When they disintegrate they release a lot of heat energy.

Results of radioactivity charges during radio.

Alpha particles

- These are Helium particles
- They are deflected by magnetic and electric field in direction showing that they are positively charged
- They are identified as H_e particles ($^{4}_{2}He$) having a mass number of 4 and atomic no. 2
- They move with a very high velocity of about $\frac{1}{10}$ of light.

Beta particles

- These are negatively charged particles
- They can also be deflected by magnetic and electric field
- They are identified as fast moving electrons similar to cathode rays
- They have no mass number but have a charge of -1
- They penetrate more than Alpha particles and have the high velocity.
- They are presented as $^{0}_{-1}e$

Gamma rays

- These are neutral particles and are never deflected by either magnetic or electric field.
- They are electromagnetic radiation similar to e x- rays
- They have no charge
- They do not have any mass
- They have a high penetrating power with greater velocity

Detection of radiation.

Use of photographic film

The radiation destroy them

- They cause surfaces for some substances to glow e.g if Beta particles which are fast moving part strike surfaces they cause it to glow.
- They also cause ionization of air molecules e.g when the fast moving electron of Beta collide with air molecule the knock off leaving charged ions.

Radioactive decay equation/reactions

(a) Alpha decay.

- An alpha particles is a Helium nucleus with a mass of 4 and atomic number 2.
- The loss of alpha particles results in reduction in mass number by 4 units and atomic no by 2 units. When an element undergoes alpha decay it produces a new element whose position is 2 places earlier.
- Most of the radioactive isotopes of element with atomic no. greater than 83 undergo alpha decay.

(b) Beta decay.

- Loss of beta particles results in increase of atomic number by one but the mass number remains the same.
- A Beta particle is a fast moving electron with no mass but a charge of -1.
- Beta decays also occurs in isotopes having atomic number over 83.
- The overall effect of Beta decay is to produce an element one place later in the periodic table.

(c) Emission of gamma rays.

- These are fast electromagnetic radiations.
- They have no mass when they are being emit there is no loss in mass or change in atomic number.

Complete the following Nuclear Reactions.

Difference between radioactive reactions and ordinary reactions

- Radioactivity reaction are affected by physical factors e.g pressure, temperature etc while chemical reactions are not affected by them.
- Radioactive reactions involve the nucleus which splits to give flesh nuclides while chemical reactions involve valence shell electrons.
- In nuclear reactions a lot of heat is given off while in chemical reactions give less heat.

Stability of the nucleus

This is a measure or an extent by which it remains dissociated and depends on neutron to proton ratio (n/p ratio) together with bonding energy. The nucleus contains protons and neutrons forming a nucleon. The protons are positively charged and continuously repelling each other with in the nucleus but they never split the nucleus and the nuclide remain stable. In forming the nucleus there is a loss in mass such that the sum of neutrons and protons mass is greater than the mass of the nucleus. The loss in mass is called mass defect which is converted into energy according to the following equation.

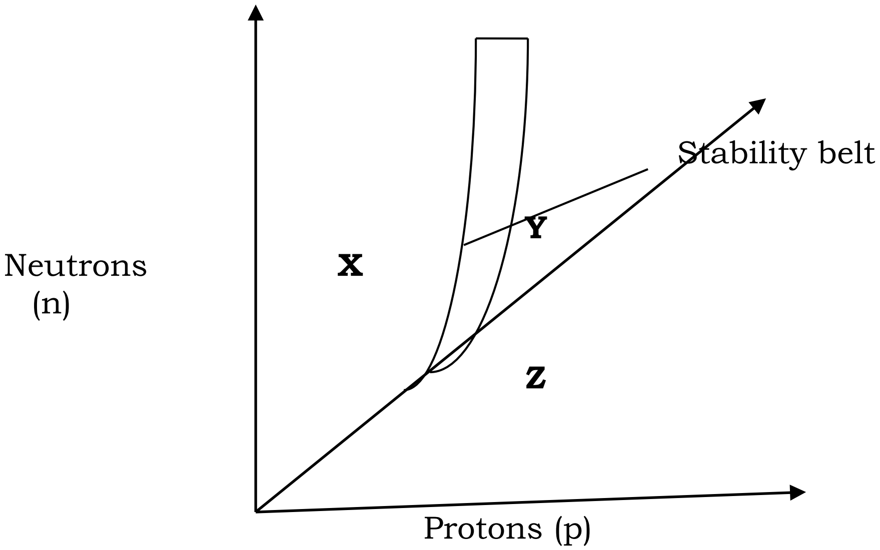
$E = mc^2$ where M is mass, C is velocity of light and E is energy. This energy is called binding energy and it keeps the protons and neutron together hence preventing the nucleus from splitting. The nucleus is said to be stable if it does not undergo radioactive and so does not emit radiation. The nucleus has a very long half time if it is to decay stable nuclei have low atomic numbers usually less than 20 and they have equal number of neutrons and protons such that the ratio $\frac{n}{p} = 1$.

The nucleus is said to be unstable if it is radioactive and emits radiation and particles forming a stable nuclei. For unstable nucleus the half time is very short ranging from fractions, seconds or minutes to a few hours. They have a very high atomic number and the number of neutrons is not equal to the number of protons i.e

$$\frac{n}{p} \neq 1$$

Heavy nuclei with atomic number between 21- 83 are unstable and undergo beta particle emission to form stable nuclei. Heavy nuclei with atomic number greater that 83 are equally unstable and they undergo alpha particle emission and to give stable nuclei.

A plot of neutron-proton number for stable and unstable nuclides.



From the graph above all stable nuclides lie in the region which is shaded

Isotopes X, Y and X are unstable and they can become stable by approaching the stability bell. X has no excess neutrons with few protons. To approach the stability belt it reduces on the number of neutrons and excess on the no of proton.

The neutron splits into an electron and a proton

$${}^{1}_{0}n \longrightarrow {}^{1}_{1}H + {}^{0}_{-1}e$$

This reduces on the number of neutrons but increases the number of protons. The electron produced as a beta particle in a process called beta particle emission. Nuclide Y has an excess of protons and neutrons which combine to form alpha particles

$$2\left({}^{1}_{1}H\right) + 2\left({}^{1}_{0}n\right) \longrightarrow {}^{4}_{2}He$$

This reduces both protons and neutrons in alpha particles emitted. Z has an excess of neutrons and protons. To attain stability it reduces on the number of protons in its nucleus but increasing the number of neutrons. It does this through capturing an electron and liberating a neutron.

$${}^{1}_{1}H + {}^{0}_{-1}e \longrightarrow {}^{0}_{1}n$$

Laws of radioactivity.

1. Radioactive nuclides disintegrates spontaneously giving new and flesh element
2. The disintegration of an element is as a result of either emission of an alpha particle or Beta or Gamma rays.
3. The rate of disintegration of a nuclides not affected by physical factors e.g concentration, temperature, pressure etc
4. The rate of disintegration of an element depend on the initial amount it present at time (t).

Decay law

It states that the rate of decay is directly proportional to the number of un decayed atom or un decayed mass of a given sample of an element.

Ie Rate of decay ∝ un decayed atoms

$\frac{-dN}{dt} \propto Nt$ -------------(1)

$\frac{-dN}{dt} \propto Nt$ -------------(2)

Where x is decay constant

$-\int \frac{dN}{Nt} = xdt$

Integration

$-\int \frac{dN}{Nt} = x\int dt$

In $Nt = \lambda t + c$--------------------(3)

If $t = 0$, $\lambda t = No = C$

Substituting in equation (3) we get

In $Ne = \lambda E$ – in No

In $Nt + No - \lambda t$

Therefore $(\frac{No}{Nt}) = \lambda t$----------------(3)

In term of logarithms to base ten

From in $(\frac{No}{Nt}) = \lambda t$

$(\frac{No}{Nt}) = e$

Taking log10 on either sides

$\text{Log } 10\ (\frac{No}{Nt}) = \text{Log}_{10}{}^{\text{ext}}$

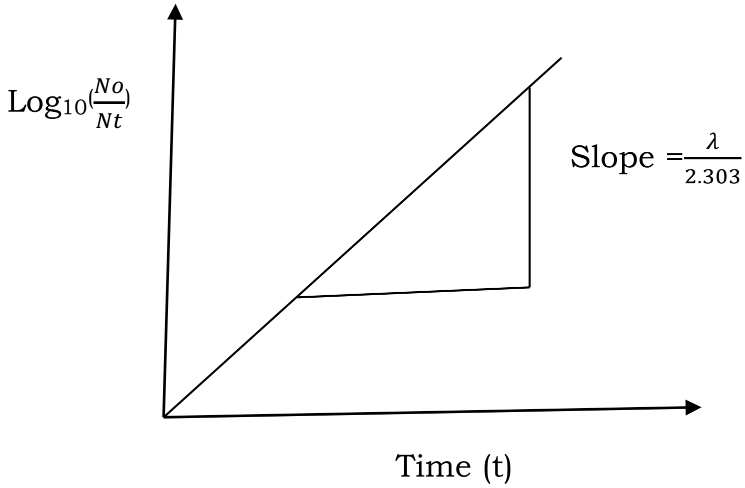
$\log 10\ (\frac{No}{Nt}) = \lambda t \times \frac{1}{\log 10}$

$\log 10\ (\frac{No}{Nt}) = \frac{\lambda t}{log^{10}}$

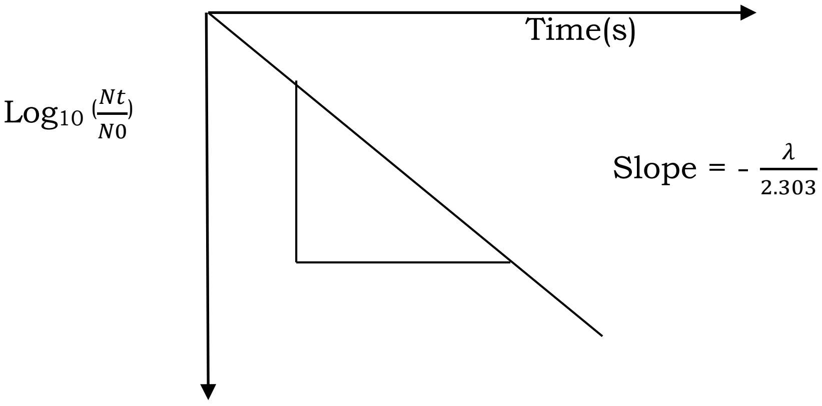
$\text{Log}_{10} \times \log_{10} (\frac{No}{Nt}) = \lambda t$

$2.303 \log_{10} (\frac{No}{Nt})\ \lambda t$

If a graph of $\log_{10} (\frac{No}{Nt})$ is plotted time, a straight from the origin is obtained with a positive gradient equal to $\frac{\lambda}{2.303}$ as shown below.



However when a graph of $(\frac{No}{Nt})$ is plotted against time, a straight line graph from the origin but with a negative gradient is obtained as shown below



Deriving an expression for half **life.**

Half life is the time taken for half of the initial amount of a substance to disintegrate to and remains constant regardless of the initial amount.

From $\quad$ In $(\frac{No}{Nt}) = \lambda t$

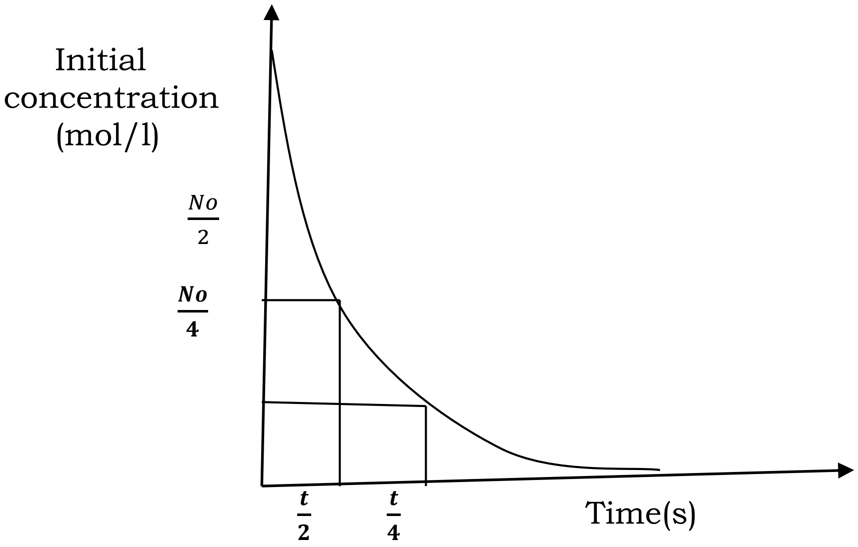
If $t = t½$, $No = ½\ No$

In $(\frac{No}{2No}) = \lambda t½$

In $(\frac{2\,No}{No}) = \lambda t½$

In 2 = $\lambda t½$, $t½ = \frac{0.693}{\lambda}$

If a graph of initial mass/ concentration is plotted against time, a curve which does not pass through the origin is obtained and the half life of the given sample can be determined.



Examples.

1. A compound W was found to contain a radioactive X which emits alpha particles and has half life of 5720 years. Calculate the % of X that would remain w after 228800 years.

Solution.

$t_{½}$ =5720 years.

t=22880 years.

No =100%

Nt= ?

$\frac{No}{Nt} = 2(\frac{t}{\frac{t1}{2}})$

$\frac{100}{Nt} = \frac{16}{1}$

Nt = 6.25%

2. (a)Define the term radio activity.

- *Radio activity refers to the spontaneous disintegration of an unstable nucleus to form a stable nucleus with emission of radiation like alpha, beta gamma rays.*

(b)Name three types of radiation emitted during radioactivity. State how they affected by nucleus of the radio isotope.

- Alpha particles

- **Effects**; when the nucleus emits an alpha particle, it loses 2 electrons and 4 neutrons hence decreases the atomic number by 2 units and the mass number by 4units and it is converted to another element of a lower atomic number by 2 units.
- Beta particles.
- **Effects;** the atomic number increases by 1unit but the mass number remains the same; the atom is converted to another with a higher atomic number by 1 unit.
- Gamma rays.
- **Effects;** the emission of gamma rays by the atom does not affect the atomic number and mass number but only energy is given out.

(c)The table below shows the mass of protactinium $^{234}_{91}Pa$ varies with time.

Mass of Pa	60.0	38.5	26.0	17.2	11.1
Time in Sec	0	40	80	120	160

(i) A graph of mass of Pa against time
(ii) Use the graph to determine mass Pa
(iii) Determine the time of 8g of Pa to decay up to 1 g

Solution.

from in $(\frac{No}{Nt}) = \lambda t$

in$(\frac{8}{1}) = 0.0108$ t

in $\frac{(8)}{0.0108} = \frac{0.0108t}{0.0108}$

t = $(\frac{2.0794}{0.0108})$

t = 192.54s

(d) The data below shows the result of the disintegration of element y.

No	**Nt**	**t(s)**
0.01	0.01	0
0.00999	0.009	30
0.0985	0.008	60
0.0997	0.0073	90
0.01000	0.0066	120
0.00989	0.0053	180
0.01010	0.0044	240
0.0975	0.0028	360
0.01056	0.0020	480
0.0104	0.0013	600

(i) Plot a graph of N_t against time (t).
(ii)Use the graph to determine half life of the element.
(iii)Decay constant of radioactive element Y

(iv) Plot a graph of log10 ($\frac{No}{Nt}$) against t.

Use it to determine.

(v) Decay constant of Y

(vi) Half life of Y

Solution

No	Nt	($\frac{No}{Nt}$)	Log10($\frac{No}{Nt}$)	($\frac{Nt}{N0}$)	Log10($\frac{Nt}{N0}$)	t(sec)
0.01	0.01	1.000	0.000	1	0	0
0.00999	0.009	1.110	0.045	0.900	-0.046	30
0.0985	0.008	12.31	0.090	0.081	-1.092	60
0.0997	0.0073	1.377	0.137	0.073	-1.137	90
0.01000	0.0066	1.515	0.180	0.660	-0.180	120
0.00989	0.0053	1.867	0.271	0.536	-0.271	180
0.01010	0.0044	2.295	0.360	0.436	-0.361	240
0.0975	0.0028	34.821	1.542	0.029	-1.538	360
0.01056	0.0020	5.280	0.723	0.189	-0.724	480
0.0104	0.0013	8.000	0.903	0.125	-0.903	600

(i) See on the graph.

(ii) Half life = 64 years

(iii) $t½ = \frac{0.613}{\lambda}$

$t½ = \frac{0.693}{\lambda}$

$\frac{64}{1} = \frac{0.693}{\lambda}$

$\frac{64\lambda}{64} = \frac{0.693}{64}$

λ = 0.0108

(iv) See on the graph.

(v) $t_{½} = 168$

but $t½ = \frac{1}{\lambda}$

$168 = \frac{0.693}{\lambda}$

$\frac{168\lambda}{168} = \frac{0.693}{168}$

λ = 0.00413

(vi) from in ($\frac{No}{Nt}$) = λt

in($\frac{8}{1}$) = 0.0413 t

in $\frac{(8)}{0.0108} = \frac{0.0108t}{0.0108}$

t = ($\frac{2.0794}{0.0108}$)

t = 192.54s.

Exercise.

1. 1000g of a related was allowed to decay to 125g after 6 min. calculate the decay constant and hence the half life of radioactive element.

   Solution.

- No= 1000g, Nt= 125g, t= 6minutes.
  In ($\frac{No}{Nt}$) = λt.
  In ($\frac{1000}{125}$) =6λ.
  λ =in ($\frac{1000}{125x\ 6}$) =0.3466min^{-1}
  t$_{½}$ = $\frac{in\ 2}{\lambda}$, t$_{½}$ =$\frac{in\ 2}{0.3466}$, t$_{½}$ =2minutes.

2. If the decay constant of a radium is 1.356 x 10^{-11}/sec, calculate the time taken for 10% of the sample decay.
   Solution.
   - λ = 1.356x10^{-11} s^{-1}, 10% decayed and 90% remained.
     In($\frac{N0}{Nt}$) = λt, in($\frac{100}{90}$) =1.356x10^{-11}
     t= in($\frac{100}{90}$) x $\frac{1}{1.356x10^{11}}$, t=7.7699x10^{9}s.
3. The half life of a radioactive element Y is 8days. Determine the time taken for 32g of Y to decay to 2g.
   Solution
   - No= 32g , Nt = 2g, t$_{½}$= 8days
     ($\frac{No}{Nt}$) =2$^{(\frac{t}{t½})}$, $\frac{32}{2}$=2$^{(\frac{t}{8})}$
   Log 16 = $\frac{t}{8}$ log2, t= $\frac{8log16}{log2}$, t=32days.

Uses of radioactivity;

- **Carbon dating**

The radioactivity of carbon 14 in archeological remains can be measured. The radio activity of a sample of a similar object can that is living can be determined. If the alf life of carbon 14 is known, then the values are used to calculate the age of the archeological.

3.303 log$_{10}$ ($\frac{No}{Nt}$) = λt

where N – is the number of radiation emitted per min.
λ = is the decay constant
t = is the time in years since the death of the object
N.B: the radioactivity of the 14C is measured by Geiger Muller which records the radiation of the sample in 1 min by making pulses or clicking on an electronic counter.

Examples.

1. Freshly killed piece of wood give 15 counts / min/ gram of carbon 14. An Egyptian mummy gives 9.5 counts/g/min of 14C .How old is the mummy case if the half of 14 C if the half life of carbon -14 is 5600years.

λ = t ½ = $\frac{1n^2}{\lambda}$
λ = $\frac{1n^2}{t\ ½}$
λ = $\frac{0.69}{5600}$
λ = 0.00012378yr^{-1}
2.303 log$_{10}$($\frac{No}{Nt}$) =λt

$$t=\frac{2.303log10^{(\frac{No}{Nt})}}{\lambda}$$

$$t = \frac{2.303log10^{(\frac{15}{9.5})}}{1.2378x10^{-4}}$$

t = 3690.75years.

2. A sample of wood from an Egyptian tomb give disintegration of 8.25min^{-1}g^{-1} if the sample of the living gives 15.3 g/min/g of 14C. Determine the age of Egyptian tomb.

Solution.

No= 8.25min^{-1}g^{-1} , No = 15.3min^{-1}g

From $\lambda = \frac{in2}{t½}$

$\lambda = \frac{0.69}{5600}$= 1.2378x10^{-4}.

2.303log$_{10}$ $(\frac{No}{Nt})$ = λt.

$$t= \frac{2.303log10^{(\frac{15.3}{8.25})}}{1.2378x10^{-4}}$$

t= 2672years.

- **It is used to treat cancer.** Cancerous tissues are destroyed by radioactivity in preference for healthy carbon 60 which emits gamma rays of 5 yrs is used.
- **Sterilization of surgical instruments**. Surgical instruments are effectively sterilized by use of radioactivity by boiling.
- **Detecting faults in metal sheet**. The thickness of metal sheet is continuously checked by the radio activity which is detected through the meal sheets.
- **Detecting underground leakages in water and oil pipes.** The level of the radioactivity on the surface can be monitored by the radioactive substance with in water being moved within the pipe.
- **Detect engine wear**; they can also be detected by measuring the rate of radioactivity I the engine oil. Normally piston rings that are made up of radioactive are used.
- **Investigating the mechanism of the reaction** e.g in esterification i.e

$$\underset{Acid}{RCOOH} + \underset{alcohol}{ROH} \longrightarrow \underset{Ester}{RCOOR} + H_2O$$

In this reaction, the O_2 in H_2O comes from either an acid or an alcohol and to prove where O_2 come is labeled H_2O and the reaction is given time to produce. On test of radioactivity of H_2O molecule given out it's found to be not radioactive. This can now lead to a conclusion that O_2 comes from acid.

Investigation of Bio chemical reaction e.g photosynthesis

$$CO_2 + H_2O \longrightarrow CH_2O + O_2$$

The O_2 of CO_2 is labeled radioactive O_2-18 and supplied to plants to carry out photosynthesis. The O_2 then given is then tested by radioactivity and its to be non radioactive. This leads to a conclusion that the O_2 evolved during photosynthesis is comes from water.

NUCLEAR FUSION AND NUCLEAR FUSION.

Nuclear fusion.

This is a process by which light nuclides combine at a very high temperature to form a heavy nuclide. This process is a companied by high amount of energy and some radiations are emitted e.g protons and neutrons.

The hydrogen bond is obtained by fusing 2 hydrogen nuclei at very high temperature of at about 10^{7k} and high amount of energy are release during fusion and this can cause explosion. The sun obtains its energy from hydrogen atoms and the sun's temperature is about $10,000,000^{0}C$ which is enough H_2 atoms to fuse.

Nuclear fission.

This is a process by which unstable nuclide is bombarded with a nuclide to disintegrate and form stable nuclides and other particles being emitted. This process is accompanied by loss of large of amount of energy. For example Uranium – 238 undergoes nuclear fission when combined with a neutron. This process produces 3 more neutrons which can accelerate the reaction. The nuclear fission of Uranium -238 is shown by the following chain reaction.

$$ {}^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{98}_{38}Sr + {}^{138}_{54}Xe + 3\,{}^{1}_{0}n $$

Uses of uranium.

- Uranium – 238 is used in atomic bombs.
- It is also used in nuclear reaction to produce thermal electricity.

Atomic emission spectrum.

When atoms of elements are subjected to electrical discharge or heated, it is observed that the element emits electromagnetic radiation which can be ultra violet light or infra red or visible spectrum. This is caused by the atoms of the element absorbing some energy and then emitting it inform of electromagnetic radiation. When the radiation is passed through a spectrometer, it is observed that un like sun light which is composed continuous spread of colours, it forms definite lines on a screen with a black back ground. In the visible part of spectrum, coloured lines are observed and each colour has a definite wave length of radiation. The mere fact that it is a line spectrum and not a continuous spectrum, it indicates that the atoms contains energy levels to which electrons move when they are excited and therefore they should absorb certain amount of energy is called **quanta of energy**. When an electron absorbs a quantum of energy, it moves from its ground energy level to higher energy level and on coming back it will emit the same amount of energy of specific frequency and wave length. the energy of radiation can be calculated using Planck's equation.

$DE = hv$ where DE is change in energy, h- is constant = 6.626×10^{8} ms^{-1}

$v = \frac{C}{\lambda}$ where C – speed of light and λ is wave length of radiation.

For most elements, the radiations are in invisible spectrum and each element produces a distinct colour of light and this enables us to identify a number of metal ions by their characteristic flame test colours e.g sodium imparts yellow colour when burnt in air, potassium gives purple/lilac, Calcium gives brick Red colour, Barium gives apple green colour.

The emission spectrum of atom elements provides evidence that electrons are distributed around the nucleus in various energy levels. Electrons occupying the same level are said to be in the same quantum shell because they absorb same quanta of energy to make them move from one level to another. The quantum shells are denoted by Principle quantum number which are 1, 2,3, 4 ……..and so on. If n=1, this means the 1st quantum shell near the nucleus. If n = 2, it means the 2nd shell etc. when we use spectrometers of high resolving power to analyze radiations, it is observed that the electron from the same quantum shell have slightly different energy and their positions in quantum shells are called sub shells/ sub energy levels/ orbitals. The orbitals are numbered using s, p, d and f. The s – orbital accommodates maximum of 2 electrons, p-orbital contains maximum of 6 electrons, d-orbital accommodates maximum of 10 electrons and f accommodates maximum of 14 electrons. Before the electrons occupy the orbitals, the following rules should be followed.

- **Paul's exclusion principle**; *it states that an orbital can take a maximum of two electrons on conditions that these electrons have opposite spins so that the magnetic effect is reinforced.*
- **Hundi's rule of maximum multiplicity;** *it states that when electrons are present in a number of degenerate orbitals (i.e orbital's of the same energy), they occupy all orbital's singly first with parallel spins pairing up in any one orbital occurs.*

An orbital *is a region in which there is greater probability of finding a particular electron although they are not confined in those particular regions.*

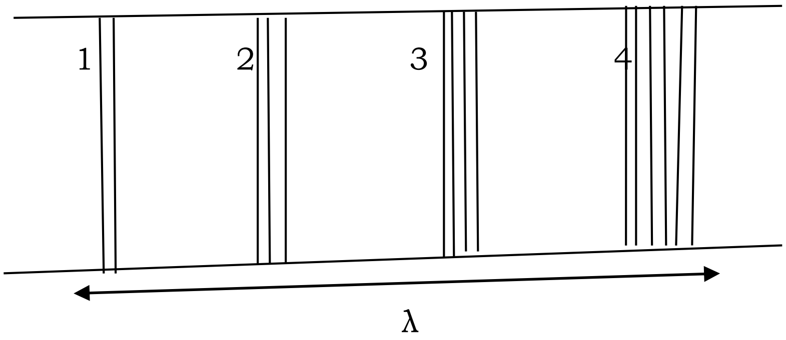
Hydrogen emission spectrum.

Emission spectrum of hydrogen atom has been explained by Bohr after careful observation he made. He suggested that despite hydrogen having one electron it has many energy levels in the space outside the nucleus. These energy levels have quantum numbers 1,2,3,4……or letters K,L,M,N. He suggested a single electron of hydrogen rotates with in energy levels. These energy levels in which the electron rotates are called "**permissible energy levels**" in which the electron does not absorb or emit radiations.

Under normal circumstance the electron will occupy an orbital near the nucleus and it is said to be in the ground state. The electron does not emit energy because it is within the permissible energy levels. When the atom is given sufficient energy, the electron "jumps" from its ground state to higher energy by absorbing energy. In this state the electron is said to be excited or promoted. In the excited state the atom us said to be unstable and would wish to get its electron back to the ground state in order to gain its stability.

The electron may return to the ground state at once and it may do so in the number of stages. In the process the electron emits energy of excitation which appears as radiation or coloured bands on the screen. When electron returns to the 1st quantum shell i.e n=1, regardless of energy level where it is coming from, it emits radiation as a line on the screen in the Lyman series. If it comes back to the 2nd quantum shell i.e n = 2, it forms Balmer series and if the electron comes to the 3rd shell i.e n=3, it forms Paschen's series and if it comes to the 4th quantum shell i.e n=4, it forms Bracket's series. This is shown on the diagram below;

The hydrogen spectrum can be represented as follows.



There are so many lines in the H_2 spectrum but the most important ones are from 1-4 which include lines in the Lyman. Balmer, Paschen and Brucket series. The lines get closer together as you move from the nucleus to decrease in the wave length of radiation emitted and eventually line emerge into a continuous spectrum. At this point the radiation emitted is in the invisible range and this one occurs at ionization when the electron is completed removed from on atom forming a gaseous ion. The emission spectrum of H_2 provides evidence for existence of energy levels within the H_2 atoms because of several lines each of which shows a particular radiation emitted. The energy levels have different wave lengths when an electron returns from them justifying the existence of different energy Levels. the wave lengths of the radiation emitted is given by;

$\frac{1}{\lambda} - Rh\ (\frac{1}{n1^2} - \frac{1}{n2^2})$ where Rh is Rydberg's constant, n^1 and n^2 are the energy levels.

In the lyman series n_1=1,n_2=2,3,4……etc
In Balmer series n_1 = 2, n_2 = 3, 4, 5..etc
In Paschen n_1 = 3 n_2 = 4, 5, 6…………etc

Examples.

1. Calculate the radiation emitted in Lyman's series if the electron turns from n=4, Rh = 1.097373 x $10m^{-1}$

Solution

From $n_1 = 1$, $n_2 = 4$

$\frac{1}{\lambda}$ = Rh $(\frac{1}{n1^2} - \frac{1}{n2^2})$

$\frac{1}{\lambda}$ = 1.097373×10^7 $(\frac{1}{1^2} - \frac{1}{4^2})$

1.097373×10^7 $(1 - -\frac{1}{4})$

$\frac{1}{\lambda}$ = 1.097373×10^7 $(\frac{3}{4})$

$\frac{1}{\lambda}$ = $1.097373 \times 10^7 \times 0.75$

$\frac{1}{\lambda}$ = 0.82302975×10^7

λ = $(\frac{1}{0.82302975 \times 10^7}) \times 10^9$ =121.5nm.

2. Calculate the radiation emitted in Balmer series if the electron turns from n=3 to n_2, Rh = 109678 m^{-1}

Solution.

$\frac{1}{\lambda} = Rh\ (\frac{1}{n2} - -\frac{1}{n^2})$.

$\frac{1}{\lambda} = 109678(\frac{1}{2^2} - -\frac{1}{3^2})$.

$\frac{1}{\lambda}$ =109678x0.138888888

$\frac{1}{\lambda}$ = 15233.05556, λ =$6.565 \times 10^{-5} \times 10^9$,=65647nm.

Similarly the energy of the radiation emitted from the higher energy level to the lower energy can be calculated as;

E = $h\upsilon$. Where h= plank's constant, V – speed of light given by $V = \frac{C}{\lambda}$

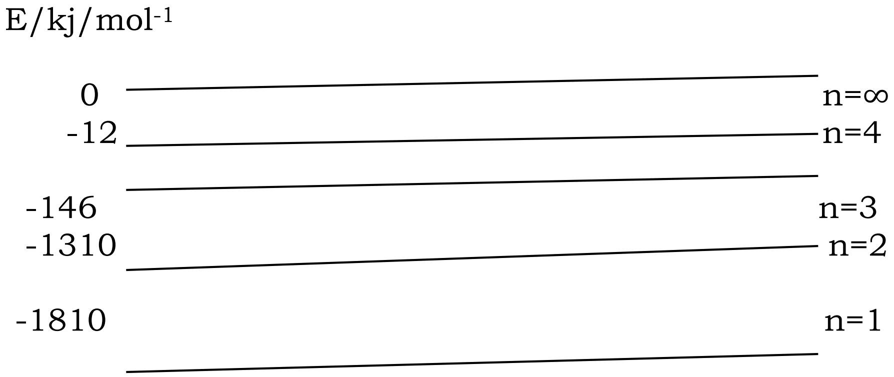
$\therefore$ E = $\frac{hC}{\lambda}$

If an electron jumps from n_1 to n_4 and the energy in n_1 is E_1 and n_4 is E_4 then the energy of excitation is given by $(E_1 - E_4) = \frac{hC}{\lambda}$.

Similarly the energy of radiation emitted when it jumps from n_4 to n_1 is given by $(E_4 - E_1) = \frac{hC}{\lambda}$.

Examples.

1. The diagram below represents some energy levels of the hydrogen spectrum.



(a) If an electron is in the ground state, calculate the maximum of amount of energy for its maximum ionization.

Solution.

E_1=-1310Kjmol^{-1}, E_∞ =okjmol^{-1}

$\Delta E = E_\infty - E_1$

= 0- $^{-}$1310

= +1310kjmol^{-1}.

(b) If the electron is in the 3rd quantum shell, n= 3, what is the frequency of radiation it can emit when coming back to the ground state h=3.99 x 10^{-13}Kjs^{-1}.

Solution.

E_3- E_1 = hv

(-145- $^{-}$1310) = 3.99x10^{-13} x V

V = $\frac{1165}{3.99X10^{-13}}$

=2.92X10^{15}s^{-1}

2.(a) Calculate the λ of light emitted in;

(i) Balmer series when the electron returns from n=5

$\frac{1}{\lambda}$ =Rh ($\frac{1}{n^2}$ – -$\frac{1}{n^2}$).

$\frac{1}{\lambda}$ = 1.097373x 10^7 ($\frac{1}{1^2}$ -$\frac{1}{5^2}$).

$\frac{1}{\lambda}$ =1.097373x10^7 x 0.96

λ=9.492x10^{-8}

(ii) Balmer series when the electron returns from n=5

$\frac{1}{\lambda}$ =Rh ($\frac{1}{n^2}$ – -$\frac{1}{n^2}$).

$\frac{1}{\lambda}$= 1.097373x10^7 ($\frac{1}{2^2}$ -$\frac{1}{5^2}$).

$\frac{1}{\lambda}$ =1.097373x10^7x0.21

λ=4.34x10^{-7}

(b)What is the energy of radiation emitted in (a) above in those series velocity of light= 3 x10^{-8} m/s.

Solution.

(i) E =hv, v=$\frac{c}{\lambda}$, E= $\frac{hc}{\lambda}$

E=$\frac{3.99x10^{-13}\,x3x10^8}{9.49x10^{-8}}$

=1261.33kjmol^{-1}

(ii) E =hv, v=$\frac{c}{\lambda}$, E= $\frac{hc}{\lambda}$

E=$\frac{3.99x10^{-13}\,x3x10^8}{4.34x10^{-7}}$

= 275.81kjmol^{-1}

BONDING AND STRUCTURE

Atoms combine so as to acquire a stable structure similar to those of noble gases and its either by transfer of electrons or by sharing them.

TYPES OF BONDS

- Ionic/ Electrovalent/ heterpolar. It occurs between electropositive and electronegative elements
- Covalent / Homopolar. It occur between electronegative elements
- Metallic. It occur between metallic elements
- Dative/ Coordinate bond
- Hydrogen bond
- Van-der-Waals bonds

ELECTROVALENT BONDING

This arises when there is transfer of one or more electrons from one atom to another
It is mainly between electropositive and electronegative elements. Formation of ions depends on loss or gain of electrons which depends on

I. Atomic number of an atom
II. Size of an atom
Size of an atom dterimines the distance between the electron and the nucleus, the further away from the nucleus, the less nuclear attraction hence a smaller ioinisation energy.
III. Ionization energy: the lower the ionization the mostly the loosely held an electron is and the more electropositive the element. E.g. the first I.E of Na is 495KJmol$^{-1.}$ Therefore it is easy to form Na^{+} and Na^{2+}
IV. Electron affinity; The electron affinity value indicates the ease with which an atom forms an ion, the greater the value of the electron affinity the easier is the ion formed

$F + e \longrightarrow F^{-}$ -44.2KJmol^{-1}

$Cl + e \longrightarrow Cl^{-}$ -389.0KJmol^{-1}

$Br + e \longrightarrow Br^{-}$ -364.0KJmol^{-1}

Therefore F^{-} is easily formed and its more electronegative

V. Polarization. When a cation approaches an anion closely. It forms an electron cloud due to electrostatic forces. At the same time the cation tends to repel the positively charged nucleus of the anion.

The distortion of the electron cloud of the anion by the cation is called ionic polarisation. The ability of the cation to polarize a nearby anion is called polarising power (polarisability)

FACTOR WHICH AFFECT PORALISATION OF ANION (FAJANS RULE)

Charge on the anion or cation

The greater the charge on the cation the greater its polarising effect

Ion (charge)	Na^+	Mg^{2+}	Al^{3+}
Ionic radius (nm)(r)	0.095	0.065	0.05
Polarising power ($\frac{z}{r}$)	10.5	30.7	60
Melting point of anhydrous chloride/^oC	801	712	180

Polarising power $\frac{z}{r}$ meseasures in the order Na^+<Mg<$^{2+}$<Al^{3+}

- Al^{3+} has a very high polarising power (60). It exerts the strongest polarisation in $AlCl_3$ resulting in a high degree of covalency because $AlCl_3$ becomes more covalent, its melting point is the lowest.
- Na+ has a low polarising power in NaCl, it remains essentially as ionic compound with very high melting point
- Similarly polarising of an ion increases with increase in its negative charge (anion repels its outer most electrons strongly and effectively).

This explains why an oxide of an oxide a metal cation is more polarized than its fluoride. Hence for a particular ion, fluorides have higher melting points than the oxides e.g. CaO has a lower MP than CaF_2

Ionic radius of the ion

Polarising power of a cation increases with decrease in the radius of the cation e.g. the polarising power of the group II cation decreases from Be^{2+} to Ba^{2+} due to increase in the radius ie compounds formed by group II cations become more ionic down the group. Polarisation is important in explaining the diagonal relationship of elements in the periodic table

	I	II	III	IV
Period 2	Li	Be	B	C
Period 3	Na	Mg	Al	Si

Diagonal relationship is the similarity in the chemistry of two element which are diagonally positioned in adjacent group of the periodic table

The chemistry of Li is similar to that of Mg

Moving across from Li to Be there is an increase in charge and decrease in size hence an increase I polarising power.

And moving down from Li to Na the charge remains the same but size hence an increase hence a decrease in polarising power.

Moving along period 3 from Na to Mg there is an increase in polarising power due to increase in charge but the polaring power of Mg is less than that of Be due to increase in size and its approximate to that of Li hence Li amd Mg have similar polarising power and thus similar chemistry.

	Radius	charge	Polarising power
Be2+	0.031	2	60
Al3+	0.05	3	60

The chemistry of Be and Al are similar in some of the properties like,

Both $BeCl_2$ and $AlCl_3$ are covalent

Both Be and Al are amphoteric

Ie $Be_{(s)} + 2H_{(aq)} + 4H_2O_{(l)} \longrightarrow \{Be(H2O)_4\}^{2+} + H_{2(g)}$

$Al_{(s)} + 3H_{(aq)} + 6H_2O_{(l)} \longrightarrow \{Al(H_2O)_6\}^{3+} + \frac{3}{2} H_{2(g)}$

$Be_{(s)} + 3OH^- + 4H_2O_{(I)} \longrightarrow \{Be(OH)4\}2- + \frac{1}{2}H_{2(g)}$

$Al_{(s)} + 4OH^- + 6H_2O_{(I)} \longrightarrow \{Al(OH)_6\}^{3-} + H_{2(g)}$

The carbides of Be and Al form methane on hydrolysis.

$Be_2C_{(s)} + 2H_2O_{(I)} \longrightarrow CH_{4(g)} + 2BeO_{(s)}$

$Al4C3(s) + 6H2O(s) \longrightarrow CH_{4(g)} + 2Al_2O_{3(s)}$

PROPERTIES OF IONIC COMPOUNDS

- Are made of ions
- Are soluble in water

- Are electrolytes in solution or molten state
- They have strong electrostatic forces of attraction between the positively charged ions thus they have very high melting and boiling points

COVALENT BONDS

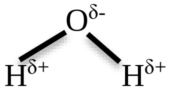
Its formed between the electronegative elements sharing the contributed electrons for two electrons from the different atoms to be shared must be unpaired and have opposite spins. When a covalent bond is formed between different atoms, electrons are not equally shared due to differences in electro negatively of the two atoms e.g. HCl, Cl is more electronegative than H. it tends to pull the bonding electrons towards itself acquiring a partial negative charge while H gets a partial positive. $H^{\delta+}$ and $Cl^{\delta+}$

HCl is said to be being electronic dipole called electric dipole movement given as

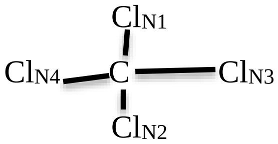
$$N = d \times q$$

Where d= distance between atoms

q= charge on the ion



In some compounds it may be polar but the overall is unpolar because of symmetrical distribution e.g. CCl_4



$\mu_1=N_2$, $N_3=N_4$

There is equal and opposite dipoles moment hence non polar $\mu_1=\mu_2$

PROPERTIES OF COVALENT COMPOUNDS

- Consists of discrete molecules not ions
- Are mainly gases and liquids with very low melting and boiling point
- Are non-electrolytes
- Are insoluble in water but dissolve in non-polar solvents like benzene

DATIVE /CO-ORDINATE BONDS

~THE END~