Ministry of Education
and Sports

THE REPUBLIC OF UGANDA

HOME-STUDY LEARNING

SENIOR

6

CHEMISTRY

August 2020

NCDC
NATIONAL CURRICULUM
DEVELOPMENT CENTRE

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NATIONAL CURRICULUM
DEVELOPMENT CENTRE

FOREWORD

Following the outbreak of the COVID-19 pandemic, government of Uganda closed all schools and other educational institutions to minimize the spread of the coronavirus. This has affected more than 36,314 primary schools, 3129 secondary schools, 430,778 teachers and 12,777,390 learners.

The COVID-19 outbreak and subsequent closure of all has had drastically impacted on learning especially curriculum coverage, loss of interest in education and learner readiness in case schools open. This could result in massive rates of learner dropouts due to unwanted pregnancies and lack of school fees among others.

To mitigate the impact of the pandemic on the education system in Uganda, the Ministry of Education and Sports (MoES) constituted a Sector Response Taskforce (SRT) to strengthen the sector's preparedness and response measures. The SRT and National Curriculum Development Centre developed print home-study materials, radio and television scripts for some selected subjects for all learners from Pre-Primary to Advanced Level. The materials will enhance continued learning and learning for progression during this period of the lockdown, and will still be relevant when schools resume.

The materials focused on critical competences in all subjects in the curricula to enable the learners to achieve without the teachers' guidance. Therefore effort should be made for all learners to access and use these materials during the lockdown. Similarly, teachers are advised to get these materials in order to plan appropriately for further learning when schools resume, while parents/guardians need to ensure that their children access copies of these materials and use them appropriately.
I recognise the effort of National Curriculum Development Centre in responding to this emergency through appropriate guidance and the timely development of these home study materials. I recommend them for use by all learners during the lockdown.

Alex Kakooza
Permanent Secretary
Ministry of Education and Sports

ACKNOWLEDGEMENTS

ABOUT THIS BOOKLET

Dear learner, you are welcome to this home-study package. This content focuses on critical competences in the syllabus.

The content is organised into lesson units. Each unit has lesson activities, summary notes and assessment activities. Some lessons have projects that you need to carry out at home during this period. You are free to use other reference materials to get more information for specific topics.

Seek guidance from people at home who are knowledgeable to clarify in case of a challenge. The knowledge you can acquire from this content can be supplemented with other learning options that may be offered on radio, television, newspaper learning programmes. More learning materials can also be accessed by visiting our website at www.ncdc.go.ug or ncdc-go-ug.digital/. You can access the website using an internet enabled computer or mobile phone.

We encourage you to present your work to your class teacher when schools resume so that your teacher is able to know what you learned during the time you have been away from school. This will form part of your assessment. Your teacher will also assess the assignments you will have done and do corrections where you might not have done it right.

The content has been developed with full awareness of the home learning environment without direct supervision of the teacher. The methods, examples and activities used in the materials have been carefully selected to facilitate continuity of learning.

You are therefore in charge of your own learning. You need to give yourself favourable time for learning. This material can as well be used beyond the home-study situation. Keep it for reference anytime.

Develop your learning timetable to ca ter for continuity of learning and other responsibilities given to you at home.

Enjoy learning

PHYSICAL CHEMISTRY

TOPIC: 1.0 PHYSICAL EQUILIBRIA

GENERAL OBJECTIVE: The learner should be able to comprehend the concept of interconversion of phases due to changes in the physical conditions and its applications.

LESSON 1.1 Systems, Phases and components

By the end of this lesson, you should be able to;
- explain the concept of physical equilibrium
- distinguish between the terms, phases, components and systems.
- discuss the characteristics of a system, phases and component
- mention different types of component systems
- give examples of one component system.
- explain the cooling curves for pure substances
- explain the term   phase diagram
- draw phase diagrams for a one component system
- explain what the different regions of a phase diagram represent.

INTRODUCTION

PHYSICAL EQUILIBRIA
It deals with balance of phases. A phase is any homogenous and physical distinct part if systems which can be separated from other part by definite boundary surface e.g. miscible liquids have one phase, immiscible liquids have two phases while water can exist in three phases. The word phase can replace the word state.

Phase equilibrium diagrams.
A phase equilibrium diagram is one that shows the relationship between the vapour pressure of a substance and temperature.

A phase equilibrium diagram for abnormal substance such as water
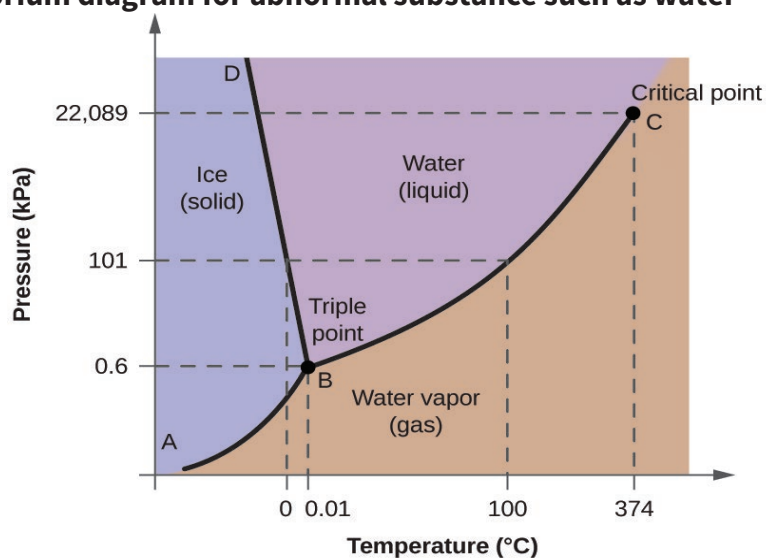
AB- sublimation curve, **BC**- evaporation / condensation CURVE

BD- Melting /freezing curve.

B- triple point. It is a point where all the three phases coexist in equilibrium.

Along AB, ice and water vapour are in equilibrium. This curve represents the effects of pressure on ice as temperature various.

Along **OC**, vapour and liquid co-exist in equilibrium. It represents the effects of increased pressure on boiling point of water.

OB- ice and liquid co-exist in equilibrium. OB represents the effects of increased pressure on the melting point of ice. It slopes towards the left (pressure axis) indicating that increase in pressure decreases the melting point and volume of ice.

Point C is the critical point i.e point beyond which the liquid and vapour phases are indistinguishable. The pressure exerted by one mole of a substances at this point is called the critical pressure and corresponding temperature is called the critical temperature. Above this point, the vapour cannot be liquefied no matter what pressure is applied.

Critical temperature is the minimum temperature above which the vapour cannot be liquefied under all conditions of temperature and pressure.

A phase equilibrium diagram for normal substance e.g carbon dioxide.
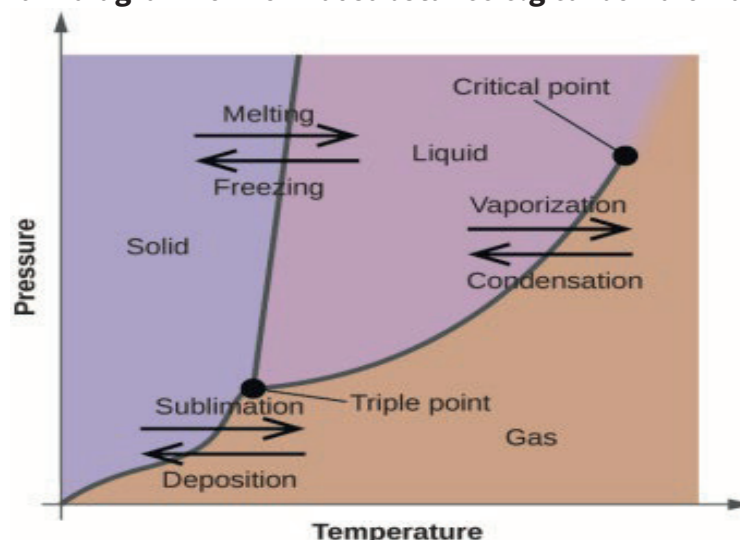
A phase equilibrium diagram for sulphur or substance that exhibit allotropy
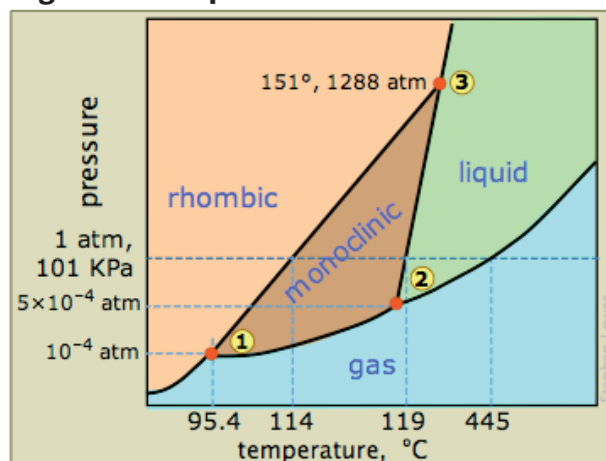
The diagram is complicated by the fact that sulfur can exist in two crystalline forms: rhombic and monoclinic.

Let's look first at the four areas:
- **Pink** — only rhombic sulfur
- **Brown** — only monoclinic sulfur
- **Green** — only liquid sulfur
- **Blue** — gaseous sulfur

The corresponding curves are:
- **lower left to ①** — the sublimation curve of rhombic S: S(rhombic)⇌S(g)
- **① to②** — the sublimation curve of monoclinic S: S(monoclinic)⇌S(g)
- **② to upper right** — the vapour pressure curve of liquid S: S(l)⇌S(g)
- **① to ③** — the transition curve for S(rhombic)⇌S(monoclinic)
- **② to ③** — the melting point curve for S(monoclinic) ⇌ S(l)
- **③ to top** — the melting point curve for S(rhombic) ⇌ S(l)

There are three **triple points**:
- ① **(95.4 °C,1×10-4 atm)** — rhombic S is in equilibrium with monoclinic S, and both have the same vapour pressure.
- ② **(119 °C,5×10−4 atm)** — monoclinic S melts; this is the triple point for Sm⇌Sl⇌Sg.
- ③ **(151 °C, 1288 atm)** — rhombic, monoclinic, and liquid S are at equilibrium.

The **critical point** — where liquid and gaseous S have the same density — is off to the right at 1041 °C and 203.3 atm

Research work
By use of internet or text book,
- Sketch cooling curves of pure substances.
- Explain the cooling curves for pure substances.
- Draw phase diagrams for mixtures
- Explain the phase diagrams for mixtures
- Explain concept of eutectic mixtures
- Compare the behaviour of eutectic mixture and a pure compound
- Give examples of substances which form eutectic mixtures.

LESSON 1.2: LIQUID- LIQUID MIXTURE

SPECIFIC OBJECTIVES:
By the end of this lesson, you should be able to**;**
- give examples of two component system.
- explain the different types of two component systems
- identify the different types of two component systems
- state Raoult's law
- explain what ideal solution is.

- give characteristics and examples of ideal solutions
- draw vapour composition diagrams for ideal solutions and real solutions.
- interpret the vapour pressure composition diagrams.
- carry out calculations on Raoult's law

INTRODUCTION

Previously you learnt that an example of **one-component system** is a **system** involving one pure **chemical** while **two-component systems**, such as mixtures of water and ethanol, have **two** chemically independent **components** and so on. Typical phases are solids, liquids and gases.

One phase system solution (miscible liquids)
Miscible liquids are liquids which dissolve in one another in all proportions to form a uniform solution. The solubility of a liquid in a liquid is governed by the same principle as a solid in a liquid, but when a liquid dissolve in another liquid, we use the word **miscible instead of soluble**.

Activity
a) *Identify examples of mixtures of miscible Liquids.*
b) *Define each of the following terms:*
   i) *Solution,*
   ii) *Solvent*
   iii) *Solute*
   iv) *Saturated solution*
   v) *unsaturated solution*

Liquid – liquid mixtures which form ideal solutions

There are hardly any liquids which form an ideal solution when mixed but some do form nearly an ideal solution.
An ideal solution is one that obeys Raoult's law exactly and possesses the following properties;
  i) The intermolecular forces of attractions between like molecules (molecules of one compound) or those between the unlike molecules (molecules of the different components) in the mixture are exactly equal and therefore the escaping tendency of the molecules of each component does not change compared to that in the pure state at the same temperature. Therefore, the boiling point of the solution is between that of two components.
  ii) When the two liquids are mixed, there is no enthalpy change.
 iii) When the two liquids are mixed to form an ideal solution, the total volume of the solution is equal to the sum of the volumes of the individual components

Raoult's law:

States that the partial vapour pressure of any volatile component of an ideal solution is equal to the vapour pressure of the pure component multiplied by the mole fraction of that component in the solution.

This law can be expressed mathematically as follows:

Suppose P^O_A, P_A and X_A are respectively the vapour pressure of pure A, Partial vapour pressure of component A in the solution, and the mole fraction of A in the solution, then

$$P_A = X_A P^o_A$$

Similarly, for liquid B we have: $P_B = X_B P^o_B$ $\qquad\qquad\qquad X_B P^O_B$

Partial vapour pressure of a component is defined as the pressure that component will exert on the walls of the container which was originally occupied by components.

For two components A and B that form on ideal solution, the total vapour pressure of the mixture at a particular temperature:

$$P_T = P_A + P_B$$
$$= (X_A P^o_A) + (X_B P^o_B)$$

Mole fraction of a component in solution is the number of moles of that component in the mixture divided by total moles in the mixture. Note that the sum of the mole fractions of all components in a mixture is 1.

$$X_A + X_B = 1$$

Thus, $X_A = 1 - X_B$

$$P_T = (P^o_A X_A) + (P^o_B X_B)$$

Becomes

$$P_T = P^o_A (1 - X_B) + (P^o_B X_B)$$
$$P_T = P^o_A - P^o_A X_b + (P^o_B X_B)$$
$$P_T = P^o_A + (P^o_B - P^o_A) X_B \qquad \text{Note: } X_A = \frac{nA}{nA+nB} \text{ and } X_B = \frac{nB}{nA+nB}$$

Where, nA = moles of A in a mixture

nB = moles of B in mixture

Activity

Components A and B form an ideal solution. The vapour pressure of pure A and pure B is 900mmHg and 500mmHg respectively at a temperature of 25°c and pressure of 760mmHg.

*Calculate the mole fraction of each component*

i)   In the solution. (Answer: $X_A = 0.65$, $X_B = 0.35$)

ii)   In the vapour above the mixture. (Answer $X_A = 0.77$ and $XB = 0.23$)

Vapour pressure – composition diagram for an ideal solution

The vapour pressure of a pure liquid increases when temperature is increased until it reaches atmosphere pressure when it begins to boil at constant temperature

For an ideal solution, the force of attraction between the molecules of individual components is the same as that between the molecules of different components.
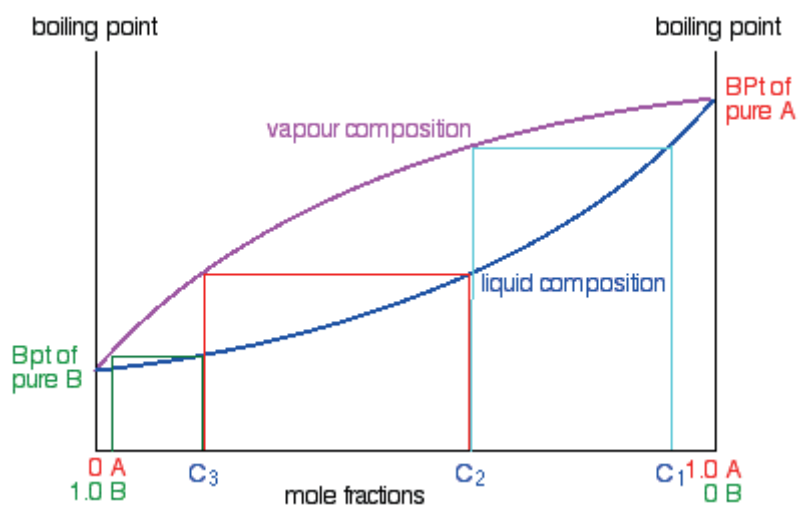
Therefore, the escaping tendency of each molecule into the vapour form is uniform.
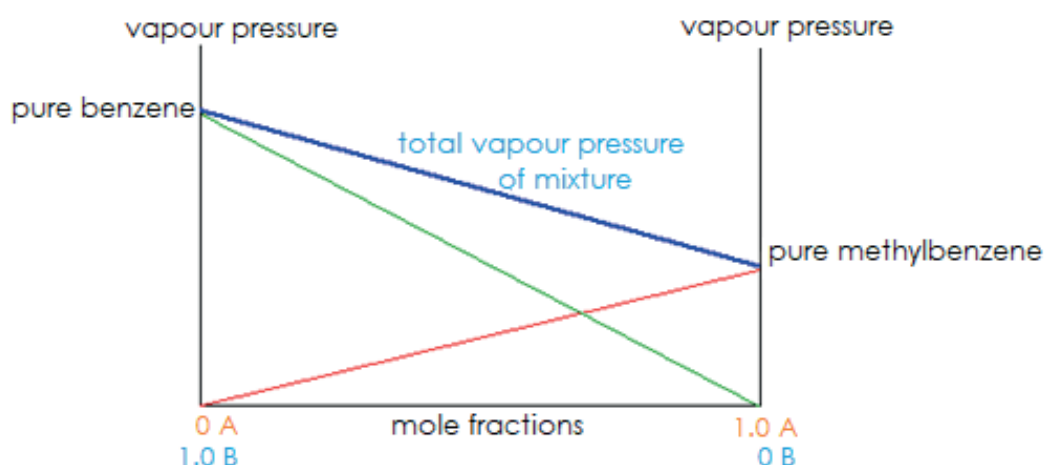
Let A = methylbenzene   B = benzene

Temperature (boiling point) – composition curve corresponding to the above   vapour pressure-composition curve is given below.

Notice that component A that had a lower vapour pressure than B now has higher boiling point than B.

If you boil a liquid mixture C_1, you will get a vapour with composition C_2, which you can condense to give a liquid of that same composition (the pale blue lines).

If you re-boil that liquid C_2, it will give a vapour with composition C_3. Again, you can condense that to give a liquid of the same new composition (the red lines).

Re-boiling the liquid C_3 will give a vapour still richer in the more volatile component B (the green lines). You can see that if you were to do this once or twice more, you would be able to collect a liquid which was virtually pure B.

The secret of getting the more volatile component from a mixture of liquids is obviously to do a succession of boiling-condensing-re-boiling operations.

It isn't quite so obvious how you get a sample of pure A out of this. That will become clearer in a while.

This process is called fractional distillation and the description above illustrates the *principal of fractional distillation*.

Fractional distillation is a technique of separating completely volatile miscible liquids by taking into account the different in their boiling points.

Effective separation can be achieved by using a long vertical column (fractionating column) attached to a distilling flask and filled with glass beads vapour from the liquid that is heated rise up the column until it condenses in the cooler parts and runs back into the vessel.
The rising vapour in the column has a more volatile component towards the top and the less volatile components at the bottom. Various fractions of the mixture can be drawn off at points of the column.

Activity
a) *explain the term fractional distillation and state its principle*
b) *State the importance of fractional distillation.*
c) *Draw a labeled diagram for the setup of apparatus that can be used to separate a mixture of miscible liquids*

Summary
- Miscible liquids are liquids that dissolve in one another in all proportions to form a uniform solution.
- Fractional distillation is used to separate a mixture of miscible liquids.
- No mixture of mixture of miscible liquids is perfectly ideal.

LESSON1.3: NON-IDEAL SOLUTION

Specific objectives: By the end of this lesson you should be able to:
- explain what real solution is
- give characteristics and examples of real solutions
- draw vapour composition diagrams for real solutions.
- differentiate between negative and positive deviation from Raoult's law.
- explain what is meant by the terms azeotropic mixtures and azeotropes
- explain what distillation is.
- explain the separation of components of azeotropes.

INTRODUCTION

A non-ideal solution (real solution) does not obey Raoult's law. The intermolecular forces of attraction between the like molecules are completely different from intermolecular forces of attraction between the unlike molecules.
The formation of non-ideal solutions is accompanied by change in total volume of mixture and evolution or absorption of heat such as solution is solid to.
There are two types of deviation from Raoult's law i.e. positive deviation and negative deviation.
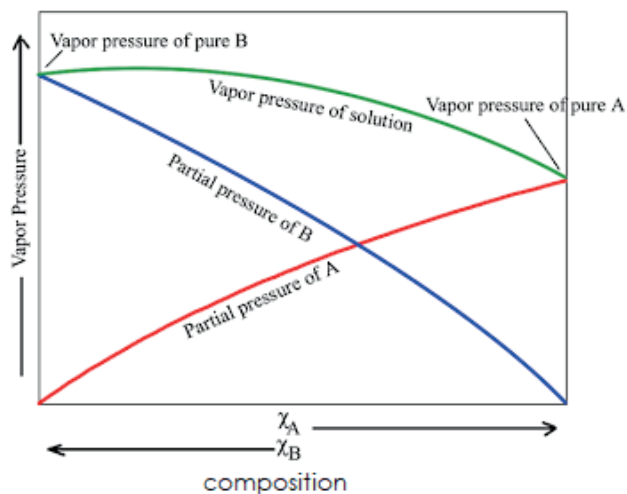
Positive deviation
It arises when the intermolecular forces of attraction between like molecules are stronger than intermolecular forces of attraction between unlike molecules. As a result, there is increased repulsion between the molecules and this increase the escaping tendency of each type of molecules from solution into the vapour phase giving a maximum vapour composition curve and a corresponding minimum boiling point composition curve.

Formation of a solution which deviates positively from Raoult's law is accompanied by absorption of heat and increase in total volume of the mixture.

Most of the liquids which deviate positively from Raoult's law, one or two must be able to form hydrogen bonds e.g. water and ethanol.

Positive Deviations from Raoult's Law
Weak solute-solvent interaction results in a vapour pressure higher than expected.

The boiling point composition diagram for a mixture that deviates positively from Raoult's law.
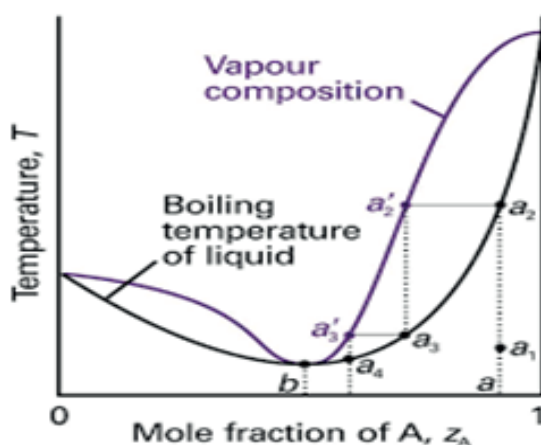
The liquid of composition **b** is called an azeotrope /azeotropic mixture/constant boiling point mixture and in this case the minimum constant boiling point mixture.

When this mixture is boiled, the temperature remains constant until all the liquid has turned into vapour and when the vapour is cooled, it forms a liquid of the same composition as one originally distilled. In this way, the azeotropic mixture behave as if it is a pure liquid yet it is not because when the external pressure is changed, the composition of the azeotropic mixture changes.

An azeotropic mixture is a mixture whose composition and boiling point remains constant at a given confining pressure with continued distillation of the mixture.

Distillation of mixture that deviates positively from Raoult's law
Fractional distillation of this mixture cannot separate the components completely because they form an azeotropic mixture. However, from the above diagram if the mixture distilled

has a composition to the right of **b** the distilled is still the azeotrope and the residue mainly **A**.

Separation of azeotropic mixtures.
1. Distillation with a third component. To separate azeotropic mixture of X and Y, a third component is introduced in which Y must be readily soluble to form an ideal solution and X must be immiscible with the third component such that a separating funnel can be used to separate the two and Y in the third component is obtained by fractional distillation e.g. an azeotropic consisting water and ethanol, benzene can be introduced as a third component.
2. By chemical method. Azeotropic mixture of ethanol and water can be separated by adding of calcium oxide which absorbs the water.
3. By absorption. It is done by addition of charcoal which absorbs one of the components.

Follow up activity.
a) *Ethanol-water system deviates positively from Raoult's law. Draw a vapour pressure-composition curve for ethanol – water system and label the phases. (Water boils at higher temperature than ethanol)*
b) *Name at least three pairs of liquids whose solution deviates positively from Raoult's law.*
c) *(C) Explain how negative deviation from Raoult's law arises. Draw labeled vapour pressure- composition diagram and the corresponding boiling point-composition diagram for a mixture of liquids that deviates negatively from Raoult's law.*
d) *State what is meant by the term a zeotropic mixture.*
e) *Use internet or text book to research and write down the description of methods of separating components of an azeotropic mixture.*

LESSON 1.4: Immiscible liquids

SPECIFIC OBJECTIVES
- Explain the total vapour of immiscible liquid mixture in terms of the vapour of the components.
- Calculate the composition of the vapour above a mixture of two immiscible liquids.
- Calculate the composition of the distillate.
- State industrial application of steam distillation

Introduction
Immiscible liquids are liquids which when mixed in any proportion form two distinct layers e.g. water and nitrobenzene
The total vapour pressure above the mixture of two immiscible liquids is equal to the sum of the vapour pressure of the liquids at a given temperature.
This total vapour pressure is independent of the relative amounts of the two components present i.e. if A and B are two immiscible liquids forming a binary mixture, then

$P_T P^o_A + P^o_B$

where, P^o_A and P^o_B are saturated vapour pressure of components A and B respectively at a given temperature.
A liquid boil when it's vapour pressure reaches the value exerted by the external pressure thus the total vapour pressure extend by an immiscible mixture of liquid will reach

atmospheric pressure at a temperature below liquids the boiling point of the most volatile constituent.

**Below is the vapour pressure curves of two liquids that are immiscible e.g water and nitrobenzene.**
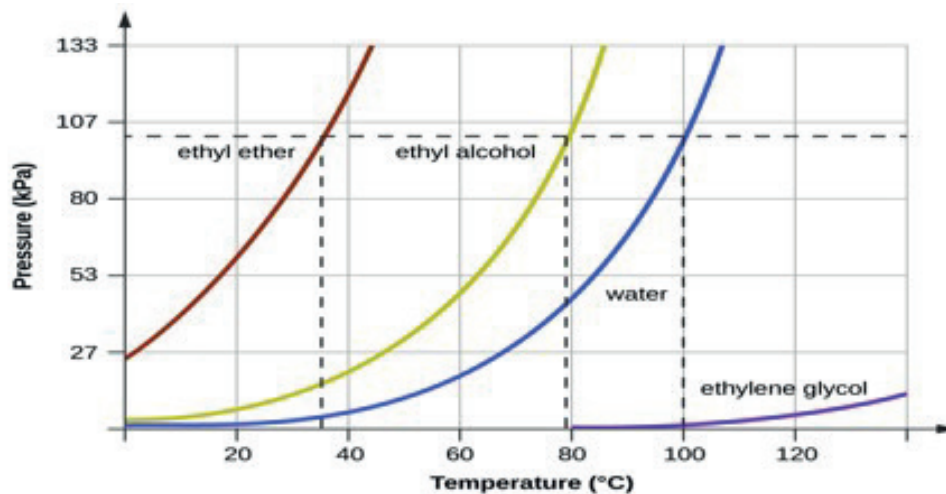
Activity

1. The vapour pressure of water and of an immiscible liquid x at different temperature are given in the table below.

Temperature / °C	92	94	96	98	100
V.P of x / kPa	6	8	12	15	17
V.P of x H_2O / kPa	74	80	88	94	109

a) On the same axes, plot graphs of vapour pressure against temperature for each liquid.

b) Determine the vapour pressure of the mixture of **x** and water at the temperature given in the table above.

c) On the same axes of the graph in (a) plot a graph of the vapour pressure of the mixture versus the temperature.

d) (d) The distillate from the mixture at 101kPa contained 16g of water and 1.1g of x. calculate the R.M.M of x using the information from the graph you have drawn.

Steam distillation (distillation of immiscible liquids)

- Pass steam from the steam jacket through a mixture containing the desired organic compound in a flask that is being maintained at a temperature just below the boiling point of water.

- When the mixture in this flask boils, it gives off steam and a vapour of the desired organic compound. The steam and the vapour are condensed and collected as a distillate.
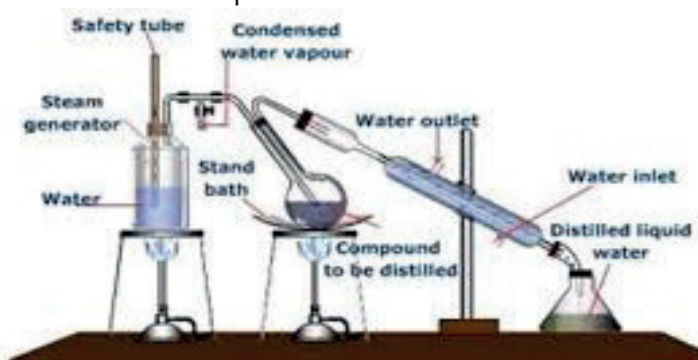
Since water and organic compound are immiscible, they are separated by means of a separating funnel or a drying agent which removes water.

Conditions for a compound to be separated by steam distillation
- The compound must be immiscible with water.
- It must have a high relative molecular mass.
- It must be able to exert high vapour pressure near the boiling point of water.
- Any impurities mixed with it must be non-volatile.

Analysis of the distillate (composition of the distillation)
The mass of each liquid in the distillate is proportional to the product of its relative molecules mass and the vapour pressure at a particular temperature i.e.

$W_A \propto RMM_A \times$ Vapour pressure A

$W_A = k$ RMM of A x vapour of A …….…………………………….… (i)

Similarly

$W_B = k$RMM of B x vapour of B …….……………………………….…. (ii)

$$\frac{W_A}{W_B} = \frac{RMM \ of \ B \ vapour \ of \ A}{RMM \ of \ A \times \ vapour \ of \ B}$$

Where, W_A = mass of component A in the distillate.
              W_B = mass of component b in the distillate.

Examples

1. **A mixture of naphthalene and water was steam distilled at 98.3°C and 753mmHg. Calculate the percentage of by mass of naphthalene in the distillated (vapour pressure of water at 98.3°C is 715mmHg).**

   Let the percentage of $C_{10}H_8$ in distillate be X
   Then let the percentage of H_2O in distillate be (100-X)

   But, $\frac{\times}{100-\times} = \frac{RMM \ of \ C_{10}H_9 \times vapour \ pressure \ of \ C_{10}H_9}{RMM \ of \ H_2O \times vapour \ pressure of \ H_2O}$

   $\frac{\times}{100-\times} = \frac{120 \times (753-715)}{18 \times 715}$

   $\frac{X}{10-X} = \frac{4864}{12870}$

   1287 = 100-X (4864)

   12870 X = 486400 – 486X
   X = 27.43

2. **A compound x was steam distilled at 80°C at 760mmHg and the distillate was found to contain 90.8% of x (vapour pressure of water at 80°C is 240mmHg) calculate the molecules mass of x.**

   $\frac{90.8}{100-90.8} = \frac{RMM \ of \ X \ vapour \ pressure \ of \ x}{RMM \ of \ H2O \ X \ vapour \ pressure \ of \ H2O}$

$$\frac{90.8}{9.2} = \frac{\text{RMM of X} \times 760 - 240}{18 \times 240}$$

90.8(18X240) = 520 RMM of x.

392,256 = 4784 RMM of x.

RMM of x = 82

Activity
a) *State the principle used in steam distillation.*
b) *Give*
   i) *the advantages of stem distillation*
   ii) *the uses of steam distillation*

LESSON 1.5:   The Distribution/Partition law.
By the end of this lesson, you should be able to:
- explain the concept of distribution law.
- experimentally determine K_D.
- carry out calculations involving distribution law.
- explain the application in; chromatography, solvent extraction and ion exchange

INTRODUCTION
This law deals with the distribution of solute between two immiscible solvents in contact with each other. It starts that when a solute irrespective of its amount is shaken between two immiscible solvents in contact with each other the solute distributes itself such that at equilibrium, the ratio of the concentrations of the solute in the two layers is constant at any given temperature.
Distribution law.
i.e. $K_D = \dfrac{C_1}{C_1}$

Where, C_1 is the concentration of the solute in solvent 1.
    C_2 is the concentration of the solute in solvent 2.
    K_D is known as the distribution or partition coefficient.

Solvents 1 and 2 are immiscible.
The distribution coefficient is defined as the ratio of concentration of a solute in one solvent to its concentration in another solvent for two immiscible solvents in contact at a particular /constant temperature.

Limitation of the law
- The solute must not dissociate or associate in any one of the solvents.
- The solute must not chemically react with any of the solvents.
- The partition law only holds at a particular temperature.
- The solute must not saturate any of the solvents.
Generally, the law only holds when the solute remains in the same molecular form in the two solvents.

Application of the partition law
- Solvent extraction
- Determination of the formula of a complex.
- Purification of the metals.

Solvent extraction
This is a process of separating substances especially organic substances from aqueous solution in which they are soluble by shaking the mixture with a suitable solvent which is immiscible with water in which the solute is more soluble in.

ACTIVITY

*$100cm^3$ of aqueous solution containing 20g of substance **x** was shaken once with $50cm^3$ of ether.*
- *i)   Calculate the mass of **x** extracted by ether.*
- *ii) Calculate the mass of **x** that would be extracted by shaking the mixture twice with $25cm^3$ of ether (K_D of **x** between ether and water is 4).*

2. The determination of formula a complex ion
The partition coefficient is used to determine the structure of a complex ion i.e. the determination of number of ligands coordinated with the metal ion.

Experimental determination of a number of ligands complexed with a metal ion
E.g. number of moles of Ammonia that form a complex ion with copper (ii) ion.
A known volume of a standard solution of excess ammonia is shaken with a standard solution of Cu^{2+} to form a complex of formula; $[Cu(NH_3)_n]^{2+}$.
The resultant solution is then shaken with $CHCl_3$ in a separating funnel repeatedly for about 5minutes while releasing pressure at intervals.
The mixture is the allowed to stand until the two layers are separate completely.
The upper deep blue aqueous layer contains both free Ammonia and ammonia that has formed a complex i.e. ammonia in a complex, in equilibrium with the free ammonia in trichloromethane layer below.

ACTIVITY

a) *Describe the application of K_D in the determination of formula of a complex.*
b) *(b)Excess aqueous ammonia was shaken with equal volume of $CHCl_3$ and 0.05M aqueous solution of Copper(II) Sulphate was added. The mixture was shaken and allowed to stand until two separate layers completely formed. It was found out that the concentration of NH_3 in $CHCl_3$ and aqueous layer were 0.21 mol l^{-1} and 0.725 mol l^{-1} respectively.*
   If distribution coefficient of NH_3 between water and trichloromethane is 25
   Determine the value of n in the complex $[Cu(NH_3)_n]^{2+}$
c) *The table below shows the result of partition of amino ethane and 0.1M Copper sulphate solution.*

$[CH_3NH_2(CHCl_3)]$	0.87	1.10	1.33	1.57	1.80
$CH_3NH_2(CHCl_3)]$	0.02	0.03	0.04	0.05	0.06

- i) *Plot a graph of $CH_3NH_2[(0.1MCuSO_4)]$*
- ii) *Determine the number of moles of aminomethane that has formed complex with Copper (ii) ions.*

TOPIC 2.0 CHEMICAL EQUILIBRIUM

GENERAL OBJECTIVE:
By the end of this topic the learner, should be able to explain the concept of reversible reactions and its applications.

LESSON 2.1 THE CONCEPT OF CHEMICAL EQUILIBRIUM AND COMPARISON BETWEEN K_c and K_p

SPECIFIC OBJECTIVES:
By the end of this lesson, you should be able to:
- explain the concept of chemical equilibrium
- distinguish between reversible and irreversible reactions
- explain dynamic equilibrium
- differentiate between homogenous and heterogeneous reversible system
- restate the law of mass action and apply it in writing equilibrium expressions
- derive a general expression relating K_c and K_p
- carry out calculations involving use of K_c and K_p
- compare concentration equilibrium constant and pressure equilibrium constant [Kc and K_p]
- compare Q and Kc to determine the direction of chemical reaction
- interpret the magnitude of value of Kc or Kp in relation to the equilibrium position

INTRODUCTION

Equilibrium exists when two opposing forces or rates balance each other.
In everyday life, such equilibrium exists in a balanced se-saw, weighing scale, when a person walks at a right speed up a down moving elevator. In chemistry, many reactions do not go to completion. The reactants combine to form a product and a point is reached when the product decomposes to form the reactants.

A point is then reached when the rate at which reactants are forming products is equal to the rate at which the product is decomposing into reactants. This is said to be the equilibrium state of the system.

The equilibrium reached is dynamic and not static because there is a constant interchange between the products and reactants and the reaction is said to be reversible.
**NB:** A dynamic equilibrium can be established in either an isolated system or a closed system.

Definition:
1. Isolated system- is one which does not exchange matter or energy with the surrounding.
2. Closed system – is one which does not exchange matter with the surrounding but exchange energy.
3. Open system – is one that exchanges both matter and energy with the surrounding therefore a dynamic equilibrium cannot be obtained in an open system.

In a closed system, a reaction will reach a state of equilibrium when the rate of the forward reaction is equal to the rate of the backward reaction.

Consider the reaction;

A+B $\rightleftharpoons$ C+D
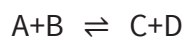
R_f = K [A] [B]

R_b = K_2 [C] [D]

At equilibrium, R_f = R_b

K_1 [A] [B] =K_2 [C] [D]

$\frac{K_1}{K_2} = \frac{[C][D]}{[A][B]}$

$K_C = \frac{[C][D]}{[A][B]}$

K_C is called **equilibrium constant** in terms of concentration of the participating.

Equilibrium constant K_C is the ratio of the product of the concentration of the products of reaction to the product of concentration of the reactants raised to their respective stoichiometric powers when the concentrations are in $moldm^{-3}$
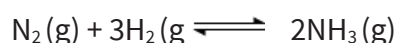
Generally, for the reaction;

n A + mB $\rightleftharpoons$ x C +y D
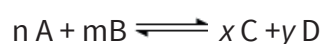
$$K_c = \frac{[C]^x[D]^y}{[A]^n[B]^m}$$

K_C is the equilibrium constant in terms of concentration of the participating species

If the reactants and products are all gases, then equilibrium constant can be conveniently given in terms of pressures e.g.,
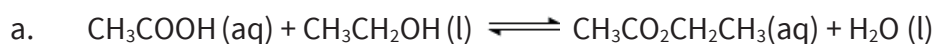
N_2 (g) + $3H_2$ (g $\rightleftharpoons$ $2NH_3$ (g)

$$K_p = \frac{P_{NH_3}^2}{(P_{N_2})(P_{H_2}^3)}$$

Where P is partial pressure and the units for K are atm^{-2}.

In terms of concentration; $K_c = \frac{[NH_3]^2}{[N_2]^2[H_2]^3}$

NB: However, if the reactants and products are I aqueous state equilibrium constant is only expressed in terms of concentration of the participating species e.g.

a. CH_3COOH (aq) + CH_3CH_2OH (l) $\rightleftharpoons$ $CH_3CO_2CH_2CH_3$(aq) + H_2O (l)

$$K_c = \frac{[CH_3CO_2CH_2CH_3][H_2O]}{[CH_3CH_2OH][CH_3CO_2H]}$$

The above reaction in which all the reactants and products are in same phase are called **homogenous equilibrium reactions.** However, in reactions where the reactant and products have different state are called **heterogeneous reactions** e.g.

a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

The concentrations of the solids hardly change and therefore are taken to be constant. Concentrations of solids hardly appear in the expression of equilibrium constant. Therefore, the above reaction;

$K_C = [CO_2]$.

In terms of the partial pressures, since the pressure exerted by a solid or liquid is negligible, then in heterogeneous equilibrium reactions, expression for K_P does not include solids and liquids e.g. in the above reaction;

$K_P = P_{CO2}$

b) $3Fe_{(s)} + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + H_2(g)$
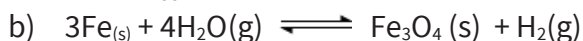
$$K_C = \frac{[H_2]^4}{P_{H_2O}^4} \qquad K_p = \frac{P_{H_2}^4}{[H_2O]^4}$$

Note: K_C or K_P value is only affected by changes in temperature and its units depend on the expression for the KC or KP and on the concentration units used or pressure with used.

LESSON 2.2 Factors that affect equilibrium reactions

SPECIFIC OBJECTIVES
By the end of this lesson, you should be able to;
- explain Le' Chatelier's principle and apply it in explaining the effects of various factors on the equilibrium of reversible chemical reaction
- experimentally determine K_c using esterification reaction
- show the importance of equilibrium constant factors on industrial processes
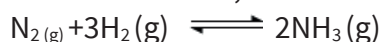
INTRODUCTION

Le Chatelier's principle

It states that when a system in equilibrium is subjected to any change, it will shift the equilibrium position in a direction that causes an opposite change.

1. Concentration
Consider the reactions;

$N_{2(g)} + 3H_2(g) \rightleftharpoons 2NH_3(g)$

When Nitrogen gas is added to the above equilibrium mixture, the position of equilibrium will shift to the right. This is the direction in which the Nitrogen added is used up by its reaction with Hydrogen to form Ammonia in attempt to restore equilibrium.

On the other hand, if some Ammonia is removed from the equilibrium mixture, the equilibrium will be distorted and hence the position of equilibrium system. Then the products will have to dissociate faster in order to replace the reactant being removed and have restore the equilibrium.

2. Pressure

Increasing pressure on a system in equilibrium will cause the equilibrium position to shift in a direction which will bring about the lowering of pressure.

Considering;

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2H_3\ (g)$$
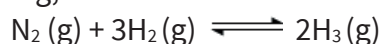
Total number of moles of reactants = 4

Moles of products = 2

Therefore, increase in pressure on the system will shift the position of equilibrium from left to right because the forward reaction proceeds with a decrease in volume i.e since PV = constant, increase in pressure can only be achieved through the corresponding decrease in volume of the system.

Note: For reactions where total number of moles of reactants = total number of moles products, pressure changes have no effect on equilibrium position. These reactions include;

$$H_{2(g)} + I_{2\ (g)} \rightleftharpoons 2HI_{\ (g)}$$

3. Temperature

The increase in temperature of a system in equilibrium will cause the position of equilibrium to shift in a direction which proceeds with absorption of heat i.e to the endothermic side.

Effect of temperature on attainment of equilibrium

Increases in temperature increases the rate of attainment of equilibrium irrespective of whether the reaction is exothermic or endothermic.

This is because increase in temperature increases the speed of reacting particles which leads to increase in their kinetic energy have more frequent collisions which are energetic will occur leading to increase in the rate of reaction and hence attainment of equilibrium in a shorter time.

Effect of concentration on attainment of equilibrium.

At high concentration of reactants, the equilibrium is attained in a shorter time. This is because when the concentrations are high, the reacting particles are close to one another

and therefore the chances of frequent collusions increase which increases the rate at which the reactants are converted to products.

Effects of a catalyst on attainment of equilibrium.
A catalyst does not change the composition of equilibrium mixture therefore it has no effect on the position of equilibrium. It also has no effect on the value of equilibrium constant. However, the catalyst affects both forward and backwards reaction to the same extent and their equilibrium position is attained more rapidly in the presence of catalyst.

Note: Pressure, concentration changes in equilibrium reaction do not have any effect on the value of the equilibrium constant because when the factors changes, there is no equilibrium in the system momentarily, but it is established after the change has been countered.

However, changes in temperature do affect the value of equilibrium constant in that;

1. If the reaction under consideration is endothermic, increase in temperature will lead to formation of more products from the reactants which means the K_C value (equilibrium constant value) will increase with increase in temperature.
2. On the other hands, if the reaction under in equilibrium constant.

Determination of equilibrium constant between ethanol and ethanoic acid.

$$CH_3CO_2H \text{ (aq)} + CH_3CH_2OH \text{ aq)} \rightleftharpoons CH_3CO_2CH_3 \text{ (aq)} + H_2O_{\text{(aq)}}$$
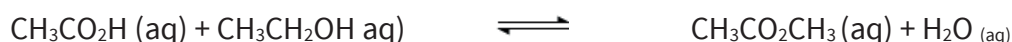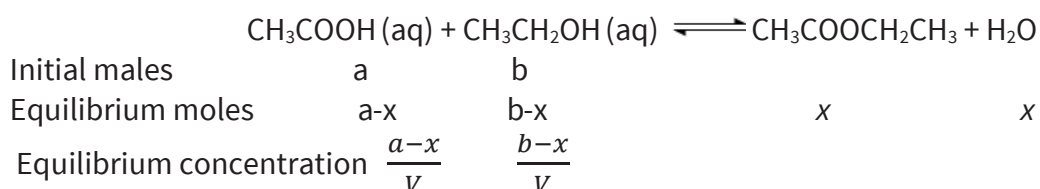
Known volume of ethanol and ethanoic acid are mixed and then heated to about 60°C

It is then allowed to stand for about 8 hours in a flask in order to keep the temperature constant.

A fixed volume of the mixture is pipette and titrated with a standard solution of Sodium hydroxide using phenolphthalein indicator.

The amount of ethanoic acid present in equilibrium mixture is determined and then the equilibrium amount of other species present at equilibrium is deduced as shown below.

Let **a** and **b** be the initial moles of ethanoic acid and ethanol respectively.

$$CH_3COOH \text{ (aq)} + CH_3CH_2OH \text{ (aq)} \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

Initial males	a	b		
Equilibrium moles	a-x	b-x	x	x
Equilibrium concentration	$\frac{a-x}{V}$	$\frac{b-x}{V}$		

$$K_C = \frac{[CH_3CO_2CH_2CH_3][H_2O]}{[CH_3CO_2H][CH_3CH_2OH]}$$

$$= \frac{[x][x]}{[(\frac{a-x}{V})][(\frac{b-x}{V})]}$$

$$= \frac{x^2}{(a-x)(b-x)}$$

ACTIVITY

When 8.28g of ethanol was mixed with 60g ethanoic acid and the mixture heated and allowed to reach equilibrium, the amount of ethanoic acid present at equilibrium, determined by titrating the mixture with a standard solution of Sodium hydroxide using phenolphthalein indicator was 49.74g.

Calculate the equilibrium constant.

If 12g of ethanoic acid were instead mixed with 13.8g of ethanol at the same temperature as in a, calculate the mass of ethylethanoate present at equilibrium.

CH_3CH_2OH = (12X2) + 16
        = 46
46g is the mass of 1mole of ethanol.

8.28g is the mass of 1mole $\frac{1}{4} \times 8.28$

        = 0.18moles
CH_3CO_2H = 12×2+16×2+4×1
      = 60
60g is the mass of 1mole of ethanoic acid.

$CH_3CO_2CH_2CH_3$ = (4x120 + (8x1) + (12x6)

      = 128

128g is the mass of 1mole of ethylethanoate

49.74g is the mass of 1mole $\frac{1}{128}$ x 49.74

      = 0.389moles

$CH_3CO_2H_{(aq)} + CH_3OH_{(aq)} \rightleftharpoons CH_3CH_2CH_{3(aq)} + H2O_{(l)}$
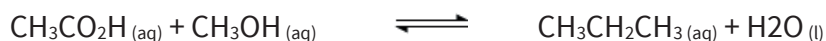
Initial moles	1	0.18	0	0
Equilibrium moles	0.829	0.089	0.171	0.171

$$K_C = \frac{[CH_3CO_2CH_2CH_3][H_2O]}{[CH_3CO_2H][CH_3CH_2OH]}$$

$$K_C = \frac{(0.171)(0.171)]}{(0.829)(0.09)}$$

= 3.93

ACTIVITY
0.3 moles of Hydrogen and 0.14 moles of Iodine were heated to 630K. if 0.2 moles of Hydrogen Iodide were formed at equilibrium. Calculate the value of equilibrium constant K_C.
*Determine the mole composition at equilibrium of the system if 0.4 moles of Hydrogen and 0.1 moles of Iodine were heated at 630K. (*K_C **= 0.5**)

Degree of dissociation

It is the fraction of 1 mole of a compound that is converted to a new substance(s) when the system has attained equilibrium.

Example.

Consider the dissociation of phosphorous pentachloride. If $\propto$ is the degree of dissociation and n is the initial moles, then at equilibrium;

$$PCl_{5\,(g)} \rightleftharpoons PCl_{3\,(g)} + Cl_{2\,(g)}$$
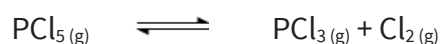
Initial moles   n   0   0

Equilibrium n(1-x) $n\propto$ $n\propto$

Total moles at equilibrium = n- $n\propto$ + $n\propto$ + $n\propto$.

$$= n+ n\propto.$$

At constant temperature, PV = nRT for no dissociation of PCl_5.

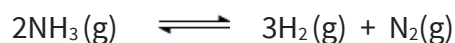However, on dissociation,

$$= (n + n\propto)RT$$

Hence, PV = nRT

But, total moles = n +$n\propto$

$$PV - nRT = n - \times RT$$

$$\propto = \frac{PV - n\mathrm{RT}}{n\mathrm{RT}}$$

$$\frac{PV}{nRT} - V$$

Consider the dissociation of ammonia.

$$2NH_3\,(g) \rightleftharpoons 3H_2\,(g)\ +\ N_2(g)$$

Initial moles n   0   0

Equilibrium mole n(1-x) $\frac{3}{2}$ n$\propto$ $\frac{1}{2}$ n$\propto$

Total moles at equilibrium = n - n$\propto$ + $\frac{3}{2}$ n$\propto$ + $\frac{1}{2}$ n$\propto$

$$= n + n\propto$$

From PV = n + n$\propto$ RT $\propto = \dfrac{PV}{nRT} - 1$

Example

1. 1 mole of phosphorus pentachloride was placed in a 10dm^3 vessel at 400°C.
   i) Calculate the pressure inside the vessel assuming that phosphorus pentachloride did not dissociate (R= 0.08 atml^{-1} K^{-1})

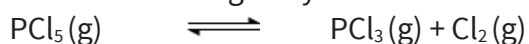 $$PV = nRT$$

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

   $$= \frac{1 \times 0.082 \times (400 + 273)}{10}$$

   = 5.52atm

   ii) When phosphorus pentachloride was allowed to dissociate, the equilibrium mixture had a total pressure of 26 atmospheres with no change in volume and temperature. Calculate the degree of dissociation if 4 moles of phosphorus pentachloride were originally used under these conditions.

   $$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

   Initial moles   4   0   0

   Equilibrium   4(1-$\propto$)   4$\propto$ 4$\propto$

   Total number moles at equilibrium = 4 - 4$\propto$ + 4$\propto$ + 4$\propto$

   $$= 4 + 4\propto$$

   From PV = nRT.

   $$PV = 4 + 4\propto + RT$$

   $$\propto = \frac{PV}{4RT} - 1$$

   $$= \frac{26 \times 10\ -\ 1}{4 \times 0.082 \times (400 \times 273}$$

   = 0.178

Effect of an inert gas on the equilibrium position of a reversible reaction.

1. A reaction in which $\Delta n = 0$ e.g. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
   i) At constant volume – addition of an inert gas to the equilibrium reaction above at constant volume has no effect on equilibrium position. This is because the inert gas its own pressure in the vessel bit pressure has no effect on the position of equilibrium for such reactions, that proceed no change in volume.
   ii) at constant pressure in the – inert gas exerts pressure but since the reaction proceeds without change in volume, it will have not affect the partial pressures of the equilibrium mixture hence it does not affect the equilibrium position.

   Reactions in which $\Delta n > 0$ e.g.
   $$2SO_{2\ (g)} \rightleftharpoons 2SO_{2\ (g)} + O_{2\ (g)}$$
   iii) Addition of an inert gas at constant volume.
   At constant volume, the concentration of species present is not affected because inert gas goes not take part in the reaction: addition of inert gas does not affect equilibrium positions of the reaction. The concentration of inert gas not takes part in the equilibrium constant expression and therefore has no effect on the value of equilibrium constant.
   iv) At constant pressure – inert gas exerts to its own pressure and at constant pressure it results in the reduction of partial pressures of the species in equilibrium mixture which therefore leads to increase in volume of the reaction mixture.
   v) This favours the forward reaction which proceeds with an increase in volume or number of gaseous molecules.
2. Reaction is which $\Delta n > 0$
   e.g. $N_2(g) + 3H_2(g) \rightleftharpoons 2H_3(g)$

Discuss the effect of adding oxygen on the o the position of equilibrium and on the value of equilibrium constant for the above reaction;
   i) At constant volume.
   ii) At constant pressure.

At constant volume, the total pressure of the system increase. This is increase the frequency of collision amongst Hydrogen, Nitrogen and Ammonia. The equilibrium is attained with a decrease in volume; the forward reaction is favored by pressure increase hence the position of equilibrium is shifted to the right. The equilibrium constant is not affected.

At constant pressure – when Argon is added, the pressure of the system increases. To keep the pressure constant, the volume must increase. There is reduced frequency of collision hence rate of attaining equilibrium decreases. The backward reaction is favored by increase in volume and so the position is shifted to the left. The equilibrium constant is not affected.

TOPIC 3.0: IONIC EQUILIBRIA

GENERAL OBJECTIVE:

By the end of this topic, you should be able to describe behaviour of acids, bases, and salts in aqueous solutions

LESSON 3.1: ACIDS, BASES AND SALTS

By the end of this lesson, you should be able to;
- explain the concept of acids and bases according to various theories.
- explain the concept of conjugate bases and conjugate acids.
- classify acids and bases on the basis of their degree of ionization.
- explain the ionisation constants for weak acids and weak bases K_a and K_b
- derive general expression for K_a and K_b
- correctly apply knowledge about K_a and K_b in calculations.
- explain auto ionization (self-ionization) of water.
- derive an expression for K_w.
- explain the concept of pH of 1-14.

INTRODUCTION

An acid is:
- A substance that donates a proton.

A base is:
- A substance that accepts a proton.
- When an acid also called the _conjugate acid of the base_ donates a proton, a base called the _conjugate base of an acid_ is formed. For example: for H_2SO_4 acid, the conjugate base is HSO_4^-

ACTIVITY: *Copy and complete the following table*:

Conjugate acid	Conjugate base
HCl	
HNO_3	
H_2O	
NH_4^+	
$[Al(H_2O)_6]^{3+}$	

- When bases accept protons, they form the *conjugate acids of the bases.* For example, ammonia accepts a proton to form the ammonium ion which by definition is a conjugate acid of ammonia.

$$NH_3(aq) +\ \ H^+(aq) \rightarrow NH_4^+(aq)$$
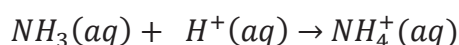
Strength of acids and bases
- The strength of an acid is measured by the ease with which it releases a proton.
- *Strong acids:* easily release protons and are completely ionized in the solvents.

- *Weak acids:* do not easily release protons, and are partially ionized in the solvents.

Factors affecting acid strength

Nature of the solvent
- The more basic the solvent, the stronger will be the acid in such a solvent because the acid will easily donate its proton. If the solvent is of weaker base strength, the acid cannot easily donate its proton to it, hence behaving as a weak acid instead.
- Hence, ethanoic acid will show much more acid properties when dissolved in ammonia than when dissolved in water, because ammonia is stronger base than water.

Proton – conjugate base bond strength
- The stronger the proton – conjugate base bond, the weaker the acid will be. This is because it is difficult to break the bond and release the proton.
- The weaker the proton – base bond, the stronger the acid will be. This is because the bond can be easily broken and the proton easily released
- Hence HI is a stronger acid in aqueous solution than HF because the $H - I$ bond is weaker than the $H - F$ bond and can easily be broken to release protons more readily than that in $H - F$

Comparing acid strength
By using their degree of dissociation.
- Degree of dissociation is the fraction of each mole of an electrolyte that exists as ions. It can also be expressed as a percentage.
- A stronger acid has a higher degree of dissociation compared to a weak one.

By using their dissociation constants, K_a, (weak acids)
- Since a weak acid partially ionizes, a solution of a weak acid has the ions and the molecules of an acid present in equilibrium with each other.
- Hence the law of mass action can be applied to give the dissociation constant.
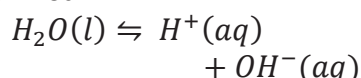   i.e. for a weak acid HX,

$$HX(aq) \leftrightharpoons H^+(aq) + X^-(aq)$$
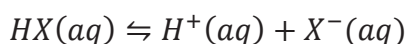
$$K_a = \frac{[H^+][X^-]}{[HX]}$$

- An acid with a higher K_a value would have ionized more than the one with the lower value. Hence an acid with a higher K_a value is a stronger acid than the one with a lower value.

Dissociation of water

- Water is a weak electrolyte because it is slightly ionized
$$H_2O(l) \leftrightharpoons H^+(aq) + OH^-(aq)$$

- By applying the law of mass action the equation obtained is
$$K = \frac{[H^+][OH^-]}{[H_2O]} \quad \ldots \ldots \ldots \ldots (1)$$

- But since the dissociation of water is very small,

$$[H_2O] \approx 1$$

- Hence, equation (1) becomes
$$K_w = [H^+][OH^-]$$

- Which is called the *the ionic product of water*
- The numerical value of the ionic product of water is given by

$$K_w = 1 \times 10^{-14} mol^2 dm^{-6}$$

pH
- This is defined as *the negative logarithm to base 10 of the hydrogen ion concentration of a given solution*
  i.e. $pH = -\log_{10}[H^+]$

pH of water
- From $K_w = [H^+][OH^-] = 1 \times 10^{-14}$
- But $[H^+] = [OH^-]$

$$\therefore [H^+]^2 = 1 \times 10^{-14}$$

$$[H^+] = \sqrt{(1 \times 10^{-14})}$$
$$pH = -\log_{10}\left(\sqrt{(1 \times 10^{-14})}\right)$$

$$\underline{pH = 7}$$

pH of acids

Strong acids
- These are completely ionized in aqueous solution.
- Thus their $pH = -\log[H^+]$

Weak acids
- Weak acids do not completely dissociate even in very dilute solution. The $[H^+] \neq [Acid]$.

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The hydrogen ion concentration depends on the degree of dissociation of the acid.

- Consider a weak acid HX which ionizes in aqueous solution as follows

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$$

Initial moles: 1   0   0

Equilibrium moles: $1-\alpha$ α α

Equilirium concetration $\dfrac{1-\alpha}{V}$ $\dfrac{\alpha}{V}$ $\dfrac{\alpha}{V}$

Applying the law of mass action:

$$K_a = \frac{[H^+][X^-]}{HX}$$

$$= \frac{\left(\frac{\alpha}{V}\right)\left(\frac{\alpha}{v}\right)}{\left(\frac{1-\alpha}{v}\right)}$$

$$K_a = \frac{\alpha^2}{v(1-\alpha)}$$

But

$$\frac{1}{v} = c$$

- For weak acids, the degree of dissociation is very small such that
$$(1-\alpha) \approx 1$$
- Hence
$$ka = C\,\alpha^2$$
- From the above equation it can be seen that
$$[H^+] = C\,\alpha$$
- Also
$$[H^+] = \sqrt{CK_a}$$

pH of bases

Strong bases

These are assumed to be completely ionized. In solution, these produce hydroxide ions in the solution and not hydrogen ions. For this reason, the pH of the solution is determined indirectly from the ionic product expression. i.e.

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

$$[H^+] = \frac{K_w}{[OH^-]}$$

Introducing
$-\log_{10}$ both sides

$$-\log[H^+]$$
$$= -\log\left(\frac{K_w}{[OH^-]}\right)$$

Hence $pH = pK_w - pOH$

But

$$p\,Kw = 14$$

Therefore
$$pH = 14 - pOH$$

Weak bases

These are partially dissociated in solution. The hydroxide ion concentration in the solution as it was with the weak acids is dependent on the base dissociation constant, K_b or the degree of dissociation ($\propto$)

Hence $K_b = C \propto^2$ **and [OH⁻] =** $C \propto$ **or   [OH⁻] = √(Kᵦ x 1/ C)**

LESSON 3.2   SALTS

SPECIFIC OBJECTIVES: The learner should be able to:
- Explain the concept of salt hydrolysis.
- Derive an expression for K_h.
- Identify the various types of salts.
- Correctly apply knowledge of K_h in calculations.
- Explain the pH of the resultant solutions derived from hydrolysis of salts.
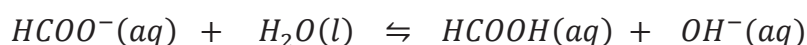
INTRODUCTION

Salt Hydrolysis

- *Is the reaction of a salt with water to give a solution, containing the acid and base that reacted to form it, and whose pH is greater or less than seven*
- Typically, salts are thought to give neutral solutions when dissolved in water. However, this is only true for salts derived from strong acids and strong bases. Other combination of salts when dissolved in water, give solutions whose pH is not exactly seven.
- Hydrolysis can occur in three different ways, all of which produce changes in pH

Salts of strong bases and weak acids
- When such salts are dissolved in water, they give alkaline solutions. (pH is greater than seven)
- Examples include: sodium ethanoate, potassium fluoride, sodium carbonate, potassium cyanide, sodium sulphite.
- The anion being a conjugate base of a weak acid, easily accepts protons from the water molecules to form an unionized weak acid and the hydroxide ion in solution. This makes the solution alkaline. Consider a salt such as sodium methanoate.
- Sodium methanoate in water dissociates into sodium and methanoate ions.

$$HCOONa\ (aq) \rightarrow HCOO^-(aq)\ \ +\ \ Na^+(aq)$$
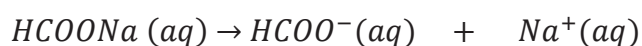
- The methanoate ions then react with water molecules

$$HCOO^-(aq)\ \ +\ \ H_2O(l)\ \ \leftrightharpoons\ \ HCOOH(aq)\ +\ \ OH^-(aq)$$

- The free hydroxide ions in the solution make it alkaline.

- From the above equation, the law of mass action can be applied, to give

$$K = \frac{[HCOOH][OH^-]}{[HCOO^-][H_2O]}$$

- But since water is in large excess, its concentration does change much so that at equilibrium $[H_2O] \approx 1$.

Hence

$$K_h = \frac{[HCOOH][OH^-]}{[HCOO^-]}$$

The above expression is called the *expression for the hydrolysis constant*, K_h, *of the salt, sodium methanoate.*

K_h is called the hydrolysis constant

pH of the solution

From the expression,

$$K_h = \frac{[HCOOH][OH^-]}{[HCOO^-]}$$

But

$$[HCOOH] = [OH^-]$$

$$[HCOO^-] \approx [salt]$$

Hence

$$K_h = \frac{[OH^-]^2}{[salt]}$$

$$[OH^-] = \sqrt{(K_h[salt])}$$

And

$$pH = 14 - pOH$$

Note

$$K_h = \frac{[HCOOH][OH^-]}{[HCOO^-]}$$

- Multiplying through the numerator and denominator by $[H^+]$

$$K_h = \frac{[HCOOH][OH^-]}{[HCOO^-]} \times \frac{[H^+]}{[H^+]}$$

- Re-arranging

$$K_h = \frac{[HCOOH]}{[HCOO^-][H^+]} \times [H^+][OH^-]$$

- But

$$\frac{[HCOOH]}{[HCOO^-][H^+]} = \frac{1}{K_a}$$

And

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

Therefore

$$K_h = \frac{K_w}{K_a}$$

Salts of weak bases and strong acids

- When such salts are dissolved in water, they give acidic solutions. (pH is less than seven)
- Examples include: ammonium chloride, ammonium nitrate, methylammonium chloride, dimethylammonium nitrate.
- The cation of the salt being a conjugate acid of a weak base, easily releases protons to form an unionized weak base and a proton in solution. This makes the solution acidic
- For example, a solution of ammonium chloride is acidic will react with strongly electropositive metals such as zinc to liberate hydrogen. This is because
- Ammonium chloride dissociates fully in water

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) \ + \ Cl^-(aq)$$
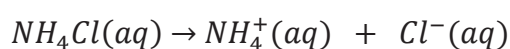
- The ammonium ions then react with water to form an acidic solution.

$$NH_4^+(aq) \ + \ H_2O(l) \ \leftrightharpoons \ NH_3(aq) \ + \ H_3O^+(aq)$$
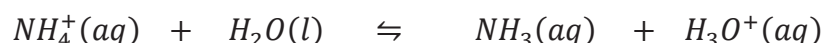
- The oxonium ions produced then react with the metal to liberate hydrogen gas

$$Zn(s) \ + \ 2H_3O^+(aq) \rightarrow Zn^{2+}(aq) \ + \ H_2(g) \ + \ 2H_2O(l)$$
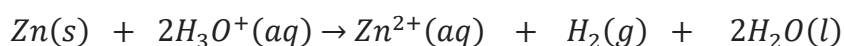
- From the above equation, the law of mass action can be applied, to give

$$K = \frac{[NH_3][H_3O^+]}{[NH_4^+][H_2O]}$$

- But since water is in large excess, its concentration does change much so that

at equilibrium $[H_2O] \approx 1$. Hence

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

- The above expression is called the *expression for the hydrolysis constant, K_h,of the salt, ammonium chloride*

pH of the solution

- From the expression,

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

- But
  $[NH_3] = [H_3O^+]$ and $[NH_4^+] \approx [salt]$

Hence

$$K_h = \frac{[H_3O^+]^2}{[salt]}$$

$$\boxed{[H_3O^+] = \sqrt{(K_h[salt])}}$$

And

$$pH = -\log[H^+]$$

- **_Note_**

It is also true that

$$K_h = \frac{K_w}{K_b}$$

Salts containing heavily hydrated cations

- A number of normal salts when dissolved in water give an acidic solution for example iron(III) chloride. This is because; the hydrated metal ion behaves as an acid. The high charge density of the cation causes greater attraction of the lone pairs in the water molecules. This attraction extends to $O - H$ bonds which becomes weaker, so that a proton is lost to the solution

$$[Fe(H_2O)_6]^{3+}(aq) \quad \leftrightharpoons \quad [Fe(H_2O)_5OH]^{2+}(aq) \quad + \quad H^+(aq)$$
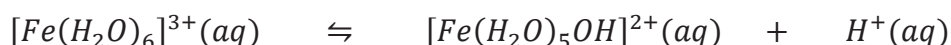
LESSON 3.2: BUFFER SOLUTION

SPECIFIC OBJECTIVES

By the end of this lesson, you should be able to;
- explain the concept of a buffer solution.
- classify buffers and give examples of each type.
- explain the action of a buffer.
- describe the preparation of a buffer.
- derive the Henderson-Hasselbalch equation.
- carry out calculations of pH of buffers.
- explain application of buffers.

This is a solution of definite pH which resists a change in its pH when a small amount of acid or alkali is added.

- A buffer solution consists of either a *weak acid and its salt with a strong base* or a *weak base and its salt with a strong acid*

Types of Buffers

Acidic buffers

- These contain a weak acid and its salt with a strong base. For example, methanoic acid and potassium methanoate, ethanoic acid and sodium ethanoate, carbonic acid and sodium carbonate.

Action of an acidic buffer

- Consider a buffer solution made of ethanoic acid and sodium ethanoate.
- Sodium ethanoate salt, ionizes fully in aqueous solution

$$CH_3COONa \ (aq) \ \rightarrow \ CH_3COO^- \ (aq) + Na^+(aq)$$

- Ethanoic acid, a weak acid partially ionizes.

$$CH_3COOH \ (aq) \ \leftrightharpoons \ CH_3COO^- \ (aq) + H^+(aq)$$

- The presence of ethanoate ions from the salt suppresses the ionization of ethanoic acid further so that the solution contains large amount on ethanoate ions and ethanoic acid molecules.
- If a small amount of the acid is added to the solution, the hydrogen ions added react with ethanoate ions to ethanoic acid molecules.
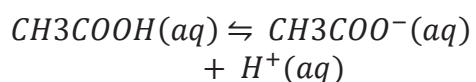
$$CH_3COO^- \ (aq) + H^+(aq) \rightarrow \ CH_3COOH \ (aq)$$

- If a small amount of the alkali is added, the excess ethanoic acid molecules react with the hydroxyl ions added to form the salt and water.

$$CH_3COOH \ (aq) + OH^-(aq) \ \rightarrow \ \ CH_3COO^- \ (aq) + H_2O(l)$$
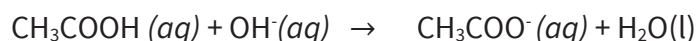
- Hence the pH of the solution remains unchanged

pH of an acidic buffer

- Ethanoic acid in the solution is partially ionized.

$$CH3COOH(aq) \leftrightharpoons CH3COO^-(aq) + H^+(aq)$$

- By law of mass action,

$$Ka = \frac{[CH3COO^-][H^+]}{[CH3COOH]}$$

- But since the acid is only slightly ionized,

$$[CH3COO^-] \approx [salt]$$

$$[CH3COOH] \approx [acid]$$

Therefore

$$K_a = \frac{[salt][H^+]}{[acid]}$$

$$[\boldsymbol{H^+}] = \frac{\boldsymbol{K_a[acid]}}{[\boldsymbol{salt}]}$$

But $\quad pH = -\log[H^+]$

Basic buffers
- These contain a weak base, and its salt with a strong acid. For example, ammonia solution and ammonium chloride, methylammonium nitrate and methylamine solution.

ACTIVITY:

Explain the action of a basic buffer such as on consisting of ammonia solution and ammonium chloride.

pH of an acidic buffer

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- Ammonia in the solution is partially ionized.

$$NH_3(aq) + H_2O(l)$$
$$\leftrightharpoons NH_4^+(aq)$$
$$+ OH^-(aq)$$
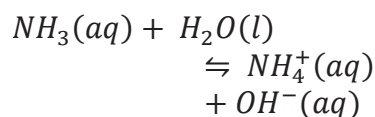
By law of mass action,

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3(aq)]}$$

But since the acid is only slightly ionized,

$$[NH_4^+] \approx [salt]$$

$$[NH_3] \approx [base]$$

Therefore

$$K_b = \frac{[salt][OH^-]}{[base]}$$

$$[OH^-] = \frac{K_b[base]}{[salt]}$$

But $pH = 14 - pOH$

Applications of buffer solutions

- ❖ Maintain constant pH of blood and tissue fluids
- ❖ In fermentation buffers prevent pH changes that would reduce the activity of enzymes
- ❖ In medicine, Solutions for intravenous injections are buffered so that pH does not change.
- ❖ in biochemical assays depend on enzymes and buffers are used to maintain the pH constant
- ❖ in industrial products such as shampoos and lotions
- ❖ in manufacture of drugs

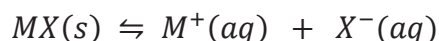## LESSON 3.3: SOLUBILITY PRODUCT

SPECIFIC OBJECTIVES:

By the end of this lesson, you should be able to;
- explain the concept of dynamic equilibrium in a saturated solution.
- explain the factors that affect solubility of sparingly soluble salts.
- derive an expression for solubility product.
- carry out an experiment to determine solubility product.
- calculate K_{sp}. and carry out calculations involving K_{sp}.
- explain relationship between ionic product, K_{sp}, and precipitation.
- explain the applications of K_{sp}.
- explain the concept of common ion effect.
- explain the application of common ion effect.

INTRODUCTION

Solubility product concept.
- This applies to a sparingly soluble salt.
- When a sparingly salt such as lead (II) sulphate is added to water, little of it dissolves and produces ions in the solution while most of it remains **not** dissolved. Thus equilibrium is set up between the solid and its ions in solution. Consider a sparingly soluble salt, MX which dissolves in water according to the equation.

$$MX(s) \leftrightharpoons M^+(aq) \ + \ X^-(aq)$$

- Since the ions are in contact with the solid, the solution is said to be saturated.
- By law of mass action,

$$K = \frac{[M^+][X^-]}{[MX]}$$

- But since the solubility of the salt is very small, the $[MX] \approx 1$.
- Hence the equation becomes

$$K_{sp} = [M^+][X^-]$$

- Which is the *solubility product expression* for a sparingly soluble salt, MX.
- The K_{sp} is called the *solubility product constant.*

- *The **solubility product** of a sparingly soluble ionic compound is the product of the molar concentration of the ions produced by the compound raised to their stoichiometric powers in a saturated solution at a given temperature.*

- ***Solubility of a solute***
  Is the mass of a solute in grams required to saturate specified amount solvent {e.g. 100g of water} at a given temperature.

- ***Saturated solution:***
  Is a solution that cannot dissolve any more solute at a given temperature in the presence of un-dissolved solute.

- The solubility of a sparingly soluble salt can be determined by conductivity measurements e.g. for barium sulphate or titration and the solubility product calculated e.g. magnesium hydroxide, calcium iodate.
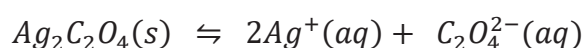
Note:

When
- $K_{sp} = [M^+][X^-]$; The solution is said to be saturated
- $K_{sp} > [M^+][X^-]$; The solution is unsaturated
- $K_{sp} < [M^+][X^-]$; Precipitation occurs

Determination of the solubility product of sparingly soluble salt such as silver oxalate

- This can be done by titration method.

Procedure

- Excess silver oxalate is added to a given volume of water in a container.
- The container is stoppered and shaken occasionally for about two hours.
- The solution is filtered to removes the excess solid
- An aliquot of the filtrate is pipetted into a conical flask and to above 60°C.
- The **hot** solution is titrated with a standard solution of potassium manganate(VII).
- The concentration of the oxalate ions in the solution is calculated.

Treatment of results

$$Ag_2C_2O_4(s) \leftrightharpoons 2Ag^+(aq) + C_2O_4^{2-}(aq)$$

- Let $[C_2O_4^{2-}] = x$
- $[Ag^+] = 2x$

- From
- $K_{sp} = [Ag^+]^2[C_2O_4^{2-}]$
- $K_{sp} = (2x)^2 x$

- $K_{sp} = 4x^3$

Factors which affect the solubility of a sparingly soluble salt

Formation of complex ion

- Consider a sparingly salt such as silver oxalate.

$$Ag_2C_2O_4(s) \leftrightharpoons 2Ag^+(aq) + C_2O_4^{2-}(aq)$$

- The solubility of this salt can be increased by adding ammonia solution. This is because ammonia reacts with silver ions to form the diamminesilver(I) complex ions.

$$Ag^+(aq) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq)$$
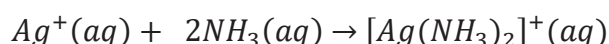
- This reduces the concentration of silver ions in equilibrium. And in order to restore the K_{sp}, more silver oxalate dissolves.
- Hence, *formation of a complex ion increases the solubility of a sparingly soluble salt.*
- The solubility of lead(II) chloride is higher in concentrated hydrochloric acid than water or dilute hydrochloric acid du formation of a complex ion, tetrachloroplumbate(II).

$$PbCl_2(aq) + 2Cl^-(aq) \rightarrow [PbCl_4]^{2-}(aq)$$
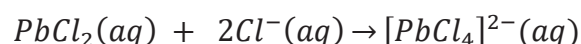
- Copper(I) salts are also more soluble in aqueous ammonia than water because of formation of the complex ion, diamminecopper(I) ion.

$$Cu^+(aq) + 2NH_3(aq) \rightarrow [Cu(NH_3)_2]^+(aq)$$
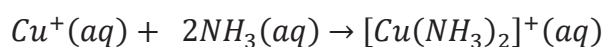
Common ion effect

- *This is the precipitation of a sparingly soluble ionic solute from its saturated solution by adding to the solution another electrolyte containing an ion common to that of the sparingly soluble compound.*
- The *common ion effect reduces the solubility of a sparingly soluble salt*.
- Consider a sparingly soluble salt such as silver chloride.

$$AgCl(s) \leftrightharpoons Ag^+(aq) + Cl^-(aq)$$
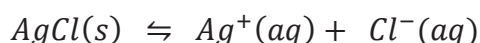
- When silver nitrate is added to such a solution, the concentration of silver ions in the solution increases, the ionic product exceeds the K_{sp}, the excess silver ions react with chloride ions to form silver chloride solid and the K_{sp} is restored.
- The same thing would occur if sodium chloride was added to a saturated solution of silver chloride

## Applications of common ion effect

Purification of common salt.

- Common salt contains calcium and magnesium chloride as impurities. Bubbling hydrogen chloride through a saturated solution of impure sodium chloride will precipitate sodium chloride while leaving calcium and magnesium chlorides in the solution

Salting out of soap

- In the preparation of soap, a concentrated solution of sodium chloride is added to the reaction mixture to precipitate soap.

Selective precipitation of compounds in qualitative analysis

- This also uses the knowledge of solubility product and common ion effect, for example the precipitation of sulphides.
- Certain metal sulphides are precipitated by passing hydrogen sulphide into a solution of the metal ion in presence of an acid while others in the presence of alkali.
- The choice of the conditions depends on the solubility product of the sulphide.
- Precipitation of sulphides such as ZnS, MnS, and NiS occurs in alkaline medium (presence of dilute ammonia).
- Hydrogen sulphide ionizes in water as follows

$$H_2S(aq) \leftrightharpoons 2H^+(aq) + S^{2-}(aq)$$
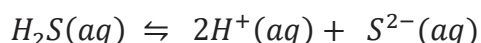
- In the presence of an alkali, hydrogen sulphide reacts with the alkali the hydrogen ions react with the hydroxide reducing their concentration in equilibrium. This causes further ionization of hydrogen sulphide and the concentration of the sulphide ions increases. The high K_{sp} of the sulphides is reached which enables them to precipitate.

- While, sulphides such as CuS, SnS and CdS with low K_{sp} values are precipitated in acidic medium (presence of dilute hydrochloric acid). The hydrogen ions from the acid suppress the ionization of hydrogen sulphide. Very low concentration of sulphide ions occur in solution but enough to reach the K_{sp} of the metal sulphides hence precipitated.

Use of potassium chromate (IV) in silver titration

- When silver nitrate solution is titrated with sodium chloride solution containing a little potassium chromate(IV), only silver chloride is precipitate as long as there are any chloride ions in the solution. The red precipitate of silver chromate(VI) appears when all the chloride ions are reacted.
- This is explained by the solubility products of the two silver salts.

$$K_{sp}(AgCl) = 1 \times 10^{-10} mol^2 dm^{-6} \quad \text{and} \quad K_{sp}(Ag_2CrO_4) = 2.5 \times 10^{-12} mol^3 dm^{-9}.$$

- Suppose the concentration of Cl^- and CrO_4^{2-} are both 0.1 $mol dm^{-3}$ then the concentration of silver ions needed to precipitate silver chloride

$$= \frac{1 \times 10^{-10}}{0.1} = 1 \times 10^{-9} \ mol dm^{-3}$$

- Concentration of silver ions needed to precipitate silver chromate

$$= \sqrt{\left(\frac{2.5 \times 10^{-12}}{0.1}\right)} = 5 \times 10^{-6} \ mol dm^{-3}$$

- Thus even if the concentration of chloride and chromate ions in the solution is the same, it is easier by adding silver ions to reach the solubility product of silver chloride than that of silver chromate in spite of the lower solubility product of the latter.

LESSON 3.4: ACID – BASE INDICATORS

By the end of this lesson, you should be able to;
- explain the action of an indicator.
- give examples of indicators.
- describe how an indicator works.
- explain the concept of pH range.
- choose a suitable indicator for acid-bases titration.
- carry out acid-bases titration.
- sketch different types of pH volume curves for acid-bases titration.

INTRODUCTION

- Acid – base indicators are substances which can change colour according to the hydrogen ion concentration of the liquid in which they are placed.
- They are weak acids; hence they are slightly dissociated when dissolved in water. The colour of the indicator depends on the colour of the un-dissociated molecules and the colour of the ions produced.

Action of an indicator

- Consider an indicator, HIn, when put in water, it ionizes as follows

$$HIn(aq) \leftrightharpoons H^+(aq) + In^-(aq)$$
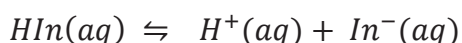
- And at this point, there are indicator molecules (HIn) and ions in the solution and the colour of the solution will be an intermediate of the two. e.g. in water methyl orange is orange, while phenolphthalein is colourless.

- ***Addition of an acid,*** increases the hydrogen ion concentration in the solution. These combine with the In^- in the solution to form the unionized HIn indicator molecules. The HIn molecules of litmus and methyl orange are red, while those of phenolphthalein are colourless.

- ***Addition of an alkali,*** provides hydroxide ions which react with the hydrogen ions from the indicator. This reduces the concentration of the hydrogen ions in equilibrium. More of the indicator molecules ions, increasing the concentration of the In^- ions in the solution, hence the colour of the solution also changes to that of the In^- ions. e.g. the In^- ions of litmus are blue, methyl orange are orange, and phenolphthalein pink

Choice of an indicator

- The true point of neutralization in any titration occurs when the amounts acid and base added together are chemically equivalent to each other. i.e. complete neutralization has taken place and a salt and water have been produced.
- However sometimes, the pH is not equal to 7 even at this point. This is because the salt formed at endpoint may undergo hydrolysis. The choice of the indicator will therefore depend on the pH of the solution at end point.
- Every indicator has a definite range of pH over which it changes colour, and if the pH at the end point of the titration falls within this range, then the indicator will be the ideal choice.

<u>**Table showing the ranges of some common indicators**</u>

Indicator	pH range
Methyl orange	2.9 – 4.6
Phenolphthalein	8.3 – 10.0
Litmus	5.0 – 8.0
Methyl red	4.2 – 6.3

- A titration between a strong acid (hydrochloric acid) and a weak base (aqueous ammonia), produces a salt, ammonium chloride which undergoes hydrolysis to form an acidic solution. Hence end point, the solution has a pH lower than seven. Methyl orange, litmus and methyl red would be ideal choices. (methyl range is commonly used)
- A titration between a weak acid (ethanoic acid) and a strong base, (sodium hydroxide) produces sodium ethanoate which hydrolyses in water to form an alkaline solution, with pH greater than seven. Phenolphthalein is the indicator of choice.
- A titration between a strong acid and a strong base forms a salt that does not undergo hydrolysis. pH of the solution at endpoint is seven and any indicator can be used for the titration.

pH CURVES

Titration of a strong acid against a strong alkali (hydrochloric *acid and* sodium hydroxide)
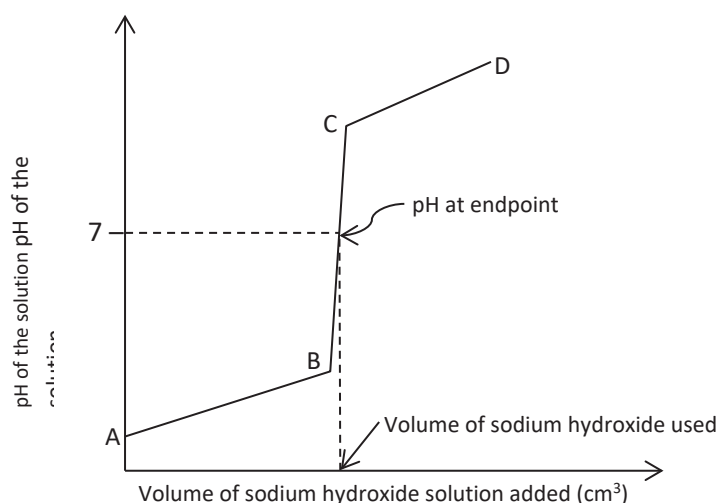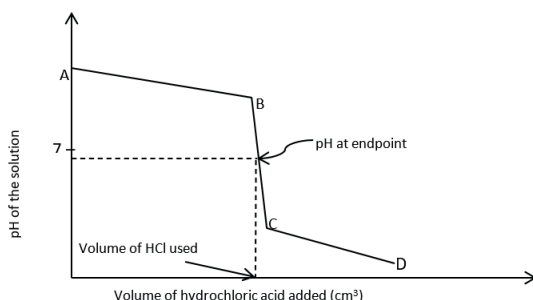

Explanation

- Initially, pH is low. Because hydrochloric acid is a strong acid the fully ionizes to give a high concentration of hydrogen ions.
- There is a gradual increase in pH between AB. This is because the acid is still in excess. The hydrogen ions gradually neutralized by the hydroxide ions from the alkali
- There is a rapid increase in pH between BC because the end point has been reached. A small amount of sodium hydroxide causes a big increase in pH.
- The pH continues to increase further between CD, due to addition of excess sodium hydroxide.
- The pH at endpoint is 7 because the salt formed (sodium chloride) does not undergo hydrolysis

Titration of a weak acid against a strong alkali (ethanoic acid sodium hydroxide
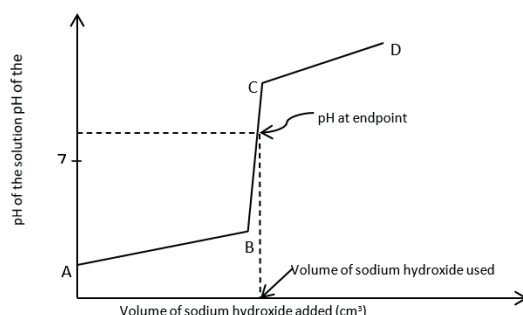
Explanation

- Initially the pH is not very low. Because ethanoic acid is a weak acid that partially ionizes to give a lower concentration of hydrogen ions
- The pH increase gradually along AB as the alkali is added because of the gradual neutralization of the excess hydrogen ions by hydroxide ions. A buffer solution is formed that does not allow pH to change rapidly.
- pH increases rapidly along BC because the end point has been reached. Small amount of sodium hydroxide causes a big change in pH.
- The pH increase along CD because of excess sodium hydroxide added.
- The pH at end point is greater than 7 because of salt hydrolysis to form an alkaline solution

Titration of a weak alkali against a strong acid (aqueous ammonia and hydrochloric)s

Explanation

- Initially at A, the pH is not very high. Because aqueous ammonia is a weak base that partially ionizes to give fewer hydroxide concentration in the solution.
- The pH then decreases gradually along AB. This is because of addition of the hydrogen ions that neutralizes the hydroxide ions. The alkali is still in excess and together with the salt formed form a buffer solution that resists a rapid change in pH.
- The pH then decreases rapidly along BC when a small amount of the acid is added because the endpoint is reached.
- Along CD pH decreases gradually because of addition of excess acid
- The pH at endpoint is less than seven because the salt formed undergoes hydrolysis to produce hydrogen ions that make the solution acidic.

TOPIC 4.0 CHEMICAL KINETICS

GENERAL OBJECTIVE:

By the end of this topic, the learner should be able to appreciate that different reactions occur at different rates and explain why they do so.

LESSON 4.1 SIMPLE RATE EQUATIONS

By the end of this lesson, you should be able to:
- Explain the concept of chemical reaction.
- Explain the law of mass action and its application.
- Explain order of a reaction and rate constant.
- Define the different terms used in kinetics.
- Relate mechanisms of reactions to kinetics.

INTRODUCTION
- Chemical kinetics is a branch of chemistry that deals with the measurement of reaction velocities/rates and determination of mechanisms by which reactants are converted into products.
- The knowledge of chemical kinetics is useful when altering the rates of chemical reaction is needed. For instance, manufacturers of fertilizers aim at speeding up the formation of ammonia from nitrogen and hydrogen whereas a car manufacturer wishes to slow down the rate at which iron rust.

Rates of reaction

Reaction rate is the speed at which a chemical **reaction** proceeds. It is often expressed in terms of either the concentration (amount per unit volume) of a product that is formed in a unit of time or the concentration of a reactant that is consumed in a unit of time.

Consider the reaction

A → product (p) ……………………………………………… (I)

The rate of the reaction or reaction velocity may be defined as the rate of disappearance of the reactant (A) or the rate of appearance or formation of the product (P) with respect to time.

$$\text{Thus rate} = -\frac{dA}{dt} = \frac{dP}{dt} = K[A]$$

Where, K, is the rate constant.

In general, for a reaction

$$aA + bB \rightarrow cC + dD \dots\dots\dots\dots\dots\dots\dots(II)$$

The rate of reaction is given as

$$\text{Rate} = -\frac{1}{a}\frac{dA}{dt} = -\frac{1}{b}\frac{dB}{dt} = +\frac{1}{c}\frac{dC}{dt} = +\frac{1}{d}\frac{dD}{dt}$$

Since the reaction depends on the concentration of the reactants, the rate equation for the reaction in (II) can be expressed in a rate equation represented as

Rate = $K[A]^x[B]^y$.

Definitions terms in a rate law
  i)   **[A]** is the molar concentration of reactant A
  ii) **x** is the order of reaction with respect to A
  iii) **y** is the order of reaction with respect to B.
  iv) The algebraic sum **(x + y)** is the overall order of the reaction. i.e. the order of the reaction is the sum of power dependence of the rate on the concentration of each reactant.
  v)   **K** is the **rate constant**, or the specific **rate constant**. It is the proportionality **constant** in the **equation** that expresses the relationship between the **rate** of a **chemical** reaction and the concentrations of the reacting substances.
Stoichiometry of a reaction is the quantitative relationships of the amount of products and reactants in a given reaction

The values of x and y are often 0 or 1 or 2 and rarely 0, 3, fraction, or negative numbers.

These values x and y are experimentally determined values and cannot be predicted until one has carried out the experiment. The order of the reaction has nothing to do with the stoichiometry of the equation for the reaction.

For example, a simple reaction between bromated (V) ions, bromide ions and hydrogen ions to give bromine is represented by the equation:

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$
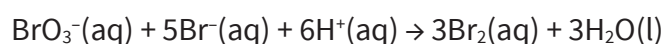
This has a complex rate equation from kinetic measurements as expressed below:

$$-\frac{d[BrO_3^-]}{dt} = K[BrO_3^-][Br^-][H^+]^2$$

Determining the order of reaction

Method 1**. Initial rate method**. The order of a reaction can be found by comparing the initial rates of two more or reactions at known initial concentrations.

Example 1

The following results obtained for a reaction between A and B; can be used to determine the order of reaction with respect to A and with respect to B and the rate constant.

Run	Concentration (moldm^{-3})		Initial rate (moldm^{-3})
	A	B	
(a)	0.50	1.0	2.0
(b)	0.50	2.0	8.0
(c)	0.50	3.0	18.0
(d)	1.0	3.0	36.0
(e)	2.0	3.0	72.0

Let the rate equation = $K[A]^x[B]^y$

To obtain x, which compare reactions in which the concentrations of B are constant but those of A vary such as (d) and (e):

$$\frac{Rate\ (e)}{Rate\ (d)} = \frac{72}{36} = \frac{K[2.0]^x[0.3]^y}{K[1.0]^x[0.3]^y}$$

$$x = 1$$

To obtain y, which compare reactions in which the concentrations of A are constant but those of B vary such as (b) and (a):

$$\frac{Rate\ (b)}{Rate\ (a)} = \frac{8.0}{32.06} = \frac{K[0.50]^x[2.0]^y}{K[0.50]^x[1.0]^y}$$

$$4 = 2^y \implies y = 2$$

Calculating the rate constant, K,

We substitute for x and y in the and any of the experimental results above, in the rate equation e.g. (a)

$2 = K\,[0.5]^1 \times [1.0]^2$

$K = 4.0 \text{dm}^6\text{mol}^{-2}\text{s}^{-1}$

Activity

1. *Tabulated are values of initial rates for the reaction*

$$2A + B \rightarrow C + D$$
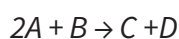
Experiment	[A]$_0$ (moldm^{-3})	[B]$_0$ (moldm^{-3})	Initial rate (moldm^{-3} min^{-1})
1	0.150	0.25	1.4×10^{-5}
2	0.150	0.50	5.6×10^{-5}
3	0.075	0.50	2.8×10^{-5}
4	0.075	0.25	7.8×10^{-5}

a) *Find the order of reaction with respect to A, the order of reaction with respect to B, and the overall order of the reaction.*

b) Find the value of the rate constant

c) Find the initial rate of the reaction when $[A]_0 = 0.120$ moldm^{-3} and $[B]_0 = 0.22$ moldm^{-3}.

Activity 2

The rate equation for a 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 is kept constant, but that of R is doubled.
   ii) the concentration of all species are halved
   iii) the concentration of all species are doubled
b) the following were obtained in a study of reaction between peroxodisulphate and iodide ions

Expt. No.	$[S_2O_8]^{2-}$ Moldm^{-3}	$[I^-]$ Moldm^{-3}	Rate Moldm^{-3} s^{-1}
1	0.024	0.024	9.60×10^{-6}
2	0.048	0.024	1.92×10^{-6}
3	0.048	0.012	9.60×10^{-6}

   i) Write the rate equation
   ii) Calculate the rate constant for the reaction and state its units
   iii)

LESSON 4.2: REACTIONS OF VARIOUS ORDERS

SPECIFIC OBJECTIVES.
By the end of this lesson, you should be able to;
- describe the experimental procedure to determine orders of reaction.
- explain the concept of half-life.

**INTRODUCTION**

1. FIRST-ORDER REACTION

A reaction is said to be first order if the rate is proportional to the first power of concentration of reactants on which the reaction kinetics depends. That is, the rate law for the first order reaction is given by

      Rate = $K[A]$

Identification of a first-order reaction

The first-order reaction can be identified from the shapes of the following graphs.

All these graphs that show that the rate of reaction is proportional to the concentration of the reactant in the chemical reaction.
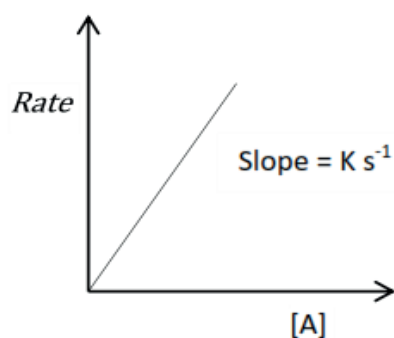
i) Rate of reaction against concentration

A straight line with a positive gradient shows that the rate is proportional concentration of the reactant and that the reaction is thus first order.

ii) The concentration of the reactant against time.
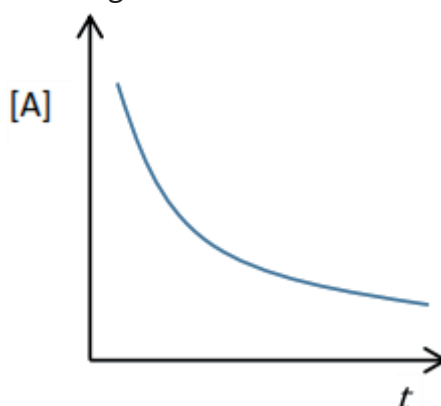
Hyperbola shows that the rate of reaction is proportional to the concentration of the reactant and thus the first-order reaction

iii) For a first-order reaction, a plot logarithm of concentration against time gives a straight line with a negative gradient.
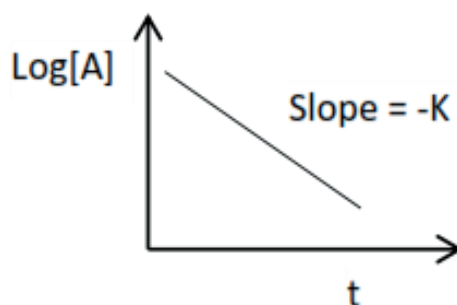
A typical example of a reaction that follows a first-order reaction mechanism is a radioactive disintegration process.

Definitions

Radioactive decay (also known as nuclear decay, radioactivity, radioactive disintegration, or nuclear disintegration) is the process by which an unstable atomic nucleus loses energy by radiation.

The integrated rate law for the first-order reaction

Consider the first-order reaction

$$A \rightarrow P$$

If the initial concentration [A] of reactant (A) at the time, t=0, is **a** moldm^{-3} and the concentration of the product, P, after time t is **x** moldm^{-3}; then concentration of A at time, t, will be (a-x) moldm^{-3}.

Then, the rate of reaction as the rate of formation of the product is represented as

$$\frac{dx}{dt} = k[a - x]$$

Or, separating variables,

$$\frac{dx}{(a - x)} = kdt$$

To get relationship between concentration and time, integrate both sides, i.e.

$$\int \frac{dx}{(a - x)} = \int kdt$$

$$-In(a - x) = kt + C$$

At *t = 0, x = 0, thus,* C = $-Ina$

Substituting for C, we derive the relationship:

$$Ina - In(a - x) = kt$$

$$In\frac{a}{a - x} = kt$$

The plot of $In\frac{a}{a-x}$ against time, t, gives a straight line and the slope of this graph is equal to ks^{-1}.
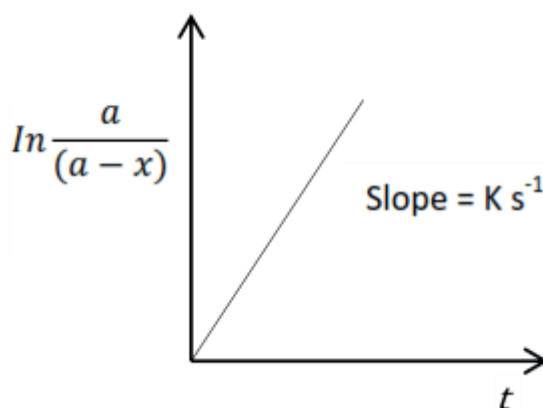
Half-life of the first order reactions

The half-life of the reaction is the time taken by a reactant to reduce to half of its initial concentration.

The expression for the half-life of a first-order reaction is obtained from the integrated rate law: i.e.

$$In \frac{a}{a - x} = kt$$

At $t = t\frac{1}{2}$, $(a - x) = \frac{a}{2}$,

Where t ½ is half-life
Then,

$$In \frac{a}{\frac{a}{2}} = kt\frac{1}{2}$$

And thus,

$$t\frac{1}{2} = \frac{In2}{k}$$

Note that, *Inx = 2.303logx*

This shows that in the first-order reaction, the half-life is independent of the initial concentration of the reactants. The time necessary for the reactants to decrease to any other given fraction can be derived in a similar manner.

2. Zero-order reactions

In a zero-order reaction, the rate is independent of the concentration of the reactants. A plot of the concentration [A] of the reactant against time has the form below:
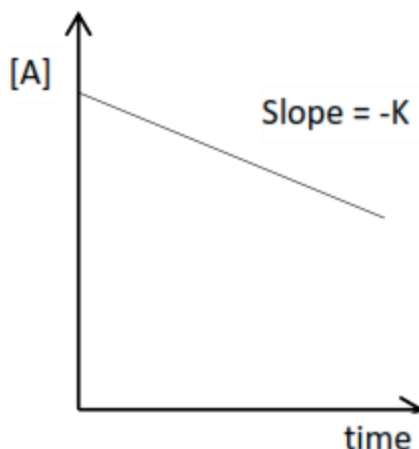
The rate equation for a zero-order reaction:

$$Rate = K[A]^0 \text{ or } Rate = K \, s^{-1}$$

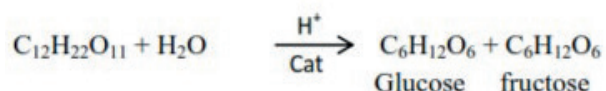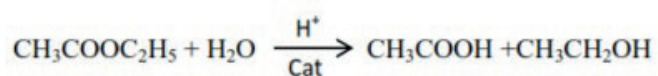Example, the reaction between iodine and propanone is a zero-order with respect to iodine.

$$CH_3COCH_3(aq) + I_2 \xrightarrow{\text{acid}} CH_3COCH_2I(aq) + HI(aq)$$

Pseudo-order reaction

A **pseudo order reaction** is a reaction that is truly **higher-order** but can be approximated to a **lower order** under special circumstances.

For instance, an elementary reaction between two reactants A and B is normally expected to be a second-order; for example, hydrolysis of an ester and inversion of sucrose.

$$CH_3COOC_2H_5 + H_2O \xrightarrow[\text{Cat}]{H^+} CH_3COOH + CH_3CH_2OH$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Cat}]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

However, if one of the reactant B is present at a very much greater concentration than that of A or else only acts as a catalyst, the concentration of B is considered constant ad the rate law becomes

Rate = K'[A]

Such a reaction is said to be pseudo-first order since the rate is proportional to the concentration of A raised to the first power. Nevertheless, it must be remembered that the new constant (K') is not a true constant because it also depends on the concentration of B. Since water is usually found in excess, the reactions are given above are in practice found to be pseudo-first-order.

Note that:

1) For a zero-order reaction, any change in concentration of the reactant does not affect the rate of reaction.
2) For a first-order reaction increasing the concentration of the reactant two or three times also increase the rate two or three times.

Activity

a) State what is meant by the term order of a reaction
b) Methylethanoate is hydrolyzed by water in the presence of an acid according to the following reaction:

$$CH_3COOCH_3 + H_2O \ (l) \ \longleftrightarrow \ CH_3CH_2OH + C\ H_3OH$$
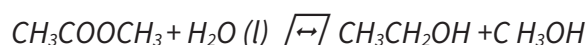
   i) State the molecularity of the reaction
   ii) State the conditions under which the reaction can be the overall first order

c) The table below shows some kinetic data for the following reaction:

Expt. No.	[A] Moldm^{-3}	[B] Moldm^{-3}	Rate Moldm^{-3} s^{-1}
1	0.20	0.20	1.2×10^{-8}
2	0.20	0.60	1.2×10^{-8}
3	0.40	0.60	4.8×10^{-8}

   i) Write the overall order of reaction
   ii) Calculate the rate constant and give its units.

LESSON 4.3: MEASURING THE RATES OF REACTIONS

By the end of this lesson, you should be able to;
- apply the knowledge of rate equations in sketching and interpreting graphs.
- discuss the relationship between a mechanism of reaction and molecularity.

- carry out designed experiments to generate kinetic data for determining order of reaction, rate of reaction and rate constants.
- explain the theories of collision.
- use theories of reaction to explain factors that affect rates of reaction

INTRODUCTION

The rate of a chemical reaction can be obtained by following some property which alters with the extent of the reaction. By analyzing the reaction mixture at suitable intervals, it's possible to determine the concentration of both the reactant and/or the product at different times and hence obtaining the rate (i.e. the rate at which the concentration of a particular substance changes with time).

In practice, the rates may be measured by observing the rate of change of physical properties such as refractive index, volume, color, and if the reaction is sufficiently slow, its rate may be found by frequent withdrawal of small portion of the reacting mixture and analyze then chemically at intervals.

Example: Iodination of propanone

An experiment to determine the order reaction with respect to iodine in the reaction of iodine with propanone in presence of an acid catalyst.

1. A fixed volume of standard Iodine solution is added to an excess of propanone solution in a flask.
2. To this mixture is added a fixed volume of dilute sulphuric acid and a stop clock started immediately.
3. At intervals of time say (every 10 minutes for 50 minutes), a specified portion is pipetted from the mixture and into a flask containing sodium hydrogen carbonate which stops the reaction by neutralizing the acid catalyst.
4. The resultant mixture is titrated with standard sodium thiosulphate using a starch indicator.
5. The volume (V_t) of thiosulphate used on the portion of the mixture after a specified time (t) is proportional to the amount of iodine remaining in the mixture.
6. The initial amount of iodine (V_0) is obtained by titrating a similar portion of the original mixture with sodium thiosulphate solution.
7. A plot of the graph of V_t against time gives a straight line as shown below showing that the order of reaction with respect to iodine is zero.
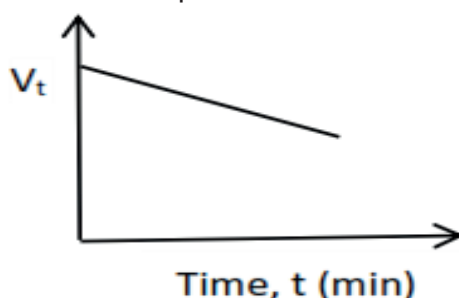
NB. The gradient gives the rate constant whose units is molcm^{-3} s^{-1}.

Activated complex

With the exception of radioactive disintegration all elementary reaction occurs via a transition state, for example, substitution reaction is expected to proceed as below

$$A + BC \quad \boxed{\leftrightarrow} \quad [A….B…..C] \quad \boxed{\leftrightarrow} \quad AB + C$$
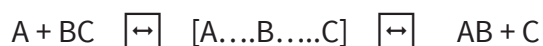
In order to form the transition state, the reactants must first acquire activation energy i.e. This is the minimum energy required for the reaction to take place. Being energy-rich, the transition species is unstable and cannot be isolated and is usually referred to as the activation complex. This may decompose either to give the product or original reactants. The energy variation during the above process may be represented by the figures below:
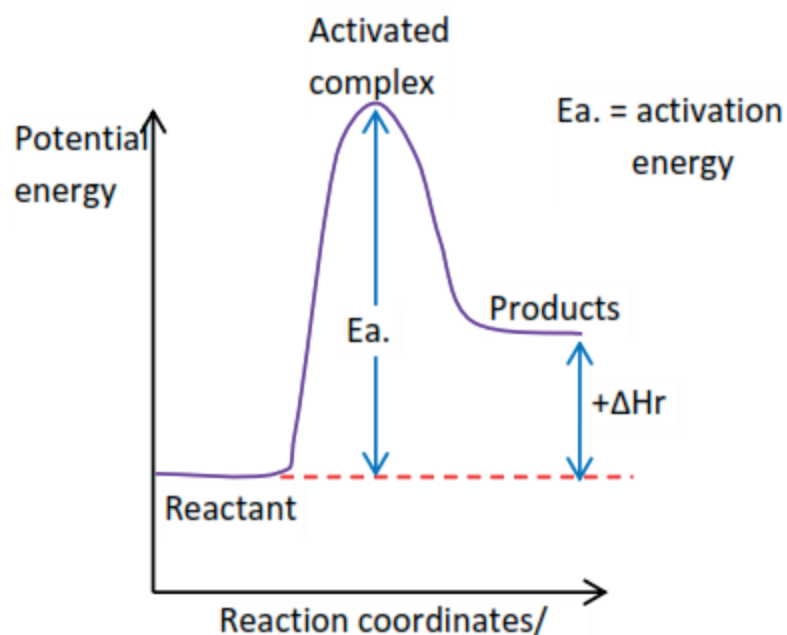
Definition

An **activated complex** is short lived intermediate involving unstable arrangement of atoms that results in the maximum **energy** point along the reaction path.

The energy diagram for the reaction for an exothermic reaction
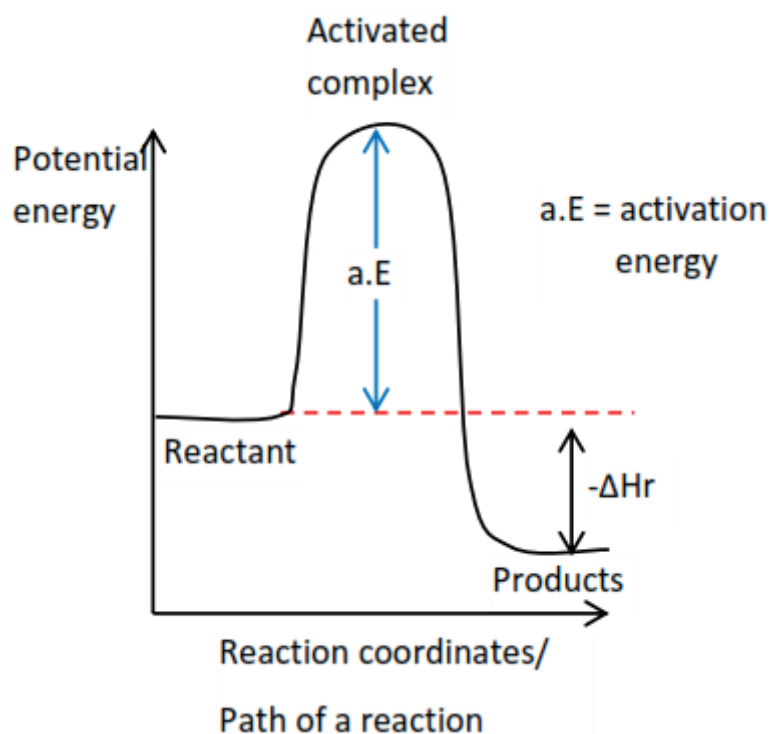
The energy diagram for the reaction for an endothermic reaction

Path of a reaction

The difference between the energy of the reactants and the product is the enthalpy of the reaction (ΔH_r) which is negative for exothermic reaction (i.e. energy given out during the reaction and the reaction mixture heats up) or positive for endothermic reaction (i.e. energy is required for the reaction to take place.)

Definition

The **molecularity** of a reaction is defined as the number of molecules or ions that participate in the rate-determining step.

The **activation energy** of a **chemical** reaction is the difference between the energy of the **activated complex** and the **energy** of the reactants.

Factors that affect the rate of reaction

The main factors which influence reaction rate are

    i)   concentration of the reactant
    ii) temperature
    iii) Pressure
    iv) presence of light
    v)   the size of the particles for solid reactants.
    vi) Catalyst

1. Particle size

The smaller the particle sizes the faster the reaction in the solid state because of increased surface area for contact. e.g.
$CaCO_3(s) + 2HCl\ (aq) \rightarrow CO_2(g) + CaCl_2(aq) + H_2O(l)$
The reaction is faster when $CaCO_3$ is in powder form than big chips.

2. Concentration

The higher the concentration of reactants; the faster is the rate of reaction due to the increase in the rate of collision among the reacting molecules.

3. Pressure

Pressure increases the rate of reaction when the reactants are in the gaseous phase because it increases the proximity and the rate of collision of the reacting molecules.

4. Temperature

Temperature increases the rate of reaction because
- Particles gain kinetic energy which increases the rate collision
- it increases the fraction of molecules with energy equal or higher than the activation energy that enables the reaction to take place in case collision take place between molecules.

The graph below shows the distribution of kinetic energies of molecules of a gas at temperatures T_1 and T_2; T_2 being higher than T_1.

Distribution of molecular kinetic energies at different temperatures
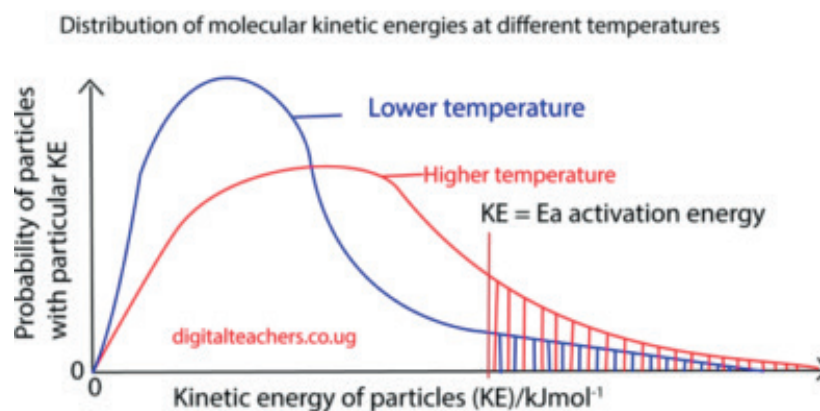
The number of molecules with energy equal to or greater then E_a increases rapidly with temperature as shown by the shaded area under graph above.

5. Light

Some reactions are catalyzed by light such as photosynthesis and formation of silver from silver salts that take place when a photographic film is exposed to light. The higher the light intensity, the higher the rate of reaction will be.

6. Surface area

Increasing surface area of the reactant increases the rate of reaction because it brings the reacting substances into more intimate contact to facilitate their interaction.

7. Catalyst

Increase the rate of reaction by lowering the activation energy

The energy diagram for the reaction for exothermic reaction in the absence and presence of a catalyst.
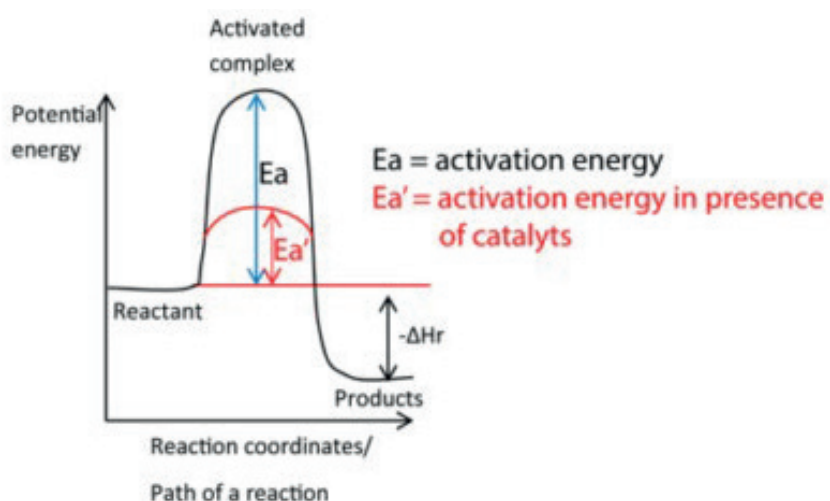
TOPIC 5.0 ELECTROCHEMISTRY

GENERAL OBJECTIVE:

By the end of this topic, the learner should be able to outline the effect of electric current on substances and the ability of the substances to generate electricity.

**LESSON 5.1** ELECTROCHEMICAL CELLS

SPECIFIC OBJECTIVES.
By the end of this lesson, you should be able to;
- explain the concept of electrode potential.
- describe the electrochemical series.
- use the electrochemical series to explain the absolute and relative electrode potential.
- describe the structure and functioning of standard hydrogen electrode.

INTRODUCTION
When a strip of metal is placed in a solution of its ions, the metal atoms tend to ionize; cations dissolve in solutions while electrons remain on the metal surface. For instance, a divalent metal, M, ionizes as follows

M(s) $\rightleftharpoons$ M^{2+} (aq) +
2e ……………………………………………………………………………..(1)
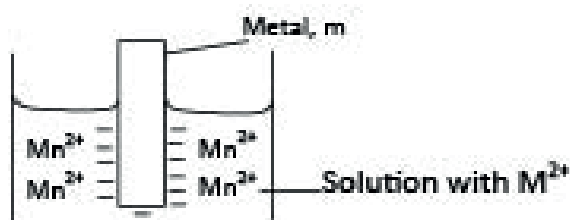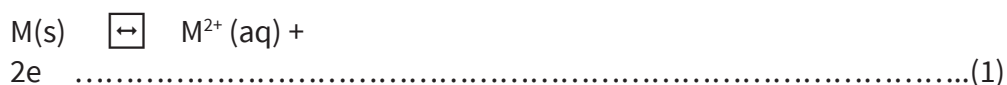
The attraction of the metal rod (containing negative charge) and the solution (containing positive charges) causes a potential difference called **electrode potential.**

The metal dipped into it's a solution containing metal ions is called electrode half-cell represented symbolically as M^{n+}/M. For example, a half-cell of zinc rod dipped in zinc ion solution is symbolized as Zn^{2+}/Zn

Electrode potential is a potential difference that is set up between a metal and its solution containing metal ions.

Factors affecting the magnitude of the potential difference
1. **The concentration of metal ions already in solution**. Since the ionization equation **(1)** is a reversible reaction, the higher the concentration of metal ions in solution, the further to the left will be the state of equilibrium and hence the smaller the electrode potential.
2. **Temperature.** Increasing temperature increases the ionization of metal atoms and thus increases the electrode potential.
3. **Pressure: applicable to gas systems**, the higher the pressure the higher the electrode potential because increased pressure increases the gas concentration at gas-liquid junction.
4. **Position of metal in electrochemical series.** Metals above hydrogen in electrochemical series, have ionization reactions that lie more to the right than left, thus, the metal tends to be negatively charged with respect to their solutions. Thus, have negative electrode potentials.

Metals below hydrogen in electrochemical series, their ionization reaction lie more to the left and their electrode potentials are positive.

Standard electrode potential (SEP)
This is the electrode potential of a metal dipped in a solution containing one mole of metal ions in a dm^3/litre of solution at 298K and 1 atmosphere. It is denoted by E^0.

Factors affecting standard electrode potential
Electrode potential involves formation of hydrated ions. It is a sum of atomization energy (which is endothermic) + ionization energy (which is endothermic) + ionic hydration energy (which is exothermic).

When atomization and/or ionization energy is high, the standard electrode potential becomes more positive.

On the other hand, when the hydration energy is higher than the sum of ionization and atomization energy, standard electrode potential is negative.

Short-hand Notation for an electrode half cells
A metal rod dipped in a solution of metal ions constitutes a half cell. The accepted short form of writing an electrode is to write is to write 'oxidized form/reduced form' of metal. For example, the zinc half-cell is written as Zn^{2+}/Zn and copper electrode as Cu^{2+}/Cu.
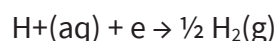
Standard Hydrogen electrode

It consists of hydrogen gas at 298K and pressure of 1 atmospheres bubbling over a strip of platinized foil (i.e. platinum coated) in a solution which is 1M with respect to H^+ ions
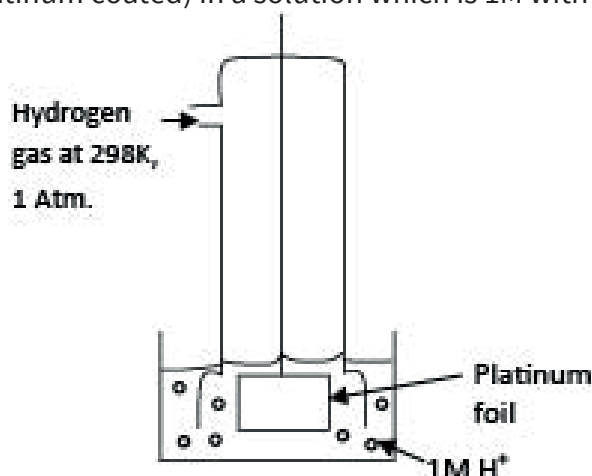
The shorthand notation for a hydrogen electrode is

$$H^+, M/ \frac{1}{2} H_2, 1 \text{ atm. Or } H^+/ \frac{1}{2} H_2.$$

And electrode reaction is

$$H+(aq) + e \rightarrow \frac{1}{2} H_2(g)$$

A potential develops on the surface of the platinum; by convention, it is assigned an arbitrary value of zero volts.

Hydrogen electrode is use as a reference electrode and the electrode potential of all other electrodes are measured relative to this.

## LESSON 5.2: Measurement of electrode potential of metal

SPECIFIC OBJECTIVES:

By the end of this lesson, you should be able to;
- describe the measurement of standard electrode potential.
- explain the term reduction potential.
- apply reduction potential to metal-metal ion convention cells.
- construct an electrochemical cell.
- write the cell notation.
- calculate the e.m.f of a cell and use it to predict spontaneity of reactions.

INTRODUCTION

A standard metal electrode is combined with a standard hydrogen electrode as shown in Fig.4.3 below
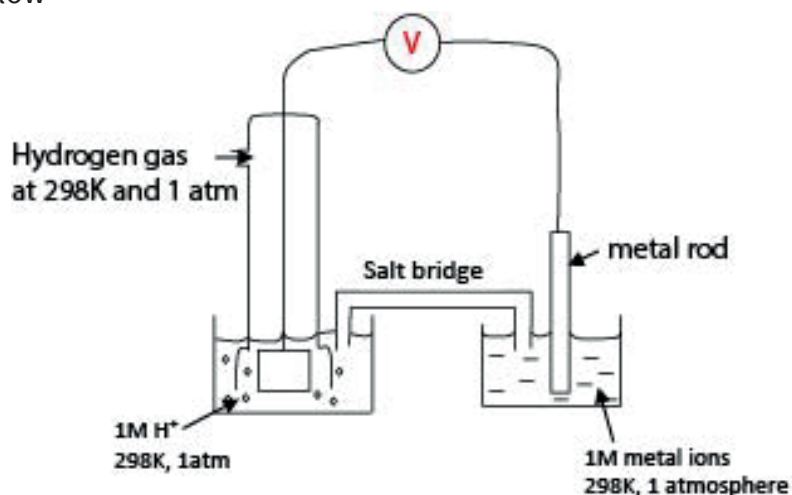
The two compartments in the figure are connected by a **salt bridge**. This contains an electrolyte such as potassium chloride, which conducts electricity but does not allow mixing of two solutions in half cells. The measurement on the high resistance voltmeter is the standard electrode of the metal since that of hydrogen half-cell is zero.

Definition

Standard electrode potential is the electrode potential value of an electrode measure with respect to a standard hydrogen electrode of 0 volts. When an electrode is immersed or dipped into a solution of 1M concentration of its ions at a standard temperature of 298K and pressure of 1 atmosphere.

Some electrode and their standard electrode potentials are given below:

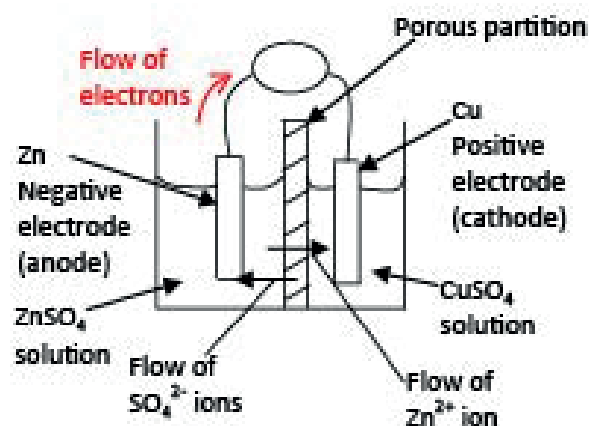| Electrode	Electrode reaction	E^o/volts
Zn^{2+}/Zn	$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$	-0.76
Cu^{2+}/Cu	$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$	+0.34
Fe^{2+}/Fe	$Fe^{2+}(aq) + 2e \rightarrow Fe(s)$	-0.44
Ag^{+}/Ag	$Ag^{+}(aq) + e \rightarrow Ag(s)$	+0.80

Galvanic or Voltaic cells or electrochemical cells

This is a type of cell in which a chemical reaction results in production of an electric current.

By combining two suitable electrodes (half cells) a cell of a particular emf may be obtained. One electrode acts as electron supplier and the other as electron acceptor.
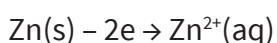
The Daniel cell

It consists of the zinc electrode dipped into 1M zinc sulphate solution and copper electrode dipped into 1M copper sulphate solution, the two solution separated by a porous partition. The cell develops an electromotive force (emf) of 1.10V.
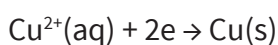

Half call reaction

At zinc electrode (anode)
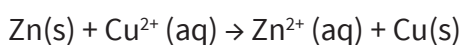
Oxidation occurs and the electrode dissolves.

$Zn(s) - 2e \rightarrow Zn^{2+}(aq)$

At the copper electrode

Reduction occurs (cathode)

$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$

Overall equation

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Cell notation

The Daniel cell can be represented as

$Zn(s)/ZnSO_4(aq)//CuSO_4(aq)/Cu(s)$

Or simply

$Zn(s)/Zn^{2+}(aq)//Cu^{2+}(aq)/Cu(s)$

The single vertical line (/) indicates a phase boundary and double vertical lines (//) indicate a porous partition between the solutions.
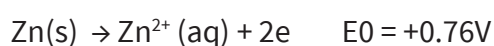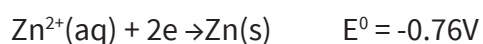
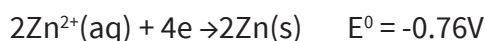**E.m.f of a cell**

The e.m.f of the above cell is given by
$E = E_{Cu} - E_{zn}$

Rules regarding electrode potentials
1. If the direction of an electrode reaction is reversed, the sign of its electrode potential must also be reversed.

$$Zn^{2+}(aq) + 2e \rightarrow Zn(s) \qquad E^0 = -0.76V$$

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e \qquad E0 = +0.76V$$

a) If an electrode reaction equation is multiplied by a positive factor. The electrode potential must **not** be multiplied by that factor. It remains unchanged.

$$Zn^{2+}(aq) + 2e \rightarrow Zn(s) \qquad E^0 = -0.76V$$
$$2Zn^{2+}(aq) + 4e \rightarrow 2Zn(s) \qquad E^0 = -0.76V$$
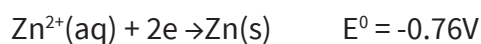
Not 1.52V

Generally, the e.m.f of a cell is defined as follow

$$E^0_{cell} = E^0_{R.H.E} - E^0_{L.H.E}$$

NB. For a positive cell e.m.f, R.H.E is for the half cell with most positive electrode potential.

Example 1

Calculate the standard e.m.f of $Zn/Zn^{2+}//Cu^{2+}/Cu$ from the data given below. Write down the half-cell reactions and cell reaction.
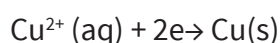
Electrode	E^0/V
Zn^{2+}/Zn	-0.76
Cu^{2+}/Cu	+0.34

Answer

$$E^0_{cell} = E^0_{R.H.E} - E^0_{L.H.E}$$
$$= 0.34 - (-0.76) = +1.10V$$

Electrode reactions

At R.H.E (cathode)

$$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$$

L.H.E (anode)

$$Zn(s) - 2e \rightarrow Zn^{2+}$$

Cell reaction

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
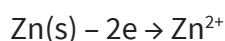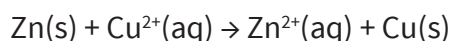
Implication of the e.m.f of a cell

For electrode; since, standard electrode potentials are reduction potentials, a negative value for E^0 implies that the reduction reaction is non-spontaneous while a positive value implies that the reduction reaction is spontaneous.

For a cell a negative value of E^0_{Cell} indicates that the cell reaction as written is non-spontaneous and instead is spontaneous in the reverse direction.

Therefore, the value of standard electrode potential may be used to predict the direction of spontaneous chemical reaction. Then when writing down or constructing a cell given two electrodes together with their standard electrode potentials, the electrode with the less negative E^0 (if both are negative or electrode with more positive value if both are positive) must be the right hand electrode of the cell and the other the left hand electrode.

Activity

a) Construct a cell using Li^+/Li and Mg^{2+}/Mg electrodes,

given that $E^0Li^+/Li = -3.04V$ and $E^0Mg^{2+}/Mg = -2.37V$.

b) Calculate the E^0cell.

c) Give the cell reaction

LESSON 5.3: STANDARD ELECTRODE POTENTIAL AND STANDARD FREE ENERGY CHANGE

SPECIFIC OBJECTIVES

By the end of this lesson, you should be able to;
- use Gibb's free energy expression to predict feasibility of reactions.
- describe the construction of Daniel cell.
- explain the functioning of a battery.
- explain the conversion of one form of energy to another.

There is a relationship between electrochemistry and thermochemistry. In the electrode reaction
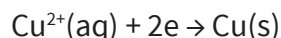
$$M^{n+} (aq) + ne \leftrightarrow M(s)$$
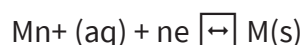
If the standard free energy change, ΔG^0 then the value of the standard electrode potential, E^o, at the same temperature is given by

$$\Delta G^0 = -nFE^0$$

Where n is the number of electrons transferred in the electrode reaction and F is the Faraday constant.

For example, $E^0 = +0.34V$ at 298K for the reaction

$$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$$

The value of ΔG^0 is given by

$$\Delta G^0 = -2 \times 96500 \times (-0.34) = 65.6kJmol^{-1}.$$
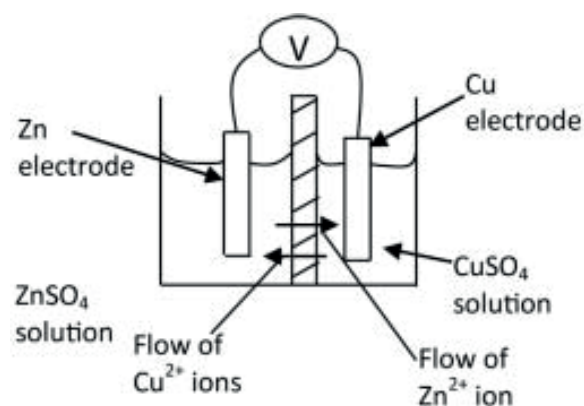
Liquid junction potential

Is a potential difference set up across a phase boundary between two solutions in a cell. It tends to oppose the cell potential i.e. it reduces it and hence the observed cell emf is less than the actual emf of the cell

$$E^o\text{cell} = E^o\text{ cell} - E^o\text{j}$$
$$\text{Observed} \quad \text{actual} \quad \text{the liquid junction}$$
$$\text{potential}$$

Causes of liquid junction potential

It is caused by the differential diffusion of charges across the porous partition between the two solutions of the cell. For example, in the Daniel cell, the Zn^{2+} ions diffuse into the $CuSO_4$ solution and Cu^{2+} diffuses into the $ZnSO_4$ solution.

The speed of migration of Zn^{2+} and Cu^{2+} cations across the phase boundary is different due to a number of factors. Some of which are either the ionic size and/or the extent to which they are hydrated. Due to this, a p.d. is set up across the boundary called Liquid Junction Potential.

This liquid junction potential may be eliminated by connecting the solutions in the two half cells by means of a salt bridge which is a glass tube containing a saturated solution of either KCl or NH_4NO_3.

NB. In the cell diagram/notation, the double lines either represent a porous partition or a salt bridge.

Types of electrodes
1. The metal/metalloid e.g. Zn^{2+}/Zn
2. The gas electrode e.g. Pt, H+/ ½ H_2
3. The metal/insoluble electrode: this type of metal coated with one of its insoluble salt surrounded by a solution containing the anion of the salt e.g. Hg/Hg_2Cl_2, KCl(aq) or Hg/Hg_2Cl_2, Cl^- This electrode is commonly known as a calomel electrode.
4. $Ag/AgCl(s)$, Cl^-

Possible electrode reactions

As R.H.E (reduction) $AgCl (s) + e \rightarrow Ag(s) + Cl^-(aq)$

As L.H.E (oxidation) $Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e$

Hg/Hg_2Cl_2, KCl(aq) or Hg/Hg_2Cl_2, Cl^- This electrode is commonly known as a calomel electrode.

Possible electrode reactions

As R.H.E (reduction) $Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$

As L.H.E (oxidation) $Hg (s) + 2Cl^- (aq) - 2e \rightarrow Hg_2Cl_2(s)$

The two electrodes $Ag/AgCl(s)$, Cl^- and Hg/Hg_2Cl_2, KCl(aq) have stable potential and are not easily affected by oxidants or reducing agents, and because of their high stability, they are sometimes used as reference electrodes since hydrogen electrode in practice is easily poisoned by oxidants and reducing agents.

- Oxidation—reducing (redox) electrodes

This type comprises a reduced species and oxidized species in the same solution, e.g. Pt/Fe^{3+}, Fe^{2+} or Pt/Cr^{3+}, Cr^{2+}.
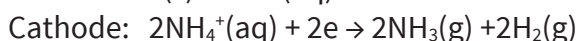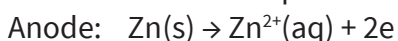
Dry cells
These were invented to overcome the difficulty of electrolytic solution leaking out of cell such as Daniel cell. In dry cell, the electrolyte is made into a paste. An example is shown below
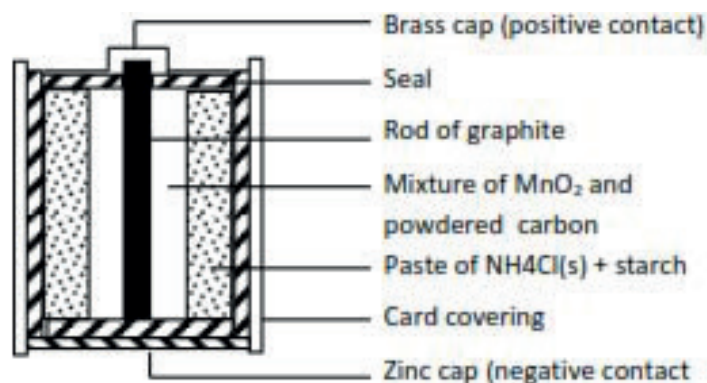
This type of cell is used in radio, flashlight and clocks as it is portable.
The initial electrode processes are
Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e$
Cathode: $2NH_4^+(aq) + 2e \rightarrow 2NH_3(g) + 2H_2(g)$

The lead-acid accumulator

The cell stores or accumulates electric charges. It consists of two lead plates dipping into a 30% solution of sulphuric acid. Both plate becomes covered with an insoluble film of lead II sulphate

First, the cell must be charged. A direct current is passed through the cell. The processes which take place are:

Charge

Positive plate

$PbSO_4(s) + 2e \rightarrow Pb(s) + SO_4^{2-}(aq)$
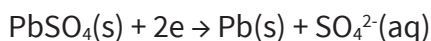
Negative plate
The plates are now different and therefore have different potentials, so that, when they are connected, an electric current will flow between them. When the cell supplies an electric current, i.e. discharge the process which take place are:

Negative plate
$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e$

Positive plates

$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e \rightarrow PbSO_4(s) + 2H_2O(l)$
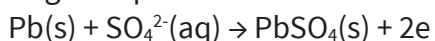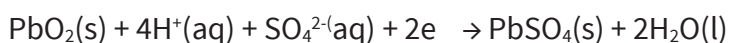
NB: the plate which is positive during the charge becomes negative during the discharge

INORGANIC CHEMISTRY

TOPIC: BONDING AND STRUCTURE

Lesson 2. 1 Types of bonding and structure.

Lesson Outcome:
By the end of this lesson, you should be able to appreciate the knowledge of bonding and structure to understand how compounds are formed by chemical means.

Introduction:

In this lesson you will understand the different types of bonding and structure, their properties and use this knowledge to explain the formation of compounds by reading attentively to the conversation between three Learners Job, Peter and Mary.

Materials you need: periodic table, internet, images, pen, book, pencil.

Mary: What are the different types of bonding and structure and how are they formed?

Job: Different types of bonding exists, these includes, covalent bond, ionic bond (electrovalent bond), metallic bonding, Hydrogen bond, and dative (coordinate) bonding.

Discussion. On different types of bonding.

Peter: Covalent bond
These are bonds formed by equal sharing of two or more electrons between two atoms in a molecule.

Each atom contributes equal numbers of electrons so that the atomic orbital overlap. The shared electrons must be unpaired with opposite spin.

Covalent bonds are usually formed between non-metal atoms due to their high electronegativity.   E.g. Ammonia, Chlorine, carbon dioxide, methane etc.

Mary: Co-ordinate/ Dative bond
This is weak covalent bond formed between an electron rich atom and electron deficient atom/ion.

The atom with lone pairs of electrons donates an electron pair therefore it is called donor atom and the atom receiving the electrons is acceptor.

Examples include:
Hydroxonium, ammonium and dimerised $AlCl_3$ and $BeCl_2$ i.e. in the vapour phase Aluminum Chloride and Beryllium chloride exist as
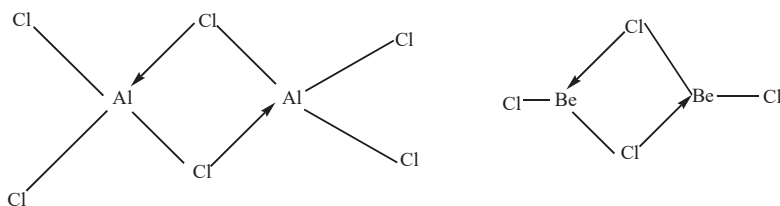
Job: Ionic bonding

Ionic bond is bond formed by electron transfer from electropositive element to another electronegative atom.

The electropositive atom loses electrons to become positively charged while the electronegative atom gains the electrons to become negatively charged.

Mary: Metallic bond

This is an electrostatic attraction between the delocalized electrons of the metal atoms and positive nucleus.

The strength of the metallic bond increases with increase in the number of delocalized electrons

Activity 2.1 *The table below shows the melting points of elements in period 3 of the periodic table*

Element	Na	Mg	Al	Si	P	S	Cl
At. no.	11	12	13	14	15	16	17
Melting point(°C)	98	650	660	1410	44	119	-101

(a)   Plot a graph of melting point against atomic number

(b)   Explain the shape of graph

Teacher: *Copy the table above and answer the questions that follow.*

Peter: Finally, Hydrogen bonding

It is a permanent bond formed by dipole-dipole attraction between the hydrogen atom and a highly electronegative atom in a molecule with at least a lone pair of electron

Compounds of Nitrogen, Oxygen and Fluorine form hydrogen bonds

Follow up activity.

(a) Distinguish between electrovalent and covalent bonding.

(b) State four applications of hydrogen bonding.

(c) Research on the structure of compounds.

TOPIC: COMPOUNDS OF GROUP VII ELEMENTS

Lesson 1.3. Compounds of group VII elements.

Lesson Outcome: A learner should be able to explain how different compounds of group VII elements are formed.

Introduction: Group VII elements form variety of compounds. These includes Hydrides, Chlorides, Oxo-acids and inter-halogens., **Kato** and **Hope.** are going to discuss the compounds. You will require a pen and paper, chemistry note book and periodic table.

Hope: How are the compounds of group VII elements formed?

Kato: Compounds of Halogens include, Hydrides/ Halogen acids.

Let us Study the table below carefully.

	HF	HCl	HBr	HI
B.E (KJmol^{-1})	556	431	336	229
B.p.t (^{o}C)	+19.9	-85	-66.7	-35.4

Kato, reads the values in the table and asks the questions below.

i)   Describe the trend in boiling point, and bond energy among the hydrides?
ii) Explain your observation?

Hope explains;

The **boiling point** increases from HCl to HI. This is because they are simple molecules held by van der -Waals whose magnitude increases with molecular mass.

However, HF has extremely high boiling point because the molecules associate by hydrogen bonding due small ionic radius of the fluoride ions.

Bond energy, decreases from HF to HI due to:

- Increased atomic radius which increases the bond length

- Decrease in electronegativity down the group thus the bonds become less polar.

Kato: **Oxo- acids / ions**

All halogens except fluorine form oxo-ions and oxo-acids e.g. HOCl, $HClO_2$, $HClO_3$ and $HClO_4$

Question.   *Draw and name the structures of the above oxo- acids.*

3. **Chloric (V) acid**

This is a powerful oxidizing agent that only occurs in aqueous solution. Its salts are more stable and can be obtained by passing chlorine gas through hot Conc. Alkali.

$$3Cl_2\,(g)\ +\ 6\,OH^-\,(aq) \longrightarrow ClO_3^-\,(aq)\ +\ 5Cl^-\,(aq)\ +\ 3H_2O\,(l)$$

The Chlorate(V) and Chloride are separated by fractional crystallization.

Hope: Interhalogen compounds

These are compounds formed between halogens with the molecular formula AB, AB_3, AB_5 and AB_7 where A- is a less electronegative atom with a vacant orbital and a higher oxidation state while B- is more electronegative.

Examples include: ICl^- - Iodine monochloride, ClF_3- Chlorine trifluoride.

Question: *Explain the shapes of the following inter-halogen compounds:*

(i) Iodine pentafluoride.

(ii) Chlorine trifluoride.

Follow up activity.

Note: Teacher gives a task to the learners.

To, *Explain the following observations:*

(a) When hydrochloric acid is exposed in air, it turns brown.

(b) A colourless solution of acidified hydrogen peroxide turns brown on addition of acidified potassium iodide.

(c) Describe how sodium chloride is manufactured

Research on the qualitative test for Cl^-, Br^- and I^- Ions. In each case suggest the reagent used and write an ionic equation for the reaction.

TOPIC: CHEMISTRY OF d-BLOCK ELEMENTS.

Lesson 4.1 Physical properties of d-block elements.

Lesson Outcome:

By the end of this lesson, you should be able to describe the trend in the physical properties of the d-block elements and interpret the graph of variation of physical properties.

Introduction:

From the electronic configuration, a transition metal is defined as that element having a partially filled 3d subshell therefore Zinc is not regarded as transition metal.

Inquiry question:

How do the physical properties among the d-block elements across the period.

In activity 1. You are given data on variation of atomic radius across the transitional elements below; write the values in your chemistry note book.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
At. Radius (°A)	1.44	1.32	1.22	1.17	1.17	1.16	1.16	1.15	1.17	1.25

Attempt the given questions.
i) Describe the trend in atomic radius across the transitional elements?
ii) Explain your observation?

Expected correct responses.

The atomic radius decreases from scandium to nickel and it slightly increases from nickel to Zinc.

As atomic number increases, the nuclear charge increases. However, the electrons are being added to inner 3d-subshell therefore these electrons are poorly shielded from the nuclear charge hence the nuclear attraction for the outer for the most electron increases resulting into increase in atomic radius/ metallic radius.

The decrease in radius coupled with increasing atomic mass causes an increase in the density and decrease in atomic volume in passing from Scandium to Nickel.

Activity 2. *The table below shows the electronegativity values for elements in d-block of the periodic table*

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Cu	Zn
At. No.	21	22	23	24	25	26	27	29	30
Electronegativity	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.9	1.6

(a) Plot a graph of electronegativity against atomic number

(b) Explain the trend of your graph in (a)

Glossary

Electronegativity is the tendency of an element to attract bonding electrons towards itself in a covalent compound.

TOPIC: CHEMISTRY OF d-BLOCK ELEMENTS

Lesson 5.1 General characteristics of d-block elements.

Lesson Outcome:

By the end of the lesson, you should be able to discuss the general characteristics of d- block elements.

Introduction: In this lesson we shall discuss the general characteristics of d-block elements. Follow the conversation between Mugaga and Diana below.

Mugaga: What are the general characteristics of d-block elements?

Diana: The general characteristics of d- block elements include;
- ability to form coloured compounds.
- they form complexes.
- catalytic activity.
- they are Paramagnetic.
- they have various oxidation states.

Mugaga: Variable oxidation states

The elements exist in variable oxidation states in variety of the compounds due to availability of the 3d-electrons which can participate in bond formation by either ionic or covalent

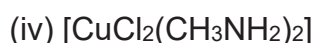The commonest stable oxidation states are in bold as shown in the table

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								+1	
	+2	+2	+2	**+2**	+2	**+2**	+2	**+2**	+2
+3	+3	+3	**+3**	+3	**+3**	+3	+3		
	+4	**+4**	+4	+4					
		+5	+5	+5					
			+6	+6	+6				
				+7					

Activity 1.
(a) Define the following terms;
  i) *Oxidation state*
  ii) *Oxidising agent*

(b) Determine the oxidation state of the transition metals in the following complex.

(i) $K_2Cr_2O_7$ (iii) $[Co(NH_3)_5SO_4]Br$

(ii) MnO_4^{2-} (iv) $[CuCl_2(CH_3NH_2)_2]$

Diana: Para magnetism

A substance that can be drawn into a strong magnetic field is known as paramagnetic substance.

Transition metals are paramagnetic due to the presence of unpaired 3d-electrons. Every spinning electron acts as a tiny magnet. However, in an orbital with 2 paired electrons, the magnetic moment of one electron cancels out.

Para magnetism increases with increase in the number of unpaired 3d-electrons.

## Mugaga: Formation of Coloured Compounds

The 3d-electrons in isolated metal atom are degenerate. i.e. Energetically alike. However, in presence of ligands, the orbitals overlap differently and spit in to two levels of different of energy. This excites electrons from a lower to higher level of energy. The frequency of light absorbed from this energy transition is from the visible region of the spectrum hence this appears as colour.

Note; Scandium and Zinc form colourless compounds therefore they are regarded as non-transition metals.

Diana: Catalytic activity

Transition elements and their compounds act as catalysts with several chemical processes

Homogeneous catalysis (where the catalyst are in the same phase with the reactants), due to variable oxidation state transition metals/ ions form with the activated complex thus providing an alternative reaction path way of lower reaction energy e.g.

$$S_2O_8^{2-}(aq) \ + \ 2I^-(aq) \ \xrightarrow{\ Fe^{2+}(aq)\ } \ 2SO_4^{2-}(aq) \ + \ I_2(aq)$$
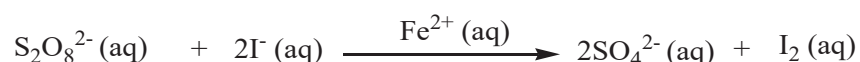
Heterogeneous catalysis (where the catalyst and reactants are in different phases), finely divided solid transition metals/ compound provide an active interface for adsorption of the reactant where they are bound to the surface by vander- Waals forces.

Examples include; V_2O_5- contact process, Iron- Haber process etc.

Mugaga: Complex formation

Transition metals form complexes due to:

- Small and highly charged ions

- Presence of vacant 3d-orbitals to accommodate lone pairs of electrons from the ligards

A ligand is anion or molecule with lone pairs of electrons linked to the central metal ion by a dative bond

Co-ordination number is the number of atoms of ligands molecules that form dative bonds in the complex ion.

A metal complex or co-ordination compound is a chemical system composed of electron donor and electron acceptor. Examples of complex include,

- $[Cu(NH_3)_4]^{2+}$Tetraamminecopper(II)ion

- $[Cr(H_2O)_4(NH_3)_2]^{3+}$ diamminetetraaquachromium(III)ion

- $[Pt(NH_3)_2NO_2Cl]^{2+}$ chloronitrodiammineplatinum(IV) ion

- $[Co(NH_3)_5SO_4]Br$ Sulphatopentaammine cobalt(III)bromide

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