

28TH SEPTEMBER 2024

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SOLUTIONS

ST. JOSEPH'S SENIOR SECONDARY SCHOOL, NAGGALAMA

SOLUTIONS TO THE A'LEVEL CHEMISTRY SEMINAR HELD ON 28TH SEPTEMBER, 2024.

- 1. (a) There is an increase in atomic radii and decrease in electronegativity from chlorine to iodine. The bonding pair of electrons in the hydrogen halogen bond becomes less strongly attracted from hydrogen chloride to hydrogen iodide. This leads to increase in bond length and hence decrease in bond strength from hydrogen chloride to hydrogen iodide, thus increasing the ease of the hydrogen halides to dissociate and release hydrogen ions in the solution from hydrogen chloride to hydrogen iodide.
- (b) The ethyl group in ethylamine has positive inductive effect and increases on the electron density on nitrogen atom. This makes the lone pair of electrons on nitrogen atom to be more easily available to accept proton from water molecules and produce more hydroxide ions in the solution.
- In 1-amino-2-bromo ethane, $[H_2CBrCH_2NH_2]$, the bromine atom has a negative inductive effect and reduces the electron density on nitrogen atom. This makes the lone pair of electrons less available to accept proton from water molecules and therefore produces less number of hydroxide ions in the solution.
- (c) There is increase in ionic radius and decrease in charge density from magnesium ion to strontium ion. The bromide ions become less polarized by the group(II) cations from magnesium ions to strontium ions. This makes the bonds to become ionic from magnesium bromide to barium bromide. As such the strength of the ionic bonds increases from magnesium bromide to strontium bromide.
- (d) Aluminium ion in Aluminium bromide has a small ionic radius and high charge, therefore high charge density and high polarizing power, it greatly polarizes the bromide ion resulting into formation of predominantly covalent character whereby there is sharing of electrons between Aluminium and bromine, by doing so Aluminium will lack two electrons to achieve its octet structure and thus reaction with halogens forms a stable complex and electrophile which attacks the benzene ring.

$$AlBr_3 + Br_2 \rightleftharpoons AlBr_4^- + Br_4^+$$

$$Br$$
 H
 $-H^+$
 Br

$$AlBr_4^- + H^+ \longrightarrow AlBr_3 + HBr$$

e) Peroxosulphate(VI) ion is a strong oxidizing agent which oxidizes iodide ions to iodine and itself reduced to sulphate ions.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

f) Hydrogen peroxide oxidizes chromate(III) ions to chromate(VI) ions

$$2Cr^{3+}$$
 (aq) + $100H^{-}$ (aq) + $3H_2O_2$ (aq) $\longrightarrow 2CrO_4^{2-}$ (aq) + $8H_2O(l)$

Or
$$2Cr(OH)_4^-(aq) + 2OH^-(aq) + 3H_2O_2(aq) \longrightarrow 2CrO_4^{2-}(aq) + 8H_2O(l)$$

g) Down the group, cationic radius increases.

For hydroxides, both lattice energy and hydration energy decrease, however, lattice energy decreases more than hydration energy and thus enthalpy of solution is negative and this makes the hydroxides increase in solubility down the group.

For sulphates, hydration energy decreases more than lattice energy and thus the enthalpy of solution is positive. Solubility of sulphates thus decrease down the group.

- 2.a)i) Distribution coeffecient is the ratio of concentrations of a solute in two immiscible solvents in contact at a given temperature.
- ii) A known volume of an aqueous ammonia of known concentration is added to a known volume of trichloromethane in a separating funnel/flask. The mixture is shaken and allowed to stand at a constant temperature

A known volume of the aqueous layer is pipetted and titrated with a standard solution of hydrochloric acid and the concentration of ammonia determined. Ammonia reacts with hydrochloric acid according to the equation.

$$NH_3$$
 (aq) + HCl (aq) $\longrightarrow NH_4Cl$ (aq)

The concentration of ammonia in the organic layer is obtained by subtraction. The distribution coefficient of ammonia between water and trichloromethane is calculated using the expression;

$$K_D = \frac{[NH_3]aq}{[NH_3]organic}$$

b) Organic layer.

Moles of HCl =
$$\frac{0.05 \times 23.10}{1000}$$

[NH₃] =
$$\frac{0.05 \times 23.10}{1000} \times \frac{1000}{20} = 0.0578M$$

$$K_D = \frac{[NH_3]aq}{[NH_3]organic}$$

$$K_D = \frac{1.442}{0.0578} = 25$$

Alternatively

Organic layer

Moles of HCl =
$$\frac{0.05 \times 23.10}{1000}$$

Moles of Ammonia in 20 cm3 = $\frac{0.05 \times 23.10}{1000}$

Moles of NH₃in 50 cm³ =
$$\frac{0.05 \times 23.10}{1000} \times \frac{50}{20}$$

$$= 2.9 \times 10^{-3}$$

Aqueous Layer

$$[NH_3]$$
 aq = 1.5- 0.0578

Initial Moles of NH₃ =
$$\frac{1.5 \times 50}{1000}$$
 = 0.075

Moles remaining in aqueous layer.

$$= 0.075 - 2.9 \times 10^{-3}$$

$$= 0.072$$

[NH₃]aq =
$$\frac{0.072}{50}$$
 x 1000.

[NH₃] CHCl₃ =
$$\frac{2.9 \times 10^{-3}}{50} \times 1000$$
.

$$K_D = \frac{0.072 \times 1000 /_{50}}{2.9 \times 10^{-3} \times 1000 /_{50}}$$

c) Organic layer.

Moles of HCl in 12.5 cm³ = $\frac{12.5 \times 0.1}{1000}$

$$[NH_3] = \frac{12.5 \times 0.1 \times 1000}{1000 \times 50} = 0.025 \text{ moles}$$

$$\frac{[NH_3]CHCl_3}{[NH_3]free} = 0.04$$

[NH₃]Free =
$$\frac{0.025}{0.04}$$
 = 0.625M

Aqueous layer

Moles of HCl in 20 cm³ = $\frac{20 \times 1}{1000}$

$$[NH_3]$$
aq = $\frac{20 \times 1 \times 1000}{1000 \times 25}$ = 0.8M

 $[NH_3]$ complex = 0.8 -0.625

0.175M

$$Cu^{2+}(aq) + 4NH_3(aq) \longrightarrow Cu(NH_3)_4^{2+}(aq)$$

$$[Cu^{2+}] = \frac{0.175}{4} = 0.0438M$$

d) Mass of silver in crude sample; = $\frac{2 \times 150}{100}$ = 3g

Let the mass extracted be Xg

$$\frac{x/_{10}}{3-x/_{150}} = 300$$

$$X = 2.857 g$$

Mass remaining; = [3-2.857] = 0.143g

% of silver remaining; = $\frac{0.143}{3}$ x 100

3.(a)Dilute nitric acid followed by ammonium oxalate solution and ethanoic acid.

BaCO₃ - white precipitate soluble in ethanoic acid

CaCO₃ - white precipitate insoluble in ethanoic acid

$$BaCO_3(s) + 2HNO_3 \longrightarrow Ba(NO)_3(aq) + H_2O(l) CO_2(g)$$

$$CaCO_3(s) + 2HNO_3 \longrightarrow Ca(NO)_3(aq) + H_2O(l) CO_2(g)$$

$$Ba^{2+}(aq) + C_2O_4^{2-} \longrightarrow BaC_2O_4$$
 (s)

Then,

$$BaC_2O_4 (s) + CH_3COOH(aq) \longrightarrow (CH_3COO)_2Ba(aq) + H_2C_2O_4 (aq)$$

$$Ca^{2+}(aq) + C_2O_4^{2-} \longrightarrow CaC_2O_4 (s)$$

(b) Neutral iron (III) chloride

OH Purple colouration,
$$CHCH_3$$
 No observable change $CHCH_3$ CH

(c) Ammoniacal silver nitrate solution and heat

$$CH_3(CH_2)_2CHO \text{ - silver mirror } , \qquad CH_3C(CH_2)_2CH_3 \qquad \text{ - no observable change}$$

(or Ammoniacal copper(I) chloride solution and heat or warm

$$CH_3(CH_2)_2CHO - \text{red precipitate} \qquad CH_3C(CH_2)_2CH_3 \qquad - \text{ no observable change}$$

$$CH_3(CH_2)_2CHO \xrightarrow{AgNO_3(aq)/NH_3(aq)} Ag(s) + CH_3(CH_2)_2COO^- \text{ (aq)}$$

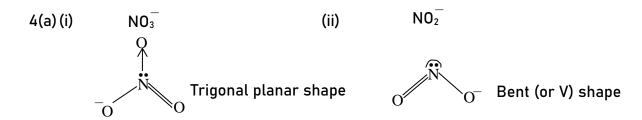
(d) Hot sodium hydroxide solution, dilute nitric acid and silver nitrate solution.

(e) Ammoniacal silver nitrate solution and heat.

$$OO$$
 O $HCOOH-silver mirror, $H-O-C-C-OH$ - no observable change$

Or, Fehlings solution and heat

HCOOH – red precipitate
$$H$$
–O–C–C–OH – no observable change H COOH $\xrightarrow{AgNO_3(aq)/NH_3(aq)}$ CO₂ (s) + Ag(s) + H₂O



(b) The bond angle in NO_3^- is bigger than that in NO_2^-

This is because in nitrate ion the nitrogen atom has three bond pairs and no lone pair. The bond pairs repel each other until minimum repulsion occurs amongst them. This occurs when the bonded species symmetrically arrange themselves around the nitrogen atom.

In nitrite ion, the nitrogen atom has one lone pair and two bond pairs. The lone pair exerts greater repulsion on the two bond pairs. This makes the bond pairs get closer to each other hence making the bond angle in nitrite ion being smaller than that in nitrate ion.

(c)(i) Nitrite ion (NO_2^-)

ii) The nitrite ion reduces iodine to iodide ions and the nitrite ion is oxidized to nitrate ion

$$NO_2^-(aq)$$
 + $H_2O(l)$ + $I_2(aq)$ $\longrightarrow NO_3^-$ + $2I^-(aq)$ + $2H^+(g)$

5.(a)(i) Acidified solution of manganate(VII) ions

- (ii) Aqueous solution of vanadium (II) ions
- (b) (i) $Pt(s)/V^{2+}(aq)$, $V^{3+}(aq)$ // $MnO_4^-(aq)$, $H^+(aq)$ $Mn^{2+}(aq)/Pt(s)$
- (ii) At positive terminal

$$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$$

At the negative terminal

$$V^{2+}(aq) \longrightarrow V^{3+}(aq) + e$$

iii)
$$E^{\theta}_{cell} = E^{\theta}_{right} - E^{\theta}_{left}$$

= +1.52 - (- 0.27) V
= + 1.79V

$$\Delta G = -nEF$$

$$= (-5 \times 1.79 \times 96500)J$$

= 863675 J/mol or 863.675 KJ/mol

(c)i)
$$Pt(s)$$
, $2Cl^{-}(aq) / Cl_{2}(g) // PbO(s) / $H^{+}(aq)$, $Pb^{2+}(aq) / Pt$$

ii)
$$E^{\theta}_{cell} = E^{\theta}_{right} - E^{\theta}_{left}$$

= (1.46 - 1.36)
= +0.10V

The E.m.f for the overall cell rotation is positive indicating that the cell produce electric current.

The e.m.f for the overall cell reaction between acidified potassium dichromate and chloride ions is

The E.m.f for the overall cell reaction is -0.03V

This means that the acidified potassium dichromate cannot oxidize the chlorine ions to chlorine since the E.m.f value has a negative sign. Therefore potassium dichromate can be acidified using dilute hydrochloric acid.

Overall cell reaction for the reaction between acidified potassium permanganate and dilute hydrochloric acid is obtained as

Since the E.m.f value for the overall cell reaction has a positive sign, this means that the manganate (VII) ions can oxidize chloride ions to chlorine.

Therefore the manganate(VII) ions cannot be acidified using dilute hydrochloric acid.

6.a). Addition polymerisation is the process by which small unsaturated molecules or molecules that contain carbon-carbon double bond combine to form a large molecule without loss of other small molecules.

Condensation polymerisation is the process by which many bifunctional molecules combine to form a large molecule accompanied by loss of other small molecules.

- b)i) Hexane-1,6-dioic acid and Hexane-1,6-diamine
- ii) Methyl-2-methylpropenoate
- c) Nylon-6,6

$$nNH_2(CH_2)_6NH_2 + nHOOC(CH_2)_4COOH \longrightarrow \frac{1}{2}HN(CH_2)_6NHCO(CH_2)_4CO \frac{1}{2}H + 2nH_2O \frac{1}{2}HN(CH_2)_6NHCO(CH_2)_4CO \frac{1}{2}H + 2nH_2O \frac{1}{2}HN(CH_2)_6NHCO(CH_2)_4COOH \frac{1}{2}HN(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH_2)_6NHCO(CH$$

Perspex

d)i) Nylon-6,6

Monomers are bifunctional

Perspex

Monomers contain carbon-carbon double bond

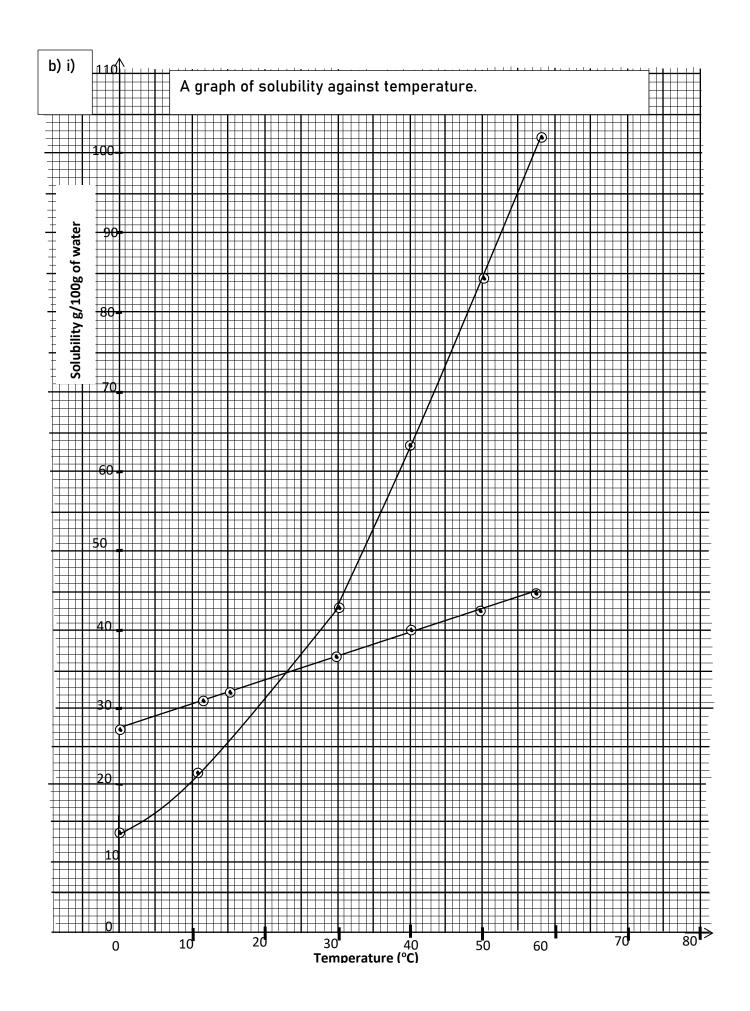
ii) In formation of nylon-6,6, there is loss of some molecules

In formation of persex, there is no loss of some molecules and the polymer is a multiplier of the monomer

e) Nylon-6,6; For making clothes, threads and fishing nets

Perspex; For making aircraft, windows and rulers.

- 7. a)i) Solute is a substance that dissolves in a solvent to form a uniform solution.
- ii) Saturated solution is one that cannot dissolve any more solute in the presence of undissolved solute at a given temperature.



- ii) Potassium chloride
- iii) At 23.5°C, the solubilities are equal.
- iv) Solubility of potassium nitrate at 30°C in 43.0g/100g of water.

Solubility of potassium nitrate at 5° C is 17g / 100g of water.

Mass of potassium nitrate that crystallized = 43 - 17

RFM of potassium nitrate $(KNO_3) = 39 + 14 + 16x3 = 101$

Number of moles of KNO₃ that crystallized = $\frac{26}{101}$

= 0.25743 moles

c)
$$2Cu^{2+}(aq) + 4I^{-}(aq) \longrightarrow 2CuI(s) + I_2(aq)$$

$$I_2 (aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^- (aq) + S_4O_6^{2-}(aq)$$

Number of moles $S_2O_3^{2-} = \frac{33.5 \times 0.118}{1000}$

= 3.953x10⁻³ moles

Mole ratio $S_2O_3^{2-}$: $I_2 = 2:1$

Number of moles of I_2 liberated = $\frac{1}{2} \times 3.953 \times 10^{-3}$

= 1.9765x10⁻³ moles

Mole ratio I_2 : $Cu^{2+} = 1:2$

Number of moles of $Cu^{2+} = 1.9765 \times 10^{-3} \times 2$

 $= 3.953 \times 10^{-3} \text{ moles}$

RFM of $CuSO_4 = 64 + 32 + 16x4 = 160$

25cm3 of diluted solution contain 3.953x10-3 moles of copper(II) sulphate

200cm³ of diluted solution contain $\left(\frac{3.953x10^{-3} x200}{25}\right)$ moles

= 0.031624 moles

Mass of $CuSO_4$ in the saturated solution = 0.031624x160

= 5.05984g

Mass of water in the saturated solution = 25.2-5.06

= 23.14q

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23.14g of water dissolve 5.06g of CuSO₄

100g of water dissolve
$$\left(\frac{5.06 \times 100}{23.14}\right)$$
g

Solubility of $CuSO_4 = 21.87g/100g$ of water.

- d) i) By boiling off most of the water such that the same solute is dissolved in less amount of water.
- ii) By increasing the temperature of the solution.
- e) i) Fractional crystallization is the process of separating two or more crystalline solids from their aqueous solution due to difference in their solubilities.
- ii) 175g of saturated solution at 100° C contain 75g of CuSO₄

∴ 50g of saturated solution contain
$$\left(\frac{75x50}{175}\right)$$
g

$$= 21.43g$$

125g of saturated solution of CuSO₄ at 30°C contain 25g of CuSO₄

50g of saturated solution of CuSO₄ at 30°C contain
$$\left(\frac{25x50}{125}\right)$$
g = 10g

: Mass of CuSO₄ that crystallized = 21.43-10

iii) Stir copper(II) sulphate into hot water until no more will dissolve. Pour the solution into a jar and wait for a few days for the crystals to grow. If one of the crystals is tied on the thread and is suspended in a hot saturated solution of copper(II) sulphate for several days. The crystal grows larger as the solution slowly evaporates.

8) a)i)
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
 $\Delta H = -ve$

ii) Temperature of 450°C.

Use of Vanadium pentoxide as a catalyst

Pressure of 2 atmosphere

- b)i) When temperature is increased to $800\,^{\circ}$ C, the position of the equilibrium will shift from the right to the left since the forward reaction is an exothermic reaction and the temperature adjusted is beyond the optimum temperature.
- ii) Acidified potassium permanganate reacts with sulphur dioxide, and reduces its concentration and as such the equilibrium position shifts from the right to the left.
- c) Let the moles of oxygen which reacted be X

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Initial moles:

1.8

2.0

0

Reacted moles;

2X

Χ

2X

Equilibrium moles;

1.8-2X

2-X

2X

Moles of oxygen that reacted; $=\frac{26}{100} \times 2 = 0.52$

$$=\frac{26}{100} \times 2 = 0.52$$

Hence

$$X = 0.52$$

Equilibrium concentration;

[SO₂] =
$$\frac{1.8 - (2 \times 0.52)}{2}$$
 = 0.38M; [O₂] = $\frac{2 - 0.52}{2}$ = 0.74M [SO₃] = $\frac{2 \times 0.52}{2}$ = 0.52M
Kc = $\frac{[SO_3]^2}{[SO_2]^2[O_2]}$
= $\frac{0.52^2}{0.338^2 \times 0.74}$
= 2.53

d)
$$2P(s) + 5H_2SO_4(l) \longrightarrow 2H_3PO_4(aq) + 2H_2O(l) + 5SO_2(g)$$

or
$$P_4(s) + 10H_2SO_4(l) \longrightarrow 4H_3PO_4(aq) + 4H_2O(l) + 10SO_2(g)$$

$$H_2S(g) + 3H_2SO_4(l) \longrightarrow 4H_2O(l) + 3SO_2(g) + S(s)$$

$$Sn(s) + 4H_2SO_4(l) \longrightarrow Sn(SO_4)_2(aq) + 4H_2O(l) + 2SO_2(g)$$

- 9. a)i) A metal which is capable of forming at least one of its stable ions with a partially filled 3d subshell.
- ii) Complex ion is either a positively charged or negatively charged ion in which the central ion is bonded to several other ligands.
- b) They form cations with high charge density which are able to attract themselves. Their ions or atoms possess partially filled or vacant orbitals in which the ligands are able to donate their lone pair of electrons and form dative bonds.
- c)i) $Co(H_2O)_6^{2+}$; Hexaaquacobalt(II)ions

ii)
$$Co(H_2O)_6^{2+}(aq) + SCN^-(aq) \longrightarrow [Co(H_2O)_5SCN]^+(aq) + H_2O(l)$$

d)i) Pink solution turns blue;

$$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$$

ii) A blue precipitate insoluble in excess and turns brown on standing

$$Co^{2+}(aq) + 20H^{-}(aq) \longrightarrow Co(OH)_2(s)$$

$$2\text{Co}(0\text{H})_2(\text{s}) + \frac{1}{2} 0_2(\text{g}) \longrightarrow \text{Co}_2 0_3.2\text{H}_2 0(\text{s})$$

Or;
$$4Co(OH)_2(s) + O_2(g) \longrightarrow 2Co_2O_3.2H_2O(s)$$

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- 10.i) Standard electrode potential is the electrode potential of an electrode which is the measure with respect to a standard hydrogen electrode under standard conditions.(298K, 1Atm, 1M concentration of ions)
- ii) it is impossible to measure an absolute standard electrode potential because it is necessary to have a second electrode as a reference electrode which also has a potential difference with respect to a solution

We can only measure relative values of standard electrode potentials using a second electrode. E.g. standard hydrogen electrode whose potential difference is arbitrarily taken to be zero (0.00v)

iii) When a metal is dipped in a solution containing its ions, the metal M dissolves so as to establish an equilibrium,

$$M(s) \rightleftharpoons M^{n+}(aq) + ne \Delta H^{o}$$

The value of standard electrode potential will depend on the overall enthalpy change. For the reaction above, it will depend on;

Atomization/ sublimation energy. $M(s) \rightleftharpoons M(g) \Delta Hatm$

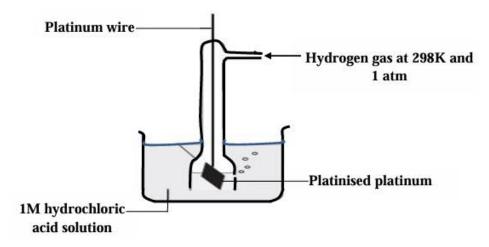
Ionization energy. $M(g) \rightleftharpoons M^+(g) + e \Delta H_{I.E}$

Hydration energy $M^+(g) \rightleftharpoons M^+(aq) \Delta H_{Hyd}$

The overall heat change, $\Delta H^o = \Delta H_{Hvd} + \Delta H_{I.E} + \Delta Hatm$

Both atomization and ionization energy are endothermic processes, hydration energy is an exothermic process. For large negative values of the electrode potentials, enthalpies of atomization and ionization should be small and the hydration energy should be large

b) A standard hydrogen electrode consists of hydrogen gas at 298K, and 1 Atm bubbling over a platinized platinum electrode suspended in 1M solution of hydrogen ions.



c) A silver plate is dipped in 1M solution of silver nitrate solution and connected to a standard hydrogen electrode via a voltmeter.

The two half cells are internally connected via a salt bridge

The E.m.f read off from the voltmeter is taken as the standard electrode potential of silver since the electrode potential of standard hydrogen electrode is arbitrarily taken to be zero volts.

d)i) Eo Cell =
$$E_R-E_L$$

= -2.87-(-2.37)
= -0.5V

ii) The cell reaction is not feasible since the E.m.f of the cell is negative.

11.

(a)
$$CH_3C \equiv CH$$
 $EX = CH_3$
 $EX = CH_3$

$$\ddot{O}H$$
 $\rightarrow H^+$ $\rightarrow CH_3$ $\rightarrow CH_3$

(c)
$$CH_3$$
 CH_2 CH_2 CH_3 CH_2 CH_3 CH_2 CH_3 CH_4 CH_2 CH_3 CH_4 CH_5 $CH_$

 $HCN \Longrightarrow \overline{C}N + H^+$

(f)
$$H_2C=CH_2 \xrightarrow{Br_2/H_2O} CH_2CH_2OH$$

Mechanism Br

(g)
$$CH_3CH_2C-Br/\bar{o}H$$
 Mechanism

$$CH_{3}CH_{2} C \xrightarrow{\mathbf{O}} CH_{3}CH_{2}C \xrightarrow{\mathbf{Br}} CH_{3}CH_{2}C \xrightarrow{\mathbf{Br}} CH_{3}CH_{2}C \xrightarrow{\mathbf{O}} C$$

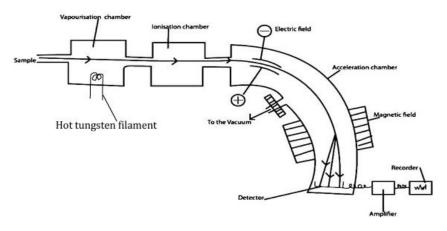
- 12. a) Relative atomic mass of an element is the ratio of the mass of its atom to a twelfth of the mass of carbon atom of carbon-12 isotope.
- b) A vaporized sample of an element allowed to enter the ionization chamber where it is subjected to a beam of electrons from an electron gun

Positively charged ions are formed, they are accelerated to the same velocity by an electric field towards the magnetic field. In the magnetic field, the ions are deflected according to their charge/mass ratio

By varying both electric and magnetic field strengths, a particular set of ions is focused onto the detector

In the detector, the ions create electric impulse in form of detector current, the magnitude of each detector current proportional to the intensity of the ion producing it

The detector currents are recorded on a photographic plate as a series of lines or peaks called mass spectrum



c)i) Relative intensity is the proportion or ratio or fraction of each isotope in a given sample

ii) R.A.M =
$$\frac{(24x8) + (25x1) + (26x1)}{9 + 1 + 1}$$
$$= 24.3$$

- iii) W has three isotopes, ²⁴W, ²⁵W, ²⁶W
- d) It produces accurate relative atomic mass
 It uses very small amount of the sample

e)
$$2.303 \log \left(\frac{No}{N}\right) = Kt$$

$$2.303 \log \left(\frac{680}{125}\right) = K350$$

$$K = 4.84 \times 10^{-3} S^{-1}$$

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

$$t_{1/2} = \frac{0.693}{4.84 \times 10^{-3}}$$

143.2 seconds

13. a) CH₃CH₂CH₂CH₂Br - 1-bromobutane

(CH₃)₂CHCH₂Br - 1-bromo-2-methylpropane

CH₃CH₂CHBrCH₃ - 2-bromobutane

- (CH₃)₃CBr- 2-bromo-2-methylpropane
- b)i) 1-bromobutane has the highest boiling point
- ii) 2-bromo-2-methylpropane has the lowest boiling point

- c) 1-bromobutane is a straight chain isomer and the molecules are closer to each other and this increases the intermolecular forces of attraction and thus more heat is required to break them
- 2-bromo-2-methylpropane is a branched isomer and increased branching gives the molecule a more spherical shape, this reduces the extent of contact between the neighboring molecules, consequently the attractive forces are reduced and therefore less energy is required to break the forces.
- d) S- 2-bromobutane

T- Butan-2-ol

e)i)

Mechanism

$$KOH + CH_3CH_2OH \longrightarrow CH_3CH_2\overline{O}K^+ + H_2O$$

 $CH_3CH_2\overline{O}K^+ \longrightarrow CH_3CH_2\overline{O} + K^+$

$$\begin{array}{cccc}
H & \nearrow Br & & H \\
CH_3C & CHCH_3 & & CH_3C=CHCH_3
\end{array}$$

$$\begin{array}{ccccc}
H & & & & & & & & & & & \\
CH_3C & & & & & & & & \\
\hline
OCH_2CH_3 & & & & & & & & \\
\end{array}$$

ii)

$$CH_{3}CH_{2}CHCH_{3} + CH_{3}COOH \xrightarrow{Conc. H_{2}SO_{4}} CH_{3}CH_{2}CHOCCH_{3}$$

Mechanism

$$CH_{3}C-OH \longrightarrow CH_{3}C-OH \longrightarrow CH_{3}C-OH \longrightarrow CH_{3}C-OH \longrightarrow CH_{2}CH_{3}$$

$$CH_{3}CH_{2}CHOH \longrightarrow CH_{3}C-OH \longrightarrow CHCH_{2}CH_{3}$$

$$CH_{3}C-O-CHCH_{2}CH_{3} \longrightarrow CH_{3}C-OH_{2}$$

f)

$$CH_{3}CH_{2}CHCH_{3} \xrightarrow{Conc. H_{2}SO_{4}} CH_{3}CH = CHCH_{3}$$

$$OH \xrightarrow{O_{3}/CCl_{4}/CO0} OH \xrightarrow{O_{3}/CCl_{4}/CO0} CH_{3}CH_{2}OH \xrightarrow{CH_{3}CH_{2}OH} CH_{3}CH_{2}OH \xrightarrow{CH_{3}COOH} CH_{3}CH_{2}OH$$

14. a) nS² nP⁵

b)i) Fluorine reacts with water vigorously to form hydrofluoric acid and oxygen gas while bromine reacts with water slightly or slowly to form hypobromous acid and hydrobromic acid

$$2F_2(aq) + 2H_2O(l) \longrightarrow 4HF(aq) + O_2(g)$$

$$Br_2(aq) + H_2O(l) \rightleftharpoons HOBr(aq) + HBr(g)$$

ii) Fluorine reacts with cold dilute potassium hydroxide to form potassium fluoride, oxygen difluoride and water

$$2F_2(aq) + 20H^-(aq) \longrightarrow 2F^-(aq) + 0F_2(g) + H_2O(l)$$

Bromine reacts with cold dilute potassium hydroxide to form potassium hydroxide to form potassium bromide, potassium hypobromite (bromate(I)) and water.

$$Br_2(aq) + 20H^-(aq) \longrightarrow Br^-(aq) + 0Br^-(g) + H_2O(l)$$

Fluorine reacts with hot concentrated potassium hydroxide solution to form potassium fluoride, oxygen gas and water

$$2F_2(aq) + 40H^-(aq) \longrightarrow 4F^-(aq) + O_2(g) + 2H_2O(l)$$

Bromine reacts with hot concentrated potassium hydroxide, potassium bromate, potassium bromide and water.

$$3Br_2(aq) + 60H^-(aq) \longrightarrow 5Br^-(aq) + BrO_3^-(aq) + 3H_2O(l)$$

c)i) Pale green solution turned to brown solution

$$Cl_2(aq) + 2FeCl_2(aq) \longrightarrow 2FeCl_3$$

ii) Brown solution turned to colorless

$$I_2(aq) + SO_3^{2-}(aq) + H_2O(l) \longrightarrow 2I^{-}(aq) + SO_4^{2-}(aq) + 2H^{+}(aq)$$

iii) Yellow precipitate

$$Br_2(aq) + H_2S(aq) \longrightarrow S(s) + 2HBr(aq)$$

iv) Grey solid dissolves to form pale yellow solution which turns colorless on standing

$$I_2(s) + 20H^-(aq) \longrightarrow I^-(aq) + I0^-(aq) + H_20(l)$$

 $3I0^-(aq) \longrightarrow I0_3^-(aq) + 2I^-(aq)$

15. a)i) Ionic product is the product of the molar concentrations of the ions that form a sparingly soluble salt raised to appropriate powers

Solubility product is the product of the molar concentrations of the ions of a sparingly soluble salt raised to appropriate powers when a solution is saturated at a given temperature.

- ii) lonic product is not affected by temperature because the ions are already in solution. However, solubility product is affected by temperature since solubility of a sparingly soluble salt is an endothermic process, increase in temperature increases the kinetic energy of the particles of the solute and thus ions can easily break off from their lattice and this increases the concentration of the ions in solution and thus solubility product increases.
- b) Excess of solid Lead(II) iodide is mixed with a known volume of distilled water. The mixture is shaken vigorously for some time until equilibrium is established at a particular temperature. The mixture is filtered to obtain a filtrate which is saturated at a given temperature. The electrolytic conductivity of the filtrate is measured using conductivity meter.

The electrolytic conductivity of pure water is also determined which can be used to determine the electrolytic conductivity of Lead(II) iodide from the formula,

Ksolute = Ksolution-Kwater

The molar conductivity of the ions of lead(II) iodide at infinite dilution are obtained from the tables in the data books and can be used to determine the molar conductivity of Lead(II) iodide at infinite dilution from the formula,

$$\Lambda \infty PbI_2 = \Lambda \infty Pb^{2+} + 2\Lambda \infty I^-$$

The solubility of Lead(II) iodide can be obtained from formula,

$$\Lambda \infty PbI_2 = \frac{KPbI_2}{C}$$

If C is the solubiblity of Lead(II) iodide, then solubility product is obtained as;

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^{-}(aq)$$

С C

$$Ksp = [Pb^{2+}][I^{-}]^{2}$$

$$= C(2C)^2$$

c) Mass of PbI₂ = 207 + 127x2 = 461.

Mass of PbI₂ that dissolved = $\frac{11.62}{100}$ x 2.5 = 0.2905 g

$$[PbI_2] = \frac{0.2905}{461} = 6.3015 \times 10^{-4} \text{ moldm}^{-3}$$

$$PbI_2(s) + (aq) \rightleftharpoons Pb^{2+}(aq) + 2I^{-}(aq)$$

$$Ksp = [Pb^{2+}][I^-]^2$$

=
$$6.3015 \times 10^{-4} \times (2 \times 6.3015 \times 10^{-4})^2 = 1.0003 \times 10^{-9} \text{mol}^3 \text{dm}^{-9}$$

d)i) The percentage of Lead(II) iodide that dissolved would be less than 11.62% because ammonium iodide is a strong electrolyte and its addition increases the concentration of the iodide ions. The excess iodide ions will react with the few Lead(II) ions to form insoluble lead(II) iodide and the equilibrium position shifts to the left

$$Pb^{2+}(aq) + 2I^{-}(aq) \longrightarrow PbI_{2}(s)$$

This is done to keep the solubility product of Lead(II) iodide constant at a particular temperature, hence its solubility reduces.

ii) The solubiblity will be more 11.62%, because magnesium ribbon reduces the lead(II) ions to lead

$$Pb^{2+}(aq) + Mg(s) \longrightarrow Pb(s) + Mg^{2+}(aq)$$

The concentration of the lead(II) ions in solution reduces, thus more lead(II) iodide dissolves to restore the concentration of lead(II) ions to keep the Ksp for lead(II) iodide constant.

e)i) Total volume of solution = 500+500 = 1000 cm³

$$[Pb^{2+}] = \frac{0.025}{1000} \times 1000 = 0.025M$$

$$[I^{-}] = \frac{0.01325}{1000} \times 1000 = 0.01325M$$

$$Pb^{2+}(aq) + 2I^{-}(aq) \longrightarrow PbI_{2}(s)$$

Ionic product = $[Pb^{2+}][I^-]^2$

=
$$0.025 \times [0.01325]^2 = 4.3891 \times 10^{-6} \text{ mol}^3 \text{dm}^{-9}$$

- ii) Precipitation will occur because the ionic product has exceeded the solubility product.
- f) Ksp for Ag₂CrO₄ = $[Ag^{+}]^{2}[CrO_{4}^{2-}]$

1.3 x 10⁻¹² =
$$[Ag^{+}]^{2}$$
 x 0.005

$$[Ag^{+}] = \sqrt{\frac{1.3 \times 10^{-12}}{0.005}} = 1.61245 \times 10^{-5} \text{moldm}^{-3}$$
Ksp for AgCl = $[Ag^{+}][Cl^{-}]$
1.8x10⁻¹⁰ = $[Ag^{+}]$ x 0.005

$$[Ag^{+}] = \frac{1.8 \times 10^{-10}}{0.005} = 3.6 \times 10^{-8} \text{ moldm}^{-3}$$

Silver chloride precipitates first because it requires a much smaller amount of silver ions to precipitate.

16.

b)

c)

$$\begin{array}{c} \text{CH} = \text{CH} \xrightarrow{\text{Na/liq. NH}_3} \text{CH} = \text{CNa} \xrightarrow{\text{CH}_3\text{CH}_2\text{CH}_2\text{CI}} \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \\ \text{Cr}_2\text{O}_7^2\text{/ H}^+\text{/ Heat} \\ \text{CH}_3\text{CH}_2\text{CH}_$$

d)

e)

$$CH_{3}CH_{2}COOH \xrightarrow{PCl_{5}} CH_{3}CH_{2}C \xrightarrow{Conc. NH_{3}} CH_{3}CH_{2}CONH_{2}$$

$$Br_{2} / Conc. NaOH warm$$

$$CH_{3}CH_{2}OH \xrightarrow{NaNO_{2} / Conc. Hcl} CH_{3}CH_{2}NH_{2}$$

f)

$$\frac{\text{NO}_2}{\text{Sn / Conc. HCl / Conc NaOH}} \underbrace{\frac{\text{NaNO}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Heat}} \underbrace{\frac{\text{NaNO}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}{5 \, ^{\circ}\text{C}}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}_{\text{Nano}_2 / \text{Conc HCl}}}_{\text{Nano}_2 / \text{Conc HCl}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}_{\text{Nano}_2 / \text{Conc HCl}}}_{\text{Nano}_2 / \text{Conc HCl}}_{\text{Nano}_2 / \text{Conc HCl}}_{\text{Nano}_2 / \text{Conc HCl}} \underbrace{\frac{\text{Nano}_2 / \text{Conc HCl}}_{\text{Nano}_2 / \text{Conc HCl}}}_{\text{Nano}_2 / \text{Conc HCl}}_{\text{Nano}_2 / \text{Conc HCl}}_{\text{Nano}_2 / \text{Conc HCl}}_{\text{Nano}_2 / \text{Conc HCl}}_{\text{Nan$$

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- ii) +2 oxidation state increases down the group while stability of +4 oxidation decreases down the group due to inert pair effect which increases with increases in atomic radius.
- b)i) Carbon, germanium and tin react with hot concentrated nitric acid to form dioxides, nitrogen dioxide and water.

$$C(s) + 4HNO_3(aq) \longrightarrow CO_2(g) + 4NO_2(l) + 2H_2O(l)$$

$$Ge(s) + 4HNO_3(aq) \longrightarrow GeO_2(g) + 4NO_2(l) + 2H_2O(l)$$

$$Sn(s) + 4HNO_3(aq) \longrightarrow Sn(g) + 4NO_2(l) + 2H_2O(l)$$

Silicon does not react with nitric acid under any conditions

Lead reacts with hot concentrated nitric acid to form Lead(II) nitrate, nitrogen dioxide and water

$$Pb(s) + 4HNO_3(aq) \longrightarrow Pb(NO_3)_2(g) + 2NO_2(l) + 2H_2O(l)$$

ii) Carbon does not react sodium hydroxide under any condition

Silicon, germanium, and tin react with hot concentrated sodium hydroxide to form silicate(IV), germinate(VI) and stannate(VI) together with hydrogen gas

$$Si(s) + 20H^{-}(aq) + H_2O(l) \longrightarrow SiO_3^{2-} + 2H_2(g) Ge(s) + 20H^{-}(aq) + H_2O(l) \longrightarrow GeO_3^{2-} + 2H_2(g) Sn(s) + 20H^{-}(aq) + H_2O(l) \longrightarrow SnO_3^{2-} + 2H_2(g)$$

Lead reacts with hot concentrated sodium hydroxide solution to form plumbate(II) and hydrogen gas

$$Pb(s) + 20H^{-}(aq) \longrightarrow PbO_2^{2-} + H_2(g)$$

c)i) Hydrogen peroxide oxidizes sulphide ions to sulphate ions which react with lead(II) ions to form lead(II) sulphate.

$$PbS(s) + (aq) \longrightarrow Pb^{2+}(aq) + S^{2-}(aq)$$

$$S^{2-}(s) + 4H_2O_2(aq) \longrightarrow SO_4^{2-}(aq) + 4H_2O(l)$$

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$$

Overall equation;
$$PbS(s) + 4H_2O_2(aq) \longrightarrow PbSO_4(s) + 4H_2O(l)$$

ii) lodide ions have a bigger ionic radius than chloride ions, iodide ions act as strong reducing agent which reduces lead(IV) ions to lead(II) ions and iodide ions oxidized to iodine

$$Pb^{4+}(aq) + 4I^{-}(aq) \longrightarrow PbI_{2}(s) + I_{2}(aq)$$

Lead(IV) oxide does not form, instead lead(II) iodide forms. The chloride ions are weaker reducing agents and thus cannot reduce lead(IV) ions to Lead(II) ions. Therefore Lead(IV) chloride can be formed from Lead(IV) ions and chloride ions.

$$Pb^{4+}(aq) + 4Cl^{-}(aq) \longrightarrow PbCl_{4}(s)$$

iii) Carbon atom in tetrachloromethane has a smaller atomic radius than silicon in silicon tetrachloride, carbon does not have accessible empty d-orbitals to accommodate lone pairs of electrons from water molecules while silicon has accessible empty d-orbitals to accommodate

lone pairs of electrons from water molecules thus silicon(IV) chloride reacts with water to form silicon(IV) oxide and hydrochloric acid.

$$SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4HCl(aq)$$

iv) Lead(IV) oxide is a strong oxidizing agent which oxidizes hydrochloric acid to chlorine and itself reduced to Lead(II) chloride which is insoluble in cold solution

$$PbO_2(s) + 4HCl(aq) \longrightarrow PbCl_2(s) + Cl_2(g) + 2H_2O(l)$$

v) Trileadtetraoxide is a mixed oxide containing lead(Ii) oxide and lead(IV) oxide, lead(IV) oxide being acid in nature does not react with nitric acid instead it is released in the solution to form insoluble solid while lead(II) oxide being basic reacts with nitric acid to form lead(II) nitrate which is a soluble compound.

$$Pb_3O_4(s) + 4HNO_3(aq) \longrightarrow PbO_2(s) + 2H_2O(l) + 2Pb(NO_3)_2(aq)$$

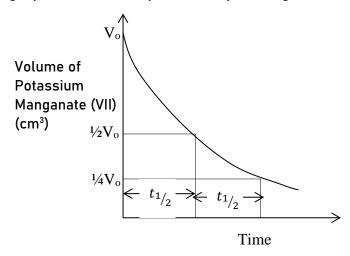
- 18.a) i) Order of reaction is the sum of the powers to which the molar concentration terms of the reactants are raised in an experimentally determined rate equation.
- ii) Molecularity is the number of chemical species taking part in the rate determining step of the reaction mechanism.
- iii) Activation energy is the minimum amount of energy possessed by the reactants for the reaction to take place.
- b) i) Rate = $K[H_2O_2]$
- ii) A known volume of hydrogen peroxide of known concentration is placed in a flask.

A small amount of Iron(III) chloride solution is added followed by a small amount of sodium hydroxide solution and a stop clock is simultaneously started.

The mixture is shaken and allowed to stand at a constant temperature. After specific intervals of time, known volumes of the reaction mixture are pipetted into other conical flasks containing dilute sulphuric acid. The base in the reaction mixture is neutralized and the reaction stops.

The mixtures are titrated against standard potassium permanganate solution. The volumes of potassium permanganate solution are directly proportional to the concentration of hydrogen peroxide remaining in the reaction mixture.

A graph of volume of potassium permanganate solution against time is plotted.

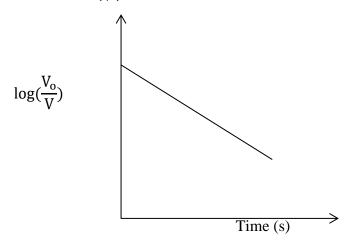


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From the graph, half-lives ate equal, implying that the reaction is first order kinetics.

0r

A graph of $\log\left(\frac{Vo}{V}\right)$ against time is plotted.



A straight line graph with negative gradient implies that the reaction is first order.

iii) Increase in temperature increases the rate of decomposition of hydrogen peroxide. Increase in temperature increases the kinetic energy of the molecules and this increases the frequency of collision of molecules. The number of molecules acquiring activation energy increases.

c)

$[H_2O_2]$ (moldm ⁻³)	0.0013	0.00076	0.00036	0.00014	0.0001
Time (min)	5	12	20	33	40
Log[H ₂ O ₂]	-2.89	-3.12	-3.44	-3.85	-4.0

On graph paper.

d)i) Initial concentration of $H_2O_2 = 10^{-2.7} = 0.001995 \text{ moldm}^{-3}$

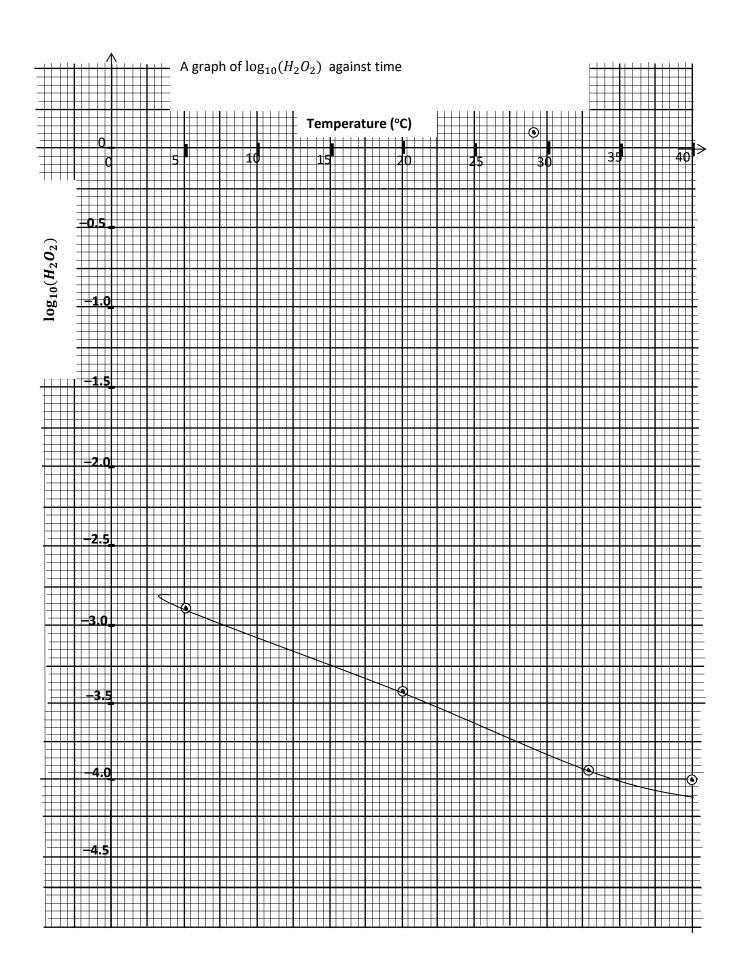
ii) Slope =
$$\frac{-4.2 - (-2.55)}{42.5 - 1.5}$$

Slope =
$$\frac{-k}{2.303}$$

K = 0.092682 min⁻¹
Half-life,
$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$= \frac{0.693}{0.092682}$$

= 7.48 minutes.



- 19. a)i) A buffer solution is a solution which resists change in pH when a small amount of an acid or a base are added to it.
- ii) Salt hydrolysis is the reaction of a salt with water to produce products that affect the pH of the water.

b) i)
$$[H^{+}] = \alpha C$$

$$= 0.025 \times 0.02 = 5.25 \times 10^{-4} \,\text{moldm}^{-3}$$

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

$$= -\log (5.25 \times 10^{-4}) = 3.28$$
ii)
$$Ka = \frac{c \times^{2}}{1-\alpha}$$

$$= \frac{0.021 \times 0.025^{2}}{1 - 0.025}$$

$$= 1.346 \times 10^{-5} \,\text{moldm}^{-3}$$

c)i) New pH = 3.28+ 2.34
= 5.62
pH = pKa +
$$log \left[\frac{[salt]}{[acid]} \right]$$

5.62 = $-log 1.346 \times 10^{-5} + log \left[\frac{[salt]}{0.021} \right]$
[Salt] = 0.11782 moldm⁻³

RFM of
$$CH_3CH_2COOK = (12x3) + (1x5) + (16x2) + (39 x1) = 112$$

Mass of $CH_3CH_2COOK = 112 \times 0.11782$ =13.1958g

ii) Addition of potassium propanoate increases the concentration of propanoate ions since potassium propanoate is a strong electrolyte. The excess propanoate ions react with hydrogen ions from the partial ionization of propanoic acid. This is done to keep the Ka the same.

$$CH_3CH_2COO^-$$
 (aq) + H^+ (aq) \longrightarrow CH_3CH_2COOH

The concentration of the hydrogen ions in solution reduces resulting into increase in pH

d)i) Ammonium ions undergo hydrolysis in aqueous solution to produce hydroxonium ions that react with magnesium ribbon to produce hydrogen gas.

$$NH_4^+$$
 (aq) + $H_2O(l) \rightleftharpoons NH_3(g) + H_2O^{3+}$ (aq)
 $Mg(s) + H_2O^{3+}$ (aq) $\longrightarrow Mg^{2+}$ (aq) + $H_2(g) + 2H_2O(l)$

ii) In benzoic acid, the carbonyl functional group is attached directly to the benzene ring. The delocalized pi electrons of the benzene ring exerts a negative inductive effect which weakens the oxygen-hydrogen bond. In aqueous solution, benzoic acid can easily donate protons and a solution has a relatively high concentration of hydrogen ions.

In propanoic acid, the ethyl group attached to the carboxyl group exerts a positive inductive effect which strengthens the oxygen-hydrogen bond and the aqueous solution of propanoic acid has a relatively low concentration of hydrogen ions.

20. (a)
$$CH_3CHO$$
 $\frac{KCN/AULH_2SO_4}{<20^9C}$ CH_3CHCN

mechanism

 $KCN + H_2SO_4 \longrightarrow KHSO_4 + HCN$
 CH_3CHCN
 CH_3CHCN

mechanism

$$CH_{3}CH_{2}C - H \longrightarrow CH_{3}CH_{2}C - H \longrightarrow CH_{3}CH_{2}C - H \longrightarrow CH_{5}CH_{2}C - H \longrightarrow CH_{$$

21. a) Steam distillation is a technique of separation of a volatile component which is immiscible with water from a mixture containing a nonvolatile impurities by passing steam through the mixture at a temperature below the boiling point of water.

-CH₃

b) The principle is that when an immiscible mixture of two liquids is heated, each liquid will vaporize independent of each other and the vapour pressure above the mixture is the sum of the

individual vapour pressures. The total vapour pressure can easily reach external atmospheric pressure and the mixture boils at temperature below the boiling points of either liquids.

c)i) The component to be steam distilled must be immiscible with water

The components to be steam must be volatile.

The impurities must be nonvolatile.

The component should have high relative molecular mass such that much of it is isolated in the distillate.

The components should exert high vapour pressure near the boiling point of water.

ii) The component is isolated in much purer state.

Decomposition of the component near its boiling point is avoided.

d)

Temperature (°C)	40	50	60	70	80	90	100	110	120
Vapour pressure of phenylamine (mmHg)	10	20	25	32	40	50	55	65	80
Vapour pressure of water(mmHg)	629	632	645	655	670	690	710	730	760
Total vapour pressure of mixture(mmHg)	639	652	670	687	710	740	765	795	840

- i) On graph paper.
- ii) At 760 mmHg, $P^{\circ}H_{2}O$ = 705 mmHg and P° amine = 55 mmHg .

$$\frac{\text{Mass of phenylamine in distillate}}{\text{Mass of water in distillate}} = \frac{\text{V. P x RMM of amine}}{\text{V. P x RMM of water}}$$

RMM of Phenylamine = 93 RMM of water = 18.

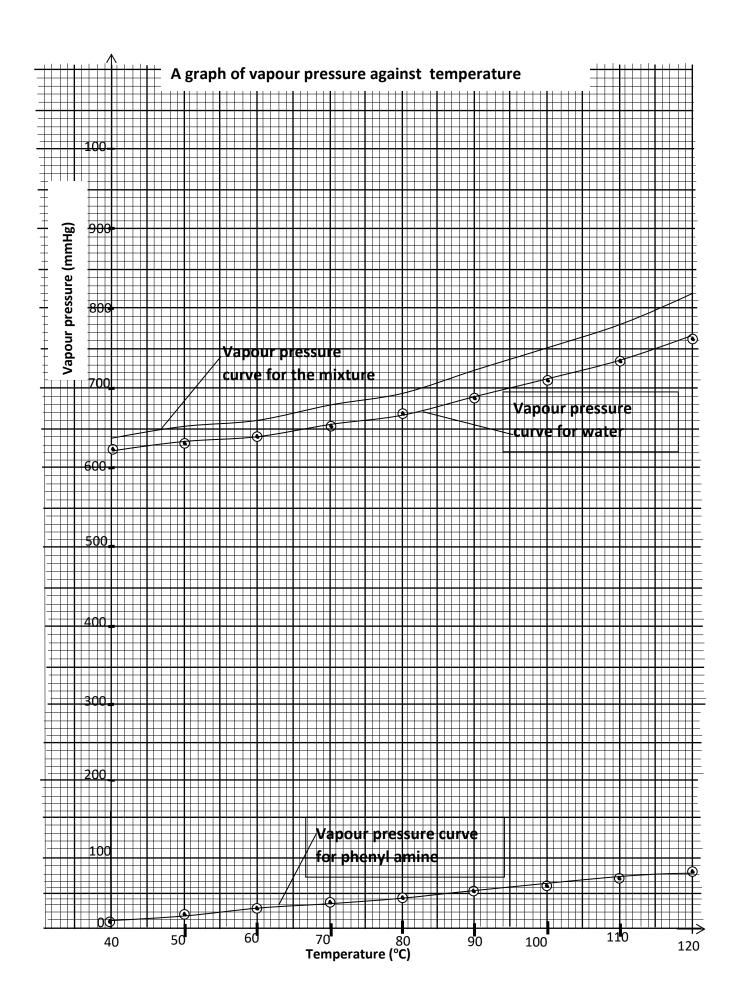
$$\frac{\text{Mass of phenylamine in distillate}}{\text{Mass of water in distillate}} = \frac{55 \times 93}{705 \times 18}$$

= 0.40307

Percentage of phenylamine = $\frac{0.4037}{1.40307} \times 100$

The ratio of ammine to water is 0.40307:1

= 28.73%



e) Let the mass extracted by 100 cm³ of ether be X g

$$K_D = \frac{[Q]Ether}{[Q]Water}$$

2.0 =
$$\frac{x}{100} \times \frac{10-x}{50}$$

$$X = 8 g$$

Mass that remained in the aqueous layer; 10 - 8 = 2 g

Percentage of Q extracted by the ether layer = $\frac{8}{10} \times 100 = 80\%$

Percentage that remained in the aqueous layer = $\frac{2}{10} \times 100 = 20\%$

- 22. a) Electropositivity of group(II) elements increases down the group. Down the group, both screening effect and nuclear charge increase due to addition of an extra shell of electrons and more protons to the nucleus respectively. However, increase in screening effect outweighs increase in nuclear charge. Thus, effective nuclear attraction decreases, and the outer electrons are not strongly attracted to the nucleus, therefore the outermost electrons can easily be lost.
- b)(i) Beryllium does not react with water under any condition. Magnesium reacts slowly with cold water forming magnesium hydroxide and hydrogen gas.

$$Mg(s) + 2H_2O(l) \longrightarrow Mg(OH)_2(aq) + H_2(g)$$

However, heated magnesium reacts vigorously with steam to form magnesium oxide and hydrogen gas.

$$Mg(s) + H_2O(g) \longrightarrow MgO(s) + H_2(g)$$

The rest of the elements react with cold water vigorously to form hydroxides and hydrogen gas.

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

$$Sr(s) + 2H_2O(l) \longrightarrow Sr(OH)_2(aq) + H_2(g)$$

$$Ba(s) + 2H_2O(l) \longrightarrow Ba(OH)_2(aq) + H_2(g)$$

$$OR X (s) + 2H_2O (l) \longrightarrow X(OH)_2 (aq) + H_2 (g)$$
 Where $(X = Ca, Sr, Ba)$

(ii) All group (II) metals react with dry air when heated to form monoxides (normal oxides) and nitrides.

$$2M(s) + O_2(g) \longrightarrow 2MO(s)$$

 $3M(s) + N_2(g) \longrightarrow M_3N_2(s)$

Where
$$M = Be, Mg, Ca, Sr, Ba$$

(iii) Beryllium does not react with nitric acid under any condition.

Magnesium reacts with very cold dilute nitric acid to form magnesium nitrate and hydrogen gas.

$$Mg(s) + 2HNO_3(aq) \longrightarrow Mg(NO_3)_2(aq) + H_2(g)$$

The rest of the metals including magnesium react with hot concentrated nitric acid to form metal nitrate, nitrogen dioxide gas and water.

$$M(s) + 4HNO_3(aq) \longrightarrow M(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

c)(i) Beryllium carbide is formed when beryllium is mixed with carbon and the mixture heated strongly at 950° C. It may also be prepared by reduction of beryllium oxide with carbon at a temperature above 1500° C.

$$2Be(s) + C(s) \longrightarrow Be_2C(s)$$

OR 2BeO (s) + 3C (s)
$$\longrightarrow$$
 Be₂C (s) + 2CO (g)

Calcium carbide is prepared by heating a mixture of calcium oxide (lime) and coke in an electric furnace at 2200 °C.

$$CaO(s) + 3C(s) \longrightarrow CaC_2(s) + CO(g)$$

(ii) Beryllium carbide reacts with dilute hydrochloric acid to form beryllium chloride and methane.

$$Be_2C(s) + 4HCl(aq) \longrightarrow 2BeCl_2(aq) + CH_4(g)$$

Calcium carbide reacts with dilute hydrochloric acid to form calcium chloride and ethyne.

$$CaC_2$$
 (s) + 2HCl (aq) \longrightarrow $CaCl_2$ (aq) + C_2H_2 (g)

d)(i) Cement is manufactured is manufactured from limestone, silica, alumina and iron ore. Silica, alumina and iron ore come from clay. These substances are mixed, and the mixture crushed into fine powder. The fine powder is heated in a kiln at 2000 °C. Other ingredients such as ash (powdered coal) and gypsum (magnesium sulphate) are added to the mixture to obtain good quality cement. Gypsum delays setting of cement.

$$\begin{array}{l} \text{CaCO}_3 \ (s) \longrightarrow \text{CaO} \ (s) \ + \ \text{CO}_2 \ (g) \\ \text{CaO} \ (s) \ + \ \text{SiO}_2 \ (s) \longrightarrow \text{CaSiO}_3 \ (s) \\ \text{CaO} \ (s) \ + \ \text{Al}_2 O_3 \ (s) \longrightarrow \text{Ca} (\text{AlO}_2)_2 \ (s) \\ \text{CaO} \ (s) \ + \ \text{Al}_2 O_3 \ (s) \ + \ \text{Fe}_2 O_3 \ (s) \longrightarrow \text{Ca} (\text{AlO}_2)_2 \ (s). \text{Ca} (\text{FeO}_2)_2 \ (s) \end{array}$$

- (ii) Concrete is a mixture of cement, sand, stones (gravel) and water. It becomes very hard on standing.
- 23. A concentrated solution of sodium chloride is electrolyzed using graphite anode and flowing mercury as the cathode.

At the anode;
$$2Cl^{-}(aq) \longrightarrow Cl_{2}(g) + 2e$$

At the cathode;
$$Na^+(aq) + e \longrightarrow Na(s)$$

$$Na(s) + Hg(l) \longrightarrow Na(s)/Hg(l)$$

The sodium amalgam is dissolved in water to form sodium hydroxide solution.

$$2Na(s)/Hg(l) + 2H_2O(l) \longrightarrow 2NaOH(aq) + 2Hg(l) + H_2(g)$$

- b)i) Animal fat or vegetable oil and sodium chloride
- ii) The animal fat or vegetable oil is heated strongly with concentrated sodium hydroxide while stirring the mixture. The liquid mixture is removed from heat source and then concentrated sodium chloride solution is added while stirring the mixture in order to precipitate out the soap. The mixture is allowed to cool and the soap formed is removed then washed.

$$H_2C$$
—O—COR OH OH OH H_2C —O—COR + $3NaOH(aq)$ \longrightarrow $3RCOONa + CH_2CH_2CH_2$ H_2C —O—COR

c) The soap lowers the surface tension between the dirt and the water. As soap is rubbed on a dirty fabric or as the dirty material is agitated with soap in the presence of water, the hydrophobic part attaches to the dirt and removes it. The hydrophilic part of soap dissolves in water. The hydrophobic part forms globules with dirt which is repelled and dispersed by water molecules hence the material being cleansed.

d)i)

d)ii) Sodium sulphate; increases the bulk of the powder making it economically profitable to the manufacturer

Sodium triphosphate; helps to form soluble calcium salts by reacting with calcium ions Sodium peroborate; gives the detergent the bleaching action.

e) Advantages.

Do not form scum with hard water

Form almost neutral aqueous solutions since they are derived from fairly strong acids and strong bases.

24. a) Temperature above which a vapour of a substance cannot be liquefied by increasing pressure

b)i) F-Solid G- Solid H- Vapour

ii) B-Transition temperature C- Tripple point D- Critical point

c) The vapor phase changed to liquid phase and volume decreased.

Number 1

Volume of pipette used =25.0 cm³

Final burette reading (cm³)	16.20	32.20	48.20
Initial burette reading (cm³)	0.00	16.20	32.20
Volume of FA1 used (cm³)	16.20	16.00	16.00

(a)(i) 16.00, 16.00

(ii)
$$\frac{16.00+16.00}{2}$$
 = 16.00

Questions

(b)(i) (Na =
$$23$$
, S = 32 , O = 16)

Molar mass of $Na_2S_2O_3 = 2x23+32x2+16x3 = 158g$

158g of $Na_2S_2O_3$ contains 1 mole of $S_2O_3^{2-}$ ions

18.96g of Na₂S₂O₃ contains
$$\frac{18.96}{158}$$
 = 0.12mole of S₂O₃²⁻ ions

 $1000 cm^3$ of FA1 contains 0.12 moles of $S_2O_3^{2-}$ ions

16.00cm³ of FA1 contains
$$\frac{0.12 \times 16}{1000}$$
 = 1.92 x10⁻³ moles of S₂O₃²⁻ ions

2 moles of $S_2O_3^{2-}$ ions react with 1 mole of iodine

 1.92×10^{-3} moles of $S_2O_3^{2-}$ ions react with $\frac{1}{2}x$ 1.92 x 10^{-3} = 9.6 x 10^{-4} moles of iodine

Moles of iodine that reacted with thiosulphate ions =9.6 $\times 10^{-4}$

- (ii) 5moles of iodine are liberated or produced by 2 moles of MnO_4
- 9.6 x 10^{-4} moles of iodine are produced by $\frac{2}{5}$ x9.6 x 10^{-4} =3.84 x 10^{-4} moles of MnO₄

25cm³ of FA3 contains 3.84 $\times 10^{-4}$ moles of MnO₄⁻

$$100 \text{cm}^3 \text{ of FA3 contains } \frac{3.84 \times 10^{-4} \times 100}{25} = 1.536 \times 10^{-3} \text{moles of MnO}_4^-.$$

(b) Moles of MnO₄⁻ in 100cm³ of FA3= moles of MnO₄⁻.in 65 cm³ of FA2 65cm³ of FA2 contains 1.536 x 10^{-3} moles of MnO₄⁻.

 $1000 \text{cm}^3 \text{ of FA2 contains } \frac{1.536 \times 10^{-3} \times 1000}{65} = 0.24 \text{moles of MnO}_4^-.$

Part II

Mass of weighing bottle +T =35.0g

Mass of weighing bottle alone =33.5g

Mass of T used =1.5g

Part III

Volume of pipette used = 25cm³ $(\frac{1}{2} \text{ mark})$

Final burette reading (cm³)	21.00	41.80	20.80
Initial burette reading (cm³)	0.00	21.00	0.00
Volume of FA2 used (cm³)	21.00	20.80	20.80

(a)(i)20.80,20.80

(ii)
$$\frac{20.80+20.80}{2}$$
 = 20.80

(b)(i) 1000cm^3 of FA2 contain 0.024 moles of MnO_4

20.80cm³ of FA2 contain
$$\frac{0.024 \text{ X} 20.80}{1000}$$
 = 4.99 x 10^{-4} moles of MnO₄⁻.

(ii) Manganate (VII) reacts with both Fe $^{2+}$ and $C_2O_4{}^{2-}$ in the ratio 1:2

Moles of MnO₄⁻ that reacted with Fe²⁺ =
$$\frac{1}{3}$$
 x 4.99 x 10⁻⁴ = 1.66 x 10⁻⁴

1 Moles of MnO₄-react with 5 moles of Fe²⁺

1.66 x 10^{-4} Moles of MnO₄-react with 5x1.66 x $10^{-4} = 8.3 \text{ x} 10^{-4} \text{moles of Fe}^{2+}$

(iii) Moles of MnO₄⁻ that reacted with C₂O₄²⁻ = 4.99 x 10^{-4} - 1.66 x 10^{-4} = 3.33 x 10^{-4}

2 Moles of MnO₄ react with 5 moles of C₂O₄²

$$3.33 \times 10^{-4}$$
 Moles of MnO₄ react with $\frac{5 \times 3.33 \times 10^{-4}}{2}$ = 8.3 x 10^{-4} moles of C₂O₄²

(b)i)Values x and y in solid T

Moles Fe²⁺
$$C_2O_4^{2-}$$
8.3 x 10^{-4} 8.3 x 10^{-4}
 8.3×10^{-4} \vdots 8.3×10^{-4}
1:1

X= 1. Y=1

Moles of Moles
$$Fe^{2+}$$
 = $C_2O_4^{2-}$ = $FeC_2O_4.nH_2O=8.3 \times 10^{-4}$

25cm³ of FA4 contains 8.3 x 10^{-4} moles FeC₂O₄.nH₂O

250cm³ of FA4 contains
$$\frac{250}{25}$$
 x8.3 x 10^{-4} = 8.3 x 10^{-3} moles FeC₂O₄.nH₂O

 8.3×10^{-3} moles $FeC_2O_4.nH_2O$ weighs 1.5g

1 moles
$$FeC_2O_4.nH_2O$$
 weighs $\frac{1.5}{8.3 \times 10^{-3}}$ = 180.7g

Molar mass of $FeC_2O_4.nH_2O = 180.7g$

56+2x12+4x16+18n = 180.7

144+18n = 180.7

n=2

Number 2

TESTS	OBSERVATIONS	DEDUCTIONS
(a)Heat two spatula end-ful of L in a dry test tube strongly until no further change.	White powdery solid reddish brown residue hot yellow on cooling colourless gas, turns moist blue litmus red and forms a white precipitate with calcium hydroxide solution colourless condensate turn anhydrous copper(II) sulphate blue	non-transition metal ions present PbO formed CO ₂ evolved CO ₃₂₋ ,C ₂ O ₄₂₋ suspected present hydrated salt

(b)To two spatula end-ful of L in a test tube add about 10cm³ of distilled water shake strongly	partly soluble	
Filter, keep both the filtrate add the residue. Divide the filtrate into four portions.	white residue	non-transition metal ions /Al³+,Ba²+,Zn²+ present
bivide the fitti die fitto four portions.	colourless filtrate	non-transition metal ions /Al ³+,Ba²+,Zn²+ present
(i) . To the first portion of the filtrate, add 2-3 drops of Barium nitrate solution followed by dilute nitric acid.	white precipitate soluble in nitric acid	PO ₄₃₋ C ₂ O ₄₂₋ , SO ₃₂₋ Suspected present
(b)(ii) . To the second portion of the filtrate, add 2-3 drops of lead (II) nitrate solution followed by dilute nitric acid.	white precipitate soluble in nitric acid	PO ₄₃₋ C ₂ O ₄₂₋ , SO ₃₂₋ Suspected present
(b)(iii) To the third portion of the filtrate, add 1-2 drops of silver nitrate solution followed by dilute ammonia solution.	white precipitate soluble in ammonia	C ₂ O ₄₂₋ SO ₃₂₋ Suspected present
(b)(iii)Use the fourth portion of the filtrate to carry out your own test to confirm the anion in the filtrate Test To the test solution I added acidified potassium manganate solution the warmed	purple solution turned colourless on warming	C ₂ O _{4²-} confirmed present
(c)Dissolve then residue in dilute nitric acid.(warm to dissolve) To the resultant solution add dilute sodium hydroxide solution drop- wise until in excess. Filter and keep both the filtrate and residue.	white residue dissolves on warming forming a colourless solution with effervescence of a colourless gas that forms a white precipitate with calcium hydroxide solution white precipitate insoluble in excess white residue colourless filtrate	non-transition metal ions /Pb ²⁺ ,Ba ²⁺ ,Zn ²⁺ present CO ₂ evolved CO ₃ ²⁻ confirmed present Mg ²⁺ , Ba ²⁺ or Ca ²⁺ Mg ²⁺ , Ba ²⁺ or Ca ²⁺
		Zn ²⁺ , Pb ²⁺ or Al ³⁺

(d). To the filtrate from part (c) add		
dilute nitric acid drop wise until the solution is just acidic.	white precipitate soluble in excess dilute nitric acid	Zn ²⁺ , Pb ²⁺ or Al ³⁺
Divide the resultants into three parts.		suspected
(d)(i)To the first portion of acidified		
filtrate, add dilute sodium hydroxide	white precipitate soluble in	Zn ²⁺ , Pb ²⁺ or Al ³⁺
solution drop-wise until in excess.	excess dilute nitric acid	suspected
(d)(ii)To the second part of acidified		
filtrate add dilute ammonia solution drop- wise until in excess.	white precipitate insoluble in excess ammonia solution	Pb ²⁺ or Al ³⁺ suspected
(d)(iii). Use the third part of acidified		Suspecteu
filtrate to carry out a test of your own choice to confirm one of the cation in the filtrate		
Test	yellow precipitate	Pb ²⁺ confirmed present
To the test solution I added potassium iodide solution		present
(e). Dissolve the residue from part (c)		
	white residue dissolves to	Mg²+, Ba²+ or Ca²+
in minimum amount of nitric acid. Divide	form a colourless solution	suspected present
the resultant solution into three parts.		
(i) To the first part add 2-3 drops dilute		
sulphuric acid	white precipitate	Ba ²⁺ or Ca ²⁺ suspected present
(ii). To the second part, add dilute		
ammonia solution drop wise until in excess.	no observable change	Ca²⁺ suspected present
(iv) Use the third part of to carry out a		
test of your own choice to confirm the second cations in L	white precipitate insoluble in ethanoic acid	Ca²⁺ confirmed present
Test		
To the test solution I added ammonium oxalate solution followed by ethanoic acid		

(f) Identify the

- (i) Cations in L \mbox{Pb}^{2+} and \mbox{Ca}^{2+}
- (ii) Anions in L $C_2O_4^{2-}$ and CO_3^{2-}

Number 3.

Number 3.		
TESTS	OBSERVATIONS	DEDUCTIONS
(a)Burn a small amount of R on a spatula end	white powdery solid melts and burns with yellow sooty flame	aromatic compound with high carbon content
(b)To about 1 spatula end-ful of R in a test - tube, add about 10 cm³ of distilled water. Shake strongly and test the mixture with litmus paper. Heat the mixture and Divide the resultant solution into 7 parts.	sparingly soluble in cold water turns blue litmus red dissolves on heating forming a colourless solution	polar aromatic compound acidic compound present
(i)To the first part of the solution, add 2 - 3 drops of acidified potassium dichromate (VI) and warm	No observable change	Primary alcohols secondary alcohol Aldehydes absent
(ii)To the second part of the solution add 2-3 drops of 2,4-dinitrophenylhydrazine solution	No observable change	Ketones absent
(iii)To the third part of the solution add 2 - 3 drops of iron (III) chloride solution	No observable change	Benzoic acid absent
(iv)To the fourth part of the solution add 1cm³ of ethanoic acid followed by 3drops of concentrated sulphuric acid and heat to boiling	No sweet fruity smell	Tertiary alcohols absent
(v)To the fifth part of the solution add little solid magnesium powder	effervescence of a colourless gas	aromatic carboxylic acids present
(vi)To the six part add 2-3 drops acidified potassium manganate(VII)	purple solution turns colourless	un-saturated compound present
(vii)To the seventh part add 2-3 drops of bromine water and shake strongly	Reddish brown solution turns colourless	un-saturated compound present
(c)Dissolve one spatula end-ful of R in about 3cm³ of ethanol, add 3 drops of concentrated sulphuric acid and heat pour the resultant solution on a Petridish containing some water	Sweet fruity smell	esters formed carboxylic acid confirmed present

(e)Comment on the nature of R. Aromatic unsaturated carboxylic acid