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1 (a) Order of reaction is the sum of powers to which the concentrations of the reactants are raised to in the rate equation ✓ 01

or

Consider the reaction

$A + B \rightarrow$ Products

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

order of reaction $= x + y$ ✓ 01

(b) (i) Rate $= K[H_2O_2]$ ✓✓ $1\frac{1}{2}$

(ii) A known volume of standard hydrogen peroxide is put in a conical flask.

A small amount of Iron (III) chloride and sodium hydroxide solution is added to the same flask and a stop clock is simultaneously started.

The mixture is shaken and allowed to stand at a constant temp.

After specific time intervals, known volumes of the reaction mixture are pipetted into a conical flask containing dilute sulphuric acid to quench the reaction.

The mixtures are titrated against standard potassium manganate (VII) solution ✓

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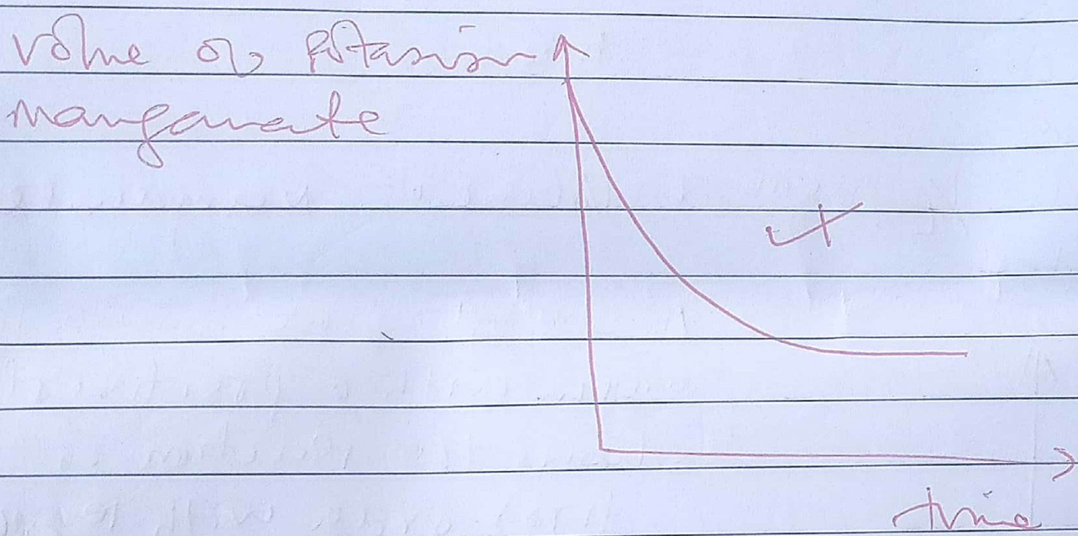
The volumes of potassium manganate (VII) solution are proportional to the concentration of hydrogen peroxide in the reaction mixture.

A graph of volume of potassium manganate (VII) solution against time is plotted



From the graph, the half lives are equal. This shows that the reaction is first order with respect to hydrogen peroxide

OR

A graph of log of volume of manganate (VII) solution against time is plotted

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(c) graph:

Axes ✓

plots ✓½

Shape ✓

Title ✓½

d (i) $t_{\frac{1}{2}}(1) = 8.5\text{min}$ ✓

(ii) $t_{\frac{1}{2}}(2) = 7.5\text{min}$ ✓

accept 8.0 ± 0.5

e (i) The times in d(i) and d(ii) are almost ✓ equal therefore the reaction is first order ½

(ii) $t_{\frac{1}{2}} = \frac{\ln 2}{k}$

$t_{\frac{1}{2}} = \frac{7.5 + 8.5}{2} = 8.0$

$k = \frac{\ln 2}{8}$ ½

or $\frac{0.693}{t_{\frac{1}{2}}}$

$= \frac{0.693}{8}$

$k = 0.087\ \text{min}^{-1}$ ✓

rej with wrong units

$-\frac{1}{2}$ for no units.

UCE

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(iii) Increase in temperature increases the rate of decomposition of hydrogen peroxide because increase in temperature increases the kinetic energy of molecules which increases the frequency of collision and the number of molecules acquiring the activation energy increases

(3½)

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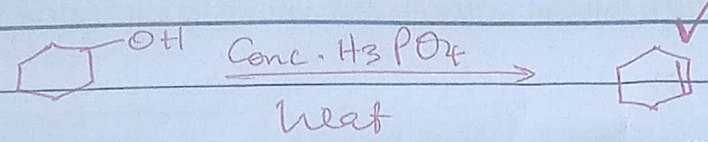
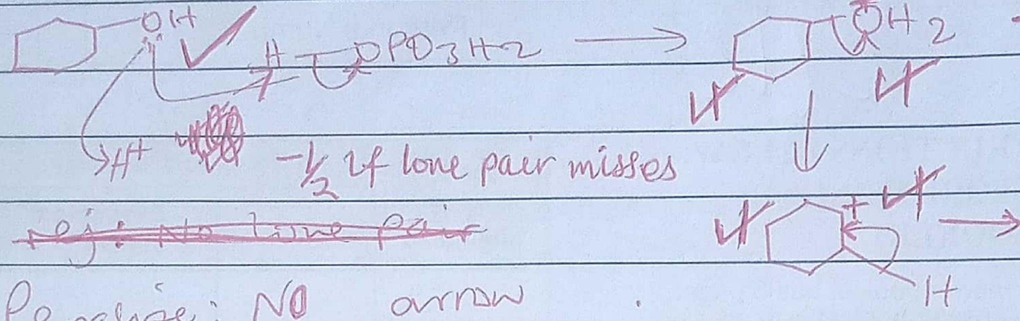
2 (a)



+ (H_2O) −½ if byproduct is wrong

Penalise wrong byproducts

Mechanism: $H-OPO_3H_2 \rightleftharpoons H^+ + {}^-OPO_3H_2$



−½ if the arrow is missing.

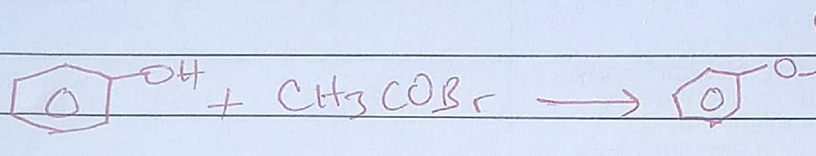
−½ if lone pair misses

~~rej: No lone pair~~

(04)

Penalise: NO arrow.

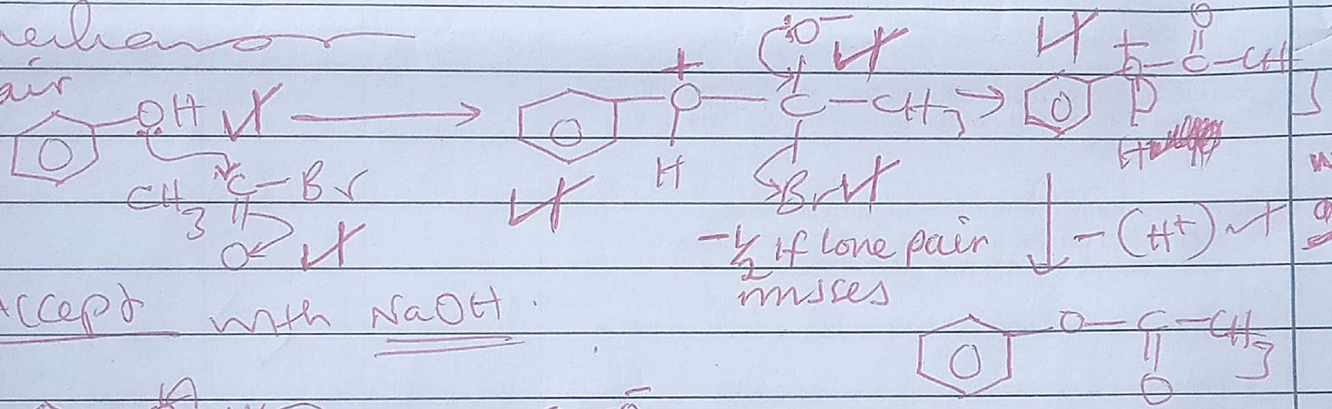
(b)



+ (HBr)

Mechanism

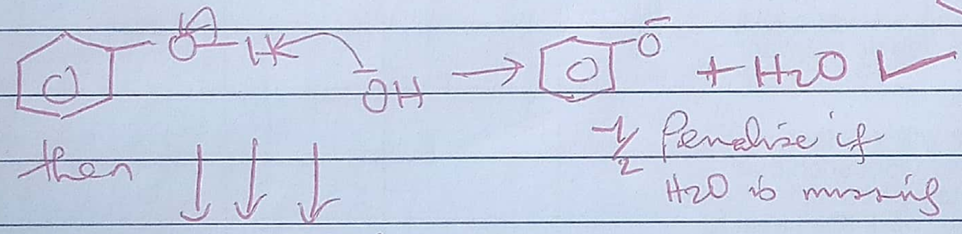
+ Lone pair has to be there



−½ if lone pair misses

w/o arrow

Accept with NaOH.



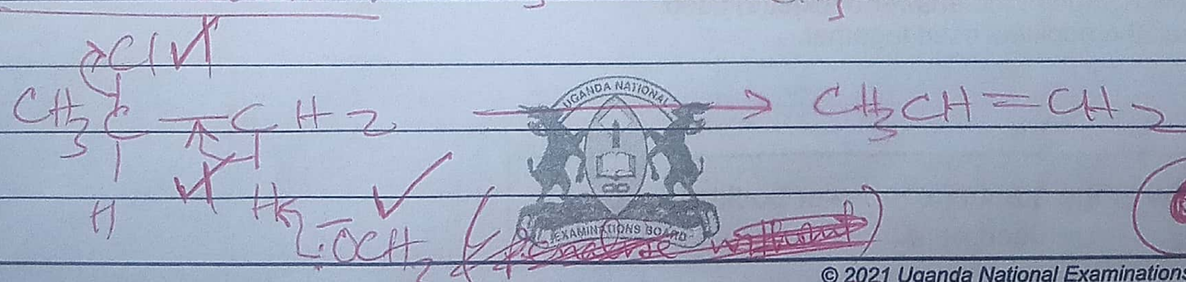
then ↓↓↓

−½ Penalise if H_2O is missing

4½

(c) $CH_3CHClCH_3 \xrightarrow[\text{heat}]{CH_3ONa/\text{alcohol}} CH_3CH{=}CH_2$ + ($NaCl + CH_3OH$)

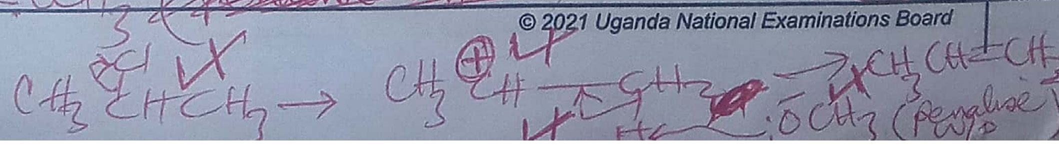
Mechanism: $CH_3ONa \rightarrow CH_3O^- + Na^+$



(~~Penalise without~~)

03

Accept: E_1



(Penalise w/o)

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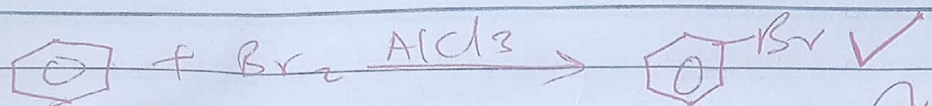
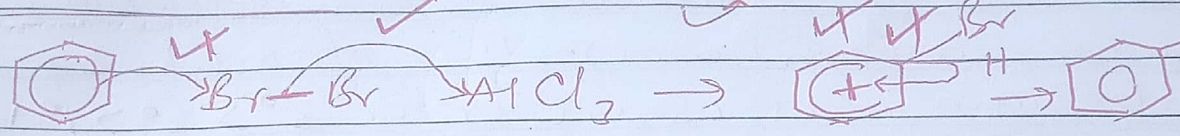
(d)



Mechanism

accept $Br^{\delta+}\cdots AlCl_3Br^{\delta-}$



(3½)

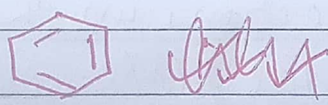
Accept

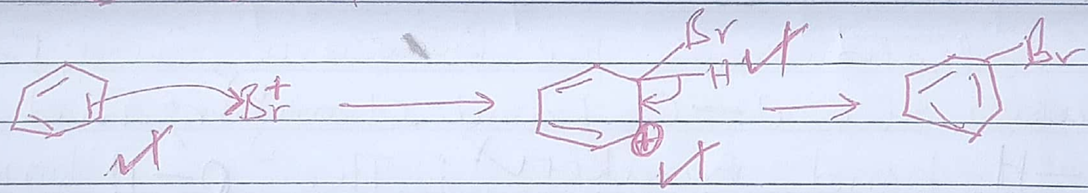
$Br{-}Br \; AlCl_3 \rightleftharpoons Br^+ + [AlCl_3Br]^-$

−½ if arrow goes to Cl

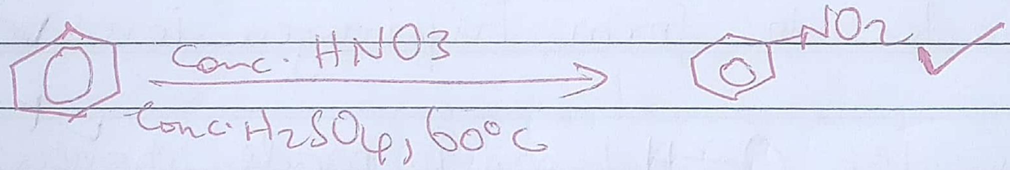
Accept

reject $AlCl_4^-$ & ...



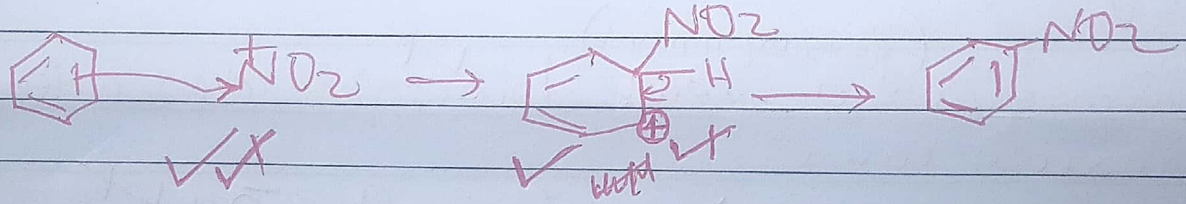


(e)



Mechanism

$HNO_3 + 2H_2SO_4 \rightleftharpoons \overset{+}{N}O_2 + H_3O^+ + 2HSO_4^-$



(5)

Accept: $H_2SO_4 + HNO_3 \rightarrow \overset{+}{N}O_2 + HSO_4^- + H_2O$.

$HNO_3 + H_2SO_4 \rightarrow H_2\overset{+}{N}O_3 + HSO_4^-$

$H_2\overset{+}{O}{-}NO_2 \rightarrow H_2O + \overset{+}{N}O_2$

$O_2N{-}\ddot{O}H \;\; H{-}OSO_3H \rightarrow H_2\overset{+}{O}{-}NO_2 \rightarrow H_2O + \overset{+}{N}O_2$

with/wo the arrows

halate(I)
hypohalite XO^-

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Very Small
smaller

3 (a) (i) Fluorine has the smallest atomic radius ✓ 01

Fluorine has the highest electronegativity ✓

Any wrong extra cancels the right ✗

Fluorine has the highest positive electrode potential

Fluorine has the low bond dissociation energy

Fluorine lacks empty d-orbitals. $\boxed{\text{Any 2}}$

(ii) Fluorine reacts with water to produce Oxygen ✓ while other ~~members~~ halogens form hypohalous ✓ acids.

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

For example:

$Cl_2(g) + H_2O(l) \rightleftharpoons HCl(aq) + HOCl(aq)$ ✓

or. $X_2 + H_2O(l) \rightleftharpoons HX(aq) + HOX(aq)$ ✓

where X = Cl, Br

Accept:

Fluorine reacts with water to form (hydrofluoric acid which is a weak acid) ✓ while others react with water to form (hydrohalic acids which are strong acids ✓)

(Same eqns).

With hot Conc alkali, fluorine forms oxygen ✓ while other halogens form halate (V) ✓

$2F_2(g) + 4OH^-(aq) \rightarrow O_2(g) + 4F^-(aq) + 2H_2O(l)$ ✓

eg. $3Cl_2(g) + 6OH^-(aq) \rightarrow ClO_3^-(aq) + 5Cl^-(aq) + 3H_2O(l)$ ✓

or $3X_2 + 6OH^-(aq) \rightarrow XO_3^-(aq) + 5X^-(aq) + 3H_2O(l)$

With cold dilute alkali, fluorine forms oxygen difluoride ✓ while other halogens form halate (I) ✓ / hypohalites

$2F_2(g) + 2OH^-(aq) \rightarrow OF_2(g) + H_2O(l) + 2F^-(aq)$ ✓

eg. $Cl_2(g) + 2OH^-(aq) \rightarrow ClO^-(aq) + H_2O(l) + Cl^-(aq)$ ✓

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→ Fluorine reacts with heated (hot) ~~silicon (IV) oxide~~ silicon dioxide to form Silicon tetrafluoride and oxygen other halogens do not under the same condition ✓

$F_2(g) + SiO_2(s) \rightarrow SiF_4(g) + O_2(g)$ ✓

– Accept reaction of HF with heated ✓ SiO_2 while other ~~chlorine~~ HX do not react ✓

$4HF(aq) + SiO_2(s) \rightarrow SiF_4(g) + 2H_2O(l)$ ✓

$6HF(aq) + SiO_2(s) \rightarrow H_2SiF_6(aq) + 2H_2O(l)$

→ ~~Heated~~ Fluorine reacts with (heated) Carbon ✓ while other halogens do not react ✓

$2F_2(g) + C(s) \rightarrow CF_4(g)$ ✓

(b) (i) Title ✓

Labelled axes ✓ with correct scale

Correct plots and the scale ✓

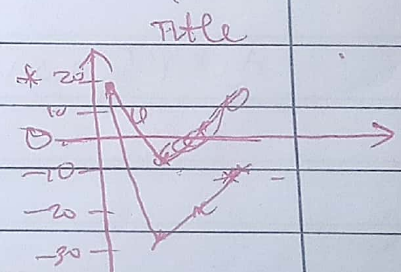
Shape ✓

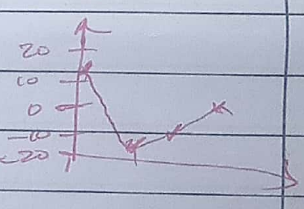
3) ref) Reject sketch.

Penalise if 2 points are wrong.

(ii) Explanation:

No graph = Do not mark.





(ii) Explanation:

Trend: Bp of hydrides increases from hydrogen ~~bromide~~ chloride to hydrogen iodide except hydrogen fluoride with an abnormally high bp ✓

or (Decreases from HF to HCl then Increases to HI) ✓

UCE

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Generally for the halides ~~from HF to HI~~ molecular mass increases down the group which increases the strength of van der waals forces;

Fluorine has a smaller atomic radius and high electronegativity. So, the H−F bond is strongly polar and molecules of HF are held by hydrogen bonds; which are stronger than the van der waals forces

8½

(C) (i) Brown solution turns to colourless solution,

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

(ii) Colourless solution turns reddish brown solution (red/ orange)/ brown gas reddish

$2HBr(aq) + Cl_2(g) \rightarrow Br_2(aq) + 2HCl(aq)$ (l) or (g).

4½

Accept ionic;

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4(a) (i) Molar conductivity is the ratio of Conductivity to concentration while electrolytic conductivity is the reciprocal of resistivity 01

OR

Molar conductivity is the conductance of a solution containing one mole of electrolyte placed between two electrodes each of $1cm^2$ cross section area and are 1cm apart while electrolytic conductivity is the conductance of a solution placed btn two electrodes ~~placed~~ each of $1cm^2$ cross section area and a placed 1cm apart

(Accept unit cross section unit distance of separation $1m^2$ C.S.A and 1M apart)

or $\Lambda_c = \frac{K}{C}$

$K = \frac{1}{\rho}$ where Λ_c = molar conductivity

K = electrolytic conductivity

c = Concentration

ρ = Resistivity

(ii) $\Lambda = \frac{K}{C}$

$\Lambda = \frac{1000K}{C}$

$K = \frac{\Lambda \cdot C}{1000}$

$K = \frac{129 \times 0.1}{1000}$

$K = 0.0129\ \Omega^{-1}\ cm^{-1}$

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Cell constant $= l/A = K \cdot R$
$= 0.0129 \times 484$
$= 6.24\ cm^{-1}$
$-\frac{1}{2}$ for no units
Deny ans if wrong units

b(i) $\Lambda^\circ AgCl = (\Lambda^\circ AgNO_3 + \Lambda^\circ KCl) - \Lambda^\circ KNO_3$
$= (133.4 + 149.9) - 145$
$= 138.3\ \Omega^{-1} cm^2 mol^{-1}$
mark w or w/o units
$-\frac{1}{2}$ for wrong units.

(ii) $K_{solute} = K_{solution} - K_{water}$
$= 3.41 \times 10^{-6} - 1.60 \times 10^{-6}$
$= 1.81 \times 10^{-6}$

From $\Lambda_c = \frac{1000K}{C}$ or $\frac{K}{C}$

$C = \frac{1000 \times 1.81 \times 10^{-6}}{138.3}$ | Accept $C = 1.3 \times 10^{-8}\ mol\ cm^{-3}$

$C = 1.3 \times 10^{-5}\ mol\ dm^{-3}$ | 1.308×10^{-5}, 1.31×10^{-5} allow

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$ rej eqn if $\rightleftharpoons$ missed
$-\frac{1}{2}$ for wrong states or missing

$-\frac{1}{2}$ no units
-1 for wrong units

$K_{sp} = [Ag^+][Cl^-]$
$K_{sp} = (1.30 \times 10^{-5})(1.30 \times 10^{-5})$
$K_{sp} = 1.69 \times 10^{-10}\ mol^2 dm^{-6}$ (or $Mol^2 l^{-2}$)
1.71×10^{-10}

C (i) The smaller the ionic radius the higher the molar conductivity ✓ because the smaller the ionic radius the higher the ionic mobility ✓

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Accept the other way round

(2½)

C (i) The smaller the ionic radius the higher the ionic mobility ✓ and hence the higher the molar conductivity ✓

(ii) For strong electrolytes;
Molar conductivity decreases with increase in concentration ✓
This is because ~~inter~~ inter-ionic distance decreases ✓; ionic interferences increases; ✓ which reduces ionic mobility ✓

For weak electrolytes;
Molar conductivity decreases with increase in concentration ✓
This is because increase in concentration decreases degree of ionisation ✓ which reduces number of ions per unit volume ✓

Accept: For both electrolytes; increase in concentration decreases the molar ~~set~~ conductivity ✓ 01

Allow: ~~increas~~ increase in dilution increases molar conductivity ✓ 01, then follow the corresponding explanations for both weak and strong electrolytes.

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5 (a) (i) mpts generally decrease down the group (or from carbon to lead)
(or carbon to tin with some slight increase to lead)
Carbon, silicon (and germanium) have giant atomic structure and strong covalent bonds btn atoms
Strength of covalent bonds decrease due to increase in atomic radius
(or increase in bond length due to increase in atomic radius)
Both tin and lead have giant metallic structures held by (~~strong~~) metallic bonds which are relatively weak than covalent bonds due to bigger atomic radii

giant covalent / giant molecular

(ii) Carbon reacts with hot conc sulphuric acid to form carbon dioxide, sulphur dioxide (and water).

$C_{(s)} + 2H_2SO_4(aq)(l) \rightarrow CO_2(g) + 2SO_2(g) + 2H_2O(l)$

Germanium reacts with hot conc H_2SO_4 to form germanium (IV) oxide, sulphur dioxide (and water)

$Ge(s) + 2H_2SO_4(aq)(l) \rightarrow GeO_2(s) + 2SO_2(g) + 2H_2O(l)$

Tin reacts with hot conc H_2SO_4 to form tin (IV) sulphate, sulphur dioxide (and water)

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

rej: hot only
sulphuric
rej: if hot conc is not there
rej: unless hot and conc are missing
Rej: correct eqn wrong condition
Ignore if cold dilute
CATEGORIC

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Lead reacts with hot conc H_2SO_4 to form lead(II) sulphate, sulphur dioxide (and water)

$Pb_{(s)} + 2H_2SO_{4(aq)(l)} \rightarrow PbSO_{4(s)} + SO_{2(g)} + 2H_2O_{(l)}$

(b)(i) $CS_{2(l)} + 3Cl_{2(g)} \rightarrow CCl_{4(l)} + S_2Cl_{2(l)}$

(or $CS_{2(l)} + 2Cl_{2(g)} \rightarrow CCl_{4(l)} + 2S_{(s)}$)

(or $CH_{4(g)} + 4Cl_{2(g)} \rightarrow CCl_{4(l)} + 4HCl_{(g)}$)

$SiO_{2(s)} + 2C_{(s)} + 2Cl_{2(g)} \rightarrow SiCl_{4(l)} + 2CO_{(g)}$

(or $Si_{(s)} + 2Cl_{2(g)} \rightarrow SiCl_{4(l)}$)

$PbO_{2(s)} + 4HCl_{(aq)} \rightarrow PbCl_{4(l)} + 2H_2O_{(l)}$

(ii) Carbon tetrachloride

No observable change

(or two separate layers)

Silicon tetrachloride

White solid

White fumes/misty fumes

(Mark misty fumes once)

Lead (IV) chloride

Brown solid

(white fumes/misty fumes)

Explanation: Carbon tetrachloride does not undergo hydrolysis; due to absence of empty d-orbitals in carbon atoms to accomodate electrons from water.

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Silicon (IV) chloride and lead (IV) chloride undergo hydrolysis

(accept equation to illustrate hydrolysis)

$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$

due to silicon or lead atoms having empty d-orbitals that accomodate electrons from water.

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6 (a)(i) Electron affinity is the enthalpy change that occurs when one mole of electrons is added to one mole of gaseous atoms to form one mole of uninegatively charged gaseous ions. ✓ 01

(ii) First ionisation energy is the energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of unipositively charged gaseous ions. ✓ 01

(iii) Enthalpy of solution is the enthalpy change when one mole of a compound/Substance / ionic cpd is dissolved in (a specified amount of) water to form an infinitely dilute solution. ✓ 01

(c) A known volume V_A of the hydrochloric acid of known concentration M_A is placed in a plastic beaker and its initial temperature noted, T_1.

penalise known amount / known mass

accept insulated lagged calorimeter

An equal volume of sodium hydroxide solution of the same molarity is measured into another plastic beaker and its initial temperature, T_2 noted.

Sodium hydroxide is then added to the flask containing hydrochloric acid and the mixture stirred; The highest/constant temperature is recorded, T_3

Assumptions:
Density of solution is equal to density of water = ($1 gcm^{-3}$)
Specific heat capacity of solution is equal to specific heat capacity of water = ($4.2 Jg^{-1}K^{-1}$ or $°C^{-1}$)
Heat capacity of the calorimeter is ignored

Treatment of results.
Initial temperature $T_i = \frac{T_1 + T_2}{2}$

Temperature change $= T_3 - T_i = \Delta T$

Mass of solution $= (V_A + V_A) cm^3 \times 1 gcm^{-3} = 2V_A$ g

Heat change $= (2V_A \times 4.2 \times \Delta T)$ J.

Number of moles of hydrochloric acid $= \frac{M_A V_A}{1000}$

$\frac{M_A V_A}{1000}$ moles of acid liberate $(2V_A \times 4.2 \times \Delta T)$ J

1 mol of acid liberates $\frac{2V_A \times 4.2 \times \Delta T \times 1}{(M_A V_A / 1000)}$

05

$\therefore$ Heat of neutralisation $= - \frac{2 \times 4.2 \times \Delta T}{M_A}$ $kJmol^{-1}$

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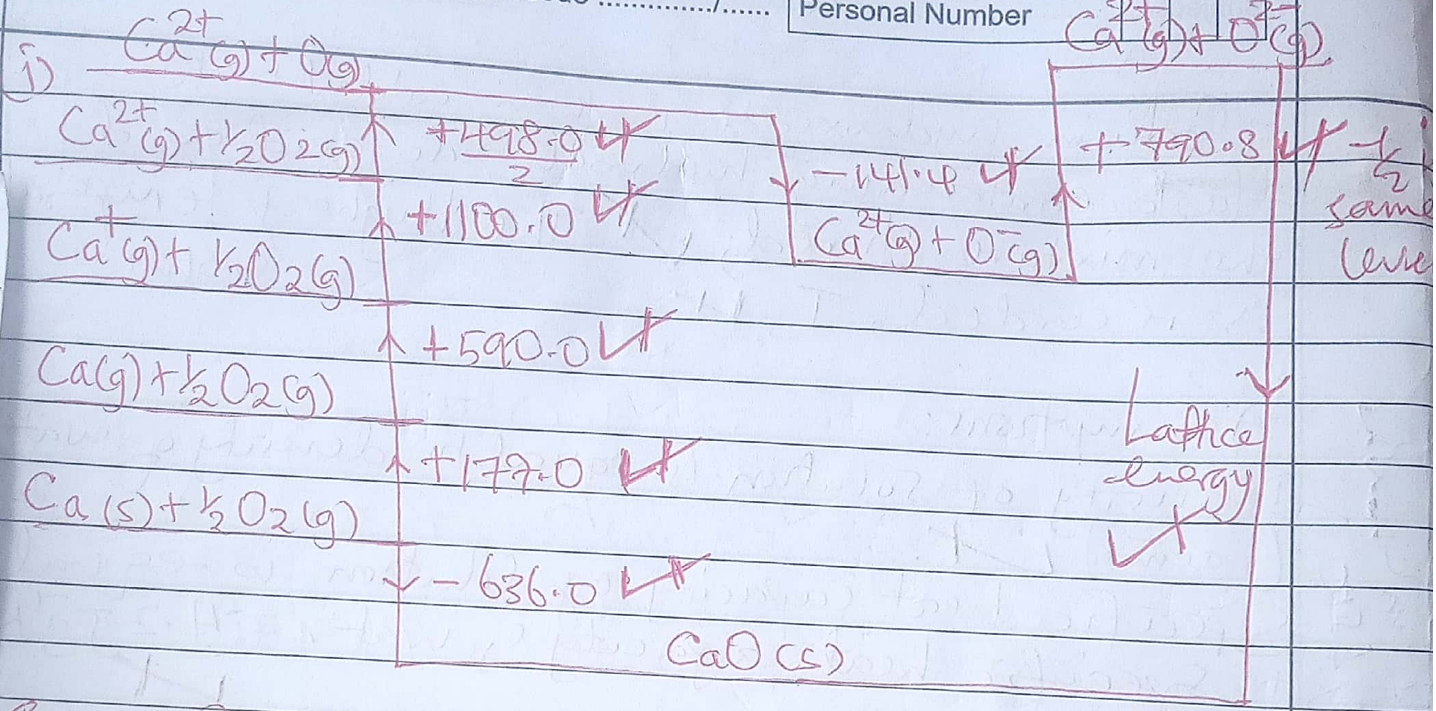
d (i)



Sign
States
Balance } check

(04)

(ii) $LE = -636.0 - (177.0 + 590.0 + 1100.0 + \frac{498.0}{2} + 790.8 - 141.4)$

$LE = -3401.4\ kJmol^{-1}$

mark with units

$-\frac{1}{2}$ for no units.

0 for wrong units.

(02)

(iii) Calcium oxide is stable because lattice energy is high.

(01)

(i) ΔH solution (LiCl) = Lattice energy + Hydration energy

$= (+843) + (-883)$

$= -40\ kJmol^{-1}$

$-\frac{1}{2}$ for no units

ΔH solution $(NaCl)$ = Lattice energy + Hydration energy

$$= (+778) + (-775)$$

$$= +3\ kJmol^{-1}$$ ✓ 01½

(ii) Sodium chloride dissolves more on heating ✓ because the enthalpy of solution of sodium chloride is positive. ✓ 01

~~use the values above~~

6 (b) When an atom loses an electron, the number of electrons reduces ✓ and the remaining electron experiences a greater nuclear ~~am~~ attraction ✓ 02

ACCEPT: - proton/electron ratio increases
- effective nuclear charge increases

NB: On treatment of results.
~~Heat of~~ If a container of mass M_c and SHC, C_c then

$$Heat = (\cancel{\ldots} \times 4.2 + M_cC_c)\Delta T$$

or

$$Heat = (2V_A \times 4.2 + M_cC_c)\Delta T \text{ joules}$$ $(2V_A \times 4.2 + M_cC_c)\Delta T$ J

Where $C = M_cC_c$ ✓
↳ Heat capacity ✓

7(a) $CH_3COCH_3 \xrightarrow{PCl_5} CH_3CCl_2CH_3$

$CH_3CCl_2CH_3 \xrightarrow{NaOH/ethanol,\ heat} CH_3C\equiv CH$

$CH_3C\equiv CH \xrightarrow{H_2/Lindlar\ catalyst} CH_3CH=CH_2$

CH_3COCH_3

↓ $LiAlH_4$/(Dry) ether or Na/ethanol or $NaBH_4/H_2O$ or methanol

(H_2/Ni, 150°C or Heat)

$CH_3CH(OH)CH_3$

↓ Conc. H_2SO_4/Heat (170–180°C) or Conc. H_3PO_4/Heat or Al_2O_3/300–400°C (heat)

(Conc & Heat)

$CH_3CH=CH_2$

↓ ($HBr/ROOR$) Penalise the word peroxide

(organic peroxide)

$CH_3CH_2CH_2Br$

↓ $\bar{O}H$(aq), Heat

$CH_3CH_2CH_2OH$

05½

Accept: ROH, EtOH, alcohol

(b) CH_3CH_2I — No Recovery

↓ KCN/ethanol, Heat (or reflux) — Accept $\bar{C}N$ or NaCN

CH_3CH_2CN

↓ H_2O/H^+, Heat (or reflux) — rej. warm

CH_3CH_2COOH

2½

OR

CH_3CH_2I

↓ Mg/(Dry) ether → ignore warm, penalise heat.

$CH_3CH_2MgI \xrightarrow{CO_2} CH_3CH_2COOMgI \xrightarrow{H_2O/H^+} CH_3CH_2COOH$

CH_3CH_2MgI ↓ 1. CO_2 2. H_2O/H^+ → CH_3CH_2COOH

$CH_3CH_2MgI \xrightarrow{HCHO} CH_3CH_2COMgI$

↓ H^+/H_2O

$CH_3CH_2CH_2OH \xrightarrow{[O]} CH_3CH_2COOH$

MnO_4^-/H^+ or $H^+/Cr_2O_7^{2-}$, Heat

02½

Do not write in this margin

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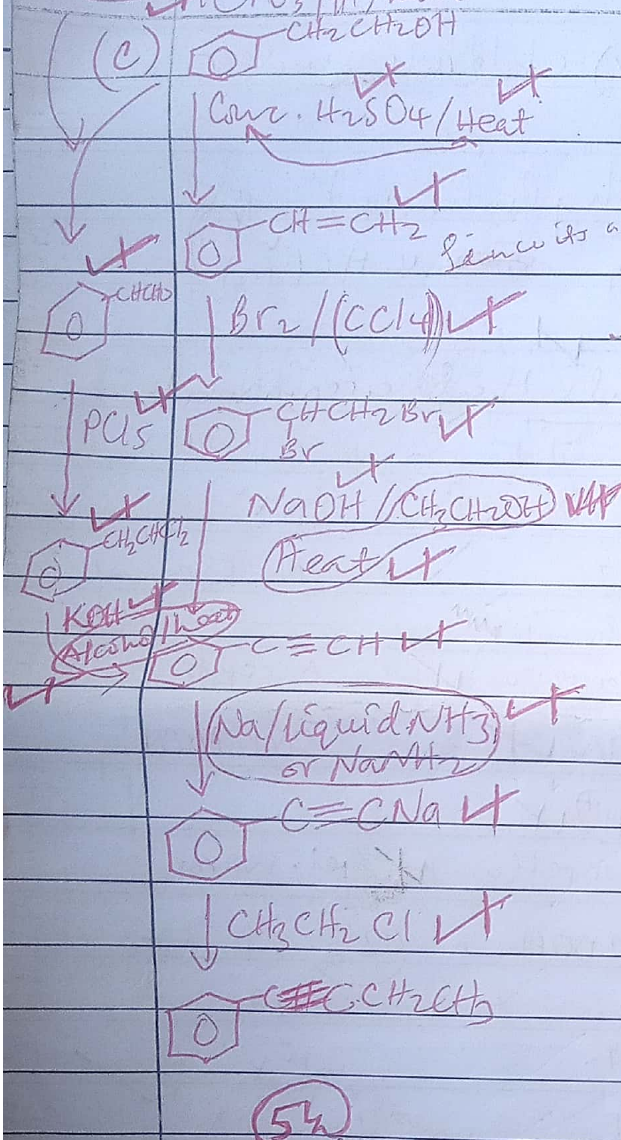
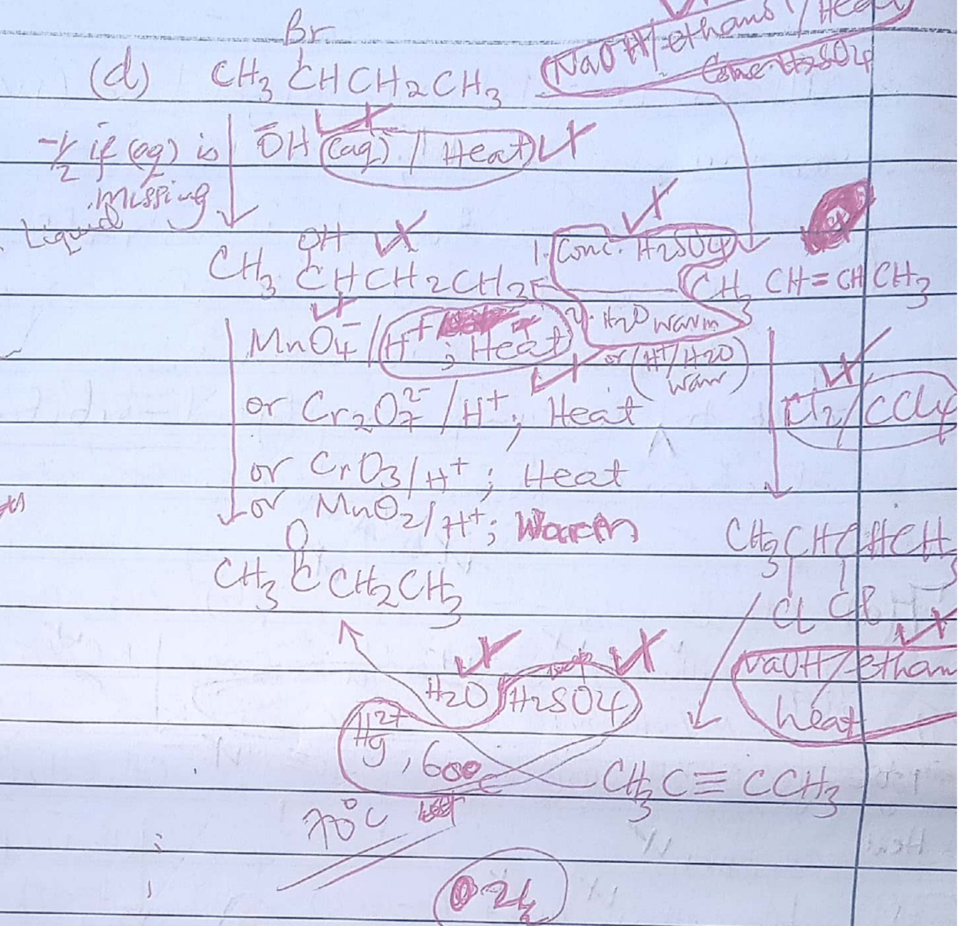
Cu/300°C
Ag/O2 500°C
MnO4-/H+ heat
MnO2/H+, warm
CrO3/H+, heat

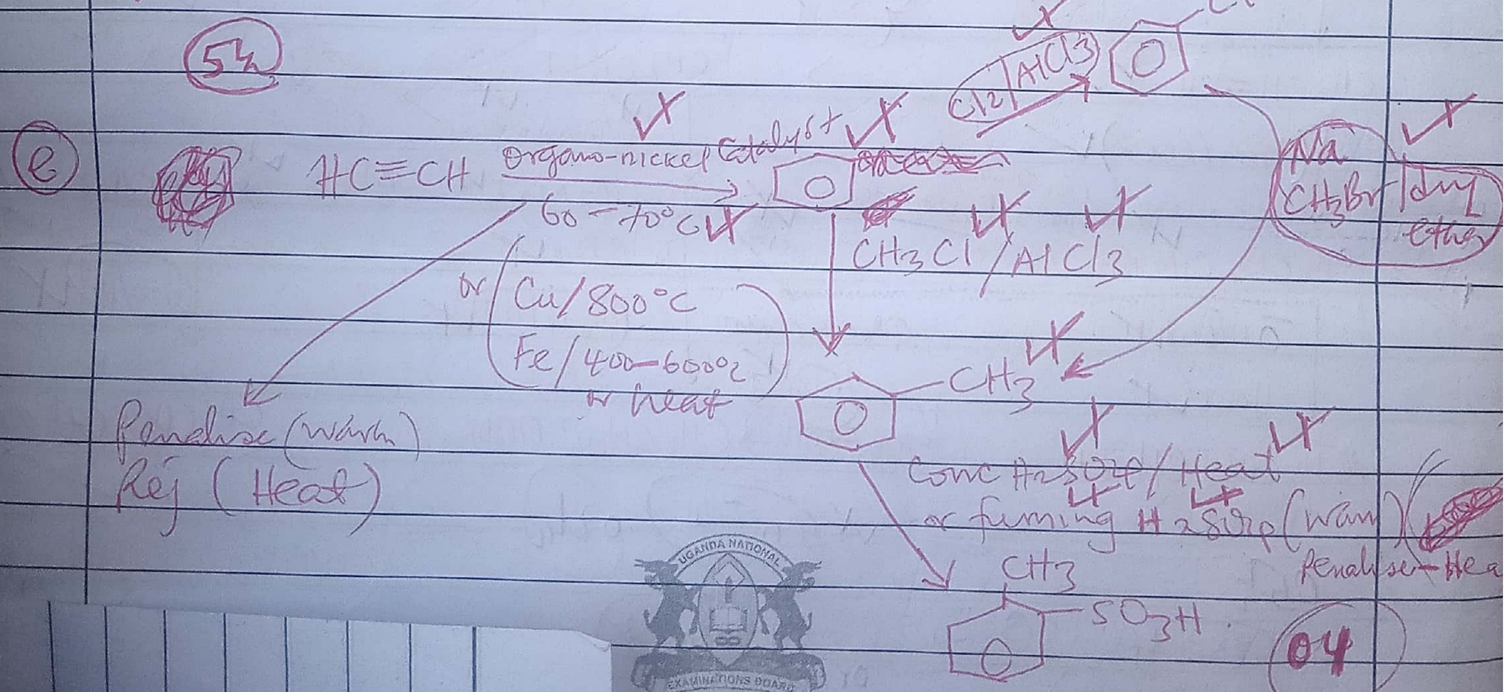
(c)



(d)



(e)



rej. dilute H2SO4

8 (a) Protons from halogen acids react with alcohols to form protonated alcohols; which loose water (or dissociate) to form carbonium ions (or carbocations); The stability of carbonium ions is in order 3° > 2° > 1° due to decrease in number of alkyl groups that have a positive inductive effect. thus favouring formation of carbonium ions. $2\frac{1}{2}$

(b) In phenol, the lone pair of electrons on the oxygen atom interacts with the delocalised (or pi) electrons of the benzene ring; this makes the C—O bond stronger; and the O—H bond weaker; The O—H bond easily breaks to form hydrogen ions

In alcohols, the O—H bond is made stronger; by the positive inductive effect of the alkyl groups 4

(c) Ammonia is a weak (Partially ionises) base; provides a few hydroxide ions

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$$

The hydroxide ions react with magnesium ions to form insoluble magnesium hydroxide

$$Mg^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Mg(OH)_2(s)$$

Magnesium hydroxide is precipitated if the ionic product exceeds the solubility product ($[Mg^{2+}][\bar{O}H]^2 > K_{sp}$)

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or

(c) $NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$

Ammonium chloride is a strong electrolyte
It produces a high concentration of ammonium ions which ~~suppress~~ supress the ionisation of ammonia. This reduces the concentration of hydroxide ions. The ionic product cannot exceed the solubility product

06

(d) Each water molecule has two O—H bonds which are polar.
Each water molecule forms four hydrogen bonds with other water molecules.
Hydrogen - fluorine bond or (H—F) is more polar than the hydrogen - oxygen bond but each hydrogen fluoride molecule forms only two hydrogen bonds with ~~each~~ other hydrogen fluoride molecules. Hydrogen bonds in water require more energy to break since they are ~~many~~ more.

04

e) The nitronium ion has two bond pairs (two bonds) and no lone pairs

The nitrite ion has two bond pairs (two bonds) and one lone pair

3½