95ALCHEMII
MARKING SCHEME

Marks

Paper II Section A

1. (a) (i) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$ — 1

Workdone $= P\Delta V$

$= \Delta(PV)$

$= RT(\Delta n)$ — 1

$= 8.31 \times 298 \times (-1\frac{1}{2})$

$= -3.7(1)$ kJ mol^{-1} — 1

(ii) $\Delta H = \Delta U + P\Delta V$ — 1

$= -140.3 \times (2.016) + (-3.71)$ — 1

$= -286.6$ kJ mol^{-1} — 1

(6)

(b) The reaction

$AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + HNO_3(aq)$

is equivalent to

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ — 1

$\Delta H = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$ — 1

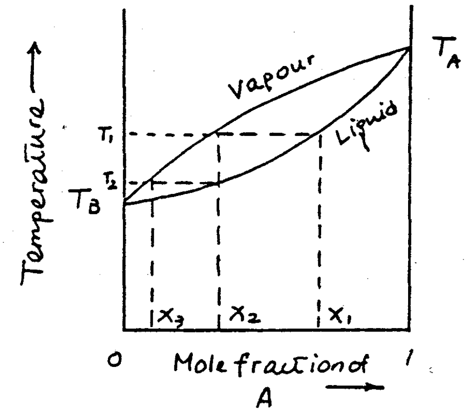
$= -127.07 - (+105.56) - (-167.15)$

$= -65.48$ kJ mol^{-1} — 2

(Accept any correct method using an energy cycle.)

(4)

(c) (i) Boiling point - composition curve



1 mark for labelling the x- and y-axis
1 mark for the liquid curve
1 mark for the vapour curve
(deduct 1 mark if $T_B > T_A$) — 3

(ii) If a solution with composition X_1 is heated to T_1 the gaseous phase in eqm. with it has the composition x_2 which is richer in B (1 marks for explanation ; 1 mark for indication on the graph) 2

This vapour is cooled to T_2 and condenses to liquid with a composition of x_2. Vaporization of this liquid leads to a new vapour with a composition x_3 which is richer in B than that with a composition x_2 and finally pure B is obtained. (1 mark for explanation; 1 mark for indication on the graph) 2

(7)

Marks

2. (a) (i) $^{228}_{88}Ra \rightarrow ^{228}_{89}Ac + ^{0}_{-1}e$ 1

(ii) $k = \frac{\ell n2}{t_{\frac{1}{2}}} = 0.104\ yr^{-1}$ 1

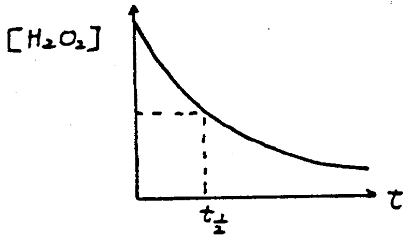
$\ell n \frac{0.5}{N_t} = 0.104\ (5)$ 1

$N_t = 0.297$ g 1 (4)

(b) (i) Withdraw a known volume of the reaction mixture and add to excess dilute H_2SO_4, titrate H_2O_2 against standard MnO_4^- ½, ½, 1

$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$

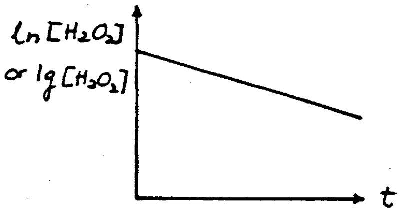
(ii) Plot $[H_2O_2]$ against t to obtain the following graph



2

for first order reaction $t_{\frac{1}{2}}$ = constant and $k = \frac{\ell n2}{t_{\frac{1}{2}}}$ 2

or, plot $\ell n[H_2O_2]$ against t to obtain a straight line (1)



(2)

for first order reaction, slope = -k (1) (6)

(c) (i) $NH_4^+ \rightleftharpoons NH_3 + H^+$

$K_a = \frac{[H^+]\ [NH_3]}{[NH_4^+]}$ 1

(ii) $NH_4^+ + CH_3COO^- \rightleftharpoons NH_3 + CH_3COOH$

$K = \frac{[NH_3]\ [CH_3COOH]}{[NH_4^+]\ [CH_3COO^-]}$ ½

$= \frac{K_a(NH_4^+)}{K_a(CH_3COOH)} = \frac{5.59 \times 10^{-10}}{1.76 \times 10^{-5}} = 3.18 \times 10^{-5}$ 1½

(iii) (1) Let $x = [NH_3] = [CH_3COOH]$

$[NH_4^+] = [CH_3COO^-] = 0.100 - x$ } 1

$K = \frac{x^2}{(0.100 - x)^2} = 3.18 \times 10^{-5}$

$x = 5.60 \times 10^{-4}$ M 1

(2) Let $y = [H^+]$

$K_a(CH_3COOH) = \frac{y(0.100 - x)}{x}$

$y = 9.96 \times 10^{-8}$ M 1

$pH = -\ell g[H^+] = 7.00$ 1

or, $K_a(NH_4^+) = \frac{y(x)}{(0.100 - x)}$

$5.59 \times 10^{-10} = \frac{y(5.60 \times 10^{-4})}{(0.100 - 5.6 \times 10^{-4})}$

$y = 9.93 \times 10^{-8}$ M (1)

pH = 7.00 (1)

(7)

Marks

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ARKING SCHEME

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3. (a) (i) $pV = nRT$ ½

$n = \frac{m}{M}$ ½

where m is the mass of dry air

$PV = \frac{m}{M}(RT)$

$M = \frac{m}{PV}(RT)$

$= \frac{d}{P}(RT)$ 1

(ii) Molar mass' of dry air

$= \frac{1.146}{98.6} \times 8.31 \times 300$

$= 28.98$ 1

Let mole fraction of N_2 be x

$28.02x + 32.0(1 - x) = 28.98$ 1

$x = 0.759$

Composition of dry air

75.9% N_2 and 24.1% O_2 1

(5)

(b) (i) $K_{sp} = [Ca^{2+}][Ox^{2-}]$

$[Ca^{2+}] = \frac{2.5 \times 10^{-2}}{2} = 1.25 \times 10^{-2}$ M

$[Ox^{2-}] = \frac{4.0 \times 10^{-6}}{2} = 2.0 \times 10^{-6}$ M 1

$[Ca^{2+}][Ox^{2-}] = 2.5 \times 10^{-8}$ mol² dm⁻⁶

$> 2.3 \times 10^{-9}$ mol² dm⁻⁶ ½

∴ Calcium ethanedioate will be precipitated. ½

(ii) Ethanedioic acid is a weak acid ½

In dilute HCl, Ox^{2-} combines with H^+ to form H_2Ox ½

With the decrease in $[Ox^{2-}]$, <u>the following eqm. shifts to right</u> 1

$CaOx \rightleftharpoons Ca^{2+} + Ox^{2-}$

∴ CaOx becomes more soluble in dilute hydrochloric acid.

(4)

(c) (i) At anode

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ 1

At cathode

$2MnO_2(s) + 2NH_4^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(g) + H_2O(\ell)$ 1

or $2MnO_2(s) + NH_4^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + OH^-(aq) + NH_3(g)$ (1)

Overall equation

$Zn(s) + 2MnO_2(s) + 2NH_4^+(aq) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2NH_3(g) + H_2O(\ell)$ 1

or $Zn(s) + 2MnO_2(s) + NH_4^+(aq) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + NH_3(g) + OH^-(aq)$ (1)

(ii) $Zn(s)|Zn^{2+}(aq) \| MnO_2(s)|Mn_2O_3(s)|C(s)$

or $Zn(s)|Zn^{2+}(aq) \mathrel{\vdots} NH_4^+(aq) \mathrel{\vdots} MnO_2(s)|Mn_2O_3(s)|C(s)$ 2

or $Zn(s)|Zn^{2+}(aq) \mathrel{\vdots} [MnO_2(s) + NH_4^+(aq)], [Mn_2O_3(s) + OH^-(aq)]|C(s)$ (2)

or $Zn(s)|Zn^{2+}(aq) \mathrel{\vdots} [MnO_2(s) + 2NH_4^+(aq)], [Mn_2O_3(s) + 2NH_3(aq)]|C(s)$ (2)

[1 mark for the correct species at cathode and anode
½ mark for using vertical solid lines to indicate phase differences.
½ mark for using vertical double line (dotted line) to represent salt bridge (porous partition).]

(iii) (1) If a current is drawn for some time, <u>$NH_3(g)$ will accumulate</u>, ½
at the cathode, the <u>equilibrium will shift to the left</u>, ½
leading to a drop in electrode potential. ½
or, if a current is drawn for some time, <u>$Zn^{2+}(aq)$ will</u> (½)
<u>accumulate</u> at the anode, <u>the eqm will shift to the left</u>, (½)
making the electrode potential of $Zn|Zn^{2+}$ less negative (½)

(2) If the cell is allowed to stand for some time, <u>NH_4^+ which is an acid</u> will react with Zn ½

$Zn(s) + 2NH_4^+(aq) \rightarrow Zn^{2+}(aq) + 2NH_3(aq) + H_2(g)$ ½

or $Zn(s) + 4NH_4^+(aq) \rightarrow Zn(NH_3)_4^{2+}(aq) + 4H^+ + 2e^-$ (½)

with decrease in $[NH_4^+(aq)]$, the electrode potential will also drop. ½

(8)

Marks

Section B

4. (a) (i) Boiling points of halogens depend on the strength of their intermolecular forces (van der Waal's forces) which is related to the strength of the instantaneous dipole of the molecule. ½ ½
Descending the group, with the increase in R.M.M., the strength of the instantaneous dipole increases. Hence more energy is needed for the boiling of the higher cogeners. ½ ½
(2)

(ii) Unusually short F-F distance leads to high repulsion due to lone pair electrons of fluorine atoms. Therefore F-F bond is weaker than expected. 1 1
(2)

(iii) I_2 forms soluble complex I_3^- with KI in solution. Therefore, I_2 appears more soluble. 1

$$I_2(s) + KI(aq) \rightleftharpoons KI_3(aq)$$ 1

or $$I_2(s) + I^-(aq) \rightleftharpoons I_3^-(aq)$$ (1)

(2)

(b) (i) O.S. of I in reactant = 0
O.S. of I in product = -1 } 1
$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$ 1

(ii) O.S. of I in I^- = -1
O.S. of I in IO_3^- = +5
O.S. of I in I_2 = 0 } 1
$5I^-(aq) + IO_3^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(\ell)$ 1
(4)

(c) (i) Trend : Bond dissociation energy decreases with increasing molecular mass of hydrogen halides. 1

Explanation : The H-X bond lengths increase as the atomic radii of the halogens increase. 1 The longer the bond, the weaker it is and the bond dissociation energy is smaller. 1

(ii) HI has the smallest bond dissociation energy, the activation energy for its decomposition is lowest 1 1
and therefore it is the most easily decomposed HX.
However, HBr and HCl do not decompose at temperatures > 400 K
From the $\Delta H^\ominus_f$ values, HI is the most unstable hydrogen halide with respect to decomposition to its elements. 1

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$ 1

(7)

Marks

5. (a) (i) As the group is descended, the next atom has another shell of electrons around the nucleus, therefore larger the atomic radius. 1

(ii) The atom has one more electron shell than the cation. 1
In M^+, the nuclear charge outweights the screening effect of the electrons and the electron cloud of M^+ experiences a stronger attraction. Therefore, the ionic radii are smaller than the atomic radii. 1

atomic radius : ionic radius ratio is highest in the case of Li, because it has the smallest size. In Li^+, the e^- experience the strongest attraction ∴ contraction in size is greatest 1

(iii) Electronic configuration of K^+ and Ca^{2+} are both

$$1s^2 2s^2 2p^6 3s^2 3p^6.$$

Both number and arrangement of electrons are the same in two cations. Ca^{2+} is doubly charged, while K^+ is singly charged, 1
the outermost e^- in Ca^{2+} experiences a stronger attraction 1
(effective nuclear charge). Hence the radius of Ca^{2+} is smaller.

(iv) The atomic radius increases as the group is descended hence the outermost-shell electrons become less strongly held and it is 1
and it is easier to remove an e^- from the (gaseous) atom of the element. 1

(v) All group I elements react with cold water to form M^+ ions 1

or $M(s) + H_2O(\ell) \rightarrow MOH(aq) + \frac{1}{2}H_2(g)$ (1)

The electrode potential of group I metal increase/becomes 1
more positive down the group with the exception of Li. 1
Therefore the reactivity increase. For Li the relatively high melting point reduces the reactivity 1
∵ activation energy for the reaction is increased.

(12)

(b) (i) Mg^{2+} is more polarizing than Na^+ due to its smaller size and 1
greater charge. The OH^- is polarized to a greater extent in $Mg(OH)_2$ 1

or, because of its high charge/radius ratio, Mg^{2+} forms more stable lattice with small anions e.g. O^{2-}, ∴ $Mg(OH)_2$ is ready to decompose (1)
to give MgO (1)

(ii) As the group is descended, the polarizing power of the cation decreases. 1
Therefore, cations of the lighter elements distort the anion electron clouds to a larger extend. 1
Anions with highly distorted electron clouds are more readily decomposed 1
than those with little distortion. Hence the thermal stability increases as the group is descended.

or the charge/ratio of cation increases as the group is ascended.
Cations with high charge/radius ratio tned to form stable (1)
lattice with small anions. ∴carbonates of Be, Mg tend to (1)
decompose to form the more stable oxides (1)

(5)

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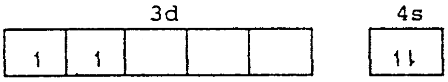
6. (a) Electronic configuration of Ti atom :

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ / [Ar]



(accept any correct form of electronic configuration. 1

(1)

(b) Ti metal : In the production of supersonic aircraft body.

or, Space shuttle. 1

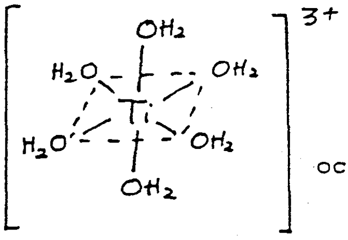
Ti compound : TiO_2 - paint filler. 1

or, Polymerisation catalyst in Ziegler/Natta process. ($TiCl_4$/$AlEt_3$) in polymerization of ethylene.

(accept any correct use of Ti and Ti compounds)

(3)

(c) (i)



octahedral 1

(ii) The colouration in transition metal ion is due to absorption of energy in UV-visible region by d-electrons when they are excited from one energy level to the other. 1

In TiO^{2+}(aq) ion, there is no d electron (d^0)/no d-d transition is possible ∴ it is colourless. 1

In $[Ti(H_2O)_6]^{3+}$ ion, the presence of 3d electron (d^1) cause the violet colour in solution due to d-d transition. 1

(iii) From the $E^{\ominus}$ values, O_2 is a stronger [O] agent than TiO^{2+}.

At standard conditions, the $E^{\ominus}$ of the following reaction is +1.23 - (+0.11) V = +1.12 V
(Deduct 1 mark for no indication of + sign) 2

$4Ti^{3+}(aq) + O_2(g) + 2H_2O(\ell) \rightarrow 4TiO^{2+}(aq) + 4H^+(aq)$ 1

∴ In the presence of oxygen, $[Ti(H_2O)_6]^{3+}$ will be oxidized to TiO^{2+}(aq)/the violet solution will turn colourless 1

(8)

Marks

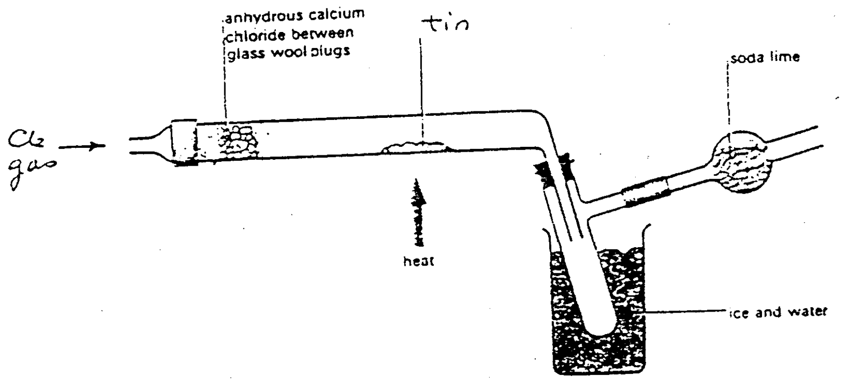
(d) Description of the preparation (3 marks)

Pass dry chlorine gas over heated tin metal ½+½

Collect $SnCl_4$ by cooling the vapour formed with ice-water 1

$$Sn(s) + 2Cl_2(g) \rightarrow SnCl_4(\ell)$$ 1

Diagram of apparatus (3 marks) 3



(1 mark for a combustion tube where Sn & Cl_2 react;
½ mark for passing dry Cl_2 over Sn;
½ mark for a drying tube at the end of the apparatus
1 mark for collection of $SnCl_4$)

(6)

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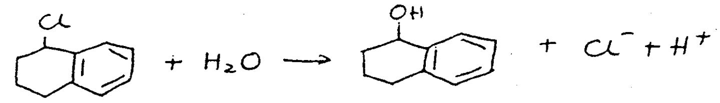
Section C

7. (a) (i) Treat compound with hot water (with or without ethanol) and then with a solution of silver nitrate(V). ½ ½

or, add $AgNO_3(aq)$ (1)

(*If NaOH used in the hydrolysis, neutralisation must preceed addition of silver nitrate, -½ mark for omission of neutralization)

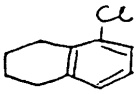


½

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)\downarrow$ ½

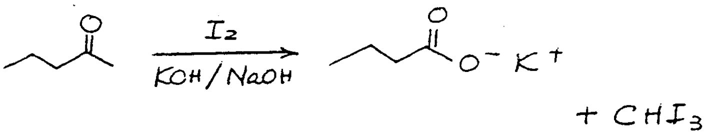
White precipitate is immediately formed. ½/0

No ppt. with



½
(3)

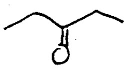
(ii) Treat compound with I_2/OH^- 1



½
½

Yellow precipitate observed ½/0

No ppt. with



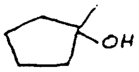
½
(3)

(iii) Treat compound with $Cr_2O_7^{2-}/H^+$ ½, ½

½

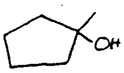
The solution changes colour from orange/yellow to green ½, ½

No reaction with



½

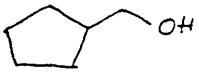
or, Treat compound with c.HCl/$ZnCl_2$ (½, ½)



gives turbidity/cloudiness (1)

(½)

No reaction with
(Very slow)

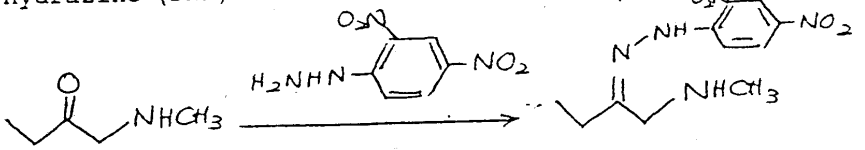


(½)

(3)

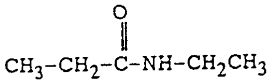
Marks

(iv) Treat compound with a solution of 2,4-dinitrophenyl hydrazine (DNP) in methanol (or ethanol)/Brady's reagent — 1



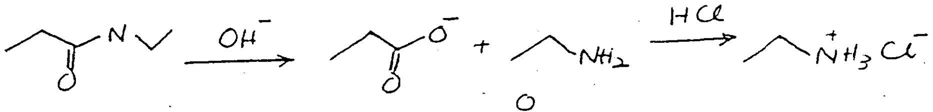
1

reed/orange/yellow precipitate is observed. — ½

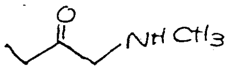


No ppt. with $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-NH-CH_2CH_3$ — ½

or, Treat compound with OH⁻(aq), gas evolved forms white fumes with HCl — (1)



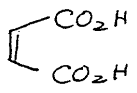
(½½½)

No observable reaction for  — (½)

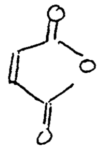
(Deduct ½ mark for each minor mistake; maximum deduction is 2 marks)

(3)

(b) (i)



D ;



E ; $HO_2C(CH_2)_2CO_2H$ — 1+1+1

(For D, 0 mark for $HO_2CCH=CHCO_2H$)

(ii) D : cis-butenedioic acid — 1

E : butenedioic anhydride — 1

(Deudct ½ mark for each minor mistake; maximum deduction is 1 mark)

(5)

35

Marks

8. (a) (i) Formula mass C_4H_9Cl = 92.562

Formula mass NaCN = 49.01

Formula mass C_4H_9CN = 83.132

No. of moles of $C_4H_9Cl = \frac{46.3}{92.562} = 0.500$ ½

No. of moles of NaCN $= \frac{30.0}{49.01} = 0.612$ ½

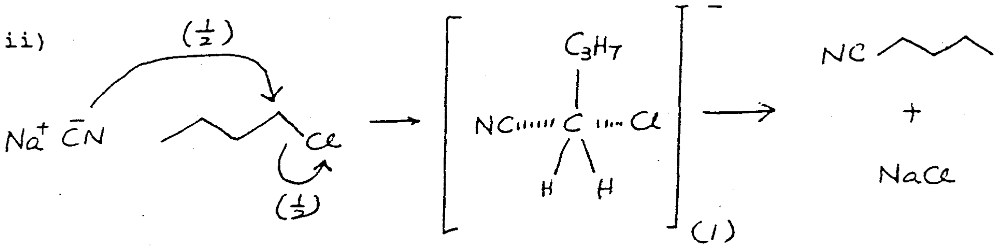
Since NaCN is in excess C_4H_9Cl is the limiting reagent

No. of moles of $C_4H_9CN = \frac{35.2}{83.132} = 0.423$ ½

$$\% \text{ yield} = \frac{\text{no. of moles of } C_4H_9CN}{\text{no. of moles of } C_4H_9Cl} \times 100 = \frac{0.423}{0.500} \times 100$$ ½

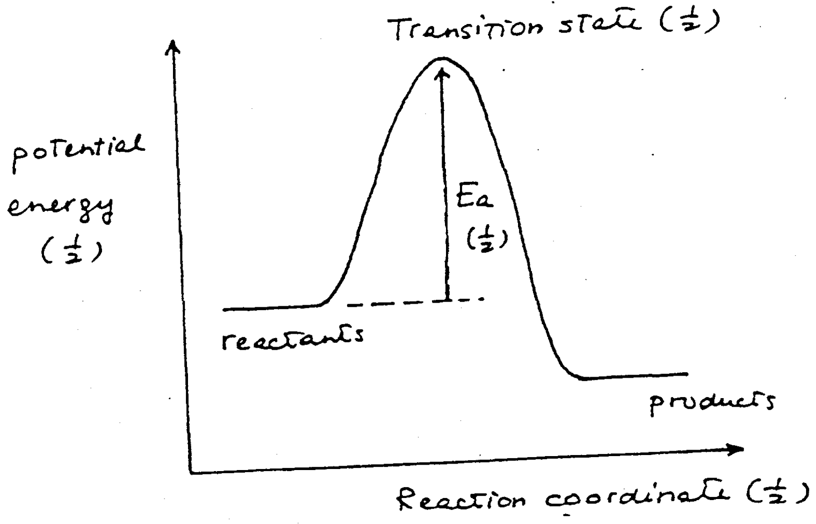
= 84.6 (84.7) 1

(ii) 2



(Deduct ½ mark for omission of charge in intermediate)

(iii) Bimolecular nucleophilic substitution (reaction)/S_N2 1



3

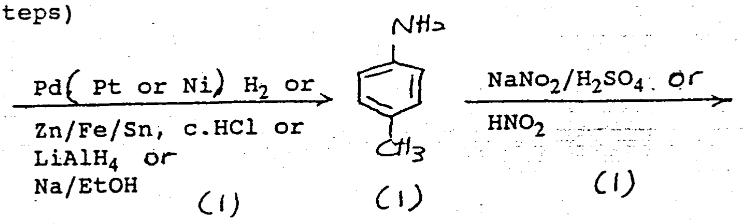
(1 mark for shape of curve)

(8)

(b) 1 mark for reagents and for intermediates

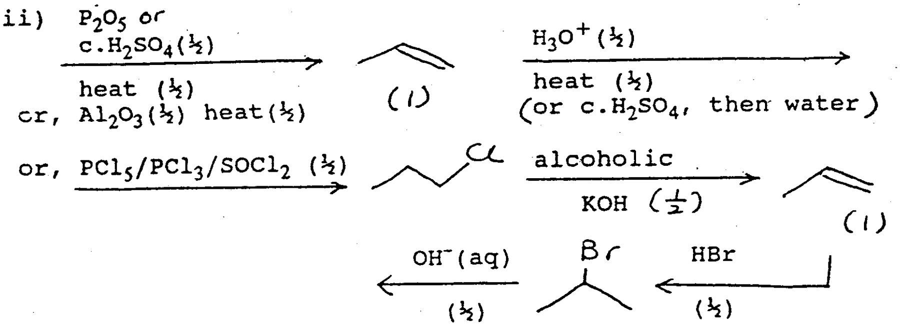
(For answers with more than 3 steps, deduct 1 mark for each extra step, i.e., 0 mark for conversions with more than 6 steps)

(i)



3

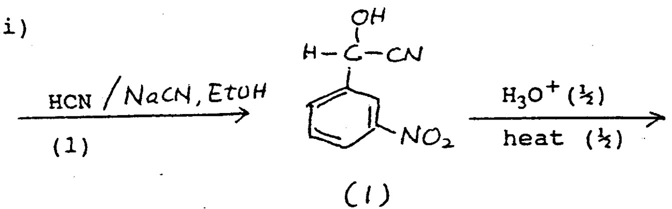
(ii)



3

(3)

(iii)



if HCN(g) (½)

3
(9)

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Marks

9. (a) (i) Mole % of C = $\frac{85.6}{12.01} = 7.13$

Mole % of H = $\frac{14.4}{1.008} = 14.29$

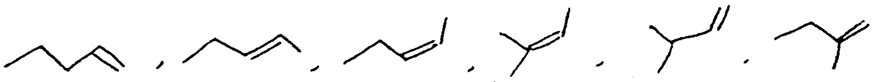
C : H = 7.13 : 14.29 = 1:2

∴ Empirical formula of G is CH_2 1

Since m.w. is between 60 and 80

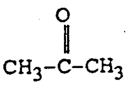
The molecular formula of G must be C_5H_{10} 1

(ii) 4



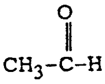
(½ mark each for 1st to 4th structure;
1 mark each for 5th and 6th structure)

(iii) Structures of H and J :



$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

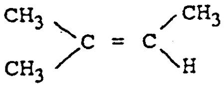
and



$CH_3-\overset{\overset{O}{\|}}{C}-H$

1+1

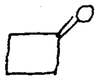
∴ Structure of G :



1

(iv) 2-methylbut-2-ene 1

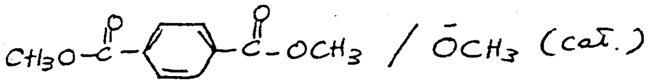
(10)

(b) (i) K :  / cyclobutanone 1

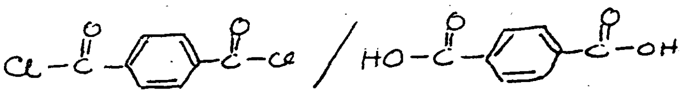
(ii) L : phosphorus(V) chloride/PCl_5/
phosphorus(III) chloride/PCl_3/
thionyl chloride/$SOCl_2$ 1

(iii) M : Pd or Ni or Pt/H_2 1
atmospheric pressure (½)
H_2/catalyst

(iv) N :



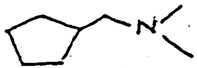
or 1



(v) P :

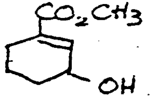
1

(vi) R :



1

(vii) S :



1

(Deduct ½ mark for each minor mistake ; maximum
deduction is 1 mark)

(7)

3(