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1991 A-level chemistry paper II marking scheme

1.(a)(i) α particle are bare helium nuclei with 2 positive charges and 4 units of mass. It can be stopped easily by a thin sheet of aluminium [2m]

β particle is fast moving electrons with 1 negative charge and negligible mass. It can be stopped by several millimeter of lead. [1m]

(ii)

$$^{238}_{92}U \rightarrow {}^{206}_{82}Pb + 8\,{}^{4}_{2}He + 6\,{}^{0}_{-1}e$$

(238 - 206) / 4 = 8 82 + 8(2) - 92 = 6

(iii) The decay constant k can be calculated from the half-life:

$\ln (2/1) = k(4.51 \times 10^9)$

$\therefore k = \ln 2 / 4.51 \times 10^9 = 1.5369 \times 10^{-10}$ year^{-1} [1m]

Let the amount of U in the mineral be x, since all Pb came from U,

The amount of U at the beginning

= amount of Pb + U at present

= 0.231x + x = 1.231x [1m]

The age of the mineral is equal to the time taken from I_0 = 1.231x to I=x

$\therefore \ln (1.231x/x) = (1.5369 \times 10^{-10})t$ [1m]

$\therefore t = 1.35 \times 10^9$ year [1m]

(b)(i) We need to have: Na(s) + 1/2Cl_2(g) **à** NaCl(s)

(ii) It is because ethanoic acid is a weak acid and is only slightly ionized [1m] and the difference is due to enthalpy change for ionization:

CH_3COOH(aq) **à** CH_3COO^-(aq) + H^+(aq) $\Delta H = + 2.1$ kJmol^{-1}[1m]

(iii The dissolving of a salt in water is a case of an enthalpy change accompanying a chemical process. The first process requires an input of energy to break the lattice (- lattice energy or - ΔL_{attice}). The second process involves the release of energy when new bonds are made between ions and water ($\Delta H_{ydration}$). In the case of NaCl, the first process is more exothermic than the second process OR the magnitude of lattice energy is larger than that of the enthalpy of hydration. [2m]

2.(a) $CH_4 < C_2H_6 < C_2H_5Cl$ [1m]

Polarizability (ease of distortion of e^- cloud) increase with increasing size (or no. of e^-)

$\therefore$ Cl > C > H [1m]

C_2H_5Cl has one highly polarizable Cl atom and has a permanent dipole moment, while C_2H_6 is less polarizable than C_2H_5Cl and has no permanent dipole moment. Thus C_2H_5Cl is expected to have stronger intermolecular forces than C_2H_6, and a higher boiling point. [1m]

The AX_4 type, tetrahedral CH_4 molecule has no permanent dipole moment, none of its atom has a very large polarizability, none of its atom has a very large polarizability, and it is expected to have the lowest boiling point. [1m]

(b)(i) CrO_4^{2-} + $4H_2O$ + $3e^-$ **à** $Cr(OH)_4^-$ + $4OH^-$ ....(1) [1m]

$S_2O_3^{2-}$ + $10OH^-$ **à** $2SO_4^{2-}$ + $5H_2O$ + $8e^-$ ....(2) [1m]

Overall equation: by 8 x (1) + 3 x (2)

$8CrO_4^{2-}$ + $3S_2O_3^{2-}$ + $17H_2O$ **à** $6SO_4^{2-}$ + $8Cr(OH)_4^-$ + $2OH^-$ [1m]

(ii) No. of moles of S2O320 = 0.2 x 40 x 10-3

Since 3 moles of $S_2O_3^{2-}$ = 8 moles of CrO_4^{2-} [1m]

$\therefore$ no. of moles of CrO_4^{2-} = (0.2 x 40 x 10^{-3}) x (8/3)

vol. of Na_2CrO_4 = (0.2 x 40 x 10^{-3})(8/3)(1/0.50) = 0.04267 dm^3

= 42.67 cm^3 [1m]

(c)(i)

Solution S:

Since	MOH	$\rightleftharpoons$	M^+	+	OH^-
Initial	0.1		0		0
At eqm.	0.1 – x		x		x

$K_b = 2 \times 10^{-5} = x^2 / (0.10 - x)$, assuming (0.1 - x) = 0.1

$\therefore x = [(2 \times 10^{-5})(0.1)]^{0.5} = 1.414 \times 10^{-3}$ M [1m]

pOH = - log [1.414×10^{-3}] = 2.85

pH = 14 - 2.85 = 11.15 [1m]

	MOH	$\rightleftharpoons$	M^+	+	OH^-
Initial	0.1		0.5		0
At eqm.	0.1 – x		0.5+x		x

$\therefore K_b = 2 \times 10^{-5} = (0.50 + x)x / (0.10 -x)$

Assuming x << 0.10, $\therefore$ 2×10^{-5} =(0.50/0.10)x

∴ x = (2 x 10^{-5}) / 5
= 4 x 10^{-6} [1m]
pOH = - log [4 x 10^{-6}] = 5.40
pH = 14 - 5.40 = 8.60 [1m]

(ii)

Solution T :

	MOH	$\rightleftharpoons$	OH^-	+	M^+
initial	0.1-0.01		0		0.5+0.01
at eqm	0.09-x		x		0.51+x - /

Assuming NO vol. change due to addition of acid
(0.51 + x)(x) / (0.09 - x) = 2 x 10^{-5}
x = (2 x 10^{-5})(0.09/0.51) = 3.53 x 10^{-6}
pOH = - log (3.53 x 10^{-6}) = 5.45
pH = 14 - 5.45 = 8.55 [3m]
* Solution T can resist the change in pH to a greater extent than solution S, it is generally known as a buffer. [1m]

3.(a)(i) Taking natural logarithm on the given expression:
ln k = ln A - Ea / RT [1m]
ln (k_2 / k_1) = Ea / R (1 / T_1 - 1 / T_2) [1m]
T1 = 273 + 370 = 643 K
T2 = 273 + 470 = 743 K
ln (4.05 x 10^{-2} / 3.91 x 10^{-4}) = Ea / 8.31 (1 / 643 - 1 / 743) [1m]
∴ Ea = 184.2 kJ mol^{-1} [1m]

(ii) T_1 = 643 K; T_2 = 273 + 450 = 723 K
ln (k_{723K} / 3.91 x 10^{-4}) = (1.842 x 10^5 / 8.31)(1 / 643 - 1 / 723) [1m]
k_{723K} = 1.77 x 10^{-2} mol^{-1} dm^3 s^{-1} [1m]

(b)(i) If a volatile solute is added to a solvent, the total vapour pressure will be the sum of the partial pressures of the solute and the solvent. If the vapour pressure of the solute is higher than the vapour pressure of the solvent, the total vapour pressure is higher and vice versa. [3m]

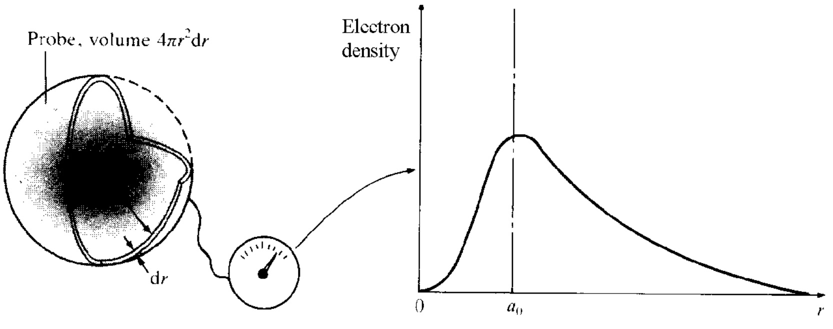
(ii)

	CH_3OH(A)	C_2H_5OH(B)
RMM	32	46
No. of moles	32/(12+4+16)=1	184/(24+6+16) = 4
Mole fraction	1/(1+4) = 0.2	4/(1+4)=0.8

[1m]

By Raoult's law P_A = X_AP_A [1/2m]
P_B = X_BP_B [1/2m]
∴P_A = (0.2)(89.2) = 17.84 mmHg [1/2m]
P_B = (0.8)(44.6) = 35.68 mmHg [1/2m]
Total vapour pressure = 17.84 + 35.68 = 53.542 mmHg [1/2m]
composition of CH_3OH in the vapour = 17.84/53.52 = 1/3
composition of C_2H_5OH in the vapour = 35.68/53.52 = 2/3 [1/2m]
i.e. composition of CH_3OH : C_2H_5OH in the vapour = (1/3) : (2/3) = 1 : 2

(c) 1s-orbital is spherical (NOT circular) [1m]
the variation is exactly the same in any direction from the nucleus / there is no angular dependence / accept diagram (a)



The most probable distance of the electron from the nucleus of the H atom is equal to the Bohr's radius, a_0. [1m]
The electron density is zero at the nucleus and at infinite distance from the nucleus / accept diagram

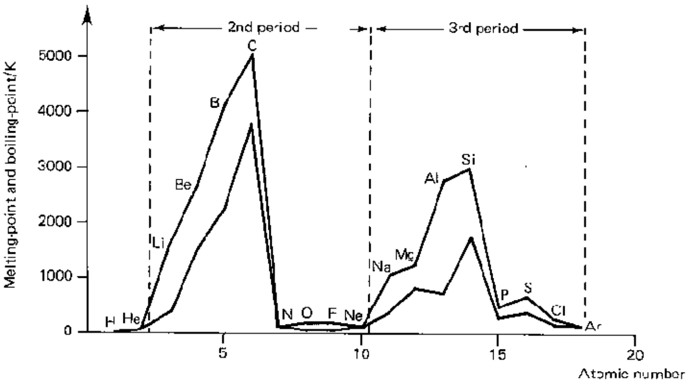
(b) [1m]

4.(a)(i) Elements in same group (having same no. of outermost shell electrons) have similar chemical properties. [1m]

Properties recur after an interval (=period) [1m]

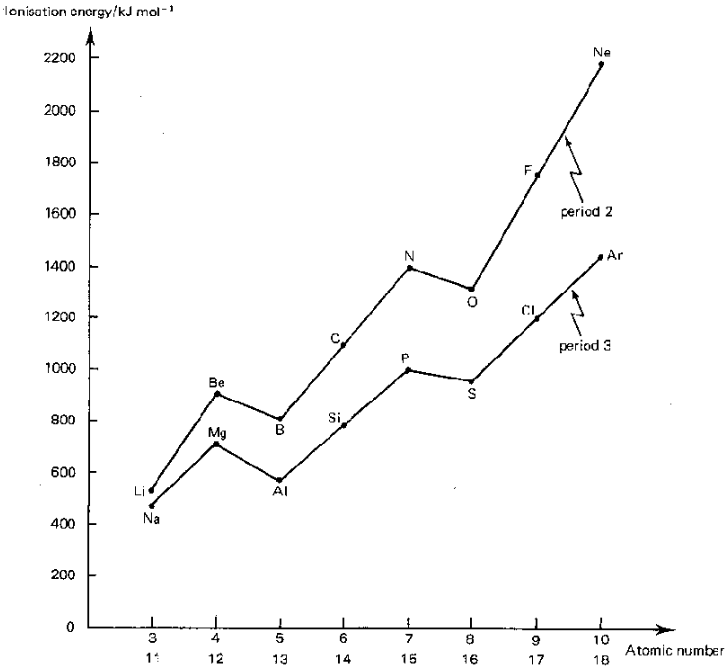
OR Element's properties are periodic functions *1m of atomic number. *1m

(ii)



Graphs show maxima for m.p. at Gp. IV [1m]
or for b.p, at either Gp. III or Gp. IV *1m
Graphs show decrease on descending Gp. III or IV [1/2m]
Graphs show minima for Gp. V - VIII [1/2m]

(iii)

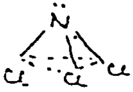


First ionisation energies of period 3 are generally lower than first ionisation energies of period 2 elements.

For I.E.: [2m]
Graph shows decrease for each group
Graph shows 2,3,3 pattern
Explanation: $2p^3$ for N (p^4 for 0 is not necessary) [1/2m]
stability of half-filled subshell [1/2m]

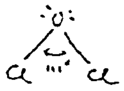
(b)(i) Example: NCl3

$NCl_3(l) + H_2O(l)$ à $NH_3(aq) + 3HOCl(aq)$



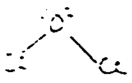
Example: Cl_2O

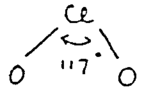
$Cl_2O(g) + H_2O(l)$ à $2HOCl(aq)$

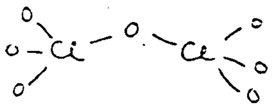


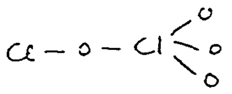
V-shaped

OR $2ClO_2 + H_2O \rightarrow HClO_2 + HClO_3$
OR $Cl_2O_6 + H_2O \rightarrow HClO_4 + HClO_3$
OR $Cl_2O_7 + H_2O \rightarrow 2HClO_4$





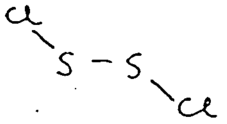




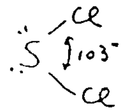
ClO_3 is the same as Cl_2O_6, which is a solid $ClO_2 + ClO_4^-$
$ClO_2 + H_2O \rightarrow$ stable in the dark

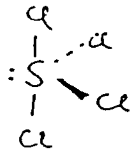
$$6ClO_2(g) + 3H_2O(l) \xrightarrow{\text{(sunlight)}} HCl(aq) + 5HClO_3(aq)$$

Other acceptable answers:
$2ClO_2(g) + 3H_2O(l) \rightarrow 2H_3O^+(aq) + ClO_2^-(aq) + ClO_3^-(aq)$
$4ClO_2(g) + 6H_2O(l) \rightarrow 4H_3O^+(aq) + ClO^-(aq) + 3ClO_3^-(aq)$
$Cl_2O_6(g) + 3H_2O(l) \rightarrow ClO_3^-(aq) + ClO_4^-(aq) + 2H_3O^+(aq)$
For oxygen chlorides, accept disproportionation reaction for oxidation states 2,4,6 but -1 or 7 for Cl.
For ClO_2 accept balanced equation for:
$6ClO_2 + 3H_2O \rightarrow HCl + 5HClO_3$
or $ClO_2 + H_2O \rightarrow$ stable (hydrate) [in the dark]
or $2ClO_2 + H_2O \rightarrow HClO_2 + HClO_3$
Example: $S_2Cl_2(l)$
$2S_2Cl_2 + 2H_2O \rightarrow 3S(s) + SO_2(aq) + 4HCl(aq)$



any sensible description, e.g. open book structure
OR SCl_2, SCl_4 (not SCl_6),





For $S_2Cl_2 + H_2O \rightarrow S + SO_2$ (or SO_3) don't need HCl
For SCl_4, reasonable answer to give SO2
For $SCl_2 + H_2O \rightarrow HOCl + HSCl$ (or accept $S + SO_2 + HCl$)
[Formula: 3 x 1/2m = 1.5m
equation: 3 x 1/2m = 1.5m, need not be balanced. Must write + H2O
electronic structure: 3 x 1/2m = 1.5m, must show lone pair(s) on S, N or O
shape: 3 x 1/2m = 1.5m draw and / or name.]

(c)(i) We expect that the X-X bond energy decreases on descending the group because the distance between the nuclear protons and the bond-pair electrons increases, so the attractive force decreases. This is so for Cl_2 and Br_2. [1m]
The F-F bond is weaker than that of Cl_2 due to non-bonding electron repulsion between lone pairs on the 2 F atoms. [1m]

(ii) Definition:
Reaction in which a single species / substance is simultaneously oxidized and reduced. [1m]
[do not accept "element" or "atom" instead of "species"]
e.g.
$H_2O + Cl_2 \rightarrow HCl + HOCl$ [1m]

Other examples might include:
$4KClO_3$(s) **à** $3KClO_4$(s) + KCl(s)
$Cl_2 + 2H_2O$ **à** $Cl^- + H_3O^+$ + HOCl
$3Cl_2 + 6OH^-$ **à** $5Cl^- + ClO_3^- + 3H_2O$ etc.

5.(a)(i) CO_2 acidic [1/2m]
SiO_2 acidic not SiO [1/2m]
SnO amphoteric [1/2m]
or SnO_2 amphoteric (1/2m)
[Name or formula acceptable. Nature incorrect, 0m]

(ii) $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$ [1/2m]
or $Ca(OH)_2 + CO_2$ **à** $CaCO_3 + H_2O$ etc.
SiO_2 + 2NaOH(aq) **à** $H_2O + Na_2SiO_3$ [1/2m]
or SiO_2 + 4HF **à** $SiF_4 + 2H_2O$ etc. (actually **à** SiF_6^{2-})
H_2O + SnO + NaOH **à** $NaSn(OH)_3$ [1/2m]
SnO + 2HCl **à** $SnCl_2 + H_2O$ [1/2m]
or $SnO_2 + 2H_2O$ + 2NaOH **à** $Na_2Sn(OH)_6$
But 4HCl + SnO_2 **ß** $SnCl_4 + 2H_2O$ unless acid is = 10 M, then also complex ion formation:
SnO_2(s) + $4H_3O^+$(aq) + $6Cl^-$(aq) **à** $SnCl_6^{2-}$(aq) + $6H_2O$(l)
[For equation showing acidic/basic/amphoteric properties, no need to balance, accept any reasonable silicate. Accept $Na_2Sn(OH)_4$ or $Si(OH)_4^{2-}$ for SnO and SnO_3^{2-} for SnO_2, but not Sn^{4+} for SnO_2]

(iii) GeO [1/2m]
amphoteric [1m]
or GeO_2 amphoteric (mainly acidic)

(b) Reason A: electronegativity difference [1m]
∴ nucleophilic attack by OH- only on Si [1m]
Reason B: state any one of the X-O, X-H bond strengths
activation energy higher for breaking C-H
Reason C: C no 2d orbital, Si has 3d orbitals (or accept C has no d orbitals)
∴ Si can form activated complex
[Any of the 3 reasons is acceptable. Answer must have fact (1 mark) then deduction (1 mark). If 2 facts from different reasons are mixed, then award only 1 mark.]
Equation:
$SiH_4 + (n+2)H_2O$ **à** $SiO_2.nH_2O + 4H_2$ [1m]
or $SiH_4 + 2H_2O$ **à** $SiO_2 + 4H_2$
$SiH_4 + 2OH^-$ **à** $SiO_3^{2-} + 4H_2$
$SiH_4 + 4H_2O$ **à** $Si(OH)_4 + 4H_2$
[eq. need not be balance, if missing H_2: -1/2m]

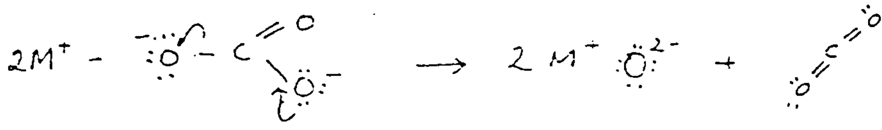
(c) As $\Delta H_{soln} = -\Delta H_{LE} + \Delta H_{HE}$ [1m]
The more negative the ΔH_{soln}, the higher the solubility of the compound [1/2m]

Small anions, e.g. OH^-, can attract manly water molecules, which leads to very exothermic hydration energy. The ΔH_{HE} of the compound will be less dependent on the cation. The ΔH_{soln} is ∴ mainly governed by the lattice energy. As the size of the cation increases down the group, the ΔH_{LE} is less exothermic for the case of Ba. The overall ΔH_{soln} will be more negative for the case of Ba(OH)2.

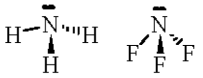
For large anions, e.g. SO_4^{2-}, the lattice energy of the compound is less dependent on the size of the cation because L.E. alpha 1/(interionic distance) and is therefore fairly constant down the group. The ΔH_{soln} is therefore governed by ΔH_{HE}. Due to the large size of Ba^{2+}, the ΔH_{HE} is less exothermic. The overall ΔH_{soln} will be less negative for the case of $BaSO_4$.

The dominating factor in energy cycle for large/small anion [1m]
Reason why LE or HE is dominating factor [1.5m]
(e.g. Know how size of anion governs LE. Magnitude of hydration energy decreases more than that of LE, so ΔH_{soln} less exothermic on descending group.)

(d) Li^+ more polarizing than Na+ [1m]
because smaller, with same charge or higher charge density or break up C-O bond easier or change in LE from Li_2CO_3 to Li_2O larger. [1m]
Charge cloud of the oxy-anion is more distorted, causing the anion to break up to give O_2 and CO_2 [1m]



(e)



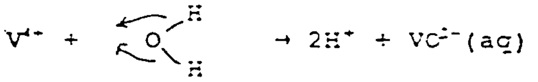
bond pair electrons nearer to F than to H [1/2m]
since F more electronegative [1/2m]
∴ bond-pair - bond-pair repulsion is smaller in NF_3 than in NH_3. [1m]

6.(a)(i) Definition:

Element which has incomplete d electron-subshell when combined in compounds (or complete in case of Zn). [1m]
OR incomplete d-electron subshell / orbitals
(between s, p blocks only: 1/2m)

(ii) Name (must be correct; NOT -ate for +ion) [1/2m]
Formula [1/2m]
Shape [1m]

(iii) Small [1/2m], highly charged [1/2m]
OR high charge density
V^{4+} ion polarizes [1/2m] H_2O molecule so strongly that it attracts electrons shared between H and O:



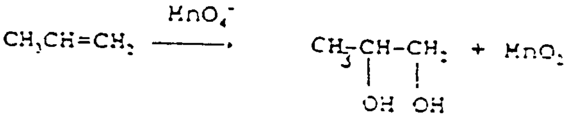
[1/2m]

(iv) (I) By mild reductants, e.g. H_2S, SO_2, Fe^{2+}, oxalate ($C_2O_4^{2-}$), Sn^{2+}, I^-. [1m]
Blue [1/2m]
(ii) Zn/HCl [1m]
Violet [1/2m]

(b) Out of syllabus

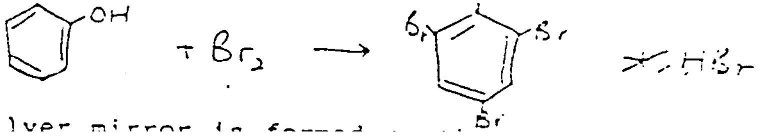
7.(a)(i) The reddish brown bromine turns colourless. [1m]
The reaction is a free-radical substitution. [1/2m]
Depending on the amount of bromine, various (colourless) substitution products are obtained.
$CH_3CH_2CH_2CH_2CH_3 + Br_2$ (hv) à $CH_3CH_2CH_2CH_2CH_2Br + CH_3CH_2CH_2CH_2CHBr_2$ etc. [1m]

(ii) The purple colour of $KMnO_4$ turns to a brown suspension of MnO_2. [1m] $KMnO_4$ is reduced and alkene is oxidized [1/2m]



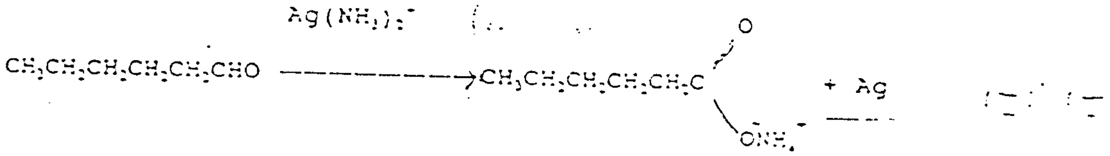
[1m]

(iii) The reddish brown solution of bromine is decolourized. [1/2m]
Tribromophenol appears as a white precipitate. [1/2m]
The reaction is an electrophilic substitution. [1/2m]



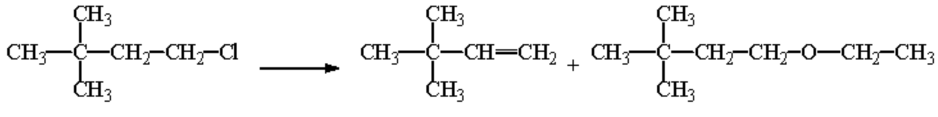
[1m]

(iv) A silver mirror is formed [1m] on the surface of the test tube (or some silver powder is formed). Ag+ is reduced by hexanal to Ag metal and deposits on the glass surface. [1/2m]



[1m]

(b)(i)



[1m each]

Q: 3,3-dimethylbut-1-ene [1m]

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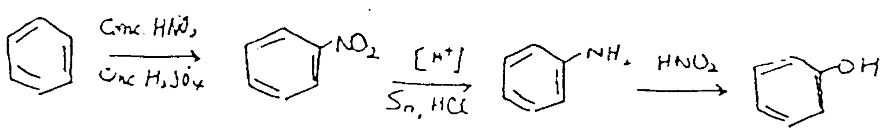
R: 1-ethoxy-3,3-dimethylbutene [1/2m]

(ii) Out of syllabus

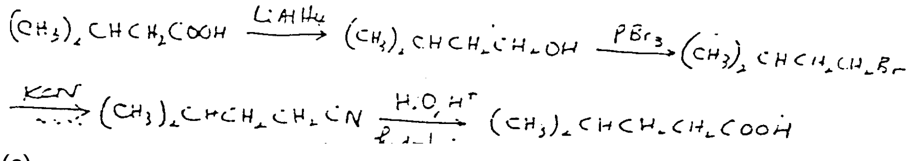
8. Any reasonable answers are acceptable.

(a)



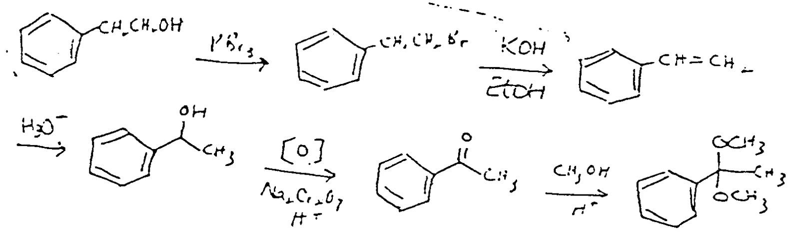
[3m]

(b)



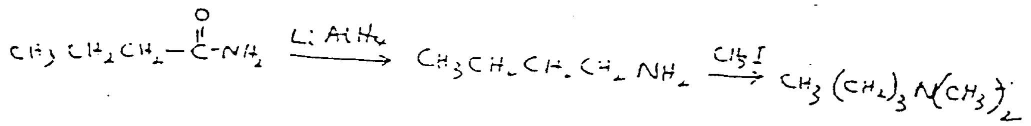
[4m]

(c)



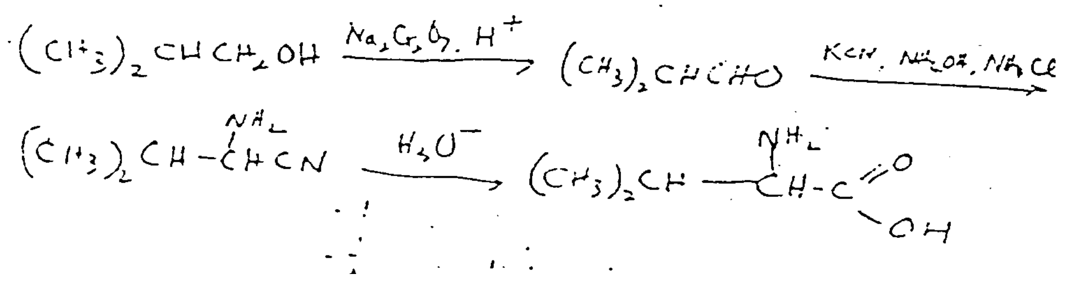
[4m]

(d)



[3m]

(e)



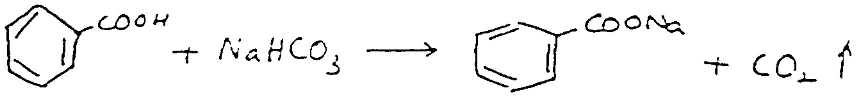
[3m]

9.(a)(i) Warm the compound with aqueous KOH, cool, acidify with nitric acid, add AgNO3

White ppt of AgCl formed for Ar-CH_2Cl

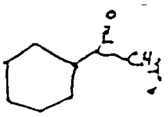
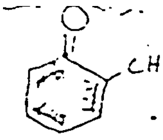
; $Ag^+ + Cl^- \rightarrow AgCl\downarrow$ [2m]

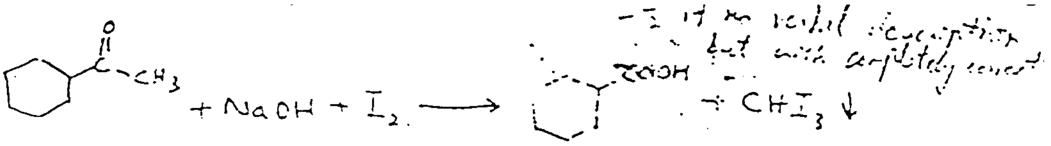
(ii) Add solution of sodium hydrogencarbonate solution to the compound. PhCOOH will react to give CO2 (effervescence observed)



[2m]

(iii) Warm the compound with iodine & NaOH

 will give yellow ppt. of iodoform, no ppt observed for 

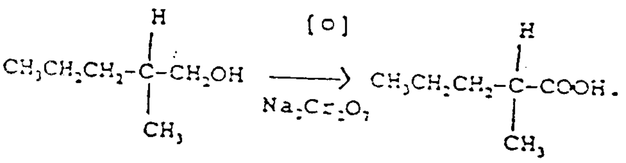


[2m]

(iv) Warm the compound with acidified $K_2Cr_2O_7$/$NaCr_2O_7$

The primary alcohol will turn the solution from orange [Cr(VI)] to green [Cr(III)]. No change in colour for the tertiary alcohol.

Primary alcohol can easily be oxidized.

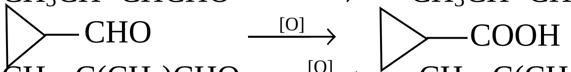


$$CH_3CH_2CH_2\text{-}C(H)(CH_3)\text{-}CH_2OH \xrightarrow[Na_2Cr_2O_7]{[O]} CH_3CH_2CH_2\text{-}C(H)(CH_3)\text{-}COOH.$$

[2m]

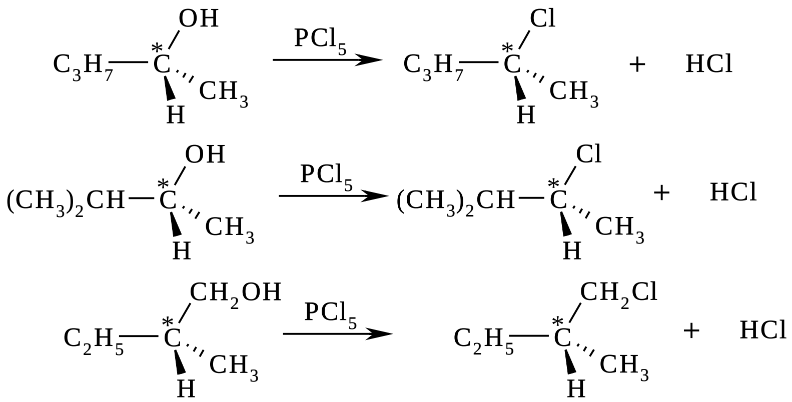
Or Add $ZnCl_2$ in conc. HCl to compound. If turbidity is observed immediately, it is the tertiary alcohol. The primary alcohol solution remains clear.

(b)(i)

J		K	
$CH_3CH=CHCHO$	$\xrightarrow{[O]}$	$CH_3CH=CHCOOH$	1+1
			(2)
$CH_2=C(CH_3)CHO$	$\xrightarrow{[O]}$	$CH_2=C(CH_3)COOH$	(2)
$CH_2=CHCH_2CHO$	$\xrightarrow{[O]}$	$CH_2=CHCH_2COOH$	(2)

Oxidation of J increase the number of oxygen atoms in product by one è oxidation of aldehyde to carboxylic acid.

(ii)

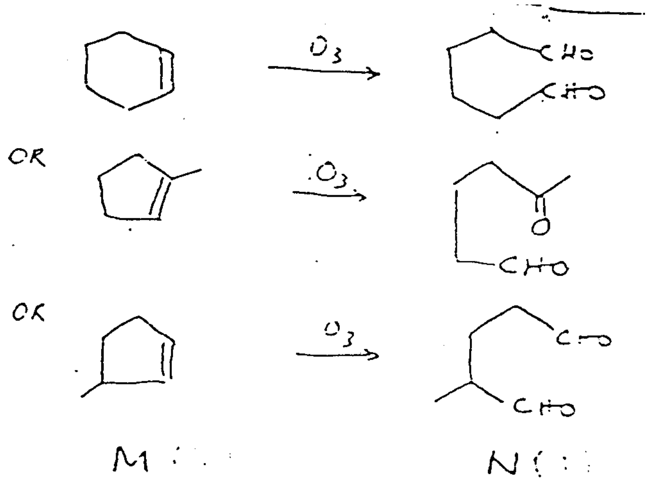


* chiral centre

L can exist as a pair of enantiomers è chiral centre in L. [1m]

L gives out HCl on reaction with PCl_5 è -OH group present. [1m]

(iii)



Ozonolysis of M without changing the carbon number è double bond forms part of a ring, i.e. cyclic alkene. [1m]