1992 AL Chemistry paper II marking scheme

1.(a)(i) For the case of hydrogen, a suitable method is to obtain the emission spectrum from a hydrogen discharge lamp.

The spectrum is obtained by passing the light emitted through a slit, a prism (or monochromator) and a recording device (or a photographic film). The wavelength (or frequency) on the spectrum should be calibrated before the experiment.

The spectrum consists of different sets of convergent lines. For the 1st high energy series of line (Lyman series), the ionization energy will be equal to the energy of the convergent limit of the lines.

(Frequency = v)

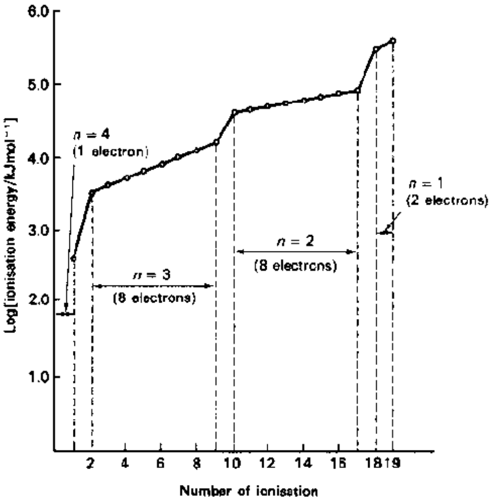
E = hv (for 1 atom) OR ionization energy = Lhv [3m]

L = Avogadro's no.

(ii) Na < F < Ne [1m]

Na has the least I.E. because there is a single 3s-electron which is not strongly attracted towards the nucleus and losing it would accomplish the completed K- and L- shell status. It is for this reason that an electron in Ne requires the highest I.E. To lose an electron means that the F atom would move further away from the completed K- and L- shell status and this requires a relatively high I.E. [1m]

(iii) There is a gradual increase in the successive ionizatioon energies in general because the nucleus becomes effectively more postively-charged as each electron is being lost. The increase is greatest when the 2nd electron is being ionized, suggesting the 2nd electron is closer to the nucleus than the first. Similar greater but less abrupt I.E.'s occur when the 10th and 18th electrons are being ionized. [3m]



(b)(i) The standard enthalpy of formation of a compound is the standard enthalpy change that occurs when one mole of the compound is made from its constituent elements under standard conditions (298 K and 1 atmospheric pressure) [1.5m]

e.g.

$C(s) + 2H_2(g) + 1/2O_2(g)$ à $CH_3OH(l)$ [1/2m]

(ii) Given: $CH_3OH(l) + (3/2)O_2(g)$ à $CO_2(g) + 2H_2O(l)$

Since $\Delta H = \Sigma(\Delta H_f)$products - $\Sigma(\Delta H_f)$reactants

Therefore $\Delta H = \Delta H_f(CO_2(g)) + 2[\Delta H_f(H_2O(l))] - \Delta H_f(CH3OH(l)) - (3/2)[\Delta H_f(O2(g)]$

$= -726.6$ kJ mol^{-1} [1m]

Since $\Delta H_f(O_2(g)) = 0$

Therefore $-726.6 = (-395.5) + 2(-285.8) - \Delta H_f(CH_3OH(l))$ [1m]

Therefore $\Delta H_f(CH_3OH(l)) = -238.5$ kJ mol^{-1} [1m] (no unit: -1/2m)

(c)(i) In aqueous acid solution the overall reaction:

$Zn(s)$ à $Zn^{2+}(aq) + 2e^-$

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$ à $2Cr^{3+}(aq) + 7H_2O(l)$

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 3Zn(s)$ à $3Zn^{2+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

E = +1.33 - (-0.76) = +2.09 V

is favourable because of the large positive E value. [2m]

The overall reaction:

$Zn(s)$ à $Zn^{2+}(aq) + 2e^-$

$2Cr^{3+}(aq) + Zn(s)$ à $2Cr^{2+}(aq)$

$2Cr^{3+}(aq) + Zn(s)$ à $Zn^{2+}(aq) + 2Cr^{2+}(aq)$

(ii)(I) An increase in the concentration of Zn^{2+}(aq) will increase the reduction potential (i.e. > -0.76 V) [1/2m] because there are more Zn^{2+}(aq) ions taking part in the reduction reaction [so that the equilibrium position shifts to the right:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$ [1m]

(II) temperature [1/2m]

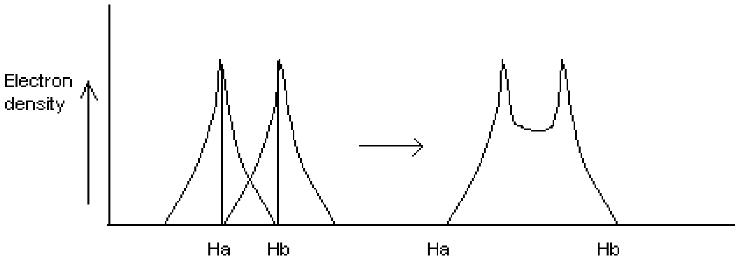
2.(a)(i) $5Cl^- + ClO_3^- + 6H^+$ **à** $3Cl_2 + 3H_2O$ [1m]

(ii) Let rate = $k[ClO_3^-]^l[Cl^-]^m[H^+]^n$

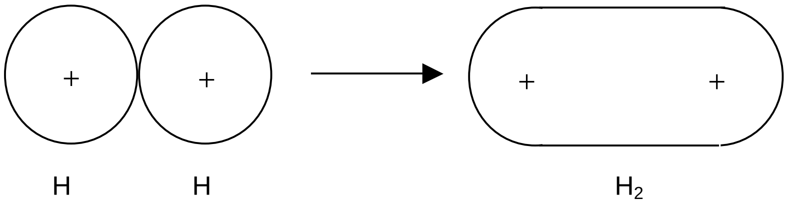
From experiments 1 & 2: [Steps must be shown]
$(1.0 \times 10^{-5} / 4.0 \times 10^{-5}) = [(0.08)^l(0.15)^m(0.20)^n] / [(0.08)^l(0.15)^m(0.40)^n]$
Therefore $1/4 = (1/2)^n$ **è** $n = 2$ [1m]
From experiments 2 & 3: [Steps must be shown]
$(4.0 \times 10^{-5} / 8.0 \times 10^{-5}) = [(0.08)^l(0.15)^m(0.40)^n / (0.16)^l(0.15)^m(0.40)^n]$
Therefore $1/2 = (1/2)^l$ **è** $l = 1$ [1m]
From experiments 1 & 4: [Steps must be shown]
$(1.0 \times 10^{-5} / 2.0 \times 10^{-5}) = [(0.08)^l(0.15)^{m(}0.20)^n] / [(0.08)^l(0.30)^m(0.20)^n]$
Therefore $1/2 = (1/2)^m$ **è** $m = 1$ [1m]

(iii) From any 1 of the set of data, e.g. experiment 1
$1.0 \times 10^{-5} = k(0.08)(0.15)(0.02)^2$
Therefore $k = [1.0 \times 10^{-5}\ mol\ dm^{-3}\ s^{-1} / (0.08)(0.15)(0.20)^2\ (mol\ dm^{-3})^4]$ [1m]
$= 2.08 \times 10\text{-}2\ mol^{-3}\ dm^9\ s^{-1}$ [1m] [-1/2m if wrong unit]

(b) The orbital occupied by the two electrons in the H_2 molecule can be obtained by taking the sum of the two hydrogen 1s atmoic orbitals. In the region between the two nuclei where there is appreciable overlap of the two 1s orbitals, the resultant electron density has an increase amplitude. It is this increased electron density that is responsible for holding two hydrogen nuclei together. [2m]



[Show only the following instead of e^- density map: 1m only]



(c)(i) Let α be the mass of X / cm^3 in D
β be the mass of X / cm^3 in E
Since distribution coefficient is 12:
Therefore $\alpha/\beta = 12$ or $\alpha = 12\beta$ [1m]
Sum of mass of X in D & E after the extraction:
Therefore $100\alpha + (50/12)\alpha = 4$ [1m]
Therefore $\alpha = 48 / 1250 = 0.0384$
Therefore mass of X in liquid D = 100α = 3.84 g [1m] (-1/2m if no unit)

(ii)(I) A liquid boils when its vapour pressure reaches the value exerted by the external pressure. Thus the total vapour pressure exerted by an immiscible mixture of liquids will reach atomspheric pressure at a temperature below the boiling-point of the most volatile constituent. [1m]

(II) P_F = vapour pressure of F = 733 mmHg
P_G = vapour pressure of G = 27 mmHg
Assuming the vapour obeys ideal gas law,
no. of moles is directly proportional to vapour pressure
Let m be mass,
M be relative molecular mass,
n be no. of moles
$P_F / P_G = n_F / n_G = (m_F / M_F) / (m_G / M_G)$ [1m]

$m_F / m_G = P_FM_F / P_GM_G$ = (733)(18) / (27(123) = 13194 / 3321 = 3.973 [1m]
% G by mass = $m_G / (m_F + m_G)$ = 1 / (3.973 + 1) = 0.2011 = 20.11% [1m]

3.(a)(i) Ice consists of covalent H_2O molecules held together by hydrogen bonding [1/2m + 1/2m]
SiO_2 solid (quartz) is an infinite three dimensional network solid in which each Si atom is covalently bonded in a tetrahedral arrangement to four O atoms. [1/2m + 1/2m]

(ii) Some of the hydrogen bonds must be overcome in order to melt ice [1m]
In order for $SiO_2(s)$ to melt, some of the strong Si-O covalent bonds have to be broken. [1m]

(b)(i) The covalent radius is defined as one-half the distance between two atoms of the same kind held together by a covalent bond. [1m]

(ii) Going down any group of the periodic table, the covalent radius increases. [1/2m]
because as the no. of filled inner shell increases / the screening effect on the outermost electrons increases / the effective nuclear charge on the outermost electrons decreases [1/2m]
Going across any period (from left to right), the covalent radius decreases [1/2m]
because the effective nuclear charge on the outermost electrons increases [1/2m]

(iii) C-C (single) bond length in CH_3-CH_3
= 2(0.077) = 0.154 nm [1m]
The C-C bond in ethane is a single bond which is longer than the carbon-carbon length in benzene because of the delocalization of electrons in the benzene ring. [1m]
The average bond order is larger than 1 in the case if benzene / there is some double bond character in the carbon - carbon bond of benzene. [1m]

(c)(i) Equivalence point is the point in the titration where moles of acid equals moles of base, corresponding to a salt solution (where the acid and base have completely reacted). [1m]
The end point is the point in a titration where a particular indicator changes colour / sharp pH changes. [1m]

(ii)(I) pH = 2.70 therefore - log $[H^+]$ = 2.70
Therefore $[H^+] = 1.9953 \times 10^{-3}$
Let a be the initial cocentration of the weak acid

Ka = $[H^+][A-] / [HA] = x^2 / (a-x) = x^2 / a = (1.9953 \times 10^{-3})^2 / a$
= 1.8 x 10-5
Since HA is a weak acid, a-x = a
Therefore a = 0.2212 M [method 1m ; answer: 1m]

(II) Let V be the volume (in cm^3) of MOH added.
The total volume of the solution at the equivalence point = 40 + V
Total no. of mol. of HA present = 0.040 x 0.2212
= 0.008847
At equivalence point, the amount of acid is the same as the amount of base. Due to hydrolysis of the salt formed, the solution is basic.

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

i.e. $[OH^-]$ = [HA] at the equivalence point
pH at equivalence point = 8.90
è $[H^+] = 1.2589 \times 10^{-9}$ M
and $[HA] = [OH^-]$ = 10-14 / $[H^+] = 10^{-14} / 1.2589 \times 10^{-9}$
$= 7.943 \times 10^{-6}$ M
Also no. of moles of A^- at equivalence point can be assumed to be equal to the no. of moles of HA in the original solution because HA is a weak acid.

Ka = $[H^+][A^-] / [HA] = 1.8 \times 10^{-5}$
$= (1.2589 \times 10^{-9})[0.008847 / (40 + V)/1000] / 7.943 \times 10^{-6}$
$1.8 \times 10^{-5} = (1.2589 \times 10^{-9} / 7.943)$ x [10-6 x 0.008847 / (40 + V)] x 1000
Therefore 40 + V = 77.89 Therefore V = 37.89 cm^3 [2m]

(III) Concentration of MOH = (0.008847 / 37.89) x 1000 = 0.2335 M [1m]

4.(a)(i)

(ii) Cu^+ d^{10} (completely filled orbitals) expect more stable
Cu^{2+} d^9 [1m]

(iii)

$$2Cu^{+}_{(aq)} \xrightarrow{disproportionation} Cu^{2+}_{(aq)} + Cu_{(s)}$$

[1/2m for disproportionation and 1/2m for products]

(iv) $Cu(NH3)_2^+$ [1m]

(v) Formation of insoluble compounds [1m]

(vi) Atoms lose electrons to form ions, whose polarizing power increases with number of electrons lost [1m]

Atoms have partially-filled d orbitals can interact with ligand oribtals by transfer of electron density [1m]

OR Complex ion formation is favoured by high positive charge on cation
small ionic cation radius
high electronegativity of cation
available orbitals of right energy to interact with ligand orbitals (any two)

(vii) $Cu(H_2O)_4^{2+} + 4NH3 \rightleftharpoons Cu(NH_3)_4^{2+} + 4H_2O$ [1m]

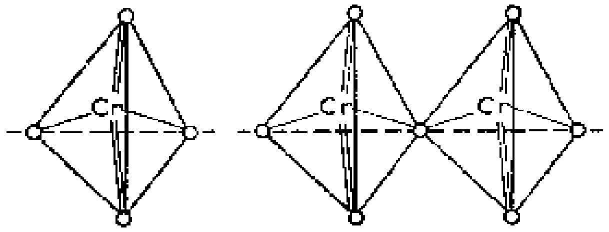
(viii) $CuEDTA^{2-}$ [1m]

(ix) For NH_3 - complex, 4 H_2O are liberated when 4 NH_3 coordinate [1m]

For EDTA - complex, 4 H_2O are liberated when 1 EDTA coordinates, so larger increase in disorder [1m]

OR the chelate effect (essentially an entropy effect)

(b)(i)



chromate tetrahedral   dichromate linked tetrahedral

[1m each]

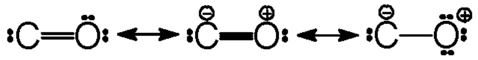
(ii) $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$ [1m]

(iii) H_2O_2
Cr^{3+} **à** CrO_4^{2-} Therefore oxidation [1m]
H_2O_2
$Cr_2O_7^{2-}$ **à** CrO_3 **à** Cr^{3+} Therefore reduction [1m]
Unstable
Deep blue

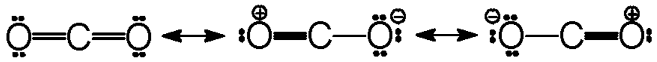
5.(a)(i) Properties such as:
catenation, e.g. hexane
multiple bonding (p_π overlap with C, N, O) e.g. ethene
formation of gaseous oxides e.g. CO_2
inertness of compounds e.g. CCl_4
(absence of divalent state)
larger bond strength e.g. E(C-H) > E(Si-H)
[1m for properties; 1/2m for example. Total: 3m]

(ii) Reasonable answers might cite:
[The eletronegativity of C (2.5) and P (2.05) are different]
properties differ because of d-orbital availability in P bonding. [1m]
[if 'different in size': 0m]

(iii)



Any 2 structures



Any 2 structures

[1/2m for each, total 2m]

(b)(i) 4,4,2 [1m]

(ii) SiO_2(s) stable, but SiO(g) exists only at high temperatures [1m]
SnO_2(s) more stable than SnO(s) [1m]

(iii) PbO(s) + 2HCl(aq) **à** $PbCl_2$(s) + H_2O(l) [1m]
H_2O + PbO + NaOH **à** $NaPb(OH)_3$ [1m]

(or $Pb(OH)_4^{2-}$ / $Pb(OH_3)^-$ / PbO_2^{2-})

(iv) heat metal, carbonate, nitrate, or hydroxide in air [1m]

(v) magnitude of E(M-X) [1m]
MII - MIV "promotion" energy. [1m]
(or inert pair effect. No argument based on M^{4+})

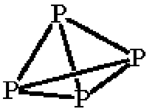
(vi) $SnCl_2 + Cl_2 \rightarrow SnCl_4$ slow but,
$PbCl_2 + Cl_2 \rightarrow PbCl_4$ only under forcing conditions
therefore <u>$SnCl_4$ forms faster</u> [1m]

(vii) $Si(s) + 2OH^-(aq) + H_2O(l) \rightarrow SiO_3^{2-}(aq) + 2H_2(g)$ [1m]
$Sn(s) + OH^-(aq) + 2H_2O(l) \xrightarrow{slow} Sn(OH)_3^-(aq) + H_2(g)$ [1m]
(or $Sn(OH)_4^{2-}$ / SnO_2^{2-})

6.A.

(a)(i) NO_3^-, NO_2^-, NH_2OH, NH_3 [4 x 1/2m = 2m]

(ii) N_2 N=N structure: (linear) diatomic molecule [1/2m]
bonding: intramolecular: covalent, multiple/triple [1m]
intermoelcular: van der Waals [1/2m]
White P_4
Structure:



discrete tetrahedral molecules [1m]
bonding: single covalent [1/2m]
van der Waals [1/2m]

(b)(i) $3Cu(s) + 8HNO_3$ (50%) $\rightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$ [1m]

(ii) $H_2S(g) + 2HNO_3$ (conc.) $\rightarrow S(s) + 2H_2O(l) + 2NO_2(g)$ [1m]
Note: On boiling, $H_2SO_4(aq)$ is formed.

(iii) $2HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + NO_3^- + HSO_4^-$ [1m]

(c)(i) The b.p. of a molecular substance depends on the strength of the intermolecular forces [1m]
NH_3 molecules are attracted by strong hydrogen bonds, whereas PH_3 molecules are attracted by weak dipole - dipole attraction only. [1m]

(ii) PH_3 [1m]
any one of the following reasons: [1m]
- greater stability of P(V) / P_4O_{10}
- lower I.E. favours oxidation
- availability of low lying vacant 3d orbitals in P
- weak P-H bond replaced by strong P-O bond (multiple bond nature)

(iii) availability of raw materials: preparation.
$N_2(g)$ atmosphere
fractional distillation
$H_2(g)$ petroleum industry (NOT accept electrolysis)
cracking / steam reforming
locate near oil refinery to save transport costs
[Any four points, max. 4m]
(use of low cost catalyst, name is not required, why it needs to be replaced; why promotor is added; copper absorbs H_2S such that can stop poisoning catalyst. max. 1m)

6.B

(a)(i) S^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-} [4 x 1/2m]

(ii) O_2 structure: (linear) diatomic molecule [1/2m]
bonding: accept or [1/2m]
intramolecular: covalent [1/2m]
intermolecular: van der Waals [1/2m]
S_8 (S) structure: ring in molecule [1/2m]

bonding: single [1/2m]
covalent [1/2m]

van der Waals [1/2m]

(b)(i) $Cu(s) + 2H_2SO_4(conc.) \rightarrow CuSO_4(s) + 2H_2O(l) + SO_2(g)$ [1m]

(ii) $H_2SO_4(conc.) + H_2S(g) \rightarrow S(s) + 2H_2O(l) + SO_2(g)$ [1m]

(iii) $2HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + NO_3^- + HSO_4^-$ [1m]

(c)(i) Intermolecular hydrogen bonding in H_2O but not H_2S [1m]

H_2S van der Waals forces only [1m]

(ii) H_2S [1m]

reasonable answer, such as higher oxidation states available for S [1m]

(iii) NOTE: NOT contact process, not the preparation of H_2SO_4

Production pf 'superphosphate' fertilizer [1m]

$Ca_3(PO4)_2 + 2H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + CaSO_4$ [2m]

acts as acid [1m]

OR Production of fertilizer (1m)

$2NH_3(aq) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$ (2m)

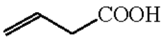
acts as acid (1m)

OR For the following industrial processes:

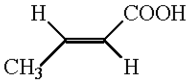
Manufacture of detergents (sulphonation)
Manufacture of dyestuffs (sulphonation)
Manufacture of drugs
Manufacture of explosives
Manufacture of rayon (arfticial silk)
Cleaning of metal before plating / galvanizing
Manufacture of lead-accumulator
(For any one of the above, 1m for function, 1m for process)

7.(a) **P** : $C_4H_6O_2$ [2m]

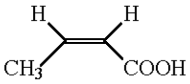
(b)



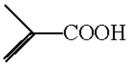
but-3-enoic acid or 3-butenoic acid



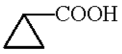
trans-but-2-enoic acid



cis-but-2-enoic acid



2-methylpropenoic acid



cyclopropanecarboxylic acid

ester: methyl but-3-enonate, etc.

[Any four structures: 4m; name of acid: 1m; name of ester: 1m]

(c) The reaction is reversible (or $\rightleftharpoons$) [1m]

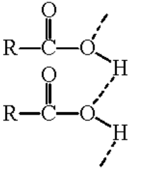
$RCOOH + CH_3OH \rightleftharpoons R\text{-}COOCH_3 + H_2O$ [1m]

Use large excess of CH_3OH; mass action to shift equilibrium [1m]

Remove H_2O as it is formed to shift equilibrium to the right [1m]

(d) Carboxylic acid has higher b.p. than its ester [1/2m]

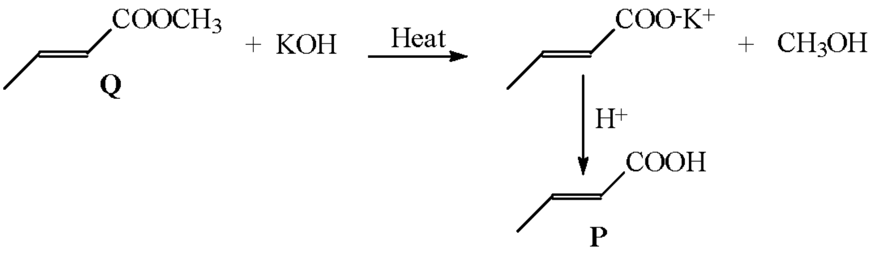
Hydrogen bonding: [1m]



or lone pair on oxygen bonded to acidic proton [1m]

Need more energy to break off H-bonding. Therefore higher b.p. [1/2m]

(e)



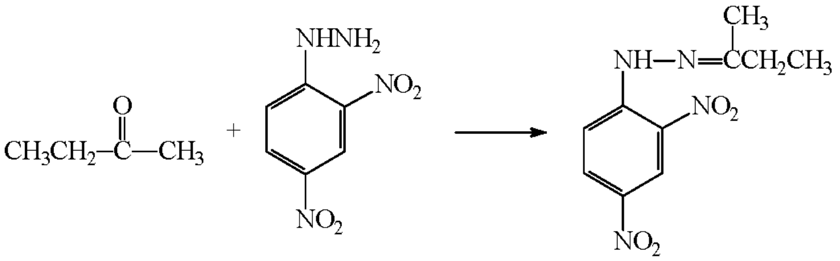
[2m]

8.(a)(i)(I) $RCOOH \xrightarrow{PCl_5} RCOCl \xrightarrow{CH_3NH_2} RCONHCH_3 \xrightarrow{LiAlH_4} RCH_2NHCH_3$ [3.5m]

(II) $RCOOH \xrightarrow{LiAlH_4} RCH_2OH \xrightarrow{PBr_3} RCH_2Br \xrightarrow{CH_3NH_2} RCH_2NHCH_3$ [3.5m]

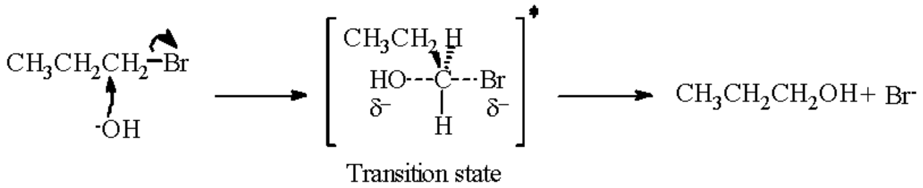
(ii) (II) is less appropriate than (I) in preparation, since

(b) Take the unknown ketone to reacts with 2,4-DNP. Get the solid derivative; purified by recrystallization; determine its m.p., compare with literature data. [2.5m]

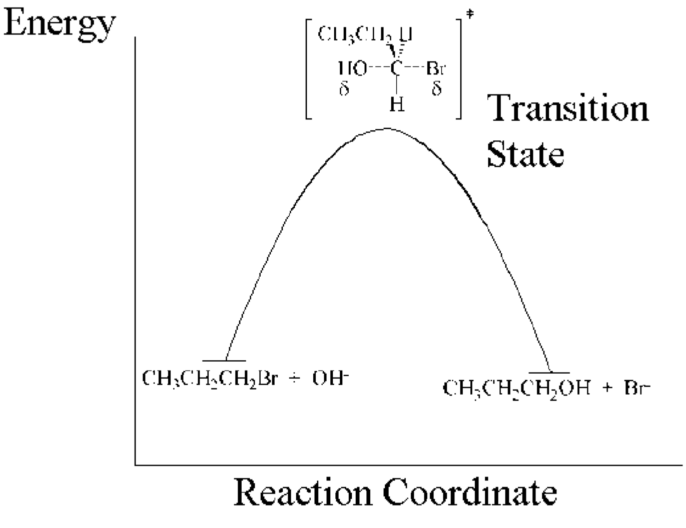


[1.5m]

(c)



[2m]

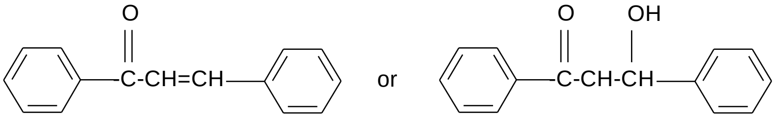


[Transition state: 1m; energy profile: 1m]

9.(a)(i)

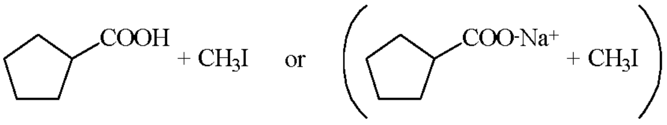
$CH_3CH_2C{\equiv}CCH_3$ or $CH_3{-}CH{=}CH{-}CH{=}CH_2$ [2m]

(ii)



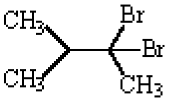
[2m]

(iii)



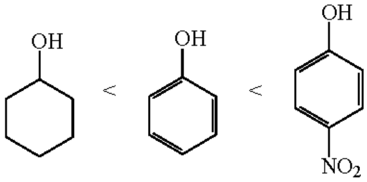
[2m]

(iv)

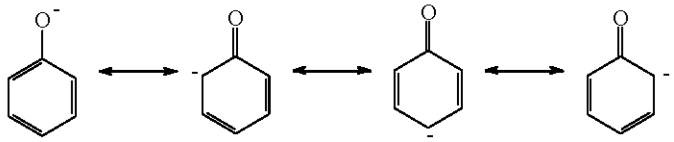


[2m]

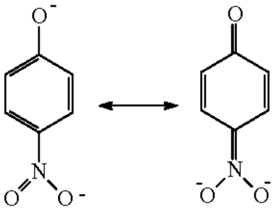
(b)



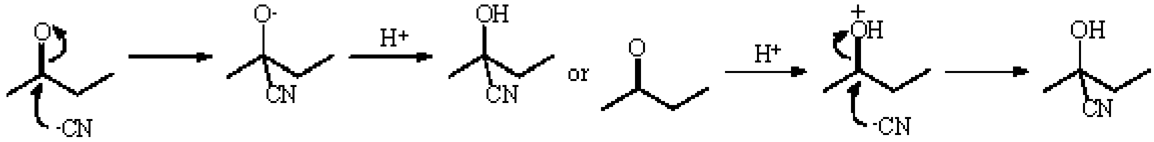
Acidity depends on the equilibrium HB $\rightleftharpoons$ B- + H+ [1m]
Phenoxide ion is stabilized by resonance, i.e.



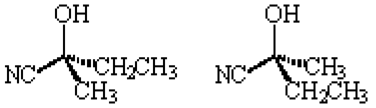
Therefore phenol is more acidic than cyclohexanol.
The nitro group in the nitrophenol attract electron (-I effect) and is capable of resonance, thus further stabilize the phenoxide ion (-M) effect [1.5m]



(c)(i) Mechanism: nucleophilic addition



[2m]
(ii) enantiomerism / optical isomerism [1m]



[1m]