ANSWER SCHEME

1 **C**

$pV = \frac{m}{Mr}RT$

$(10^5 \times 5.7 \times 10^{-3}) = \frac{18.0}{Mr}(8.31)(273)$

$Mr = 71.6$

Let a be the %mass of $^{35}Cl_2$

$\left(\frac{a}{100} \times 70\right) + \left[\frac{1-a}{100} \times 74\right] = 71.6$

$a = 60$

2 **B** From the first 2 properties, **E** must be a main group metal.

Hence, option C and D are incorrect.

Since it was obtained by removing electrons from the same orbital, **E** must be either a metal in Group 1 or 2.

3 **A** Since its shape is trigonal pyramidal, that must mean that around O there are 3 bp and 1lp.
The 3 bp are formed between one electron from F and 1 from O and the lp belongs to O.
With only 5 valence electrons around O than the usual 6, the entire ion is short of 1 electron and hence n = 1

4 **C**

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
10 cm^3 $CH_4 \equiv \boxed{10\ cm^3}\ CO_2$

$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$
20 cm^3 $C_2H_6 \equiv \boxed{40\ cm^3}\ CO_2$

50 cm^3 CO_2

5 **B** Amount of $MnO_4^- = \frac{37.5}{1000} \times 0.02 = 7.5 \times 10^{-4}$

$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$
Amount of MnO_4^- : amount of electrons: amount of **G** ion :
7.5×10^{-4} : 3.75×10^{-3} : 1.25×10^{-3}
3: 1

Given that ion of **G** is oxidised to GO_3^-, O.N. +5,
Original O.N of ion of **G** is +5 –3 = +2

6 **B** Assuming ideal gas behaviour (*i.e.* pV = nRT),

1) value of pV of L = $n_LRT_L = 3x$
   value of pV of J = $n_JRT_J = x$
2) J deviates from Ideal gas behaviour more than L, indicating more significant/stronger intermolecular forces of attraction between J molecules than L

(*i.e.* $\frac{n_LT_L}{n_JT_J} = 3$)

×1: $\frac{n_LT_L}{n_JT_J} = \frac{0.5 \times (273+50)}{0.5 \times (273+25)} = 1.08$

✓2: J=NH_3 (stronger hydrogen bonds between NH_3 molecules)
L = CH_4 (weaker id-id attractions between CH_4 molecules)
$\frac{n_LT_L}{n_JT_J} = \frac{1.5 \times (273+25)}{0.5 \times (273+25)} = 3$

×3: J = H_2 (weaker id-id attractions between CH_4 molecules)
L=SO_2 (stronger pd-pd bonds between NH_3 molecules)
$\frac{n_LT_L}{n_JT_J} = \frac{0.75 \times (273+25)}{0.25 \times (273+25)} = 3$

7 **A** K: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ Cl: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

✓1: K has one more quantum shell, valence electrons are further away from nucleus. Increase in shielding effect by inner shell electrons outweighs the increase in nuclear charge hence, decreased attraction between nucleus and valence electrons / decreased nuclear attraction. Thus, the atomic radius of potassium is greater than atomic radius of chlorine atom.

×2: Similarly, the 4s electron is further away from the nucleus, decreased nuclear attraction between nucleus and valence electrons, thus, less energy is required to remove an outermost/valence electron.

×3 K^+: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Cl^-: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Both are isoelectronic, with potassium having a bigger nuclear charge. Hence, there is great nuclear attraction between nucleus and valence electrons. Thus the ionic radius of potassium is smaller than that of chlorine.

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8 D reaction 1 $Br_2(aq) + 2NaOH(aq) \rightarrow NaBr(aq) + NaOBr(aq) + H_2O(l)$

$$\underset{0}{Br_2}(aq) + 2NaOH(aq) \rightarrow \underset{-1}{NaBr}(aq) + \underset{+1}{NaOBr}(aq) + H_2O(l)$$

reaction 2 $3NaOBr(aq) \rightarrow 2NaBr(aq) + NaBrO_3(aq)$

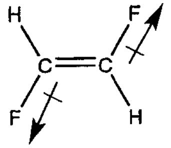
$$3\underset{+1}{NaOBr}(aq) \rightarrow 2\underset{-1}{NaBr}(aq) + \underset{+5}{NaBrO_3}(aq)$$

Reaction 1: Br in Br_2 is oxidised to OBr^- and reduced to Br^-

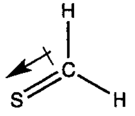
Reaction 2: Br in OBr^- is oxidised to BrO_3^- and reduced to Br^-.

Hence both are disproportionation reactions.

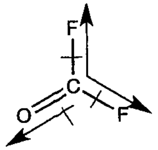
9 D A: Dipole moments cancel out.



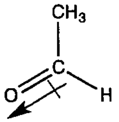
B: Dipole moment is smaller than that in D since S is less electronegative than O.



C: Dipole moment is smaller than that in D as the net dipole moment of C–F bonds reduces the dipole moment of C=O bond



D:



10 B $\boxed{LE \propto \left|\frac{q_+ \times q_-}{r_+ + r_-}\right|}$

	sodium	magnesium	oxygen	bromine
Charge	+1	+2	-2	-1
Ionic size	0.186	0.160	0.140	0.195

	MgO	$MgBr_2$	Na_2O	NaBr
LE ∝	13.33	5.63	6.13	2.62

Based on the above formula, MgO will be 2nd least exothermic

11 C ΔH $= (5(BE(N{=}N) + BE(N{=}O) + 2BE(C\text{-}H) + BE(C{\equiv}C)) - (2BE(O\text{-}H) + 4BE(C{=}O) + 5(N{\equiv}N))$

$= (5(418 + 686) + 2(410) + (840)) - (2(460) + 4(805) + 5(944))$

$= -1680\ kJ\ mol^{-1}$

12 C Since average IMF in water are much stronger than the average IMF in steam, and average IMF in ice are slightly stronger than the average IMF in water

✓1: The numerical value of ΔH_b is greater than ΔH_m

×2 ($H_2O(l) = H_2O(g)$) <u>**ΔH_b is positive**</u> as the energy required to break stronger IMF in liquid water is more than energy released when forming IMF between steam molecules ($H_2O(s) = H_2O(l)$), <u>**ΔH_m is positive**</u> as the energy required to break stronger IMF in solid water is more than energy released when forming IMF between liquid water molecules.

✓3: The intermolecular forces in ice and water are similar – hydrogen bond

13 A Let the rate equation be rate = $k[N]^n[P]^q$.

Comparing Experiment 2 and 3, keeping [N] constant,

$$\frac{6.4\times10^{-3}}{1.6\times10^{-3}} = \frac{k(0.006)^n(0.8)^q}{k(0.006)^n(0.4)^q} \Rightarrow q = \text{order of reaction w.r.t [P]} = 2$$

(correct; reject Option D)

Comparing Experiment 1 and 2,

$$\frac{1.6\times10^{-3}}{1.6\times10^{-3}} = \frac{k(0.006)^n(0.4)^1}{k(0.003)^n(0.4)^1} \Rightarrow n = \text{order of reaction w.r.t [N]} = 0$$

Since the order of reaction w.r.t [N] is not one, the half–life of N is not constant.

(correct; reject Option C)

The rate equation is <u>rate = $k[P]^2$</u> and hence, the units of $k = mol^{-1}\ dm^3\ min^{-1}$.

(correct; reject Option B).

The rate equation implies that the rate–determining step involves 2 units of P only. Hence, this also implies that N is involved in other steps and thus, the reaction is not a one-step reaction.

14 D

×A Reaction rate is defined as the speed at which a chemical reaction proceeds, defined as the change in concentration of a reactant or product per unit of time.

×B At higher concentration, particles are closer together per unit volume.

×C At higher concentration, the kinetics energy of the particles remain the same.

✓D With more collisions per second, the rate will increase.

15 **A**

	$ROH(l)$	+	$CH_3COOH(l)$	=	$CH_3COOR(l)$	+	$H_2O(l)$
Initial amt	3		2		0		1
change	-0.5		-0.5		+0.5		+0.5
Eqm amt	2.5		1.5		0.5		1.5
Eqm [ ]	$\frac{2.5}{V}$		$\frac{1.5}{V}$		$\frac{0.5}{V}$		$\frac{1.5}{V}$

$$K_c = \frac{[CH_3COOR][H_2O]}{[CH_3COOH][ROH]}$$

✓A $K_c = \frac{[\frac{0.5}{V}][\frac{1.5}{V}]}{[\frac{1.5}{V}][\frac{2.5}{V}]} = 0.2$

×B $\Delta H^\circ < 0$ i.e exothermic, When temperature decrease, POE will shift to the right, favouring the exdothermic reaction to release heat. Hence, the [CH_3COOH] will reduce below 1.5 mol.

×C K_C has no units.

×D The equilibrium amount of ester is the not the same as the equilibrium amount of water. (See working above)

16 **B** $2\,CO\,(g) + O_2\,(g)$ □ $2CO_2\,(g)$ $\Delta H < 0$

At time = t_1, shape of graph shows a gradual increase in CO and decrease in CO_2, indicating POE shifts to the left.

Possible changes include

- increasing temperature as increasing temperature will favour endothermic reaction, i.e. backward reaction thus POE shifts left
- remove O_2 as removing O_2 will result in POE shifting left.

(Cancel A and D)

At time = t_2, shape of graph shows a sharp increase in both CO and CO_2, indicates a decrease in the volume of system. When volume of system decrease, pressure of system increase. POE shifts to the right side with lesser mol to reduce the pressure.

(Cancel C)

Addition of catalyst will not result in any equilibrium shift.

Addition of an inert gas at constant volume will not result in any equilibrium shift as partial pressure of the other gases remains the same.

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17 **D** Amount of $NH_4^+ = \frac{100}{1000} \times 0.10 = 0.01$ mol (excess)

Amount of $OH^- = \frac{40}{1000} \times 0.15 = 0.006$ mol

In resulting solution,
Amount of NH_4^+ left 0.01 – 0.006 = 0.004 mol
Amount of NH_3 formed = 0.006 mol

$$pOH = pK_b + lg\left(\frac{[NH_4^+]}{[NH_3]}\right)$$

$$pOH = 4.75 + lg\left(\frac{0.004}{0.006}\right) = 4.57$$

pH = 14 – 4.57 = 9.43

18 **B** **×A** Since solubility of Group 2 hydroxides increases down the group, [M^{2+}] and [OH^-] increases, $K_{sp} = [M^{2+}][OH^-]^2$, value of K_{sp} increases down the group.

✓B $Mg(OH)_2\,(s) = Mg^{2+}\,(aq) + 2OH^-\,(aq)$

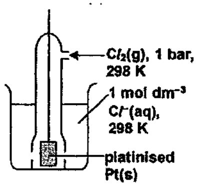
$$K_{sp} = [Mg^{2+}][OH^-]^2 = \boldsymbol{X}$$
$$(\boldsymbol{S})\,(2\boldsymbol{S})^2 = \boldsymbol{X}$$
$$\boldsymbol{S} = (\frac{\boldsymbol{X}}{4})^{\frac{1}{3}}$$
$$[OH^-] = 2\,\boldsymbol{S} = 2(\frac{\boldsymbol{X}}{4})^{\frac{1}{3}} = (2\boldsymbol{X})^{\frac{1}{3}}$$

Thus $pH = 14 - (-lg(2\boldsymbol{X})^{\frac{1}{3}}) = 14 + lg\,(2\boldsymbol{X})^{\frac{1}{3}}$

×C the solubility of magnesium hydroxide will decrease due to the common ion, Mg^{2+}, in $Mg(NO_3)_2$. Thus solubility will be lesser than $\boldsymbol{S}$.

×D K_{sp} will not change unless there is a change in temperature.

19 **B** Reduction potential is measured under standard conditions of 1 moldm^{-3} of any aqueous solution 298K and 1 bar.



$Cl_2\,(g) + 2e^- = 2Cl^-\,(aq)$ E°

×A Adding water will reduce [Cl^-], and E° becomes more positive.

✓B
×C Electrode potential depends on the nature of the electrode, temperature of the solution and the concentration of metal ions in the solution. It does not depend on the size of the electrode.

×D Adding Ag^+ will result in the precipitation of $AgCl$, this reduces [Cl^-], and E° becomes more positive.

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20 **A**

21 **A**

$$Cu(NO_3)_2\,(aq) \xrightarrow[\text{I}]{NH_3(aq)} Cu(OH)_2\,(s) \xrightarrow[\text{II}]{\substack{\text{excess}\\ NH_3(aq)}} Cu(NH_3)_4^{2+}\,(aq) \xrightarrow[\text{III}]{CN^-(aq)} Cu(CN)_4^{3-}\,(aq)$$

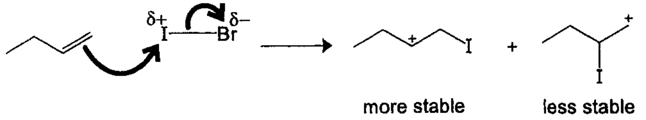
✓1
✓2 Step III involves both a ligand exchange where NH_3 has been displaced by CN^- (indicating that CN is a stronger ligand than NH_3) and a redox reaction where Cu in $Cu(NH_3)_4^{2+}$ has been reduced from +2 to +1 in $Cu(CN)_4^{3-}$.

✓3 Step I shows the precipitation of $Cu(OH)_2$ solid.

22 **D**

23 **D** Type of reaction: <u>electrophilic addition</u>

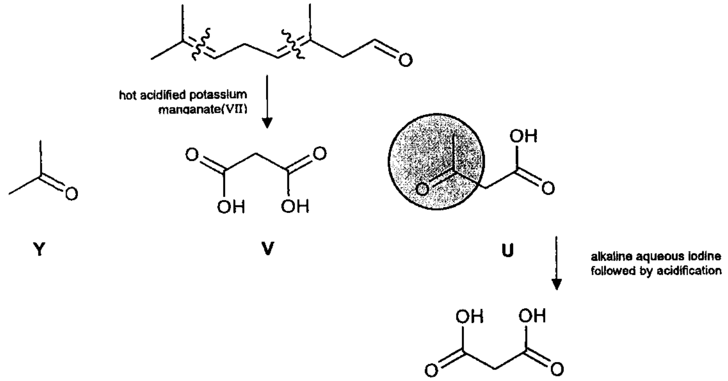
Since iodine is less electronegative than Br, iodine will bear the δ+ charge and functions as the electrophile.



The <u>product must contain I atom</u>. (reject D)

Br^- and CH_3O^- can function as nucleophile to attack either carbocation to give the products in Option A to C.

24 **A**



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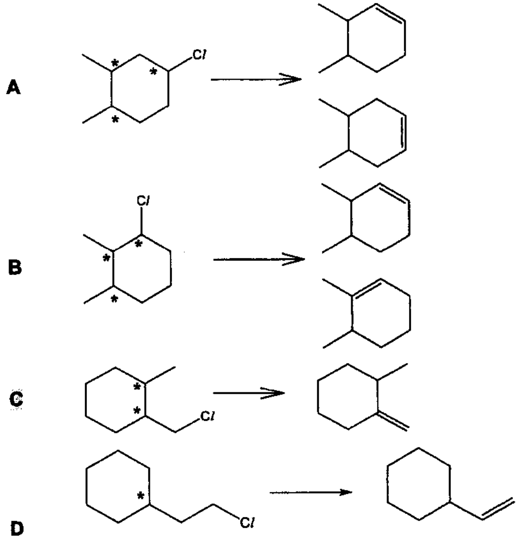
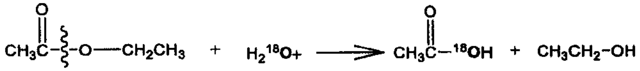
25 **C**



Starting compound has a plane of symmetry, thus cannot rotate polarised light

26 **D**

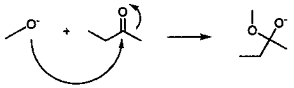


$$CH_3\overset{O}{\overset{\|}{C}}\text{-}O\text{—}CH_2CH_3 + H_2{}^{18}O + \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\text{—}{}^{18}OH + CH_3CH_2\text{-}OH$$

27 **C**

×1 Methanol acts as a Bronsted acid, i.e. donates H^+, in step1. It does not accept any lone pair from OH^-, hence, not acting as a Lewis acid.

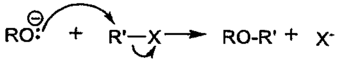
✓2 Step 2 is a nucleophilic addition reaction.

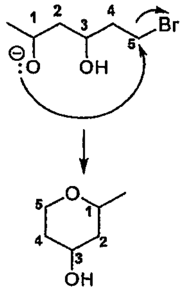


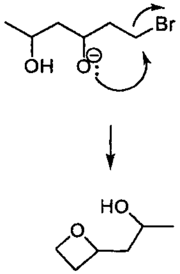
✓3 KOH is used as a catalyst in step 1 and regenerated in step 3..

×4 Step 3 is not a redox reaction. It is an acid-base reaction.

28 **B**

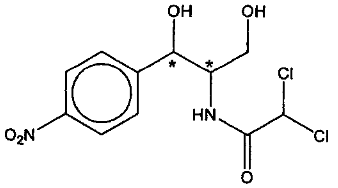




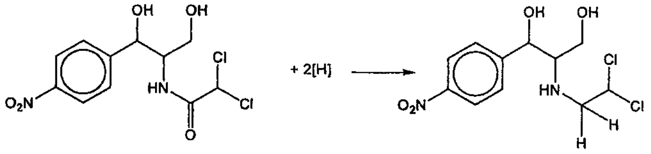


not stable due to ring strain

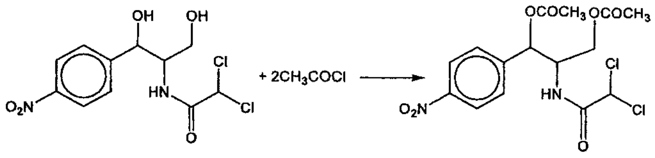
29 **D**



A: correct. It has 2 chiral carbon, hence 4 stereoisomers.



B: correct.



C: correct.

D: incorrect. No reaction.

30 **C** Since Z is a nonapeptide, it has the structure:

(*N–terminus*) ___ – ___ – ___ – ___ – ___ – ___ – ___ – ___ – ___ (*C–terminus*)

Using the fragments obtained from the hydrolysis using the two enzymes:

Arg–Ile–
Arg–Ile–Ser–Lys–
Ser–Lys–Trp–Ile–
Trp–Ile–Lys–
Lys–Leu–Arg
Leu–Arg

Arg–Ile–Ser–Lys– Trp–Ile–Lys– Leu–Arg

BP-707

Answers for JPJC 2025 H2 Chem Prelim Paper 2

1 Nitrogen is found in inorganic compounds such as the oxides of nitrogen, NO_2 and NO.

(a) NO_2 can be produced from the thermal decomposition of gaseous N_2O_5.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g) \qquad \Delta H_{1'}$$

Table 1.1 gives some data relevant to this question.

Table 1.1

process	ΔH° / kJ mol^{-1}
standard enthalpy change of formation of $N_2O_5(g)$	+11.3
standard enthalpy change of formation of NO(g)	+89.0
$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$	–58.1

(i) Explain what is meant by standard enthalpy change of formation.

It is the heat change when 1 mole of substance is formed from its constituent elements in their standard states under the standard conditions of 298 K and 1 bar. [1]

(ii) Use data from Table 1.1 to calculate $\Delta H_{1'}$. You may find it helpful to draw an energy cycle.

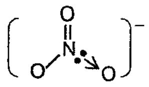
$$\begin{tikzcd}
2N_2O_5(g) \arrow[r, "\Delta H_{1'}"] & 4NO_2(g) + O_2(g) \\
2N_2(g) + 5O_2(g) \arrow[u, "2(+11.3)"] \arrow[r, "4(+89.0)"'] & 4NO(g) + 3O_2(g) \arrow[u, "4(-58.1)"']
\end{tikzcd}$$

$$\Delta H_{1'} = -2(+11.3) + 4(+89.0) + 4(-58.1)$$
$$= +101 \text{ kJ mol}^{-1}$$

[2]

(iii) In the solid state, N_2O_5 has an ionic structure and consists of the ions, NO_2^+ and NO_3^-.

Draw and name the shapes of NO_2^+ and NO_3^-.

ion	NO_2^+	NO_3^-
diagram of shape	$[O{=}N{=}O]^+$	
name of shape	linear	trigonal planar

[3]

(b) Nitrogen dioxide, NO_2, and dinitrogen tetraoxide, N_2O_4, exist in dynamic equilibrium with each other.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +58 \text{ kJ mol}^{-1}$$

At 50 °C and a pressure of 1.68×10^5 Pa, 4.60 g of the equilibrium gaseous mixture occupies 1.00 dm^3.

(i) Assuming the gaseous mixture behaves ideally, calculate the average relative molecular mass, M_r, of the gaseous mixture.

$$M_r = \frac{4.60 \times 8.31 \times (273 + 50)}{1.68 \times 10^5 \times 1.00 \times 10^{-3}}$$
$$= 73.5$$

[1]

(ii) Using the following relationships, calculate the mole fraction of N_2O_4, m, and the mole fraction of NO_2, n, in the mixture.

$$m + n = 1$$
$$\text{Average } M_r = 92m + 46n$$

$73.5 = 92m + 46n$

$73.5 = 92(1 - n) + 46n$

$73.5 = 92 - 92n + 46n$

$46n = 18.5$

$n = 0.402$

$m = 1 - 0.402 = 0.598$ [1]

(iii) Hence calculate the partial pressures of N_2O_4 and NO_2 in the mixture.

$P_{N_2O_4} = 0.598 \times 1.68 \times 10^5 = 1.00 \times 10^5$ Pa

$P_{NO_2} = 0.402 \times 1.68 \times 10^5 = 6.75 \times 10^4$ Pa

[1]

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(iv) Write an expression for equilibrium constant, K_p, for the reaction, and calculate its value. Include units in your answer.

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}}$$

$$K_p = \frac{(6.75\times10^4)^2}{1.00\times10^5} = 4.54 \times 10^4 \text{ Pa (or 45.4 kPa)}$$

[3]

(v) State and explain the effect of increasing the temperature on the average M_r of the equilibrium mixture.

Increasing the temperature will shift the position of equilibrium in $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ to the right to favour the endothermic reaction so as to absorb some heat.

Hence, there is a higher mole fraction of NO_2, so the average M_r will decrease.

[2]

(c) With the aid of suitable equations, describe and explain the role of NO_2 in the oxidation of atmospheric sulfur dioxide.

NO_2 acts as a homogeneous catalyst in the oxidation of atmospheric SO_2 since both NO_2 and SO_2 have the same gaseous phase.

Step 1 : $NO_2 + SO_2 \rightarrow NO + SO_3$

Step 2 : $NO + \frac{1}{2}O_2 \rightarrow NO_2$

[2]

[Total: 16]

2 Copper(I) salts in aqueous solution are unstable as shown by equation 1.

equation 1 $2Cu^+(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$

(a) (i) Using relevant data from the *Data Booklet*, calculate $\Delta G^\ominus$, in kJ mol^{-1}, for the above reaction.

$Cu^{2+} + e^- \rightleftharpoons Cu^+$ +0.15

$Cu^+ + e^- \rightleftharpoons Cu$ +0.52

$E^\ominus_{cell} = +0.52 - (+0.15) = +0.37$ V

$\Delta G^\ominus = -nFE^\ominus_{cell} = -(1)(96500)(0.37) = -35705$

$= -35.7$ kJ mol^{-1}

[2]

(ii) Deduce the sign of $\Delta S^\ominus$ for the reaction and explain your answer.

$\Delta S^\ominus$ is negative (or $\Delta S^\ominus < 0$) as there is a decrease in disorderliness since the more disordered aqueous ions react to form a more ordered solid Cu.

OR number / amount of aqueous ions decreases from 2 to 1 as the reaction proceeds.

[1]

(iii) Hence, determine if the reaction in equation 1 is exothermic or endothermic. Explain your answer.

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

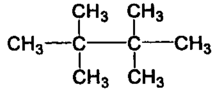
$\Delta S^\ominus < 0$, $-T\Delta S^\ominus > 0$, $\Delta G^\ominus < 0$,

so $\Delta H^\ominus < 0$. Forward reaction is exothermic.

[1]

(b) Some copper(I) compounds are used as reagents in organic reactions where new carbon-carbon bonds are formed. Larger alkanes can also be formed through the reaction of alkanes with some halogens. However, the yield of the larger alkanes obtained through such a reaction is low.

(i) Trace amount of alkane A is obtained when 2-methylpropane reacts with bromine in the presence of ultraviolet light.



A

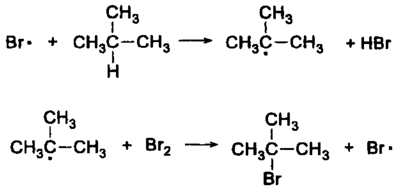
Outline the mechanism of this reaction, clearly showing how A is formed in the above reaction.

(Free radical substitution)

Initiation:

$$Br_2 \xrightarrow{uv} 2Br\cdot$$

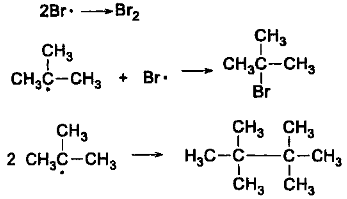
Propagation:



$$Br\cdot + (CH_3)_3CH \rightarrow (CH_3)_3C\cdot + HBr$$

$$(CH_3)_3C\cdot + Br_2 \rightarrow (CH_3)_3CBr + Br\cdot$$

Termination:



$$2Br\cdot \rightarrow Br_2$$

$$(CH_3)_3C\cdot + Br\cdot \rightarrow (CH_3)_3CBr$$

$$2\,(CH_3)_3C\cdot \rightarrow (CH_3)_3C\text{–}C(CH_3)_3$$

[3]

(ii) Chloroalkanes can be formed by the above mechanism but not iodoalkanes. Use relevant data from the *Data Booklet* to explain why iodoalkanes cannot be formed.

Iodoalkanes cannot be made by free–radical substitution as the first propagation step is MORE endothermic
($\Delta H = 410 - 299 = +111$ kJ mol^{-1})

OR LESS energy is evolved from the formation of the WEAK H–I bond (299 kJ mol^{-1}) compared to that of H–Br (366 kJ mol^{-1}). [1]

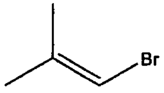
(iii) Iodoalkanes can be made by warming a bromoalkane with a solution of sodium iodide in dry propanone, in which sodium bromide is almost insoluble.

$$CH_3CH_2CH_2Br + NaI \rightleftharpoons CH_3CH_2CH_2I + NaBr$$

Suggest why the above reaction produces a high yield of $CH_3CH_2CH_2I$ despite the C–I bond being weaker than the C–Br bond.

Sodium bromide being insoluble in propanone can be precipitated, causing the [NaBr] to be low. This will cause the position of equilibrium to shift to the right to form more NaBr, allowing the reaction to go to almost to completion. [1]

(iv) A student wanted to distinguish 2–bromo–2–methylpropane, $(CH_3)_3CBr$, from compound **B** shown below.



compound **B**

The student suggested the following method:

Step 1: To 2 cm^3 of each compound, add an equal volume of NaOH(aq).

Step 2: Then add 1 cm^3 of $AgNO_3$(aq).

Step 3: Then add excess of dilute HC*l*(aq).

Identify and explain two improvements to the student's proposed method.

Improvement 1: Heating is required in step 1.

Heating is necessary to break the C–X bond via nucleophilic substitution to give X$^-$ for precipitation with silver nitrate.

Improvement 2: Mixture should be acidified before adding $AgNO_3$.

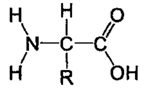
Any excess NaOH will react with Ag$^+$ to form a brown Ag_2O precipitate, making it difficult to observe the white AgC*l* ppt.

Improvement 3: HNO_3 should be used to acidify the mixture.

C*l*$^-$ in HC*l* gives white ppt with $AgNO_3$, giving wrong conclusion. [2]

[Total: 11]

3 Amino acids are the fundamental building blocks of proteins and play crucial roles in various biological processes. Amino acids are crystalline solids with high melting points, are water-soluble, and exist as zwitterions. The general structure of an α–amino acid is given below.



where R represents the side–chain on the α–carbon of amino acid.

(a) Explain why amino acids exist as crystalline solids at room temperature.

A lot of energy is required to overcome the strong ionic bonds / electrostatic forces of attraction between –NH_3^+ and –COO$^-$ of the zwitterionic form. Hence, amino acids have high melting point and exist as solid at room temperature. [1]

(b) The Strecker synthesis is one method to prepare α-amino acids in the laboratory by reacting readily available aldehydes or ketones in the presence of NH_4C*l* and KCN.

However, the Strecker synthesis lacks chirality control, producing racemic mixtures. This poses serious issues in pharmaceuticals, where specific enantiomers are crucial for safety and biological compatibility.

Alanine (2–aminopropanoic acid) can be prepared from the Strecker synthesis as shown in Fig. 3.1.

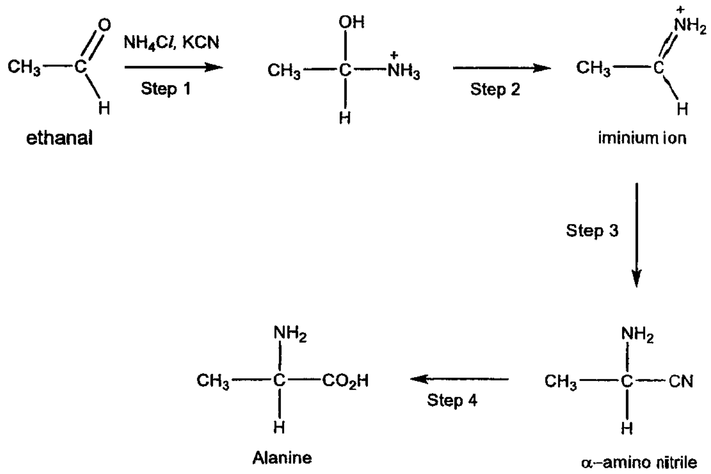


Fig. 3.1

(i) State the type of reaction that occurred in steps 2 and 4.

step 2: elimination

step 4: hydrolysis [2]

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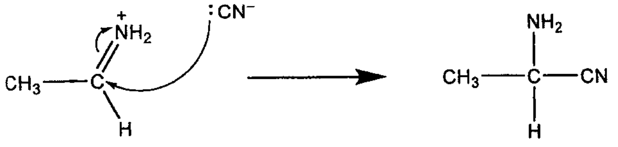
(ii) Step 3 in the Strecker synthesis involves the reaction of the iminium ion and CN^- to form the α-amino nitrile. This reaction is similar to the reaction between CN^- and carbonyl compounds.

State and describe the mechanism for step 3. In your answer, show relevant lone pairs of electrons and show the movement of electrons by curly arrows.

Type of mechanism: Nucleophilic Addition



iminium ion

α–amino nitrile

[2]

(iii) Using your answer in **(b)(ii)**, explain why alanine formed by the Strecker Synthesis method exists as a racemic mixture.

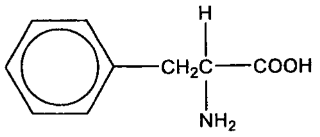
Alanine contains a chiral centre at the α-carbon.

There is equal probability for the CN^- to attack either side of the trigonal planar C of $C{=}NH_2^+$ in the iminium ion, hence forming a 1:1 mixture of enantiomers (racemic)

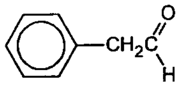
[1]

(iv) Phenylalanine can also be formed via the Strecker synthesis.

Suggest the structure of the starting compound necessary for step 1 of the Strecker synthesis to obtain phenylalanine.

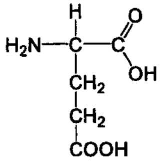


phenylalanine



[1]

(c) Glutamic acid is a non-essential α-amino acid vital for protein synthesis and is the main excitatory neurotransmitter in vertebrates.



Glutamic acid

Glutamic acid has pK_a values of 2.1, 4.1 and 9.5.

(i) Explain the difference in the pK_a values of the two carboxylic acid groups on glutamic acid.

Since the electron–withdrawing N of $-NH_2$ is closer to α–COO^- / α–COOH, the negative charge on α–COO^- is dispersed more and hence, α–COO^- is more stable than the side–chain –COO^-.

Hence, the α–COOH is a stronger acid and has a lower pK_a than side–chain COOH.

[2]

The following graph in Fig. 3.2 was obtained when protonated glutamic acid was titrated with aqueous potassium hydroxide.

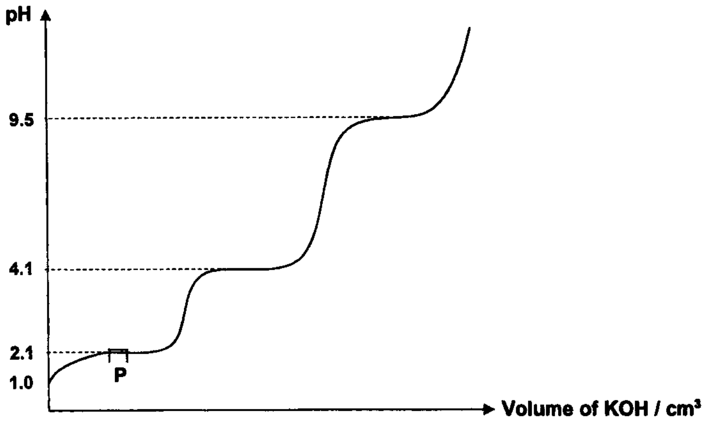
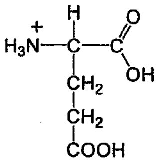


Fig 3.2

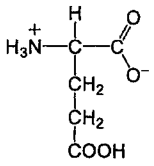
(ii) The pH of the solution changes only gradually around point **P** as aqueous KOH is added to the glutamic acid solution.

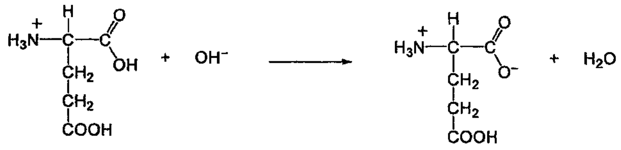
Identify the 2 major species present at point **P** and write an equation to illustrate how glutamic acid can maintain the pH of a solution at 2.1 when a small amount of OH^- is added.

At pH 2.1, the major species present are



and





[2]

(iii) State what is meant by the term *zwitterion*.

Zwitterion is a species which contains both positive and negative charge such that there is / but has no overall electrical charge.

[1]

(iv) Indicate on Fig. 3.2 with a cross (x) to show the point at which the predominant species of glutamic acid in the solution is the zwitterion. Explain your answer.

Point indicated on the graph between 2.2 – 4.

the α-COOH is deprotonated / exists as α-COO^- but the side-chain -COOH and α-NH_2 remain protonated.

Hence, glutamic acid exists as a zwitterion.

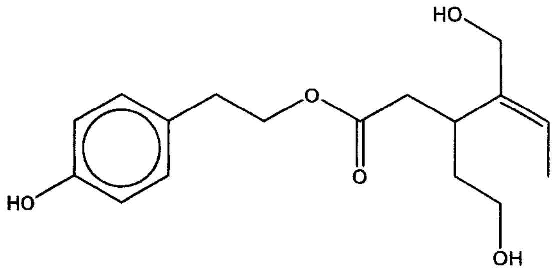
[2]

[Total: 14]

---

4 Oleocanthal, $C_{17}H_{20}O_5$, is a naturally occurring compound found in olive oil, known for its anti-inflammatory and antioxidant properties. When oleocanthal is reacted with $NaBH_4$, compound **C** is formed.

Fig. 4.1 shows the structural formula of a molecule of compound **C**.



Compound **C**

Fig. 4.1

(a) **(i)** The molecule of compound **C** contains sp^2 hybridised carbon atoms.

Describe how sp^2 hybridised orbitals are formed.

They are formed by mixing one s orbital and two p orbitals to form three identical sp^2 hybrid orbitals of the same energy and arranged in a trigonal planar arrangement. [1]

(ii) State the number of sp^2 hybridised carbon atoms in a molecule of compound **C**.

9 [1]

(iii) Deduce the number of stereoisomers of compound C.

4. [1]

(iv) Write the equation for the reduction of oleocanthal by $NaBH_4$ to give compound C.

Use [H] to represent the reducing agent and use the molecular formula of oleocanthal and compound C in the equation.

$C_{17}H_{20}O_5 + 4[H] \rightarrow C_{17}H_{24}O_5$ [1]

(v) State the number of moles of $H_2(g)$ that will be evolved when 1 mol of compound C reacts with an excess of sodium metal.

1.5 mol

[1]

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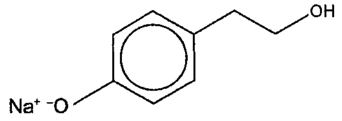
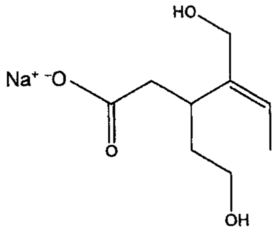
(b) Draw structures of the organic compounds formed when compound **C** is

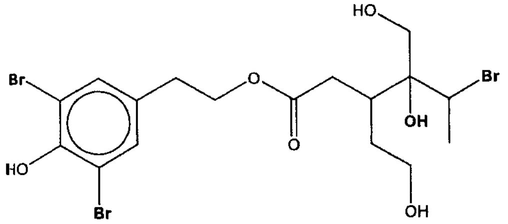
(i) heated with excess dilute NaOH(aq)



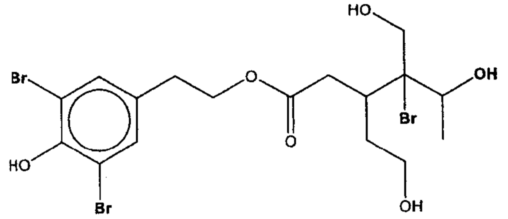


[2]

(ii) reacted with excess Br_2(aq).



OR



[2]

(c) Hexan-1-ol, $C_6H_{13}OH$, is one of the compounds that contribute to the aroma of olive oil.

A student used the apparatus shown in Fig. 4.2 to carry out an experiment to determine the enthalpy change of combustion of hexan-1-ol.

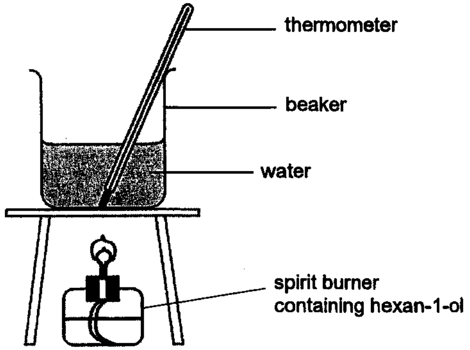


Fig. 4.2

The experimental results obtained are shown in Table 4.1.

Table 4.1

mass of water in beaker / g	250
initial temperature of water / °C	31.0
final temperature of water / °C	44.5
initial mass of spirit burner and hexan-1-ol / g	50.91
final mass of spirit burner and hexan-1-ol / g	50.34

(i) Using data from Table 4.1, calculate the heat, in kJ, gained by the water in this experiment. The specific heat capacity of water is 4.18 J g^{-1} K^{-1}.

Heat gained by water = 250 × 4.18 × (44.5 – 31.0)

= 250 × 4.18 × 13.5 = 14107.5 J = 14.1 kJ

[1]

(ii) The enthalpy change of combustion of hexan-1-ol is –3980 kJ mol^{-1}. Calculate the percentage efficiency of heat transfer in this experiment.

Amount of heat that should be produced by hexan-1-ol assuming no heat loss

$$= \frac{50.91 - 50.34}{6(12.0) + 14(1.0) + 16.0} \times 3980$$

$$= \frac{0.57}{102.0} \times 3980$$

$$= 22.241 \text{ kJ}$$

Percentage efficiency of heat transfer = $\frac{14.1075}{22.241} \times 100\% = 63.4\%$ [2]

(d) Olive oil primarily contains triesters, which do not vapourise easily. Hence, raw olive oil is unsuitable as a direct fuel for diesel engine as the triesters present will accumulate and clog the engine components. Olive oil can be converted into biodiesel through a chemical process called transesterification. The resulting esters from this process are more suitable for use as fuel in diesel engines.

One transesterification reaction is shown in Fig. 4.3.

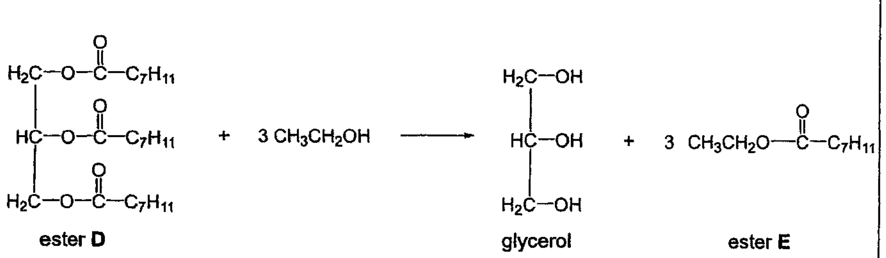


Fig. 4.3

(i) Explain why ester **E** is more suitable than ester **D** to be used as a fuel in diesel engines.

Ester E is more volatile / has a lower boiling point than D

because the instantaneous dipole-induced dipole attractions between its molecules are weaker and need less energy to overcome than those of D since E has less number of electrons per molecule. [2]

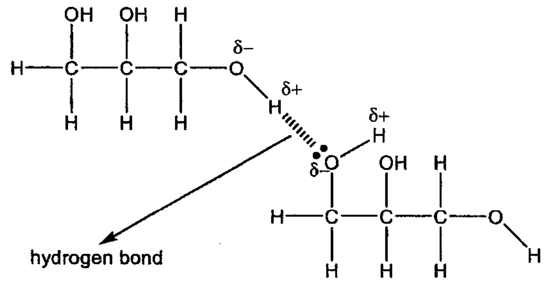
A large amount of glycerol is generated as a by-product in the production of biodiesel from natural oils. Efforts are being made to convert glycerol into more useful organic products.

(ii) Give the systematic name of glycerol.

propane-1,2,3-triol [1]

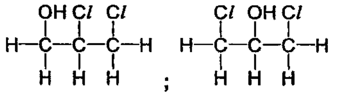
(iii) The properties of glycerol are affected by the intermolecular forces present between glycerol molecules.

Draw a labelled diagram to name and show the strongest intermolecular force present between two molecules of glycerol.



[1]

(iv) Glycerol can react with hydrogen chloride to form dichlorinated products. Draw the structures of all possible dichlorinated products from this reaction. **Ignore any stereoisomers.**



[2]

[Total: 18]

5 Silver is known for forming a range of sparingly soluble salts, such as silver carbonate and the silver halides. Their low solubility in water makes them useful in qualitative analysis and photographic processes.

(a) The values of the solubility products of some silver salts at 298 K are given in Table 5.1.

Table 5.1

salt	K_{sp} value
AgBr	5.0×10^{-13}
Ag_2CO_3	6.3×10^{-12}

(i) Write an expression for the solubility product, K_{sp}, of Ag_2CO_3.

$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$

$K_{sp} = [Ag^+]^2[CO_3^{2-}]$

[1]

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(ii) Ag_2CO_3 solid was stirred in 100 cm^3 of water until no more Ag_2CO_3 solid can dissolve.

Calculate the mass of Ag_2CO_3 that was dissolved in this sample of water.

	$Ag_2CO_3(s)$	=	$2Ag^+(aq)$	+	$CO_3^{2-}(aq)$
Eqm conc/ mol dm^{-3}			$2x$		x

$$6.3 \times 10^{-12} = (2x)^2(x)$$

$$x = \sqrt[3]{\frac{6.3\times10^{-12}}{4}} = 1.16 \times 10^{-4}$$

$$\text{Amount of } Ag_2CO_3 \text{ dissolved} = \frac{100}{1000}\times1.16\times10^{-4} = 1.16 \times 10^{-5} \text{ mol}$$

$$\text{Mass of } Ag_2CO_3 \text{ dissolved} = 1.16 \times 10^{-5} \times (2(107.9) + 12.0 + 48.0)$$

$$= 3.21 \times 10^{-3} \text{ g}$$

[3]

(iii) A solution contains 0.10 mol dm^{-3} each of Br^- and CO_3^{2-}. AgBr and Ag_2CO_3 can be precipitated by adding $AgNO_3(aq)$ dropwise to the solution.

Which salt will precipitate out first, AgBr or Ag_2CO_3? Explain your answer with appropriate calculations.

For first trace of precipitation, Ionic Product = K_{sp}

Minimum concentration of Ag^+ to see first trace of AgBr ppt

$$= \frac{K_{sp}(AgBr)}{0.10} = \frac{5.0\times10^{-13}}{0.10} = 5.00 \times 10^{-12} \text{ mol dm}^{-3}$$

Minimum concentration of Ag^+ to see first trace of Ag_2CO_3 ppt

$$= \sqrt{\frac{K_{sp}(Ag_2CO_3)}{0.10}} = \sqrt{\frac{6.3\times10^{-12}}{0.10}} = 7.94 \times 10^{-6} \text{ mol dm}^{-3}$$

AgBr will precipitate first since the minimum $[Ag^+]$ required for precipitation is lower.

[2]

(b) AgBr is soluble in concentrated $NH_3(aq)$ but sparingly soluble in dilute $NH_3(aq)$.

Consider the following two equilibria at 298K.

equilibrium 1 $AgBr(s) = Ag^+(aq) + Br^-(aq)$
equilibrium 2 $Ag^+(aq) + 2NH_3(aq) = [Ag(NH_3)_2]^+(aq)$

Use the concepts of Le Chatelier's principle **and** solubility product, as applied to equilibria 1 and 2, explain why AgBr is soluble in concentrated $NH_3(aq)$ but sparingly soluble in dilute $NH_3(aq)$.

Calculations are **not** required.

Initial $[Ag^+]$ is low.

- In dilute NH_3, there's not enough NH_3
- to complex enough Ag^+ to reduce $[Ag^+]$ sufficiently (or reduce $[Ag^+]$ sufficiently through forming stable $Ag(NH_3)_2^+$ complex), so ionic product for AgBr is still greater than its K_{sp}.
- In concentrated NH_3, the high concentration of NH_3 causes the position of equilibrium in equilibrium 2 to shift to the right, to form $[Ag(NH_3)_2]^+$ complex
- $[Ag^+]$ decreases and position of equilibrium in equilibrium 1 shifts to the right.
- The Ionic Product (I.P) for AgBr is now significantly lower until I.P is less than its K_{sp}, hence the POE for Eqm 1 shifts completely to the right, AgBr dissolves completely, forming a colourless solution, $Ag(NH_3)_2^+$.

[3]

(c) Silver chloride and silver bromide can be used in photography.

(i) In a photographic film, AgBr crystals precipitated into a gelatine base as 'grains'.

Calculate the number of silver ions in a grain of AgBr of mass 2.5×10^{-12} g. Give your answer to 2 significant figures.

$$\text{Number of } Ag^+ \text{ ions} = \frac{2.5\times10^{-12}}{107.9+79.9}\times6.02\times10^{23} = 8.0 \times 10^9$$

[1]

(ii) In photography, a bromide ion absorbs light of a specific wavelength and loses an electron for the photographic process.

$$Br^- \rightarrow Br + e^-$$

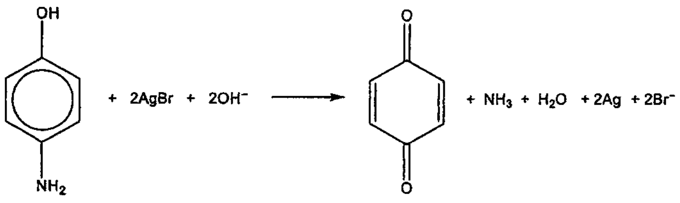
Predict whether it would require more energy or less energy to initiate this process in Ag*Cl* compared to AgBr. Explain your answer as fully as you can.

It will require more energy.

Despite Cl^- has a lower nuclear charge, it has less shielding effect since there is less quantum shell of electrons. The electron to be removed is closer to the nucleus and is more strongly attracted to the nucleus.

[2]

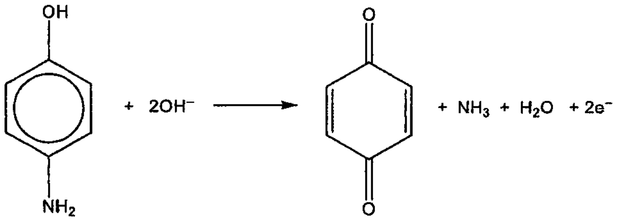
Rodinal is used as a photographic developer. It develops a latent photographic image through reducing silver ions in AgBr to silver atoms in alkaline conditions.



rodinal

1,4-benzoquinone

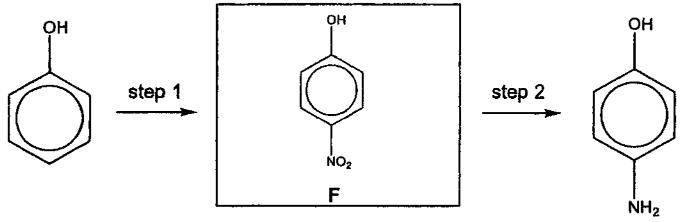
(iii) Write a half-equation for the oxidation of rodinal to 1,4-benzoquinone under the conditions described for the development of latent photographic image.



[1]

(iv) Rodinal can be synthesised from phenol.

State the reagents and conditions for steps **1** and **2** and draw the structure of compound **F** in the box provided.



rodinal

step 1: dilute HNO$_3$

step 2: Sn, conc HC*l*, followed by NaOH(aq)

[3]

[Total: 16]

BP~717

Answer Scheme Paper 3
Section A

1 Nitrogen, a Period 2 element, forms a wide variety of compounds with diverse structures, oxidation states, and properties. These include ammonia, ammonium salts, amines, and nitrates, all of which play important roles in industry, agriculture, and the environment.

(a) The enthalpy changes involved in the formation of ionic and covalent compounds vary across the period.

(i) Explain why the first ionisation energy of nitrogen is more endothermic than that of carbon and oxygen. [2]

C: $1s^2\ 2s^2\ 2p^2$ N: $1s^2\ 2s^2\ 2p^3$ O: $1s^2\ 2s^2\ 2p^4$

Comparing C and N:

N has a higher nuclear charge, while the shielding effect caused by inner shell electrons remains approximately constant. Therefore, it has a smaller atomic radius, and valence electrons experience a stronger nuclear attraction. Consequently, N has a higher first ionisation energy compared to C.

Comparing N and O:

Less energy is required to remove one of the paired 3p electrons in oxygen due to the larger interelectronic repulsion. Thus, O has a lower first ionisation energy than N.

(ii) Some Period 3 elements can react with chlorine to produce chlorides, for example, NaC*l* and SiC*l*$_4$.

Describe and explain what happens when NaC*l* and SiC*l*$_4$ are separately added to excess water. State the pH of the resultant mixtures and give relevant equations. [3]

NaCl is an ionic chloride and will dissolve/hydrate in water to form a solution of pH 7.

$NaCl \rightarrow Na^+(aq) + Cl^-$

$SiCl_4$ is a covalent chloride and has energetically accessible vacant 3d orbitals that allow the water molecule to form dative bonds.

Thus $SiCl_4$ hydrolyse in water to form an acidic solution of pH 1-2.

$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$

---

1 (b) Ammonia (NH_3), ammonium nitrate (NH_4NO_3), and ethanamide (CH_3CONH_2) are important compounds that can be used as fertilisers due to their high nitrogen content.

Arrange these three compounds in order of increasing pH value of their aqueous solution. Explain your answer. [3]

$NH_4NO_3 < NH_2CONH_2 < NH_3$

NH_4NO_3 will dissociate into NH_4^+ and NO_3^- ions in solution. NH_4^+ will undergo hydrolysis to produce H^+ ions, forming an acidic solution. Thus, the pH value of NH_4NO_3 solution is less than 7.

NH_3 will be basic due to the availability of lone pair electrons on N for protonation. Thus, the pH value of the solutions will be higher than 7.

CH_3CONH_2 will be neutral due to the delocalisation of the lone pair of electrons on N into the neighbouring π electron cloud of the electron-withdrawing C=O group, the lone pair of electrons in urea is not available for protonation than NH_3. Thus, it is a weaker base compared to NH_3, hence, lower pH value.

(c) Aqueous iron(III) nitrate, $Fe(NO_3)_3(aq)$, is yellow in colour.

(i) Explain why the solution of iron(III) nitrate is yellow in colour. [3]

The presence of ligands cause the d orbitals to split into 2 different energy levels with a small energy gap, ΔE, that corresponds to the visible light region of the electromagnetic spectrum.

Visible light is absorbed when an electron transits from a lower energy d orbital to a higher energy d orbital which is unfilled or partially filled.

Hence, the colour observed is the complement of the colours absorbed.

(ii) Using data from the *Data Booklet*, predict what will be observed when aqueous iron(III) nitrate is added to potassium iodide, KI, giving a balanced equation for the reaction that occurs. [3]

From Data Booklet:

$\boxed{Fe^{3+}} + e^- \rightleftharpoons Fe^{2+}$ $E = +0.77\ V$

$I_2 + 2e^- \rightleftharpoons \boxed{2I^-}$ $E = +0.54\ V$

$$E^\ominus_{cell} = (+0.77) - (+0.54)$$
$$= +0.23\ V > 0 \text{ (reaction is energetically feasible)}$$

Obs: Yellow solution of Fe^{3+} turn pale green and brown solution of I_2 formed

Eqn: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

(iii) A sample of $Fe(NO_3)_3(aq)$ was added to aqueous sodium hydroxide. A red-brown precipitate formed immediately and remained unchanged upon standing.

When a solution of $SCN^-(aq)$ is added to the resulting precipitate, the precipitate dissolves and blood red solution of $[Fe(SCN)(H_2O)_5]^{2+}$ complex is formed. The formation of the blood red complex is non-reversible.

Explain the above observations and include relevant equations. [3]

Fe^{3+} reacts with OH^- to form red-brown precipitate of $Fe(OH)_3$

$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$

When SCN^- is added, a ligand exchange reaction occurs. The stronger SCN^- ligand replaces the weaker H_2O ligand to form a stronger dative bond and a more stable complex.

$$Fe(H_2O)_6^{3+} + SCN^-(aq) \rightarrow Fe(H_2O)_5(SCN)^{2+} + H_2O$$

The precipitate in the solution is sparingly soluble.

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq) \text{ --- (1)}$$

This decreases concentration of Fe^{3+} in the solution, causing position of equilibrium (1) to shift left and thus precipitate dissolves.

[Total: 17]

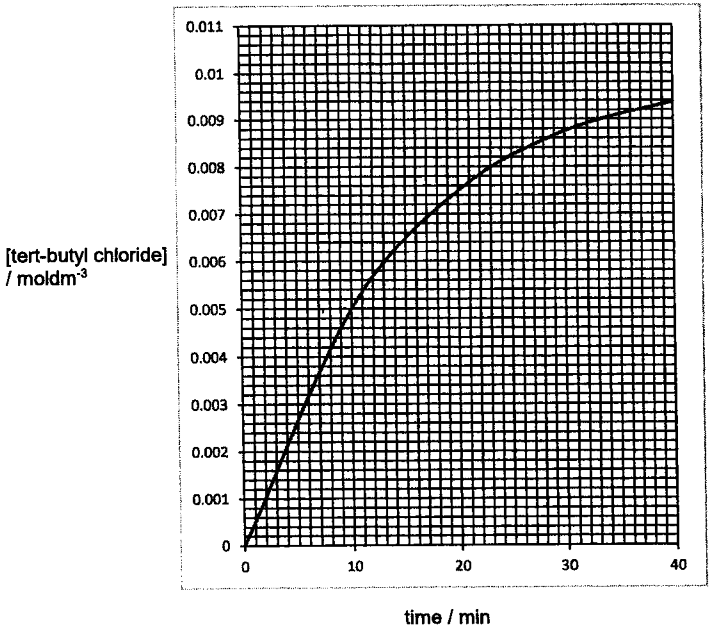
---

2 Lucas Test, named after an American chemist, Howard Luca, is a simple qualitative test, using concentrated HC*l* in the presence of $ZnCl_2$, to classify alcohols by observing the rate of turbidity, indicating the formation of insoluble alkyl halides.

(a) The rate of the Lucas Test is investigated, using tert-butanol, $(CH_3)_3COH$.

$$(CH_3)_3COH + HCl \xrightarrow[0 \text{ to } 10\,^{\circ}C]{ZnCl_2} (CH_3)_3CCl$$

When 1 dm^3 of 0.0100 mol of tert-butanol is reacted with 5.00 mol of HC*l* in the presence of $ZnCl_2$, the concentration of tert-butyl chloride, $(CH_3)_3CCl$, formed over time is shown in the graph below.



(a) (i) Define the term *order of reaction*. [1]

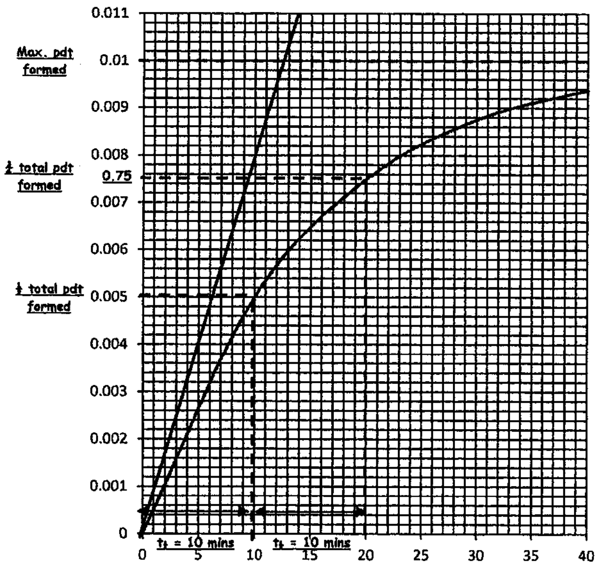
order of reaction with respect to a reactant is the power to which the concentration of the reactant is raised to in the rate equation

OR

In an experimentally determined rate equation: rate = $k[A]^m[B]^n$ where A and B are the reactants, the orders of reaction with respect to [A] and [B] are m and n respectively

(ii) The same graph was obtained when the test was repeated with 7.5 mol of HC*l*.

Using the information provided and the graph, deduce the orders with respect to $(CH_3)_3COH$ and HC*l*. Show clearly your working and any construction lines on the graph. [3]



Since 1st $t_{\frac{1}{2}}$ = 2nd $t_{\frac{1}{2}}$ = 10 mins, the half life of the reaction is (approximately) constant. The reaction is 1st order w.r.t $(CH_3)_3COH$ and

When concentration of HCl is increased by 1.5 times/changed, the rate of reaction remains the same, thus, the reaction is 0 order w.r.t HCl.

(iii) Hence, write the rate equation for the Lucas Test, and calculate a value for the rate constant. Include units in your answer. [3]

Rate = $k[(CH_3)_3COH]$

Since it is a overall first order reaction

$k = \ln 2 / t_{\frac{1}{2}} \quad = \ln 2 / 10 = \underline{0.0693 \text{ min}^{-1}}$

OR

Initial rate method:

y-intercept at 16 mins

Initial rate = 0.011 / 16 = 0.000688 mol dm^{-3} min^{-1}

K = 0.000688 / 0.01

$= \underline{0.0688 \text{ min}^{-1}}$

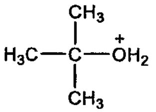
---

2 (b)

$$(CH_3)_3COH + HCl \xrightarrow[0 \text{ to } 10\ ^\circ C]{ZnCl_2} (CH_3)_3CCl$$

The Lucas Test, as shown above, follows a nucleophilic substitution reaction mechanism as follows:

- Tert-butanol reacts with HC*l* to generate the following reaction intermediate in the first step.



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\overset{+}{O}H_2$$

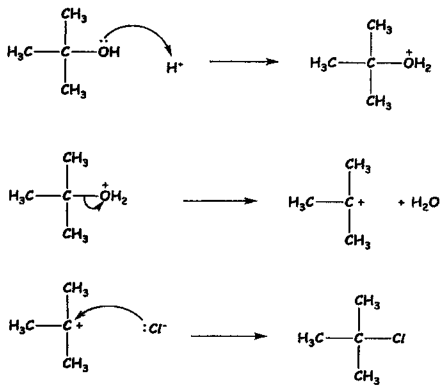
- This intermediate subsequently loses water to form a carbocation, which reacts further to form the product, tert-butyl chloride.
- HC*l* is acting as a Lewis acid in the first step and as a source for ***nucleophile*** in the subsequent steps.

(i) Define the term, *nucleophile.* [1]

Nucleophile is defined as <u>electron-rich species</u> that <u>can donate an electron pair</u>.

(ii) Use the data and information given above, draw the mechanism for the Lucas Test.

Show all relevant curly arrows, charges and structure of the intermediates. Include an equation for the formation of the reaction intermediate. [3]



(iii) Suggest two reasons why the reaction between $(CH_3)_3COH$ and concentrated HC*l* follows a S_N1 mechanism rather than a S_N2 mechanism. [2]

1. S_N1 is preferred because the tertiary carbocation intermediate, $(CH_3)_3C^+$ formed has three electron-donating alkyl groups that disperse the positive charge to a larger extent and stabilise it.
2. S_N2 is not preferred because the presence of 3 bulky alkyl groups prevents the backside approach of the nucleophile, resulting in steric hindrance.

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(c) $ZnCl_2$ is a *Lewis acid* and functions as a catalyst for the Lucas Test.

$FeCl_3$ is a stronger *Lewis acid* compared to $ZnCl_2$. However, it causes multiple side reactions to occur and is thus not preferred.

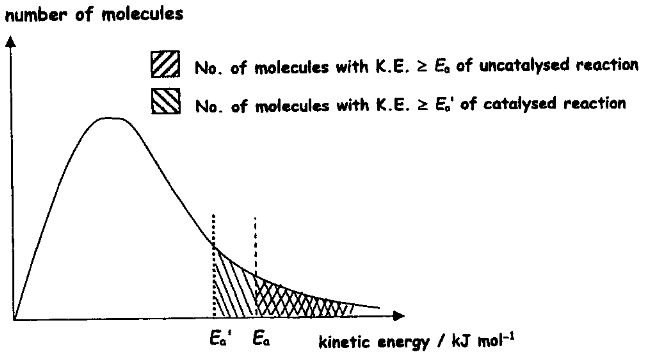
(i) Define the term *Lewis acid*. [1]

A Lewis acid is an electron pair acceptor.

(ii) By considering the electronic configuration of Zn^{2+} and Fe^{3+}, suggest two reasons why $FeCl_3$ is a stronger Lewis acid compared to $ZnCl_2$. [2]

1. Fe^{3+} ions have a higher charge and a smaller radius compared to Zn^{2+} ions. As such, the Fe^{3+} ion is more likely to attract an electron pair and behaves as a stronger Lewis acid.
2. Fe^{3+} ion has available low-lying 3d orbitals which easier to accept an electron pair. Zn^{2+} ion has fully filled 3d orbitals. The next available orbital is 4s, which has a higher energy level and is less accessible.

(iii) Explain, with the aid of an appropriate diagram, how $ZnCl_2$ increases the rate of the Lucas Test. [3]



A catalyst provides an alternative reaction pathway with lowered activation energy.

When catalyst is used, the proportion of molecules possessing energy greater or equal to the lowered activation energy increases.

Frequency of effective collision increases, rate increases.

[Total: 19]

3 (a) Describe the variation in the acid-base behaviour of Al_2O_3 and P_4O_{10} by reference to their reactions with H_2SO_4 and NaOH respectively.

Write equations for any reactions described. [3]

Both Al_2O_3 and P_4O_{10} can act as acidic oxide and react with NaOH.

$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq)$

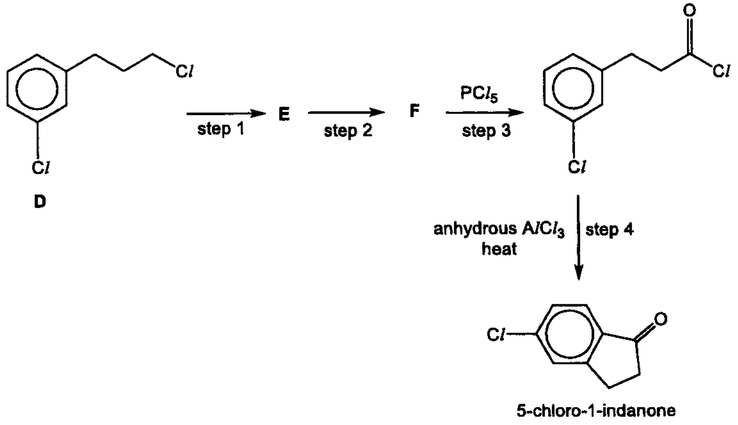
$P_4O_{10}(s) + 12OH^- \rightarrow 4PO_4^{3-} + 6H_2O$

However, only Al_2O_3 can act as basic oxide to react with H_2SO_4, but P_4O_{10} cannot.

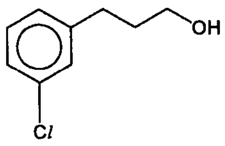
$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$

(b) 5-chloro-1-indanone is mainly used as a chemical intermediate in pharmaceuticals, agrochemicals, and material sciences. It serves as a building block for drugs, pesticides like indoxacarb, and advanced materials such as fluorescent dyes.

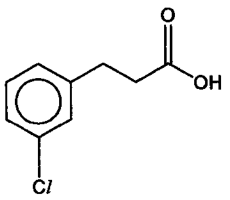
5-chloro-1-indanone can be synthesised from compound D as shown below.



(i) Deduce the structures of organic product **E** and **F**. [2]



E



F

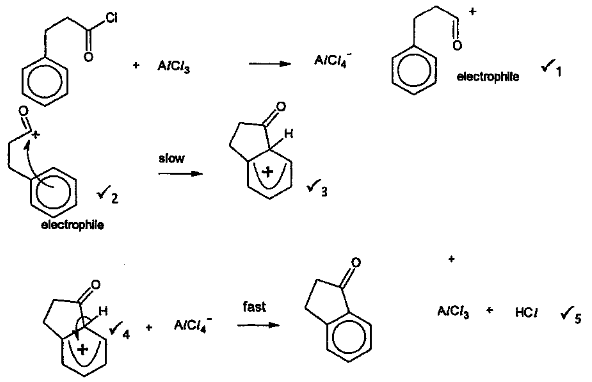
(ii) Suggest reagents for step 1 and for step 2. [2]

Step 1: NaOH(aq), heat

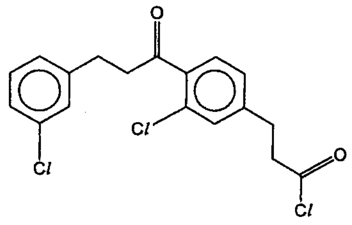
Step 2: acidified $K_2Cr_2O_7$, heat

(iii) Name and describe the reaction mechanism for Step 4. [3]

Electrophilic substitution [1]



(iv) In step 4, another by-product **M** can be formed.



M

By considering the structure of the starting reactant and the overall entropy change of the reaction, explain **two** reasons why the formation of 5-chloro-1-indanone is preferred over **M**. [2]

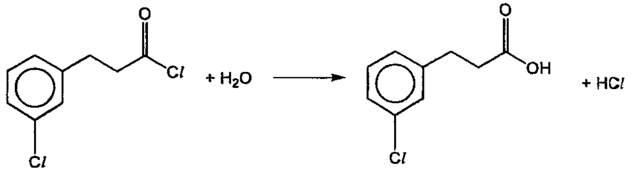
1. Intramolecular reaction is faster and favoured due to the close proximity of the acyl chloride and aromatic ring.
2. Intramolecular reaction increases the number of molecules ($\Delta S > 0$), whereas intermolecular reaction does not, making the former more favoured.

(v) In Step 4, anhydrous $AlCl_3$ must be used, and no water can be introduced. With the aid of appropriate equations, explain why this is so. [1]

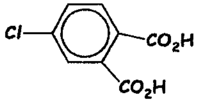
The catalyst $AlCl_3$ will hydrolyse in water, and cannot generate the +ve charged electrophile for the reaction.

$AlCl_3 + 6H_2O \longrightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

OR Acyl chloride will hydrolyse in water to form carboxylic acid, thus, no longer can form the +ve charged electrophile for the reaction.



(vi) When 5-chloro-1-indanone is oxidised with acidified $KMnO_4$, CO_2 is evolved as a side product. Suggest the structure of the organic product formed. [1]

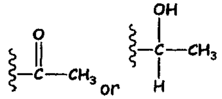


(c) Compound **G**, $C_5H_9NO_3$, is a neutral compound that contains 2 chiral centres.

Samples of compound **G** are reacted separately with

- NaOH(aq) and heat to from product **H** and a pungent gas
- 2,4-DNPH forming an orange precipitate **J**, $C_{11}H_{13}N_5O_6$
- Fehling's reagent to form a brick red precipitate
- Alkaline aqueous iodine and heat forming a yellow precipitate
- $K_2Cr_2O_7$ in the presence of sulfuric acid and heat to form an organic compound, **K**, $C_5H_6O_5$.
- An excess of $LiAlH_4$ forming an organic compound **L**, $C_5H_{13}NO_2$

Deduce the structures for **G**, **H**, **J**, **K** and **L**, explaining the reactions described. [10]

Observation	Type of reaction	FGs
G is neutral	-	G contains amide
G + NaOH(aq) → H and pungent gas	Alkaline hydrolysis	G contains primary amide
G + 2,4-DNPH → orange ppt J	Condensation	G contains aldehyde or ketone
G + alkaline I_2(aq) →	Oxidation / positive iodoform test	G contains either 
G + Fehling reagent → brick red ppt	Oxidation	G contains aliphatic aldehyde
G + $K_2Cr_2O_7$ → K	Oxidation Acid hydrolysis	K contains carboxylic acid G contains aldehyde G contains alcohol
G + $LiAlH_4$ → L	Reduction	L contains amine G contains amide

G	J	H

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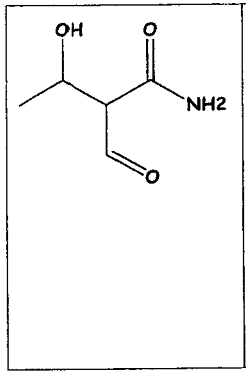
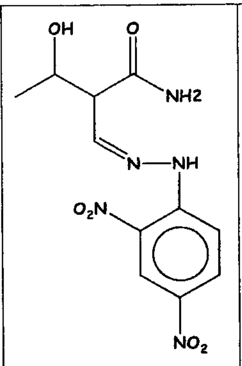
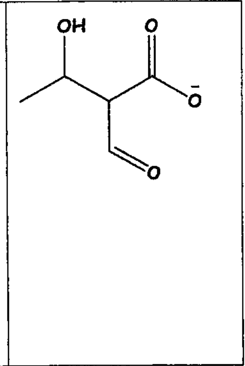
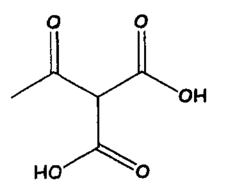
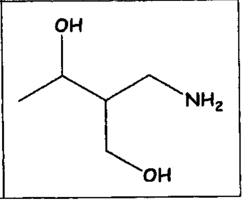
		

K	L
	

[Total: 24]

Section B

Answer one question from this section.

4 Aluminium-air batteries are used as back-up power supplies in many telephone exchanges. The structure of one such battery is shown in **Fig 4.1** below.

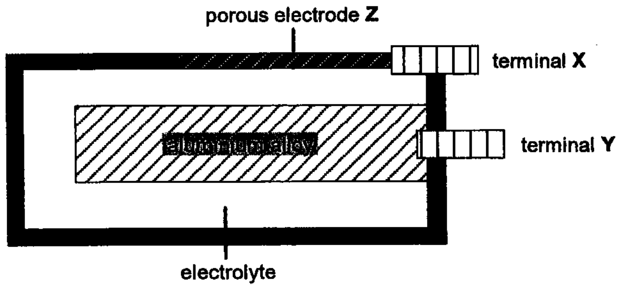


Fig 4.1

The electrolyte used is aqueous potassium hydroxide. During discharge, oxygen in air is reduced while aluminium is oxidised as shown by the following equation:

$$Al(s) + 4OH^-(aq) \rightarrow [Al(OH)_4]^-(aq) + 3e^-$$

(a) **(i)** State, with a reason, the polarity of terminal **Y**. [1]

Terminal Y is connected to the aluminium alloy and electrons are being produced when aluminium is oxidised.

Hence, terminal Y is *negative*.

(ii) Write a balanced equation with state symbols for the reaction that takes place at the porous electrode **Z**. [1]

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

(iii) State why electrode Z must be porous. [1]

To allow $O_2(g)$ to diffuse through and interact with the electrolyte to be reduced.

(iv) In this battery, aluminium may be replaced by zinc.

Using data from the *Data Booklet*, suggest an advantage of using aluminium rather than zinc. [1]

- $E^\ominus(Al^{3+}/Al)$ is more negative than $E^\ominus(Zn^{2+}/Zn)$ so the operating voltage of the battery is higher. OR
- Al produces more electrons per mol of metal, so more electrons/electricity can be produces for the same mass of metal used.

4 **(a)** **(v)** When aqueous potassium hydroxide is replaced by aqueous sodium chloride, it is noticed that white $Al(OH)_3$ solid is formed around the aluminium electrode instead.

Explain why it is formed. [1]

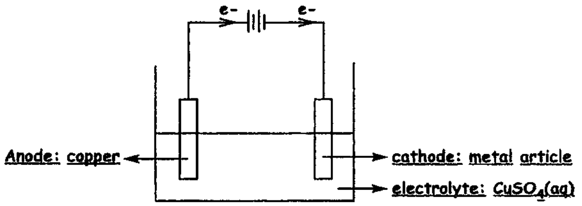
There is insufficient hydroxide ions formed from the reduction of oxygen to form the soluble complex ion.

(b) The aluminium-air battery was used as an electrical source to electroplate an article with copper.

(i) Draw a labelled diagram of an electrolytic cell setup to show how an article can be electroplated with copper.

In your diagram, state clearly the choice of anode, cathode, electrolyte to be used and the direction of electron flow.

You may use the standard battery symbol ⊣⊢ to represent the aluminium-air battery in your diagram. [2]



(ii) If the mass of aluminium electrode in the aluminium-air battery as described earlier in **(a)** decreased by 5.4 g, calculate the mass of copper that was deposited on the article. [2]

$$\text{amount of } Al \text{ reacted} = \frac{5.4}{27.0} = 0.200 \ mol$$

$$\text{amount of electrons formed} = 3 \times 0.200 = 0.600 \ mol$$

Since $Cu \equiv 2e$

$$\text{amount of } Cu \text{ formed} = \frac{1}{2} \times 0.600 = 0.300 \ mol$$

$$\therefore \text{mass of } Cu \text{ formed} = 0.300 \times 63.5 = 19.1 \ g$$

(iii) The electroplating process took 468 min.

Calculate the current delivered by the aluminium-air battery. [1]

Using $Q = It = nF$

$I(468 \times 60) = (0.600)(96500)$

$I = 2.06 \ A$

(iv) In some batteries, graphite can be used as electrodes.

Describe and explain, in terms of structure and bonding, how graphite can serve this role. [2]

Graphite has a giant covalent structure, with each C atom is covalently bonded to 3 other atoms with delocalised electrons along/within the layers over the structure.

Graphite can conduct electricity due to the presence of mobile delocalised electrons.

(c) A ligand exchange reaction occurs when aqueous ammonia is added to a solution of green $Ni^{2+}(aq)$.

$$Ni(H_2O)_6{}^{2+}(aq) + xNH_3(aq) \rightarrow [Ni(NH_3)_x(H_2O)_{6-x}]^{2+} + xH_2O(l)$$

The formula of a nickel-ammonia complex that is blue in colour can be found using a colorimeter.

Eleven tubes containing 20 cm³ of 0.05 mol dm⁻³ of $Ni^{2+}(aq)$ had 0.4 mol dm⁻³ aqueous ammonia added. The first tube has 2 cm³ of aqueous ammonia added, the second tube 4 cm³ and so on. Distilled water was added to bring the total volume to 50 cm³.

Each tube was then placed in a calorimeter and the absorbance recorded. The absorbance intensity is proportional to the concentration of the complex.

The results are shown in Fig 4.1 below.

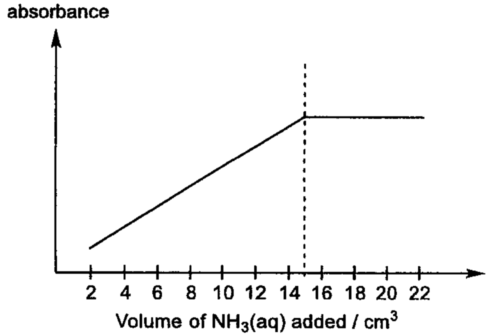


Fig 4.2

(i) Explain why the absorbance value in **Fig 4.2** remains constant after 15 cm³ of $NH_3(aq)$ is added. [1]

All the $Ni^{2+}(aq)$ present in the sample has been completely reacted and thus no more complex will be formed. As such, amount/concentration of the complex remains a constant and thus the graph shows no change in absorbance.

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(ii) Deduce the formula of the complex based on the stoichiometry information that could be inferred from the graph. [2]

amount of Ni^{2+} in each test tube $= \frac{20}{1000} \times 0.05$

$= \mathbf{1.00 \times 10^{-3}}$ **mol**

amount of NH_3 at 15 cm^3 $= \frac{15}{1000} \times 0.4$

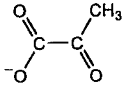
$= \underline{\mathbf{6.00 \times 10^{-3}}}$ **mol**

mol ratio of Ni^{2+} to $NH_3 = \mathbf{1.00 \times 10^{-3} : 6.00 \times 10^{-3} = 1:6}$

$\therefore$ **x = 6**

Formula of the complex is $[Ni(NH_3)_6]^{2+}$

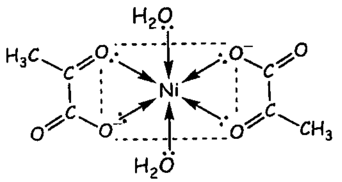
(iii)



ligand **Z**

Z is a bidentate ligand, and experiments show that two mole of **Z** react with each mole of $[Ni(H_2O)_6]^{2+}$ to form an octahedral complex.

Given that the complex has no dipole moment, draw the structure of the complex formed, showing the 3-dimensional arrangement around the nickel ion. Indicate the overall charge, if any, on this complex. [2]



(d) Nickel (Ni) readily forms a tetracarbonyl complex, $Ni(CO)_4$, where four carbon monoxide (CO) molecules act as ligands.

$$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$$

(i) State two physical properties of nickel, apart from the colour of the metal, in which it differs from calcium. Explain the reasons for those differences. [2]

The melting point of Ni is higher compared to that of *Ca*. As compared to *Ca*, more energy is required to overcome the stronger metallic bonds between the Ni^{2+} ions and the sea of delocalised electrons, since both 3d and 4s electrons are involved in the metallic bonding.

The density of Ni is higher compared to that of *Ca*, because Ni has a smaller atomic radius (or cationic radius) and a larger A_r than *Ca*. Since density is the mass per unit volume, assuming that the atoms are spherical in shape, Ni will have a higher density as compared to

Ca. In addition, having a smaller atomic radius also means that its structure is more closely packed.

(ii) Explain why carbon monoxide, CO, is poisonous. [1]

Stronger *CO* ligand displaces the weaker O_2 ligand by forming a stronger dative bond with Fe^{2+} in the haem group of haemoglobin to give a more stable complex.

This results in the inability of haemoglobin to transport oxygen to the cells and thus accounts for the toxic nature of *CO*.

[Total: 20]

5 Cobalt is a brittle and hard transition metal with magnetic properties similar to those of iron. One of the characteristic properties of transition metals is their ability to form complexes.

(a) The compound **B** can act as a *bidentate ligand* can form a complex with Co^{3+} ions in the mole ratio 3:1.

$$\underset{\textbf{B}}{H_2NCH_2CH_2NH_2}$$

Compound B can be made using ethene and appropriate inorganic reagents by the following 2-step synthesis.

$$\underset{\text{ethene}}{H_2C{=}CH_2} \xrightarrow{\text{step 1}} A \xrightarrow{\text{step 2}} \underset{\textbf{B}}{H_2NCH_2CH_2NH_2}$$

(i) What can be understood by the term *bidentate ligand*? [1]

Bidentate ligand is a ligand that contain two groups that have a lone pair of electrons each that can form two dative bonds to the central metal cation.

(ii) Suggest the structure of compound L and the reagents and conditions for Step 1 and 2. [3]

Structure of L: $BrCH_2CH_2Br$

Step 1: $Br_2(l)$

Step 2: excess NH_3, ethanol, heat in sealed tube

(iii) State the coordination number of the cobalt(III) complex. [1]

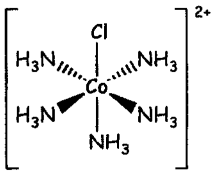
6

(b) Two different complexes can be obtained by reacting aqueous cobalt(III) chloride with ammonia under various conditions.

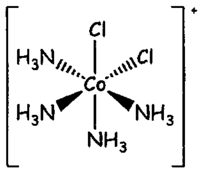
Different proportions of chloride are precipitated when each of the complexes is treated with aqueous silver nitrate.

complex	empirical formula	No. of moles of Ag*Cl* precipitated per mole of complex	Does the complex have a dipole moment?
S	$CoCl_3(NH_3)_5$	2	yes
T	$CoCl_3(NH_3)_4$	1	yes

Suggest the structures of complexes S and T, showing clearly the three dimensional arrangement of the ligands around the metal ion center. [2]



complex S



complex T

(c) When an aqueous solution of the ligand **Q** is mixed with an aqueous solution of cobalt salt, the flowing equilibrium is set up:

$$Co^{3+}(aq) + 6\,\mathbf{Q}(aq) \rightleftharpoons Co\mathbf{Q}_6^{3+}(aq)$$

A similar equilibrium occurs with the ligand **R**, forming $Co\mathbf{R}_6^{3+}(aq)$.

Solutions **X**, **Y** and **Z** were made by mixing 0.1 mol dm^{-3} solutions of Co^{3+}, **Q** and **R**. The table below gives the volumes of each used.

	Volumes of 0.1 mol dm^{-3} solution / cm^3		
Solution	$Co^{3+}(aq)$	**Q**(aq)	**R**(aq)
X	4	96	0
Y	4	0	96
Z	4	48	48

The visible absorption spectra of the three solutions **X**, **Y** and **Z** are shown below:

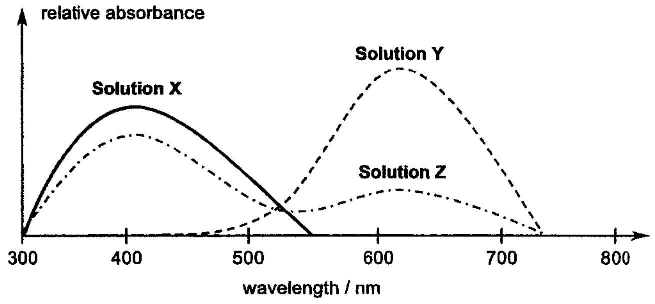


Fig 5.1

The wavelength at which the maximum absorbance is observed is inversely proportional to the energy gap between the two sets of d orbitals in an octahedral complex.

(i) The spectra show that the peak in the curve for solution **Y** is at a longer wavelength than is the peak in the curve for solution **X**.

What deduction can be made from this fact about the size of the d-orbital splitting in the two complexes? [1]

The size of the d-orbital splitting in $Co\mathbf{Q}_6^{3+}(aq)$ is larger than that in $Co\mathbf{R}_6^{2+}$.

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5 (c) (ii) The absorbance of a solution at a particular wavelength is proportional to the concentration of the ion responsible for the absorption.

Use this information and the given absorption spectra in **Fig 5.1** to suggest and explain which ligand, Q or R, forms the stronger bond with Co^{3+}. [2]

From the spectrum of solution **Z**, when there are equal proportions of ligands **Q** and **R**, the relative absorbance of $Co\mathbf{Q}_6^{3+}$ is higher, and hence the proportion of $Co\mathbf{Q}_6^{3+}$ in the mixture is higher.

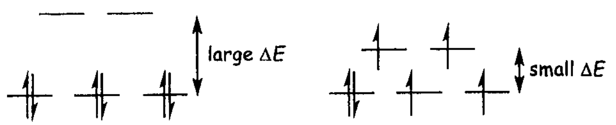
Hence, the stability of $Co\mathbf{Q}_6^{3+}$ in the mixture is higher, thus **Q** forms a stronger bond with Co^{3+}.

(iii) The energy gap between the two levels of d orbitals in an octahedral complex depends on the strength of the ligand. The energy gap in turn affects how electrons occupy the d subshell in the complex. Electrons in the d subshell may occupy all the orbitals singly before pairing up or they may fill up the d orbitals in the lower energy level before filling up the d orbitals in the higher energy level.

Paramagnetic materials have one or more unpair electrons in their electron configuration. These unpaired electrons spin and create a magnetic dipole moment, making the molecule magnetic.

By considering the electronic configuration of Co^{3+} and your answers in **(c)(ii)**, suggest and explain which of the two complexes, $Co\mathbf{Q}_6^{3+}$ or $Co\mathbf{R}_6^{3+}$, have the higher tendency to be paramagnetic. [2]

The electron arrangement due to the size of the d orbital splitting:



From **(c)(ii)**, since **Q** forms a stronger dative with the metal ion center, it is the stronger ligand. As such, the energy gap between the two sets of d orbitals is larger.

There is a higher probability of the electrons filling up the d orbitals in the lower energy level first. This will result in the complex to not have any unpaired electrons.

Hence $Co\mathbf{Q}_6^{3+}$ have a higher tendency to not be paramagnetic / $Co\mathbf{R}_6^{3+}$ have a higher tendency to be paramagnetic.

5 (d) Many transition metals and their compounds are useful catalysts.

An aqueous solution of Co^{2+} can catalyse the reaction between iodide and peroxodisulfate, $S_2O_8^{2-}$ whereas Ca^{2+} cannot.

(i) Why is it necessary to catalyse the reaction between iodide and peroxodisulfate? [1]

Both ions are negatively charged and the electronic repulsion increases the activation energy thus the reaction is very slow.

(ii) Explain why Ca^{2+} is not suitable as a catalyst. [1]

Co^{2+} has variable oxidation states and can function as homogenous catalyst while Ca^{2+} only has one oxidation state.

(iii) With reference to the *Data Booklet*, show how Co^{2+} can catalyse the above reaction. [2]

From Data Booklet

$Co^{3+} + e^- \rightleftharpoons Co^{2+}$ $E^\ominus = +1.89$ V

$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\ominus = +2.01$ V

Step 1: $2Co^{2+} + S_2O_8^{2-} \rightarrow 2Co^{3+} + 2SO_4^{2-}$

$E^\ominus_{cell} = (+2.01) - (+1.89)$

$= +0.12\ V > 0$ (*reaction is energetically feasible*)

Step 2: $Co^{3+} + 2I^- \rightarrow I_2 + Co^{3+}$

$E^\ominus_{cell} = (+1.89) - (+0.54)$

$= +1.35\ V > 0$ (*reaction is energetically feasible*)

5 (e) Stellite alloys are cobalt–chromium alloys prized for their hardness, wear, and corrosion resistance. The corrosion resistance is largely due to the chromium content, which forms a stable, protective Cr_2O_3 oxide layer. In contrast, cobalt does not form a stable protective oxide and therefore reacts more readily in acidic environments.

A 5.00 g sample of the cobalt–chromium alloy is being analysed to determine its cobalt content. The sample is dissolved in excess dilute sulfuric acid, forming a pink solution containing Co^{2+} ions while chromium remains as green insoluble Cr_2O_3 sludge.

The resulting solution was made up to 100 cm^3 and a 25.0 cm^3 aliquot of this solution is titrated with 0.120 mol dm^{-3} $KMnO_4$ in acidic solution. The volume of $KMnO_4$ required for complete reaction is 22.0 cm^3.

Calculate the percentage by mass of Co in the alloy. [4]

amount of MnO_4^- reacted $= \underline{\frac{22.0}{1000} \times 0.120} = \mathbf{2.64 \times 10^{-3}}$ **mol**

$MnO_4^- + 5Co^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Co^{3+} + 4H_2O$

Since 1 $MnO_4^- \equiv \mathbf{5}$ Co^{2+}

amount of Co^{2+} reacted $= \underline{\mathbf{5 \times 2.64 \times 10^{-3}}} = \underline{\mathbf{1.32 \times 10^{-2}\ mol}}$

amount of Co^{2+} in original solution $= \underline{\mathbf{1.32 \times 10^{-2} \times \frac{100}{25}}} = \mathbf{5.28 \times 10^{-2}}$ **mol**

mass of $Co = \underline{\mathbf{5.28 \times 10^{-2} \times 58.9 = 3.11g}}$

percentage by mass of $Co = \mathbf{\frac{3.11}{5} \times 100\% = 62.2\%}$

[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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