Suggested Solutions

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

14 September 2023
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/10
2	/12
3	/14
4	/14
5	/25
Total	/75

This document consists of **25** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

1 (a) A fluorophore is a fluorescent chemical compound that can re-emit light upon light excitation. Fluorophores typically contain several combined aromatic groups, or planar or cyclic molecules with several π bonds.

Derivatives of trans-stilbene have been recently studied due to their well-known fluorophore properties and they are generally more stable than cis-stilbene. The structure of cis-stilbene is shown in Fig. 1.1.

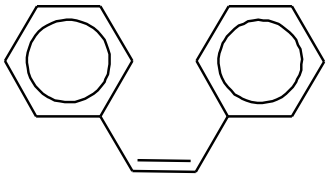


Fig. 1.1

(i) Explain why the melting point of trans-stilbene is higher than that of cis-stilbene.

[1]

Trans-isomer has higher symmetry and **packs more closely** into a crystal lattice. **More energy** is required to break the stronger intermolecular forces of attraction in crystal lattice in the trans–isomer than the cis–isomer.

(ii) Based on the structure of stilbene, suggest a reason why trans-stilbene is more stable than cis-stilbene.

[1]

It has two bulky phenyl groups far from each other, making this compound more stable than cis isomers due to **less steric hindrance**.

(b) Aluminium chloride, $AlCl_3$, is used as a halogen carrier in order for chlorination of benzene to take place in stilbene.

$$AlCl_3 + Cl_2 \rightleftharpoons AlCl_4^- + Cl^+$$

(i) Name the type of bond formed when $AlCl_3$ reacts with Cl_2. Explain how this bond is formed.

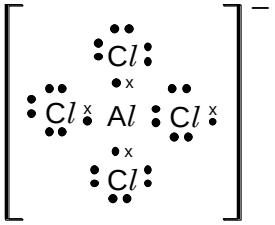
[2]

Dative bond. **Al atom has a vacant** low-lying **orbital** in its valence shell so it can **accept an electron pair from Cl_2**.

(ii) Draw the dot-and-cross diagram for the $AlCl_4^-$ ion.

Use the VSEPR theory to state and explain the shape of the ion and the bond angle present.

[3]



There are **4 bond pairs and 0 lone pairs** around the central aluminium atom. As the repulsion between the 4 bond pairs are similar in strength, the shape around the central aluminium atom is thus **tetrahedral** to **minimise repulsion** between them. The bond angle is **109° .**

(c) Orange street-lamps contain sodium with a small amount of neon. Light is produced when the gaseous atoms are ionised in an electric field.

$Ne(g) \rightarrow Ne^{+}(g) + e^{-}$ $\quad 1^{st}$ I.E = +2080 kJ mol^{-1}
$Na(g) \rightarrow Na^{+}(g) + e^{-}$ $\quad 1^{st}$ I.E = +494 kJ mol^{-1}

(i) Explain the difference in the first ionisation energies of neon and sodium.

[2]

Na has **an additional electron shell** compared to Ne, hence Na **experiences stronger shielding effect**. **Despite having a higher nuclear charge**, the electron to be lost from Na is **further away** and **experiences weaker attraction from the nucleus** .

(ii) When the lamps are switched on, they first emit a red glow characteristic of neon, but after some time, the orange glow of sodium predominates.

Suggest why neon is ionised first even though its first ionisation energy is much higher than that of sodium.

[1]

Sodium is in the **solid state** and energy is required to **vapourise sodium** first before the atoms can be ionised.

[Total: 10]

2 Compound **M** has molecular formula, $C_6H_8O_2$.

M reacts with an excess of hot concentrated $KMnO_4$ to produce two different organic molecules **L** and **K**.

(a) **K** has molecular formula $C_2H_2O_4$ and is further oxidised to form CO_2.

(i) Name **K**.

[1]

ethanedioic acid

(ii) Write an equation for the oxidation of **K** to form CO_2, using [O] to represent the oxidising agent.

[1]

$(CO_2H)_2$ + [O] → $2CO_2$ + H_2O

(b) **L** has molecular formula $C_4H_6O_3$.

When pure samples of **L** are separately added to two different reagents, the observations in Table 2.1 are recorded.

Table 2.1

test	reagent	observation
1	alkaline aqueous iodine	pale yellow precipitate
2	phosphorus(V) chloride	misty acid fumes

(i) Name the type of reaction occurring to **L** in test 1.

[1]

oxidation

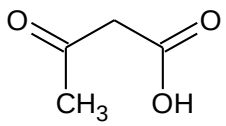
(ii) Based on the observation for test 2, name two functional groups that could be present in **L**.

[1]

alcohol or **carboxylic acid**
reject hydroxyl / −OH groups

(iii) Deduce the structure of **L**.

[1]

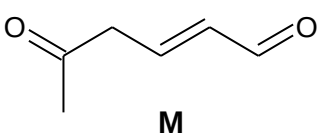


L

test	reagent	observation	deductions
1	alkaline aqueous iodine	pale yellow precipitate	Oxidation reaction. **L** contains either the $-CH(OH)CH_3$ or $-COCH_3$ group. Since **L** is a product of strong oxidation of **M**, **L** contains the $-COCH_3$ group.
2	phosphorus(V) chloride	misty acid fumes	Nucleophilic substitution reaction. Since **L** is a product of strong oxidation of **M**, **L** contains either a tertiary alcohol or a carboxylic acid group. Since **L** has molecular formula $C_4H_6O_3$, **L** has 3 oxygen atoms and contains the carboxylic acid group.

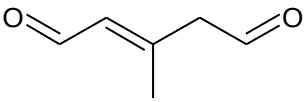
(c) Suggest a possible structure of **M**, $C_6H_8O_2$, showing the skeletal formula.

[2]



M

OR



M

OR

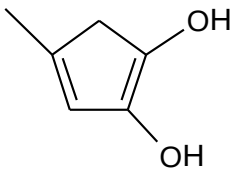


Fig. 2.1 shows a reaction scheme of compound **N**.

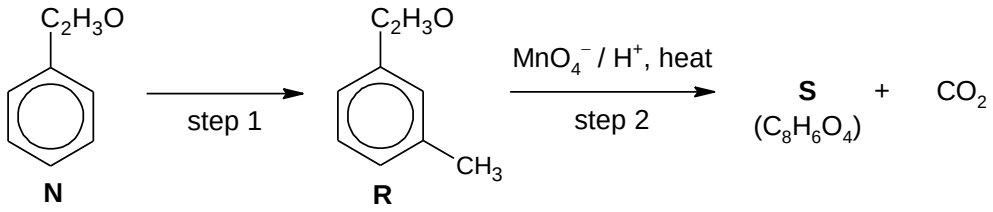


Fig. 2.1

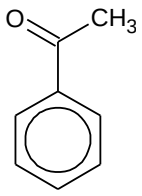
(d) **(i)** **N** reacts with 2,4-dinitrophenylhydrazine to give an orange precipitate. Explain this observation.

[1]

N undergoes **condensation** reaction with 2,4-DNPH.
N contains either **a ketone or an aldehyde** functional group.

(ii) **R** is the major product of the reaction occurring in step 1.
Use this information and your answer in **(d)(i)** to deduce the structure of **N**. Explain your answer.

[2]



N

From **(d)(i)**, the $-C_2H_3O$ group has to contain the ketone or aldehyde functional group so it can be $-COCH_3$ or $-CH_2CHO$.

Since **incoming CH_3^+** electrophile is **directed to the 3-position**, $-C_2H_3O$ has to be the **electron-withdrawing $-COCH_3$ group** which deactivates the benzene ring.

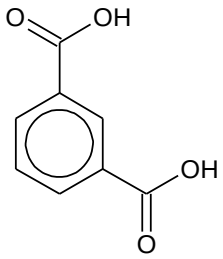
(iii) State the reagents and conditions required for step 1.

[1]

CH_3Cl, anhydrous **$AlCl_3$**

(iv) Suggest the structure of compound **S**.

[1]

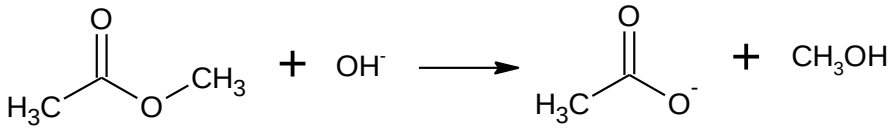


S

[Total: 12]

3 **(a)** A series of kinetics experiments was carried out at a constant temperature to study

the mechanism of ester hydrolysis under basic conditions. The overall chemical reaction is described below.



The initial rates of reaction with varying ester concentrations were measured at $[OH^-]$ = 0.90 mol dm^{-3} and $[OH^-]$ = 1.50 mol dm^{-3}. Fig. 3.1 shows the graph of the results obtained.

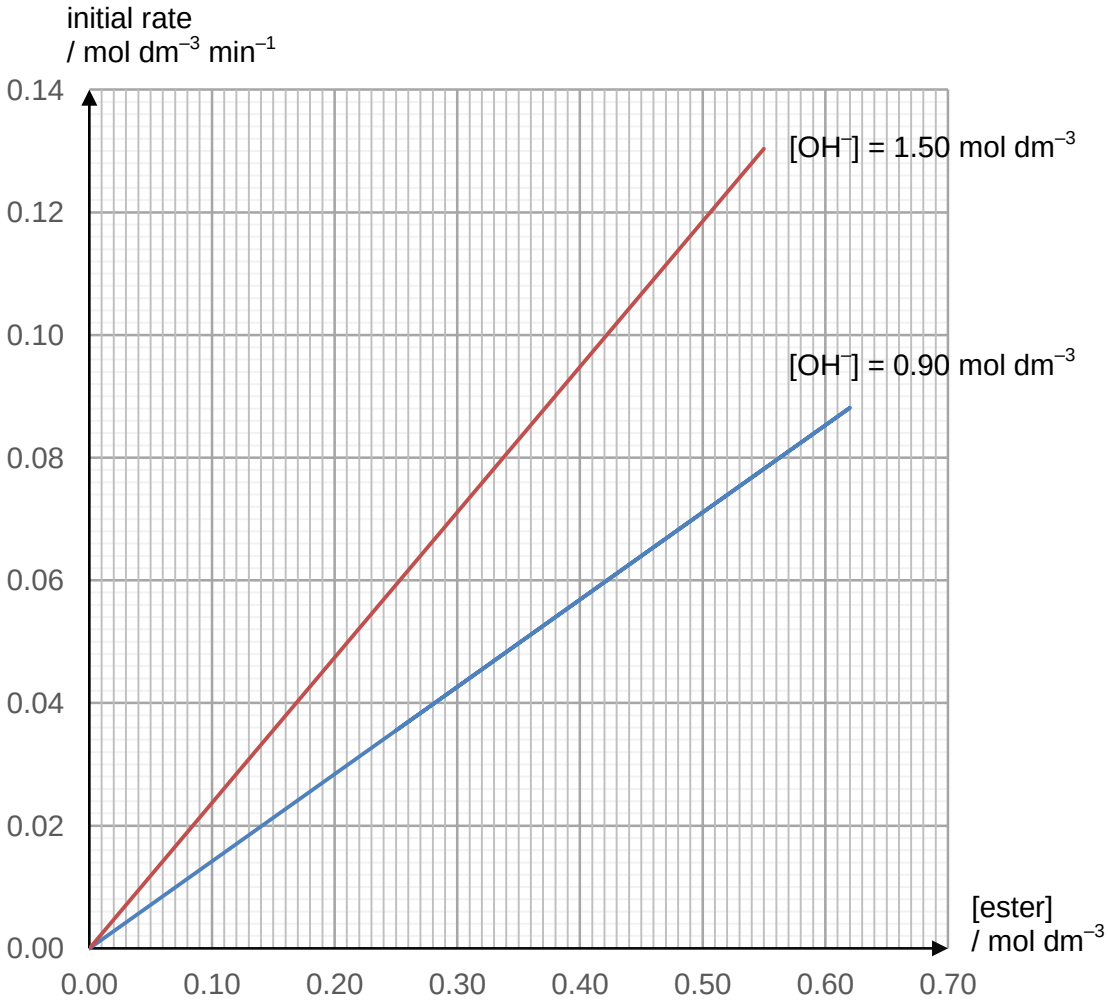


Fig. 3.1

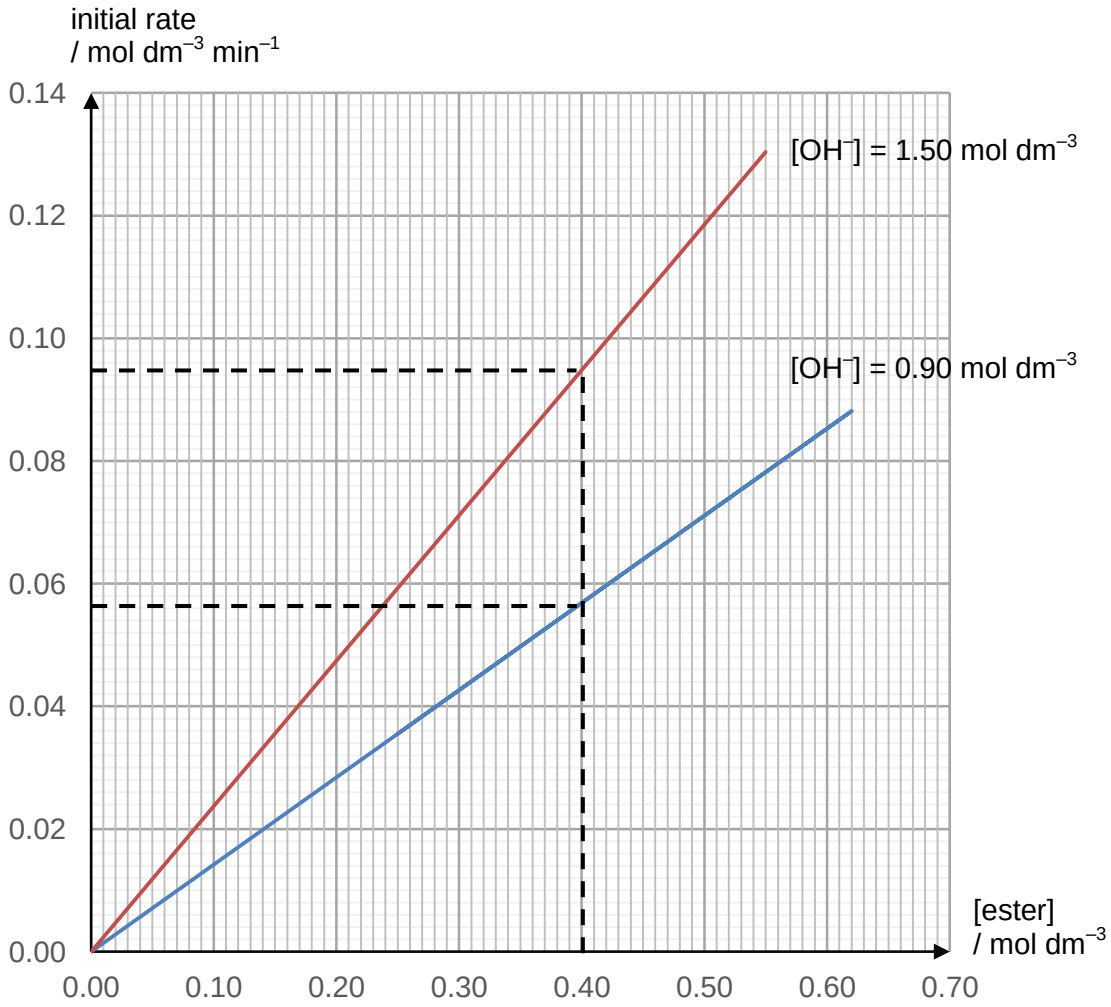
(i) By quoting relevant data from Fig. 3.1, determine the order of reaction with respect to each reactant. Show your reasoning clearly.

[2]

When $[OH^-]$ is constant, the graph of initial rate against [ester] is a **straight line with a positive gradient passing through the origin**. Hence rate is **directly proportional** to [ester] and the reaction is **first order** w.r.t. [ester].

When [ester] = 0.40 mol dm^{-3}, when $[OH^-] \times \frac{5}{3}$ from 0.90 mol dm^{-3} to 1.50 mol dm^{-3}, initial rate also $\times \frac{5}{3}$ from 0.056 mol dm^{-3} min^{-1} to 0.095 mol dm^{-3} min^{-1}.

Hence rate is **directly proportional** to $[OH^-]$ and the reaction is **first order** w.r.t. $[OH^-]$



(ii) Using your answer in **(a)(i)**, write the rate equation for the reaction.

[1]

rate = k[OH$^-$][ester]

(iii) Using your answer in **(a)(ii)** and relevant data from Fig. 3.1, calculate the value of the rate constant under the experiment conditions. State its units.

[1]

rate = k[OH$^-$][ester]
$0.130 = k \times 1.5 \times 0.55$
$k = 0.158\, mol^{-1}\, dm^3\, min^{-1}$

(b) The proposed mechanism for the hydrolysis reaction is shown in Fig. 3.2.

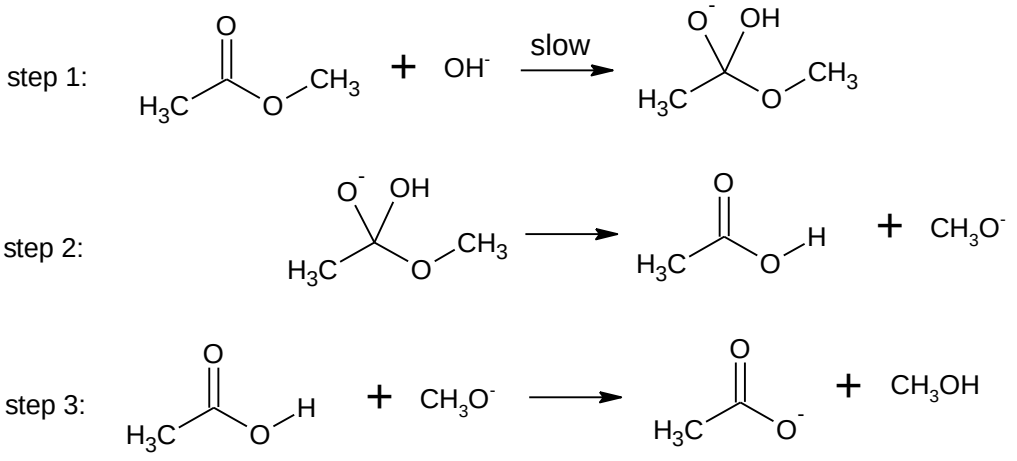


Fig. 3.2

(i) Deduce if the mechanism shown in Fig. 3.2 is supported by the experimental data in Fig. 3.1.

[1]

Yes, **one ester molecule and one OH^- ion** is involved in the **slow step**.

(ii) State the type of reaction occurring in step 2 of the mechanism.

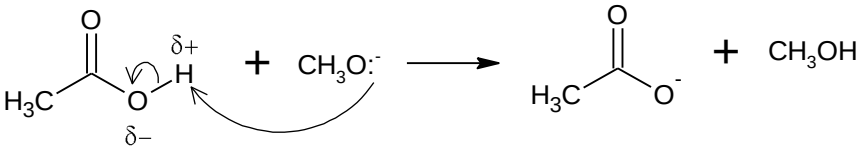
[1]

Elimination

Step 3 is an acid-base reaction.

(iii) On Fig. 3.2, draw curly arrows to describe the mechanism of step 3. You should show relevant lone pairs and dipoles.

[1]



(iv) Suggest why the CH_3O^- ion is a stronger base than the CH_3COO^- ion.

[2]

The CH_3COO^- anion is stabilised by the **delocalisation of negative charge over two (highly electronegative) oxygen atoms**. This **decreases the charge density** on the O atom.

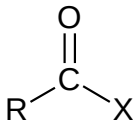
The **oxygen lone pair is less available for donation to H^+**, hence CH_3COO^- anion is a weaker base.

(v) State a reagent that can be used to show that carboxylic acid is a stronger acid than alcohol. Describe the observation in each case.

[2]

Reagent	Carboxylic acid	Alcohol
Na_2CO_3	Effervescence is observed. CO_2 evolved.	No effervescence observed.
NaOH	Temperature of the mixture increases.	No change in temperature.
Mg	Effervescence is observed. H_2 evolved.	No effervescence observed.

The ease of hydrolysis of carboxylic acid derivatives depends on the relative strength of electronic effect and resonance effect exerted by the group (X) bonded to the carboxyl carbon (C=O).



The electronic effect of the group (X) causes the carboxyl carbon to be more electrophilic while the resonance effect causes the carboxyl carbon to be less electrophilic.

(c) **(i)** State the reagents and conditions necessary for hydrolysis of esters and acid chlorides.

[1]

Hydrolysis of esters: **heating with dilute base / dilute acid**
Hydrolysis of acid chlorides: **water (**at room temperature)

(ii) By considering your answer in **(c)(i)**, comment on the relative strength of electronic effect and resonance effect for the esters and acid chlorides.

[2]

Since esters require **heating and/or stronger nucleophile (OH^-) and/or catalyst (H^+)**, the carboxyl carbon is less electrophilic hence **resonance effect is stronger** for esters.

Since acid chlorides require **a lower reaction temperature and/or a weaker nucleophile (H_2O) and/or does not require a catalyst**, the carboxyl carbon is more electrophilic hence **electronic effect is stronger** for acid chlorides.

[Total: 14]

4 Table 4.1 shows the pK_b values of urea, propylamine and hydroxylamine at 25°C.

Table 4.1

name of compound	structural formula	pK_b
urea	$CO(NH_2)_2$	13.9
propylamine	$CH_3CH_2CH_2NH_2$	3.46
hydroxylamine	NH_2OH	8.06

(a) Using data in Table 4.1, state and explain the relative basicity of urea, propylamine and hydroxylamine.

[3]

The greater the pK_b value, the weaker the base. Hence, urea, which is an amide, **is the least basic** while **propylamine is the most basic**. **Basicity increases** with the **availability of lone pair on N atom** to accept a H+.

For urea, **p orbital of the N atom overlaps side-on with the p orbitals of the adjacent C=O group**, allowing **the lone pair of electrons on the N atom to be delocalised**, making the lone pair unavailable / decreasing the availability of the lone pair on N atom to form a dative bond with a H^+ ion.

For hydroxylamine, the presence of the **electronegative oxygen atom exerts an electron withdrawing effect**, resulting in the lone pair on N to be less available

than propylamine.

For propylamine, the **electron donating propyl group increases the electron density of the lone pair on N**, increasing the availability of the lone pair on N.

(b) Fig. 4.1 shows the change in pH when 0.1 mol dm^{-3} of aqueous propylamine, $CH_3CH_2CH_2NH_2(aq)$ is titrated with 0.2 mol dm^{-3} $HCl(aq)$.

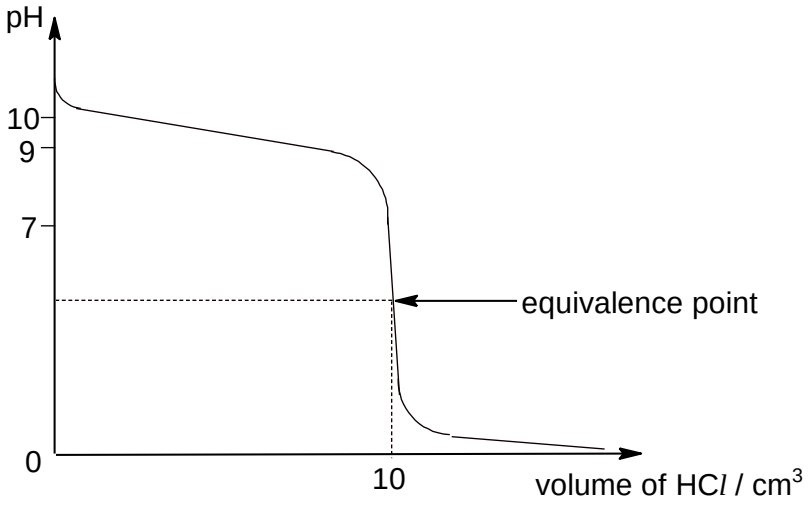


Fig. 4.1

(i) Identify the two major species present in this solution over the pH range 9.0 to 10.0.

[1]

$CH_3CH_2CH_2NH_2$ and $CH_3CH_2CH_2NH_3^+$

(ii) Explain why the slope of the graph only changes gradually over the pH range 9.0 to 10.0.

[1]

When a small amount of H^+ is added,
$CH_3CH_2CH_2NH_2 + H^+ \rightarrow CH_3CH_2CH_2NH_3^+$

The **added H^+ is removed by $CH_3CH_2CH_2NH_2$** as $CH_3CH_2CH_2NH_3^+$. Hence **pH remains fairly constant** resulting in the slope of the graph changes gradually.

(iii) Suggest, with the aid of an equation, why the pH at the equivalence point is less than pH 7 in this titration.

[1]

$CH_3CH_2CH_2NH_3^+ + H_2O \rightleftharpoons CH_3CH_2CH_2NH_2 + H_3O^+$

At equivalence point, the main organic compound in the solution is **$CH_3CH_2CH_2NH_3^+$**. Since it is the conjugate acid of a weak base, it **partially dissociates in water to release H^+** / **undergoes salt hydrolysis** causing the solution at equivalence point to be weakly acidic.

(iv) Using data in Table 4.1 and Fig 4.1, calculate the pH of the solution at equivalence point at 25 °C.

[2]

$pK_a = 14 - pK_b$

= 14 – 3.46 = 10.54

$K_a = 10^{-10.54} = 2.88 \times 10^{-11}$ mol dm^{-3}

Total volume of solution at equivalence point
= 10 + 20 (stoichiometric amount of propylamine is required to neutralise HC*l*)
= 30 cm^3

$[H^+] = \sqrt{2.88 \times 10^{-11} \times \frac{0.002}{0.03}} = 1.39 \times 10^{-6}$ mol dm^{-3}

pH = $-\log_{10}(1.39 \times 10^{-6})$ = **5.86**

(c) Fig. 4.2 shows the synthetic route of 1,3-diaminopropane from ethene.

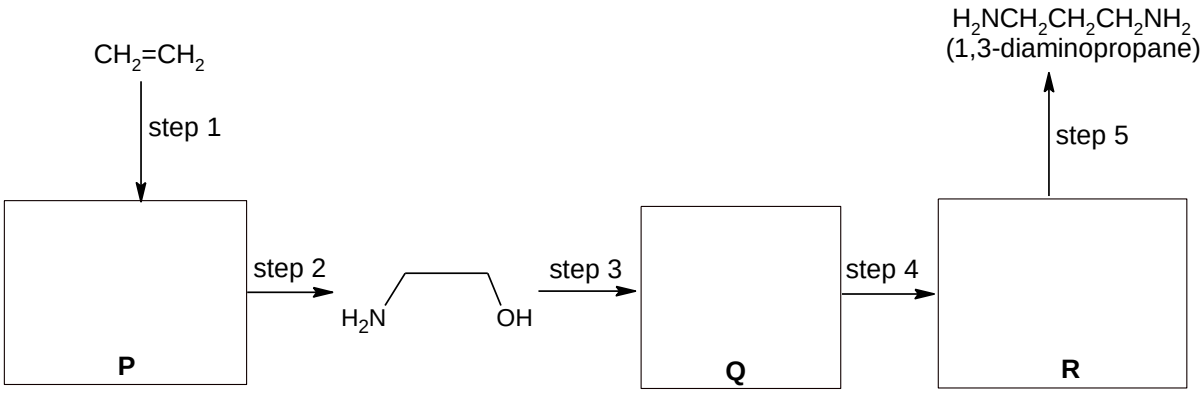
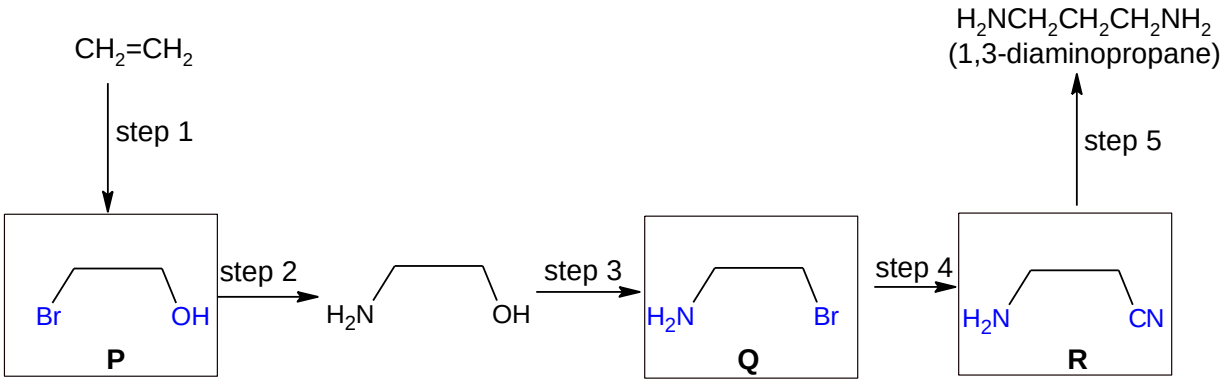


Fig. 4.2

(i) Draw structures of compounds **P**, **Q** and **R** in the boxes provided in Fig. 4.2.

[3]



(ii) Suggest reagents and conditions for steps 2, 4 and 5.

[3]

step	reagents and conditions
2	Excess NH_3 in ethanol, heat in sealed tube
4	KCN in ethanol, heat under reflux
5	$LiAlH_4$ in dry ether / H_2, Ni catalyst, heat under pressure

[Total: 14]

5 (a) Vaccines usually contain proteins that can denature at room temperature. Hence, they need to be refrigerated when being transported or stored. This increases cost and makes distribution difficult. A recently developed process called "ensilication" can prevent warmed−up vaccines from degrading. This is achieved by encasing protein molecules in a silica shell. Ensilicated vaccine allows the structure to remain intact even when heated to 100°C or stored at room temperature for up to three years.

"Ensilication" of the vaccines involves

Process 1 Hydrolysis of colourless liquid, tetraethyl orthosilicate, $Si(OCH_2CH_3)_4$, to form orthosilicic acid, $Si(OH)_4$.

Process 2 Decomposition of orthosilicic acid into silica, SiO_2 in the presence of protein/antibody catalyst.

Process 3 At the end of the process 2, a suspension of silica nanoparticles loaded with protein is formed. The protein can be released using a solution of sodium fluoride and hydrochloric acid, which breaks up the silica.

(i) Write an equation to represent the standard enthalpy of formation of tetraethyl orthosilicate, $Si(OCH_2CH_3)_4(l)$.

[1]

$Si(s) + 2O_2(g) + 8C(s) + 10H_2(g) \rightarrow Si(OCH_2CH_3)_4(l)$

(ii) Write a balanced chemical equation for process 2.

[1]

Process 2: $Si(OH)_4 \rightarrow SiO_2 + 2H_2O$

FYI
Process 1: $Si(OCH_2CH_3)_4 + 4H_2O \rightarrow Si(OH)_4 + 4CH_3CH_2OH$

(iii) The equation for process 3 is given below.

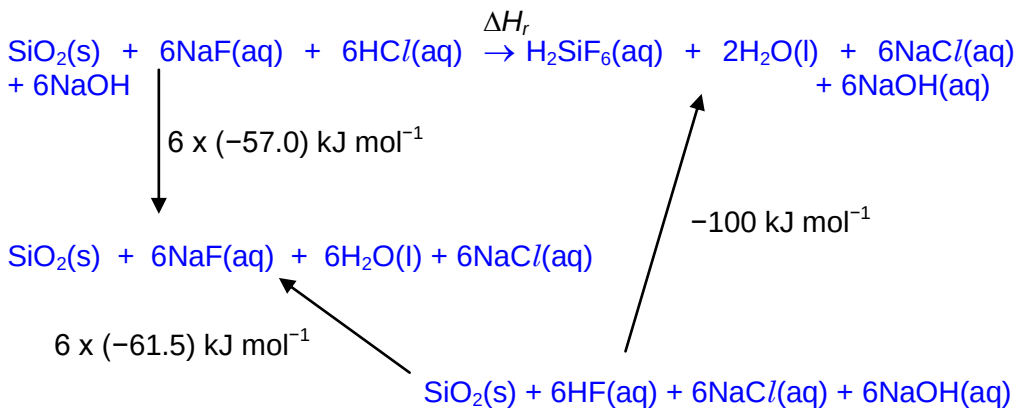
$$SiO_2(s) + 6NaF(aq) + 6HCl(aq) \xrightarrow{\Delta H_r} H_2SiF_6(aq) + 2H_2O(l) + 6NaCl(aq)$$

Using the data in Table 5.1, draw an energy cycle and calculate the enthalpy change of reaction, ΔH_r, in process 3.

Table 5.1

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$	$\Delta H_1^{\ominus} = -57.0$ kJ mol^{-1}
$SiO_2(s) + 6HF(aq) \rightarrow H_2SiF_6(aq) + 2H_2O(l)$	$\Delta H_2^{\ominus} = -100$ kJ mol^{-1}
$NaOH(aq) + HF(aq) \rightarrow H_2O(l) + NaF(aq)$	$\Delta H_3^{\ominus} = -61.5$ kJ mol^{-1}

[3]



By Hess' Law,

ΔH_r = [6 x (−57.0)] –[6 x (−61.5)] + (−100)

= **−73.0 kJ mol^{-1}**

(iv) Process 2 is thermodynamically favoured but slow, which is why a catalyst is required. The standard Gibbs free energy change for the reaction in process 2 is given by the equation

$$\Delta G^{\ominus} = -R(1680 + 0.605T)$$

Determine $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for the reaction.

[2]

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

Comparing this with the equation given,

$\Delta H^{\ominus}$ = −1680 x 8.31 = **−14000 J mol^{-1}**

$\Delta S^{\ominus}$ = 0.605 x 8.31 = **+ 5.03 J mol^{-1} K^{-1}**

(b) The magnetic dipole moment of a substance measures the strength and direction of its magnetism. An electron has an electron magnetic dipole moment generated by the electron's spin.

The magnetic property of a substance can be determined by examining its electron configuration. If the substance contains unpaired electrons, then it is paramagnetic and attracted to a magnetic field. Increasing the number of unpaired electrons increases the relative paramagnetism.

If all electrons are paired, the substance is diamagnetic and it is weakly repelled by a magnetic field.

Table 5.2 shows the relative paramagnetisms of some iron complexes.

Table 5.2

formula of complex	relative paramagnetism

$[Fe(H_2O)_6]^{2+}$	4
$[Fe(H_2O)_6]^{3+}$	5
$[Fe(CN)_6]^{4-}$	0
$[Fe(CN)_6]^{3-}$	1

(i) Using Table 5.2, state if $[Fe(CN)_6]^{4-}$ would be attracted or repelled by a magnetic field. Explain your answer in terms of the number of unpaired electrons.

[1]

$[Fe(CN)_6]^{4-}$ would be **repelled** by a magnetic field. Relative paramagnetism is 0. =>The complex ion contains **no unpaired electrons**.

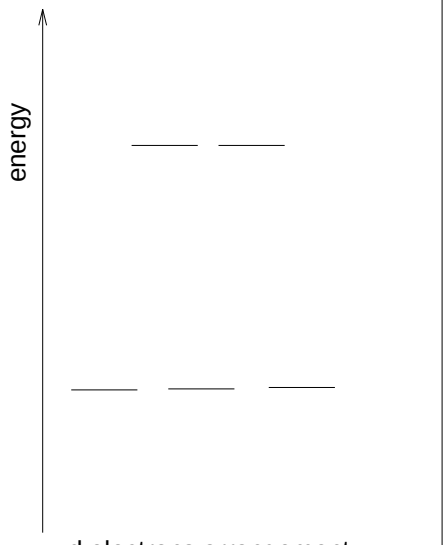
(ii) Write down the electronic configuration of the iron(II) ion in $[Fe(CN)_6]^{4-}$.

[1]

Electronic configuration of iron(II) ion in $[Fe(CN)_6]^{4-}$ is **$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^6$**

(iii) Using your answer in **(b)(i)** and **(ii)**, complete the diagram in Fig. 5.1 to show how the d electrons in the octahedral $[Fe(CN)_6]^{4-}$ complex are arranged in the five non−degenerate d−orbitals.

[1]



d electrons arrangement in $[Fe(CN)_6]^{4-}$

Fig. 5.1

d electrons arrangement in $[Fe(H_2O)_6]^{2+}$

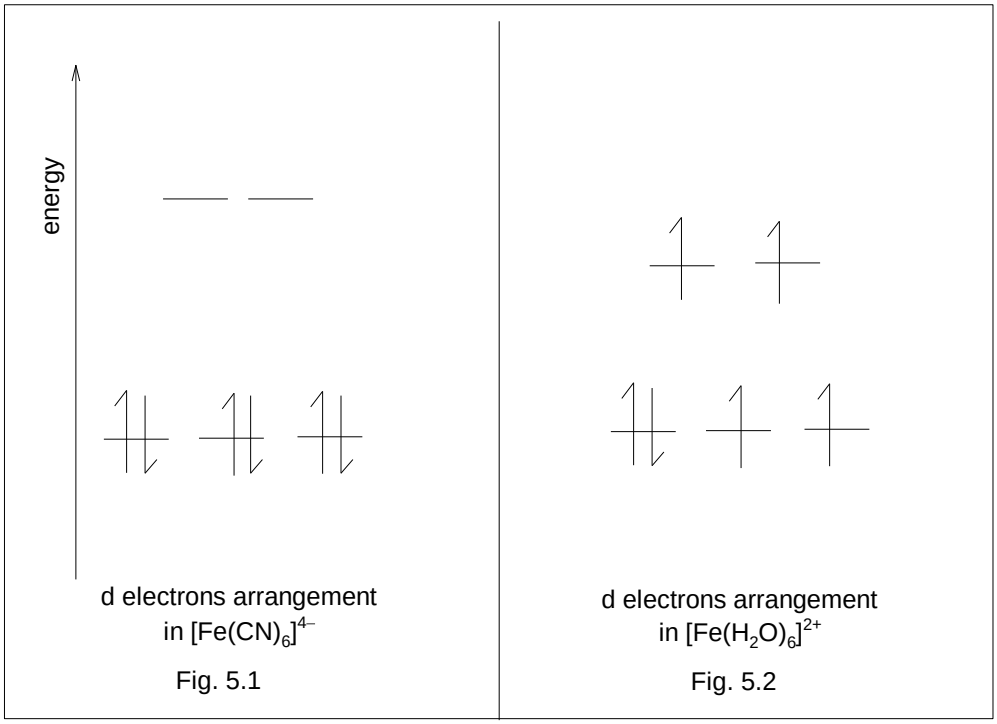
Fig. 5.2

(iv) In Fig. 5.2 above, draw another diagram, to the same scale as that in Fig. 5.1, to show how the d electrons in the octahedral $[Fe(H_2O)_6]^{2+}$ complex are arranged in the five non−degenerate d−orbitals.

Hence, state which ligand, H_2O or CN^-, splits the five degenerate d−orbitals

to a larger extent.

[2]



d electrons arrangement in $[Fe(CN)_6]^{4-}$

Fig. 5.1

d electrons arrangement in $[Fe(H_2O)_6]^{2+}$

Fig. 5.2

There are also 6 d electrons in $[Fe(H_2O)_6]^{2+}$. They occupy the five d orbitals singly first before pairing. There are (4) unpaired electrons in the 3d orbitals, giving rise to its paramagnetism.

Energy gap between the two sets of non−degenerate d−orbitals is relatively **smaller** than in $[Fe(CN)_6]^{4-}$. This allows the d electrons to be arranged singly in the five non-degenerate orbitals before pairing.

(c) Redox Flow Batteries (RFB) are rechargeable flow batteries. They are one of the most promising systems for large−scale energy storage, especially in applications based on renewable energies. This type of electrochemical system has flexible operation, fast responsiveness, moderate maintenance cost and is scalable.

Among different types of RFB, Vanadium Redox Flow Batteries (VRFB) have gained more attention. The battery takes advantage of the four oxidation states of vanadium that are stable in aqueous acidic solutions in the absence of oxygen. A schematic diagram of a VRFB is shown in Fig. 5.3. Two redox couples, V^{3+}/V^{2+} and VO_2^+/VO^{2+} in 2 mol dm^{-3} sulfuric acid are stored in electrolyte tanks. Upon operating, the redox species are pumped into the system into each of the half compartments of the cells. The conversion between chemical energy and electrical energy occurs while the electrolytes containing redox species are flowing through the electrochemical cell.

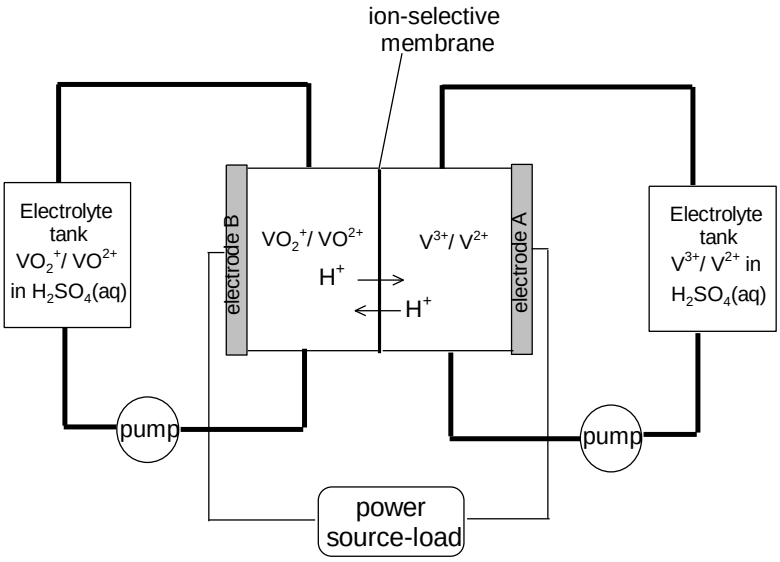


Fig. 5.3

(i) Complete Table 5.3 by stating the polarity of each electrode and writing the equation of the reaction taking place during discharging.

[2]

Table 5.3

electrode	polarity of electrode	equation of reaction taking place during discharge
A	negative	$V^{2+} \rightarrow V^{3+} + e^-$
B	positive	$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$

(ii) By using relevant data from the *Data Booklet*, calculate the $E^{\ominus}_{cell}$ and hence the change in standard Gibbs energy of the reaction occurring during discharging.

[2]

$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$
$= (+1.00) - (-0.26) =$ **+1.26 V**

$\Delta G^{\ominus} = -nF\Delta E^{\ominus}_{cell}$
$= -1 \times 96500 \times (+1.26)$
$= -121590$ J mol^{-1}
$=$ **−122 kJ mol^{-1}**

(iii) When the VRFB is operating at temperatures above 40 °C, vanadium(V) ions in solution tend to precipitate out as V_2O_5.

State and explain how the E_{cell} of the system at 50 °C would compare with

that under standard conditions.

[2]

At 50 °C, vanadium(V) ions in solution tend to precipitate out as V_2O_5. **[VO_2^+] decreases**.

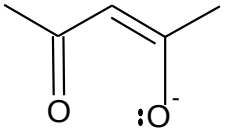
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$ +1.00 V

Above equilibrium position shifts to the **left**, $E_{cathode}$ or $E_{VO_2^+/VO^{2+}}$ **becomes less positive than +1.00 V,**

E_{cell} becomes **less positive than +1.26 V**.

(d) Metal complexes RFB have been studied to achieve higher energy density. Among these, vanadium(III) acetylacetonate, $V(acac)_3$, attracted wide attention due to its good reversibility and a voltage of 2.20 V−2.60 V in various solvents.

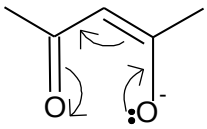
Structure of the acetylacetonate ion is shown below.



The negative charge can be delocalised over both oxygen atoms and the carbon−carbon double bond.

(i) Using curly arrows, show how delocalisation of electrons occurs in an acetylacetonate ion.

[1]



(ii) Suggest the number of delocalised electrons in an acetylacetonate ion.

[1]

6

(iii) Acetylacetonate ion behaves as a bidentate ligand. State the coordination number of the V^{3+} ion in the $V(acac)_3$ complex.

[1]

6

(e) An acidified solution, **S**, containing $VO_2^+(aq)$ was divided into two equal portions.

An excess of powdered zinc was added to one portion. The mixture was stirred until the reaction was complete, and then filtered. The filtrate was solution **T**. A 25.0 cm^3 sample of solution **T** required 37.5 cm^3 of 0.0200 mol dm^{-3} $KMnO_4$ for complete oxidation to $VO_2^+(aq)$.

25.0 cm^3 of another portion of solution **S** was reacted with a reducing gas, **R**. The resultant solution **Q** required 25.0 cm^3 of 0.0200 mol dm^{-3} $KMnO_4$ for complete

oxidation to VO_2^+(aq).

(i) Using relevant data from the *Data Booklet*, determine the oxidation state of vanadium in solution **T** and hence calculate the concentration of VO_2^+(aq) in solution **S**.

[2]

electrode reaction	$E^\ominus$ / V
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$V^{3+} + e^- \rightleftharpoons V^{2+}$	−0.26
$V^{2+} + 2e^- \rightleftharpoons V$	−1.20
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76

For the first portion of solution S:

Reaction 1: Reduction of VO_2^+ by Zn.

The $E^\ominus$ value for Zn^{2+}/Zn of −0.76 V is **more negative than all of the above vanadium redox couples except $E^\ominus(V^{2+}/V)$**. Hence, VO_2^+ will be reduced to V^{2+}. Oxidation state of vanadium in solution **T is +2.**

OR
$E^\ominus_{cell}$ = (−1.20) −(−0.76) = **−0.44 V < 0**.

Since $E^\ominus_{cell} < 0$, **reaction is not spontaneous**.

Zn will **not further reduce V^{2+} to V** as $E^\ominus_{cell} < 0$.
Oxidation state of vanadium in solution **T is +2.**

Reaction 2: $KMnO_4$ then oxidises V^{2+} back to VO_2^+.

(oxidation) $V^{2+} + 2H_2O \rightarrow VO_2^+ + 4H^+ + 3e^-$
(reduction) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$5V^{2+} \equiv 3MnO_4^-$

Moles of MnO_4^- = 0.0200 x (0.0375 dm^3) = 7.50×10^{-4} mol

Moles of V^{2+} present = $\frac{5}{3}(7.50 \times 10^{-4}) = 1.25 \times 10^{-3}$ mol

$V^{2+} \equiv VO_2^+$

Concentration of VO_2^+ = (1.25×10^{-3}) / (0.025 dm^3) = **0.0500 mol dm^{-3}**

(ii) Using your answer in **(e)(i)**, determine the oxidation state of vanadium in solution **Q** and hence suggest a suitable reducing gas **R**.

[2]

Moles of MnO_4^- required = 0.0200 x (0.025 dm^3) = 5.00×10^{-4} mol

Let the oxidation state of vanadium in Q be x.

Moles of V^{x+} in **Q** = 0.0500 x (0.025 dm^3) = 0.00125 mol

$5V^{x+} \equiv 2MnO_4^-$

2 mol of MnO_4^- gained 10 mol of electrons from 5 mol of V^{x+}

Each mol of V^{x+} lose 2 mol of electron. Since final oxidation state of V is +5. Oxidation state of vanadium in **Q** is + 3.

Suitable gas **R** is **SO_2(g) or H_2(g)**

[Reduction potential of SO_4^{2-}/SO_2 = +0.17 V; H^+/H_2 = 0.00 V. They are less positive than reduction potential of VO^{2+}/V^{3+} = +0.34 V]

[Total: 25]