Name:		Centre/Index Number:		Class:	

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.

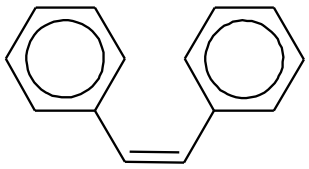

Fig. 1.1

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

……

……

……

……
[1]

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

……

……

……

……
[1]

(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]

(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]

(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.

……

……

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……

……
[2]

(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]

[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]

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

……
[1]

(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]

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

……
[1]

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

[1]

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

[2]

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

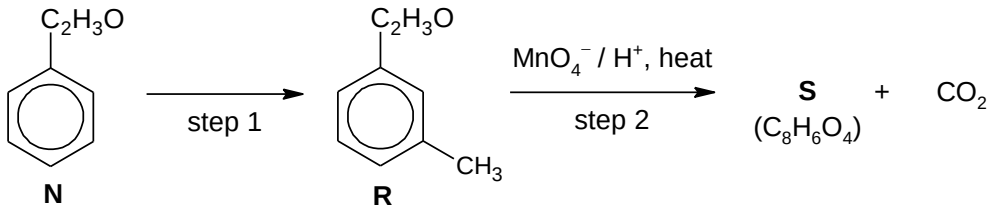


Fig. 2.1

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

……

……
[1]

(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]

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

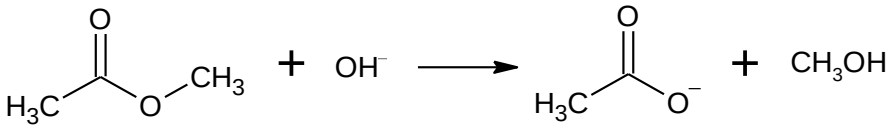
……
[1]

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

[1]

[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.

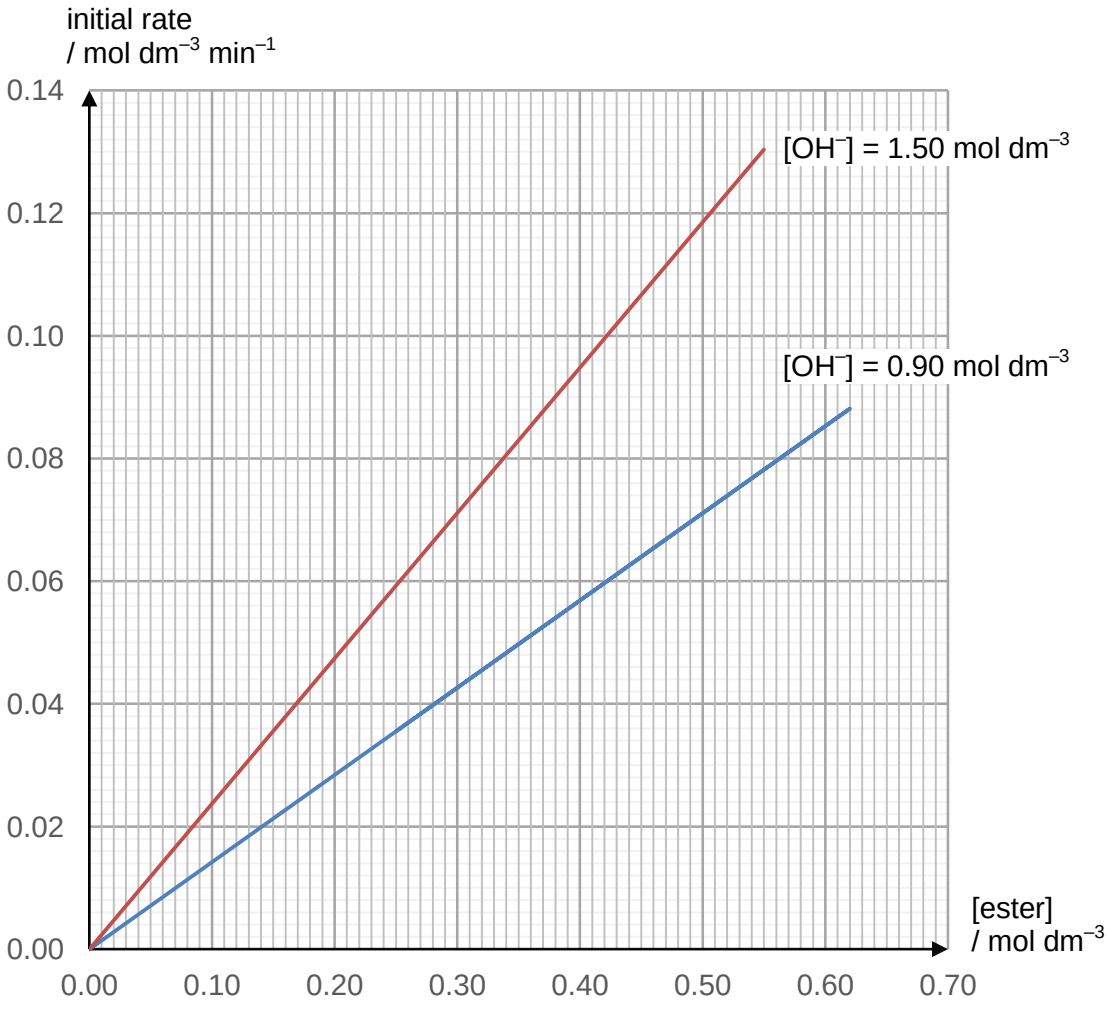


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Fig. 3.1

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

……

……

……

……

……

……

……

……
[2]

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

……
[1]

(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]

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

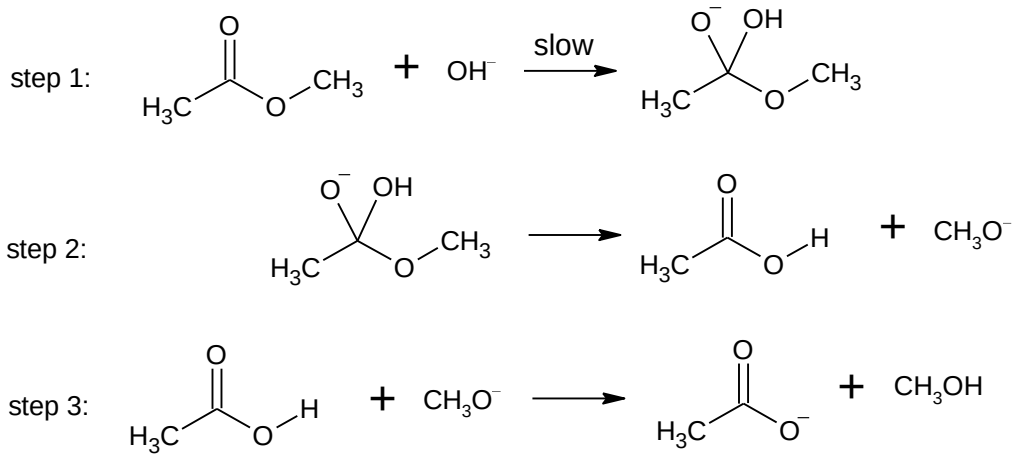


Fig. 3.2

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

……

……
[1]

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

……
[1]

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]

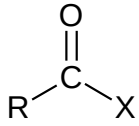
(v) State a reagent that can be used to show that carboxylic acid is a stronger acid than alcohol. Describe the observation in each case.

reagent ……

observation for carboxylic acid	observation for alcohol

[2]

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.

hydrolysis of esters ……..

hydrolysis of acid chlorides ……...
[1]

(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]

[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.

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……

……

……

……

……

……

…… [3]

(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} HC*l*(aq).

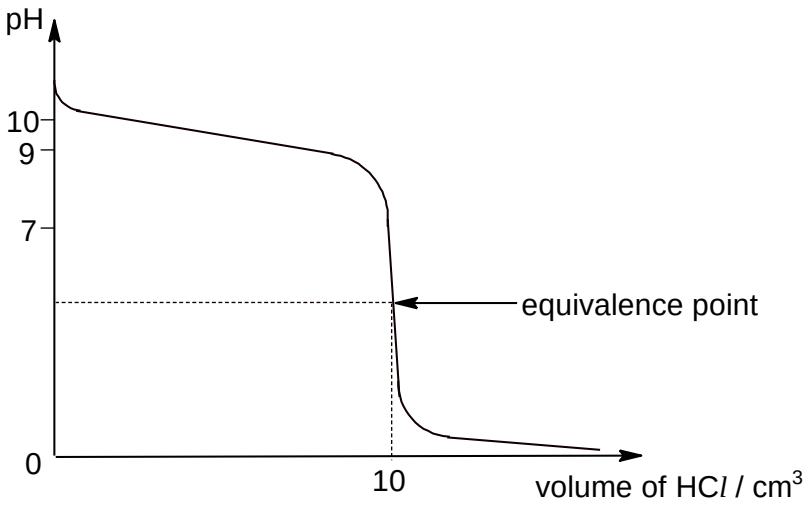


Fig. 4.1

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

……
[1]

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

……

……

……
[1]

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

……

……

……
[1]

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

[2]

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

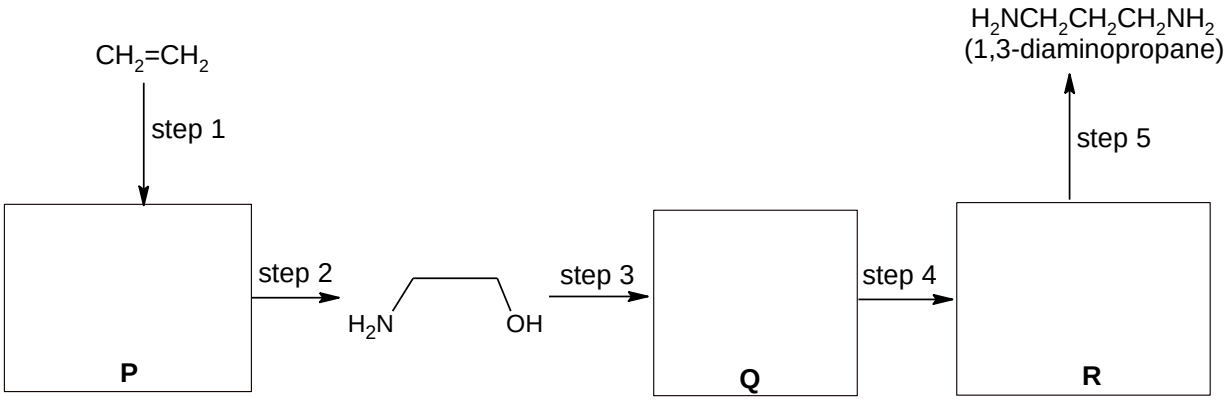


Fig. 4.2

(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.

step	reagents and conditions
2	
4	
5	

[3]

[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]

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

……
[1]

(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]

(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]

(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.

……

……

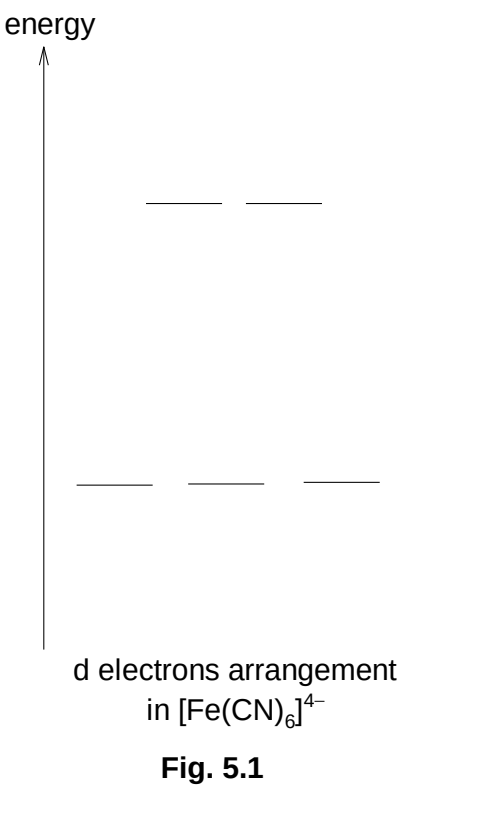
……
[1]

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

……
[1]

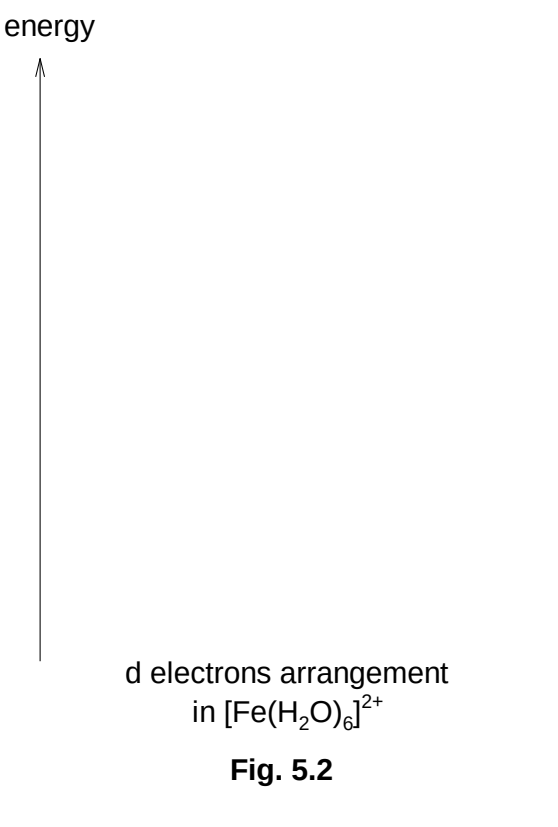
(iii) Using your answer in **(b)(i)** and **(ii)**, complete the diagram in Fig. 5.1 to show how the d electrons in the octahedral $[Fe(CN)_6]^{4-}$ complex are arranged in the five non−degenerate d−orbitals.

[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]

(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.

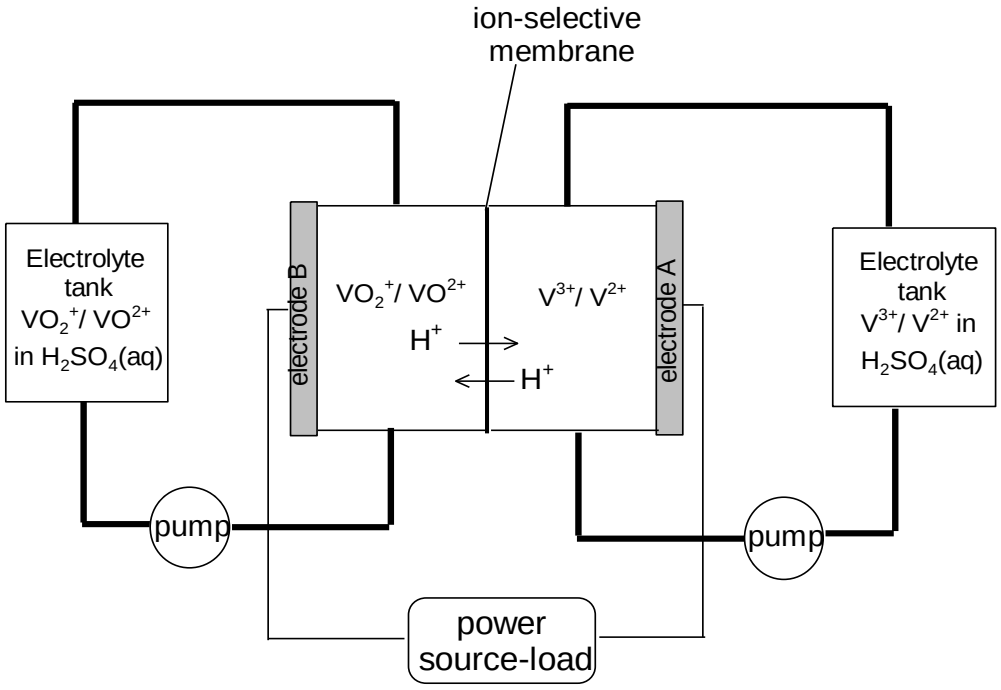


Fig. 5.3

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

Table 5.3

electrode	polarity of electrode	equation of reaction taking place during discharge
A		

B		

[2]

(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]

(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.

……

……

……

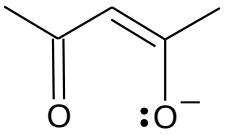
……

……

……
[2]

(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]

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

…… [1]

(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]

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

Oxidation state of vanadium in solution **Q** ……

Reducing gas **R** …….... [2]

[Total: 25]