

Answer **all** the questions.

- 1 Born–Haber cycles provide a model that chemists use to determine unknown enthalpy changes from known enthalpy changes. In this question, you will use a Born–Haber cycle to determine an enthalpy change of hydration.

- (a) Magnesium chloride has a lattice enthalpy of $-2493 \text{ kJ mol}^{-1}$.

Define in words the term *lattice enthalpy*.

.....

.....

.....

..... [2]

- (b) The table below shows the enthalpy changes that are needed to determine the enthalpy change of hydration of magnesium ions.

enthalpy change	energy/ kJ mol^{-1}
lattice enthalpy of magnesium chloride	-2493
enthalpy change of solution of magnesium chloride	-154
enthalpy change of hydration of chloride ions	-363

- (i) Why is the enthalpy change of hydration of chloride ions exothermic?

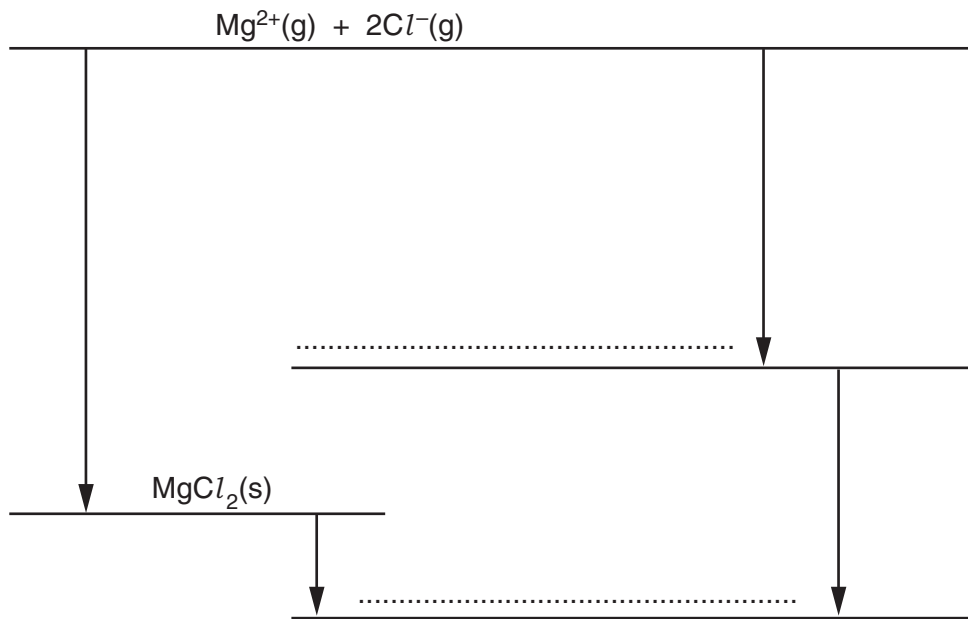
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.....

..... [1]

- (ii) In this part, you will use the Born–Haber cycle to determine the enthalpy change of hydration of magnesium ions.

On the two dotted lines, add the species present, including state symbols.



[2]

- (iii) Calculate the enthalpy change of hydration of magnesium ions.

answer = kJ mol^{-1} [2]

- (c) The enthalpy change of hydration of magnesium ions is more exothermic than the enthalpy change of hydration of calcium ions.

Explain why.

.....

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.....

.....

..... [2]

[Total: 9]

(c) An industrial chemist carries out some research into the $\text{NO}/\text{O}_2/\text{NO}_2$ equilibrium used in **Stage 2** of the manufacture of nitric acid.

- The chemist mixes together 0.80 mol $\text{NO}(\text{g})$ and 0.70 mol of $\text{O}_2(\text{g})$ in a container with a volume of 2.0 dm^3 .
- The chemist heats the mixture and allows it to stand at constant temperature to reach equilibrium.
The container is kept under pressure so that the total volume is maintained at 2.0 dm^3 .
- At equilibrium, 75% of the NO has reacted.

(i) Write an expression for K_c for this equilibrium.

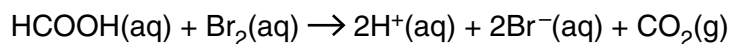
[1]

(ii) Calculate the equilibrium constant, K_c , including units, for this equilibrium.

$K_c = \dots\dots\dots$ units $\dots\dots\dots$ [5]

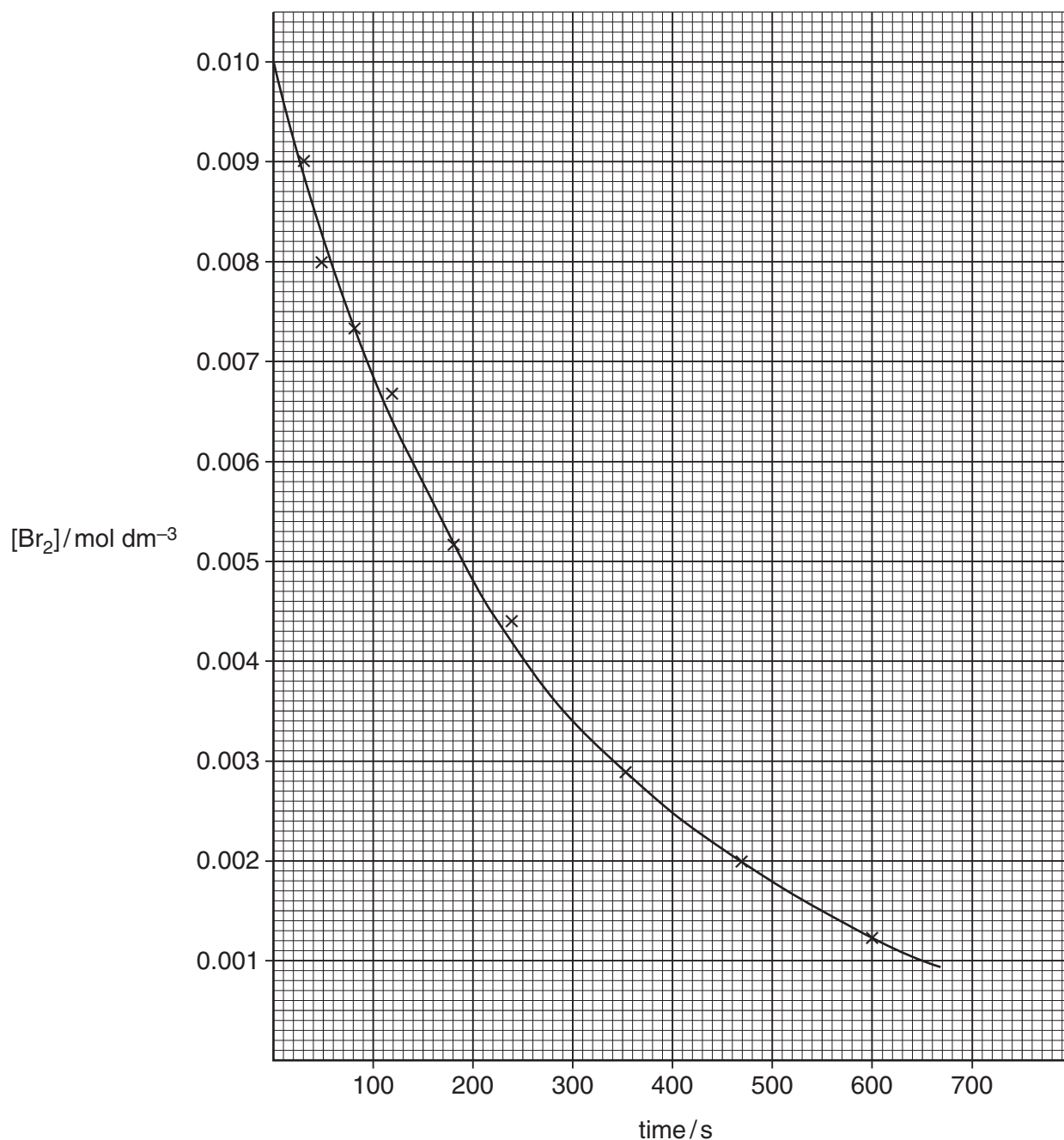
[Total: 11]

- 3 In aqueous solution, methanoic acid, HCOOH , reacts with bromine, Br_2 .



A student carried out an investigation on the rate of this reaction. The student used a large excess of methanoic acid which ensured that its concentration was effectively constant throughout. During the reaction, bromine is used up and its orange colour becomes less intense. The intensity of the bromine colour can be measured with a colorimeter to give the bromine concentration.

The graph below was plotted from the experimental results.



- 4 Chemists and biochemists use pK_a values to compare the strengths of different acids. pK_a is a more convenient way of comparing acid strengths than K_a values.

pK_a values of several naturally occurring Brønsted–Lowry acids are shown in **Table 4.1** below.

common name and source	systematic name	structural formula	pK_a (at 25°C)
benzoic acid (from bark resin)	benzenecarboxylic acid	C_6H_5COOH	4.19
acetic acid (from vinegar)	ethanoic acid	CH_3COOH	4.76
pyruvic acid (formed during metabolism)	2-oxopropanoic acid	$CH_3COCOOH$	2.39
lactic acid (from milk)	2-hydroxypropanoic acid	$CH_3CHOHCOOH$	3.86

Table 4.1

- (a) (i) What is meant by the term *Brønsted–Lowry acid*?

..... [1]

- (ii) What is meant by the *strength* of an acid?

In your answer, include an equation for one of the acids in **Table 4.1**.

.....

 [2]

- (iii) Place the four acids in **Table 4.1** in order of increasing strength.

weakest acid
 ↓

 strongest acid [1]

- (iv) Aqueous benzoic acid was mixed with aqueous lactic acid. An equilibrium mixture was formed containing conjugate acid–base pairs.

Complete the equilibrium below to show the components in the equilibrium mixture.



(b) Aqueous pyruvic acid was reacted with an aqueous solution of calcium hydroxide.

(i) Write an equation for this reaction.

..... [1]

(ii) Write an ionic equation for this reaction.

..... [1]

(c) The pH of an acid solution can be calculated from its pK_a value.

Calculate the pH of a $0.0150 \text{ mol dm}^{-3}$ solution of pyruvic acid at 25°C .

Show **all** your working.

Give the pH to **two** decimal places.

pH = [4]

(d) Oxalic acid (ethanedioic acid), $C_2H_2O_4$, is present in the leaves of rhubarb plants. Oxalic acid has two dissociations with $pK_a = 1.23$ and $pK_a = 4.19$.

(i) Draw the structure of oxalic acid.

[1]

(ii) Predict the equations that give rise to each dissociation.

$$pK_a = 1.23$$

$$pK_a = 4.19$$

[2]

(e) Acid buffers are used to give many sweets their 'magic tang'. A sweet manufacturer carried out tasting tests with consumers and identified the acid taste that gives the 'magic tang' to a sweet.

The manufacturer felt sure that sweets with the 'magic tang' would sell better. He asked the company's chemists to identify the chemicals needed to give the required taste. The chemists' findings would be an important factor in the success of the sweets.

The team of chemists identified that a pH of 3.55 was required and they worked to develop a buffer at this pH.

The chemists decided to use one of the acids in **Table 4.1** (page 8) and a salt of the acid to prepare this buffer.

- Deduce the chemicals required by the chemists to prepare this buffer.
- Calculate the relative concentrations of the acid and its salt which the chemist needed to make this buffer.
- Comment on the validity of the prediction that the pH of the sweet would give the sweets the 'magic tang'.

- 5 Chemists use three energy terms, enthalpy, entropy and free energy, to help them make predictions about whether reactions may take place.

(a) The table below shows five processes. Each process has either an increase in entropy or a decrease in entropy.

For each process, tick (✓) the appropriate box.

process		increase in entropy	decrease in entropy
A	$C_2H_5OH(l) \rightarrow C_2H_5OH(g)$		
B	$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$		
C	$NH_4Cl(s) + aq \rightarrow NH_4Cl(aq)$		
D	$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$		
E	$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$		

[2]

(b) At 1 atm (101 kPa) pressure, ice melts into water at 0°C.

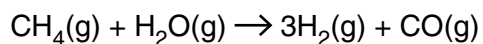
Complete the table below using the symbols '+', '-' or '0' to show the sign of ΔH and ΔS for the melting of ice at 0°C and 1 atm.

For each sign, explain your reasoning.

energy change	sign +, - or 0	reasoning
ΔH		
ΔS		

[2]

- (c) Much of the hydrogen required by industry is produced by reacting natural gas with steam:



Standard entropies are given in the table below.

substance	$\text{CH}_4(\text{g})$	$\text{H}_2\text{O}(\text{g})$	$\text{H}_2(\text{g})$	$\text{CO}(\text{g})$
$S^\ominus/\text{J K}^{-1}\text{ mol}^{-1}$	186	189	131	198

- (i) Calculate the standard entropy change, in $\text{J K}^{-1}\text{ mol}^{-1}$, for this reaction of natural gas with steam.

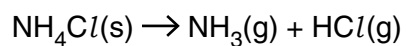
$$\Delta S^\ominus = \dots\dots\dots \text{J K}^{-1}\text{ mol}^{-1} \quad [2]$$

- (ii) State **two** large-scale uses for the hydrogen produced.

1.

2. [1]

- (d) Ammonium chloride, NH_4Cl , can dissociate to form ammonia, NH_3 , and hydrogen chloride, HCl .



At 298 K, $\Delta H = +176 \text{ kJ mol}^{-1}$ and $\Delta G = +91.2 \text{ kJ mol}^{-1}$.

- Calculate ΔG for this reaction at 1000 K.
- Hence show whether this reaction takes place spontaneously at 1000 K.

Show **all** your working.

$\Delta G = \dots\dots\dots \text{ kJ mol}^{-1}$ [4]

[Total: 11]

15
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TURN OVER FOR QUESTIONS 6, 7 AND 8

- (b) A student dissolves nickel(II) sulfate in water. A green solution forms containing the complex ion $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

The student then reacts separate portions of the green solution of nickel(II) sulfate as outlined below.

- Concentrated hydrochloric acid is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a lime-green colour and contains the four-coordinate complex ion **A**.
 - Aqueous sodium hydroxide is added to the green solution of nickel(II) sulfate. A pale-green precipitate **B** forms.
 - Concentrated aqueous ammonia is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a violet colour and contains the complex ion **C**.
C has a molar mass of 160.7 g mol^{-1} .
- (i) Draw a 3-D diagram for the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ion.
Show a value for the bond angles on your diagram.

[2]

- (ii) Suggest the formulae of **A** and **B**.

A

B [2]

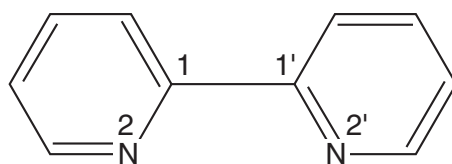
- (iii) Deduce the formula of **C**.

C [1]

- (iv) Write an equation for the formation of **C** from $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

..... [2]

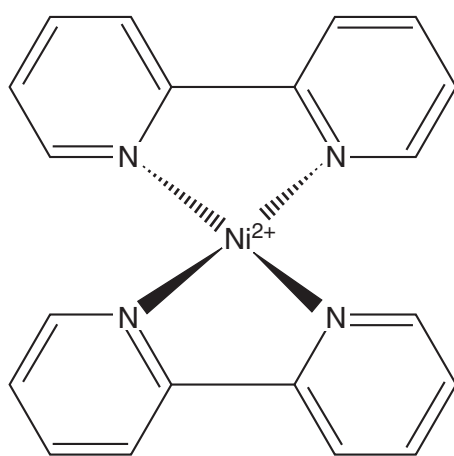
- (c) 2,2'-Bipyridine (or 'bipy') is a bidentate ligand that forms complexes with many transition metals. The structure of 2,2'-bipyridine is shown below.



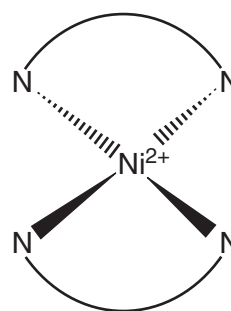
2,2'-bipyridine

In the naming of bipyridines, the numbering starts at the carbon atom that links to the other ring.

2,2'-Bipyridine forms a complex, $[\text{Ni}(\text{bipy})_2]^{2+}$. The structure of $[\text{Ni}(\text{bipy})_2]^{2+}$ is shown in Fig 6.1 below.



structure



simplified diagram



Fig 6.1

- (i) What is the molecular formula of 2,2'-bipyridine?

..... [1]

- (ii) What is the coordination number of the $[\text{Ni}(\text{bipy})_2]^{2+}$ complex ion?

..... [1]

- (iii) 2,2'-Bipyridine forms a complex with the transition metal ruthenium with the formula $[\text{Ru}(\text{bipy})_3]^{2+}$. This complex exists as two stereoisomers.

Draw 3-D diagrams to predict the structures for these stereoisomers of $[\text{Ru}(\text{bipy})_3]^{2+}$. You can represent the 2,2'-bipyridine ligands as in the simplified diagram for $[\text{Ni}(\text{bipy})_2]^{2+}$ in **Fig 6.1**.

[2]

- (iv) 4,4'-Bipyridine (4,4'-bipy) can also form complexes with transition metal ions. Because of its structure, 4,4'-bipyridine can bridge between metal ions to form 'coordination polymers'. For example, nickel(II) can form a coordination polymer with 4,4'-bipyridine containing $\{[\text{Ni}(\text{H}_2\text{O})_4(4,4'\text{-bipy})]^{2+}\}_n$ chains.

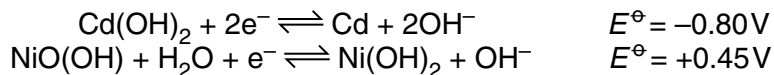
Draw a 3-D diagram to predict the repeat unit in this coordination polymer of nickel(II). Your diagram should show the complete structure of 4,4'-bipyridine and all coordinate bonds.

[3]

[Total: 21]

- 7 Nickel–cadmium cells (NiCd cells) are much used as rechargeable storage cells. NiCd cells have been a popular choice for many electrical and electronic applications because they are very durable, reliable, easy-to-use and economical.

The electrolyte in NiCd cells is aqueous KOH. The standard electrode potentials for the redox systems that take place in NiCd cells are shown below.



- (a) Define the term *standard electrode potential*, including all standard conditions in your answer.

.....

.....

.....

.....

..... [2]

- (b) What is the standard cell potential of a NiCd cell?

answer = V [1]

- (c) When a NiCd cell is being used for electrical energy, it is being discharged.

- (i) Construct the overall cell reaction that takes place during discharge of a NiCd cell.

.....

.....

..... [2]

- (ii) Using oxidation numbers, show the species that have been oxidised and reduced during discharge of a NiCd cell.

oxidation

.....

reduction

..... [2]

(d) NiCd cells are recharged using a battery charger.

(i) Suggest the reactions that take place in the NiCd cell during the recharging process.

.....
..... [1]

(ii) As the cell approaches full charge, the aqueous KOH electrolyte starts to decompose, forming hydrogen gas at one electrode and oxygen gas at the other electrode.

Predict half-equations that might take place at each electrode for the decomposition of the electrolyte to form hydrogen and oxygen.

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..... [2]

[Total: 10]

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