OCR
RECOGNISING ACHIEVEMENT

ADVANCED GCE
CHEMISTRY A
Equilibria, Energetics and Elements

F325

Candidates answer on the question paper.

OCR Supplied Materials:
- *Data Sheet for Chemistry A* (inserted)

Other Materials Required:
- Scientific calculator

Monday 31 January 2011
Morning

Duration: 1 hour 45 minutes

OCE/23216

Candidate forename	Max	Candidate surname	

Centre number						Candidate number				

INSTRUCTIONS TO CANDIDATES

- The insert will be found in the centre of this document.
- Write your name, centre number and candidate number in the boxes above. Please write clearly and in capital letters.
- Use black ink. Pencil may be used for graphs and diagrams only.
- Read each question carefully. Make sure you know what you have to do before starting your answer.
- Write your answer to each question in the space provided. If additional space is required, you should use the lined pages at the end of this booklet. The question number(s) must be clearly shown.
- Answer **all** the questions.
- Do **not** write in the bar codes.

INFORMATION FOR CANDIDATES

- The number of marks is given in brackets **[ ]** at the end of each question or part question.
- Where you see this icon you will be awarded marks for the quality of written communication in your answer.

  This means for example you should:
  - ensure that text is legible and that spelling, punctuation and grammar are accurate so that meaning is clear;
  - organise information clearly and coherently, using specialist vocabulary when appropriate.
- You may use a scientific calculator.
- A copy of the *Data Sheet for Chemistry A* is provided as an insert with this question paper.
- You are advised to show all the steps in any calculations.
- The total number of marks for this paper is **100**.
- This document consists of **24** pages. Any blank pages are indicated.

Answer **all** the questions.

1 Hydrogen, H_2, reacts with nitrogen monoxide, NO, as shown in the equation below.

$$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$$

A chemist carries out a series of experiments and determines the rate equation for this reaction:

$$\text{rate} = k[H_2(g)][NO(g)]^2$$

(a) In one of the experiments, the chemist reacts together:

- 1.2×10^{-2} mol dm^{-3} $H_2(g)$
- 6.0×10^{-3} mol dm^{-3} NO(g)

The initial rate of this reaction is 3.6×10^{-2} mol dm^{-3} s^{-1}.

Calculate the rate constant, k, for this reaction. State the units, if any.

$3.6\times10^{-2} = k \times 1.2\times10^{-2} \times (6\times10^{-3})^2$

$\frac{3.6\times10^{-2}}{4.32\times10^{-7}} = k$

$k = 83333.3$

$k = \frac{[\ ]\ s^{-1}}{[\ ][\ ][\ ]}$

$mol^{-2}\ dm^{+6}\ s^{-1}$

$k =$ ..... units ..... [3]

(b) Predict what would happen to the initial rate of reaction for the following changes in concentrations.

(i) The concentration of $H_2(g)$ is doubled.

RATE DOUBLES

..... [1]

(ii) The concentration of NO(g) is halved.

RATE 1/4 'S

..... [1]

(iii) The concentrations of $H_2(g)$ and NO(g) are **both** increased by four times.

4×4^2

$= 64$

..... [1]

(c) The chemist carries out the reaction between hydrogen and nitrogen monoxide at a higher pressure.

(i) Explain, with a reason, what happens to the initial rate of reaction.

↑ PRESSURE ↓ VOLUME, ↑ CONC^{n}
MORE PARTICLES PER VOL
MORE COLLISION FREQUENCY
FASTER RATE [1]

(ii) State what happens to the rate constant.

NO CHANGE [1]

(d) This overall reaction between hydrogen and nitrogen monoxide takes place by a two-step mechanism. The first step is much slower than the second step.

Suggest a possible two-step mechanism for the overall reaction.

step 1: $H_2 + 2NO \longrightarrow N_2O + H_2O$

step 2: $H_2 + N_2O \longrightarrow N_2 + H_2O$ [2]

[Total: 10]

2 Iron and platinum are transition elements. They both form ions that combine with ligands to form complex ions. Some of these complexes are important in biological systems.

(a) Complete the electron structures of:

an atom of Fe: $1s^2 2s^2 2p^6$ ..... $3s^2 3p^6 3d^6 4s^2$ .....

an ion of Fe^{2+}: $1s^2 2s^2 2p^6$ ..... $3s^2 3p^6 3d^6$ ..... [2]

(b) State **one** property of Fe^{2+}, other than the ability to form complex ions, which is typical of an ion of a transition element.

..... CATALYST .....

..... [1]

(c) Aqueous iron(II) sulfate takes part in redox reactions.

Using oxidation numbers, show that both reduction and oxidation have taken place in the redox reaction of aqueous iron(II) sulfate shown below.

$$6FeSO_4 + 7H_2SO_4 + Na_2Cr_2O_7 \rightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O$$

2+ 3+

..... OXIDATION : Fe +2 → +3 .....

.....

..... REDUCTION : Cr +6 → +3 .....

.....

..... [2]

(d) Hexaaquairon(II) ions, $[Fe(H_2O)_6]^{2+}$, take part in a ligand substitution reaction with ammonia.

$$[Fe(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Fe(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$

Write an expression for the stability constant, K_{stab}, for this equilibrium.

$$K_{STAB} = \frac{[[Fe(NH_3)_6]^{2+}]}{[[Fe(H_2O)_6]^{2+}][NH_3]^6}$$

[2]

(e) Haemoglobin is a complex of iron(II).

(i) Explain how ligand substitutions allow haemoglobin to transport oxygen in the blood.

O_2 MOLECULE FORMS DATIVE COVALENT BOND WITH Fe^{2+}

BOND BREAKS + O_2 RELEASED WHEN REDUCED

[2]

(ii) In the presence of carbon monoxide, less oxygen is transported in the blood.

In terms of stability constants, suggest why.

COMPLEX ION WITH CO HAS MUCH HIGHER K_{STAB} THAN COMPLEX ION WITH O_2

∴ D.C. BOND IS STRONGER BETWEEN CO + TM THAN O_2 + TM.

[2]

(f) Platin, $Pt(NH_3)_2Cl_2$, is a complex of platinum(II) that has two stereoisomers. One of these stereoisomers is used in medicine.

(i) Platin is a neutral complex.

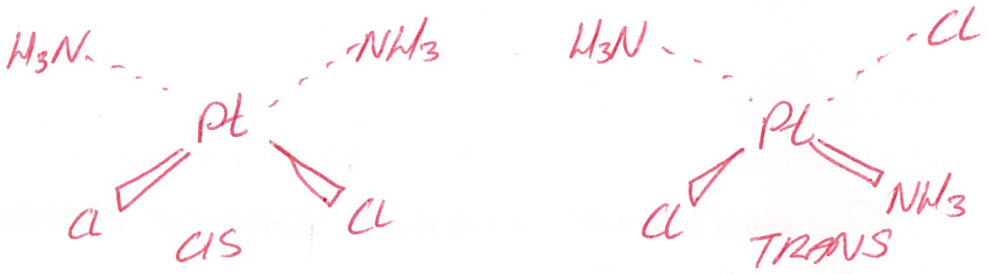
Explain why platin is neutral.

$Cl^{1-} \times 2 = -1$

$Pt + 2NH_3 + 2Cl^- = 0$

$Pt : +2$ [1]

(ii) Draw diagrams of the two stereoisomers of platin and describe its bonding.



LIGAND DONATES LONE PAIR OF e's FORMING A DATIVE COVALENT BOND WITH Pt. [3]

(iii) Describe the action of platin in the treatment of cancer patients.

- BINDS TO FAST GROWING CELLS ie CANCEROUS
- STOPS REPLICATION. [1]

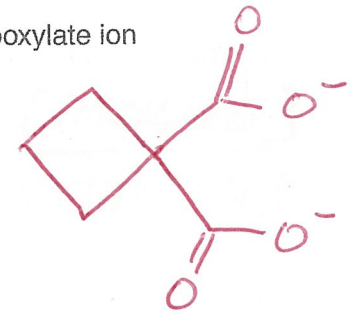
(g) The use of platin in medicine can cause unpleasant side effects for patients.

In the search for alternatives, chemists often start with the current drug and modify its properties by chemically changing some of the groups.

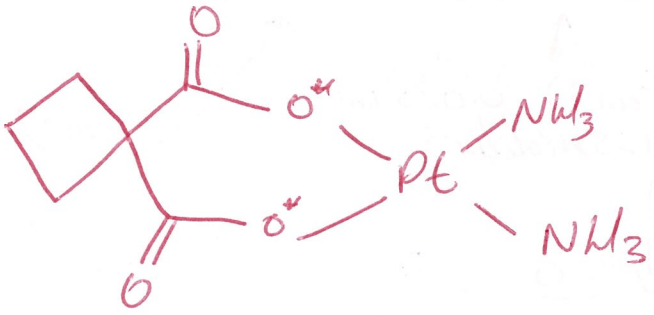
A recent discovery is a drug called carboplatin. The structure of carboplatin is similar to platin except that a single 1,1-cyclobutanedicarboxylate ion replaces the two chloride ligands in the structure of platin.

Draw the structures of,

- the 1,1-cyclobutanedicarboxylate ion
- carboplatin.



1,1-cyclobutanedicarboxylate ion



carboplatin

[2]

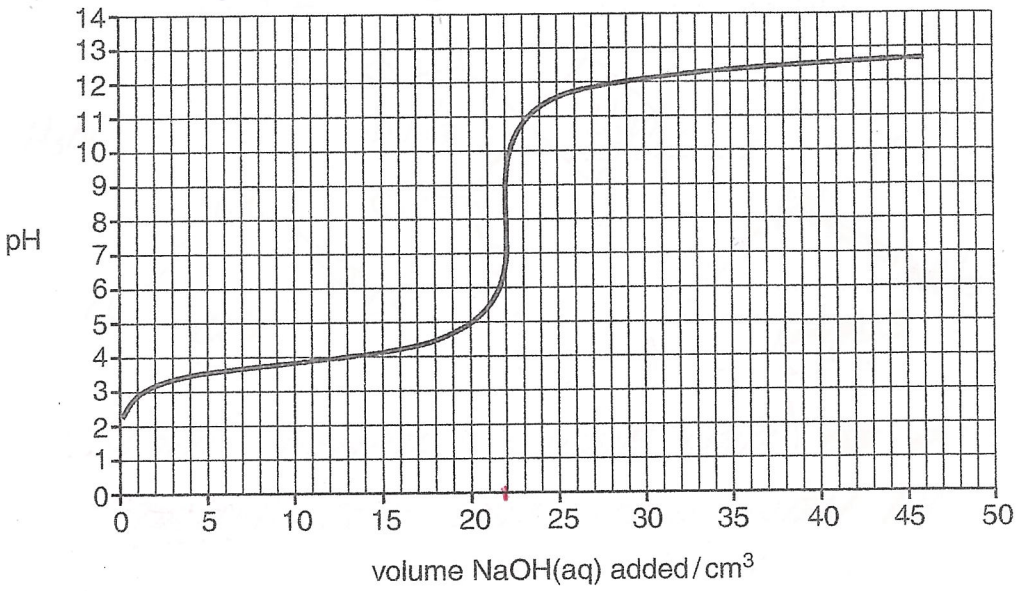
[Total: 18]

3 Glycolic acid, $HOCH_2COOH$, and thioglycolic acid, $HSCH_2COOH$, are weak acids.

(a) Glycolic acid reacts with bases, such as aqueous sodium hydroxide, NaOH(aq), to form salts.

A student pipetted 25.0 cm^3 of 0.125 mol dm^{-3} glycolic acid into a conical flask. The student added NaOH(aq) from a burette. A pH meter and data logger were used to measure continuously the pH of the contents of the conical flask.

The pH curve that the student obtained is shown below.



1 mol of glycolic acid reacts with 1 mol of sodium hydroxide.

(i) Write the equation for the reaction that takes place in the titration.

$HOCH_2COOH + NaOH \rightarrow HOCH_2COO^-Na^+ + H_2O$ [1]

(ii) Determine the concentration, in mol dm^{-3}, of the NaOH.

(25 cm^3) 0.025 dm^3
0.125 Mol dm^{-3}

(22 cm^3) 0.022 dm^3

MOLES = C × V
= 0.125 × 0.025
= 0.003125

1:1

0.003125

$C = \frac{MOLES}{V} = \frac{0.003125}{0.022}$
= 0.142

concentration of NaOH = 0.142 mol dm^{-3} [2]

(iii) The student decided to carry out this titration using an acid–base indicator.

What important factor does the student need to consider when deciding on the most suitable indicator to use for this titration?

INDICATOR MUST CHANGE COLOUR IN THE VERTICAL SECTION ON PH CURVE.

..... [1]

(b) The 0.125 mol dm^{-3} glycolic acid had a pH of 2.37.

(i) What is the expression for the acid dissociation constant, K_a, of glycolic acid?

$$K_a = \frac{[H^+][HOCH_2COO^-]}{[HOCH_2COOH]}$$

[1]

(ii) Calculate K_a for glycolic acid.

$$K_a = \frac{[0.00427]^2}{[0.125]}$$

$$= 1.46 \times 10^{-4}$$

$[H^+] = 10^{-pH}$

$= 0.00427$

$[H^+] = [A^-]$

K_a = 1.46×10^{-4} units $mol\,dm^{-3}$ [3]

(iii) Calculate the percentage molar dissociation of the glycolic acid.

$$\% = \frac{[H^+]}{[HOCH_2COOH]} \times 100 = \frac{0.00427}{0.125} \times 100$$

percentage dissociation = 3.4 % [1]

(c) A buffer of glycolic acid and ammonium glycolate is used in a facial cleanser.

Explain, using equations,

A) • how a solution containing glycolic acid and glycolate ions can act as a buffer
B) • how this buffer could be prepared from ammonia and glycolic acid.

In your answer you should explain how the equilibrium system allows the buffer solution to control the pH.

A) $HOCH_2COOH \rightleftharpoons H^+ + HOCH_2COO^-$

LARGE RESERVOIR LARGE RESERVOIR

ADDITION OF H^+

$\uparrow [H^+]$ EQ^M MOVES TO LHS IN ORDER TO REMOVE ADDED H^+.

pH MAINTAINED.

ADDITION OF OH^-

OH^- REACTS WITH H^+ ION $\rightarrow H_2O$

$\therefore [H^+]\downarrow$

EQ^M MOVES TO RHS TO REPLACE USED H^+ pH MAINTAINED

B) $HOCH_2COOH + NH_3 \rightarrow HOCH_2COO^- \; NH_4^+$

$\uparrow$

MUST BE IN EXCESS TO LEAVE A LARGE RESERVOIR

REACTION IS PARTIALLY NEUTRALISES ACID TO GIVE A LARGE RESERVOIR OF $HOCH_2COO^-$

[7]

(d) Ammonium thioglycolate, $HSCH_2COONH_4$, is the ammonium salt of thioglycolic acid, $HSCH_2COOH$.

When ammonium thioglycolate is dissolved in water, an acid–base equilibrium is set up. The equilibrium lies well to the left-hand side.

$$HSCH_2COO^-(aq) + NH_4^+(aq) \rightleftharpoons HSCH_2COOH(aq) + NH_3(aq)$$

BASE 1 ACID 2 ACID 1 BASE 2

In the spaces above,

- label one conjugate acid–base pair as '**Acid 1**' and '**Base 1**'
- label the other conjugate acid–base pair as '**Acid 2**' and '**Base 2**'. [2]

(e) Ammonium thioglycolate is used by hairdressers to perm hair.

Hair is a protein and its shape is largely the result of cross-linked disulfide bonds, –S–S–. The formula of the protein in hair can be represented as R–S–S–R.

Perming of hair involves two stages.

Stage 1

- Hair is first wound around curlers and a solution of ammonium thioglycolate is applied to the hair.
- In this process, each disulfide bond is broken by two thioglycolate ions to form two molecules containing thiol groups, –S–H, and one other product.

Stage 2

- After 15–30 minutes, the hair is rinsed with a weak solution of hydrogen peroxide, H_2O_2.
- The hydrogen peroxide reforms disulfide bonds that lock the hair in the shape of the curlers. The hair is now 'permed'.

Suggest equations for the two processes that take place during perming.
In your equations, use R–S–S–R to represent the protein in hair.

Stage 1

$$2\,HSCH_2COO^- + R\text{-}S\text{-}S\text{-}R \rightarrow$$

$$2\,R\text{-}SH + {}^-OOCCH_2\text{-}S\text{-}S\text{-}CH_2COO^-$$

Stage 2

$$H_2O_2 + 2R\text{-}SH \rightarrow R\text{-}S\text{-}S\text{-}R + 2H_2O$$

[2]

[Total: 20]

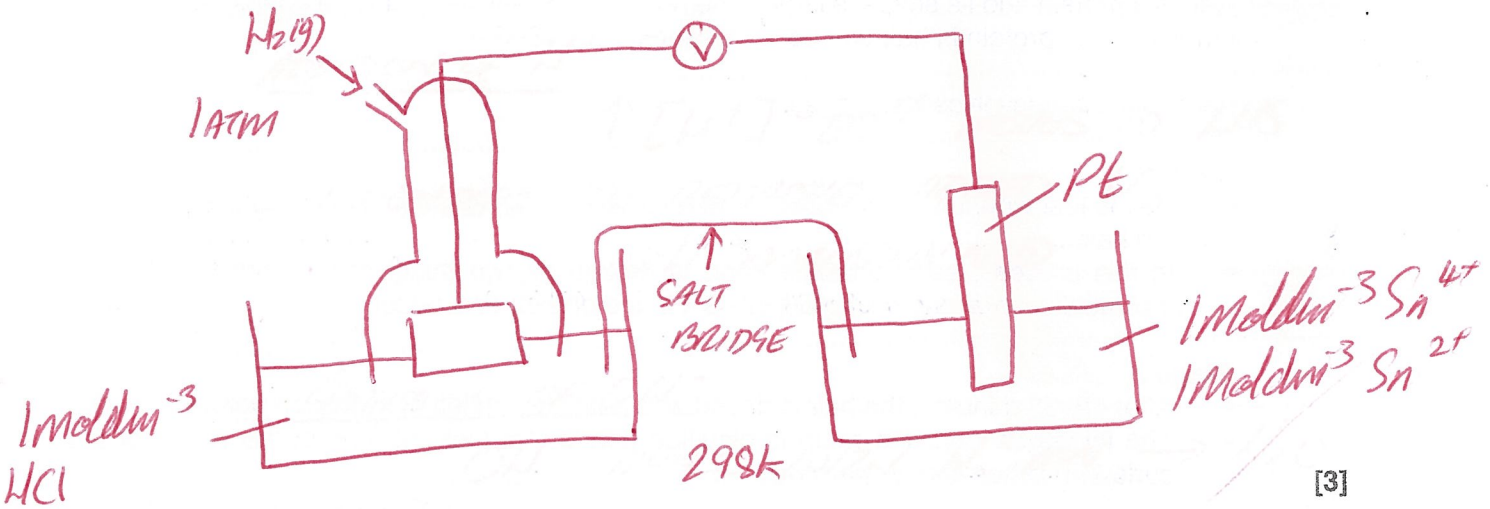
4 Redox reactions are used to generate electrical energy from electrochemical cells.

(a) **Table 4.1** shows three redox systems, and their standard redox potentials.

redox system	$E^{\ominus}$/V
$Cu^{+}(aq) + e^{-} \rightleftharpoons Cu(s)$	+0.52
$Cr^{3+}(aq) + 3e^{-} \rightleftharpoons Cr(s)$	−0.74
$Sn^{4+}(aq) + 2e^{-} \rightleftharpoons Sn^{2+}(aq)$	+0.15

Table 4.1

(i) Draw a labelled diagram to show how the standard electrode potential of a Sn^{4+}/Sn^{2+} redox system could be measured.



[3]

(ii) Using the information in **Table 4.1**, write equations for the reactions that are feasible.

Suggest **two** reasons why these reactions may **not** actually take place.

$2Cr + 3Sn^{4+} \longrightarrow 2Cr^{3+} + 3Sn^{2+}$

$Cr + 3Cu^{+} \longrightarrow Cr^{3+} + 3Cu$

$Sn^{2+} + 2Cu^{+} \longrightarrow Sn^{4+} + 2Cu$

CONDITIONS MAY BE NON-STANDARD IE NOT 1moldm^{-3}

HIGH ACTIVATION ENERGY

[5]

(b) Modern fuel cells are being developed as an alternative to the direct use of fossil fuels. The 'fuel' can be hydrogen but many other substances are being considered.
In a methanol fuel cell, the overall reaction is the combustion of methanol.

As with all fuel cells, the fuel (methanol) is supplied at one electrode and the oxidant (oxygen) at the other electrode.

Oxygen reacts at the negative electrode of a methanol fuel cell:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

(i) Write an equation for the complete combustion of methanol.

$CH_3OH + 1\frac{1}{2}O_2 \rightarrow CO_2 + 2H_2O$ [1]

(ii) Deduce the half-equation for the reaction that takes place at the positive electrode in a methanol fuel cell.

$CH_3OH + 1\frac{1}{2}O_2 \rightarrow CO_2 + 2H_2O$

$2H_2O \rightarrow O_2 + 4H^+$

$H_2O + CH_3OH \rightarrow CO_2 + 4H^+$ [1]

(iii) State **two** advantages of vehicles using fuel cells compared with the combustion of conventional fossil fuels.

LESS CO_2

GREATER EFFICIENCY

[2]

(iv) Suggest **one** advantage of using methanol, rather than hydrogen, in a fuel cell for vehicles. Justify your answer.

IT IS A LIQUID : EASIER TO STORE

[1]

[Total: 13]

5 Entropy changes are an important factor in determining the feasibility of reactions.

(a) You are provided with equations for four processes.

A $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
B $H_2O(l) \longrightarrow H_2O(g)$
C $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$
D $2C(s) + O_2(g) \longrightarrow 2CO(g)$

For each process, explain why ΔS has the sign shown below.

A: sign of ΔS: negative

reason for sign: (-)VE 3 → 2 MOLES OF GAS

B: sign of ΔS: positive

reason for sign: (+)VE l → g

C: sign of ΔS: negative

reason for sign: (-)VE g → l

D: sign of ΔS: positive

reason for sign: (+)VE s/g → g AND (3 → 2 MOLES) l → 2 MOLES GAS [4]

(b) Calcium oxide, CaO, is used to make cement. Calcium oxide is manufactured by the thermal decomposition of calcium carbonate.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad \Delta H = +178\,kJ\,mol^{-1}$$

Standard entropies of $CaCO_3(s)$, CaO(s) and $CO_2(g)$ are given in the table below.

substance	$CaCO_3(s)$	CaO(s)	$CO_2(g)$
S / J K^{-1}mol^{-1}	89	40	214

- Using the information in the table, show that the entropy change, ΔS, for the decomposition of calcium carbonate is 0.165 kJ K^{-1} mol^{-1}.
- Show that calcium carbonate is stable at room temperature (25 °C).
- Calculate the minimum temperature needed to decompose calcium carbonate.

Show all your working.

$\Delta S = S_p^\ominus - S_R^\ominus$

$= (40 + 214) - 89$

$= 165\ J\,Mol^{-1}\,K^{-1}$

$= 0.165\ kJ\,Mol^{-1}\,K^{-1}$

$25°C = 298K$

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

$= 178 - (298 \times 0.165)$

$= 178 - 49.17$

$= 128.8\ kJ\,Mol^{-1}$

$\Delta G > 0 \therefore$ IS NOT FEASIBLE

$\therefore$ STABLE

[7]

[Total: 11]

6 The dissociation of water is a reversible reaction.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The ionic product of water, K_w, measures the extent of dissociation of water.

K_w varies with temperature. Therefore, it is always important to quote the temperature at which measurements are being taken.

Fig. 6.1 shows the variation of K_w between 0 °C and 60 °C.

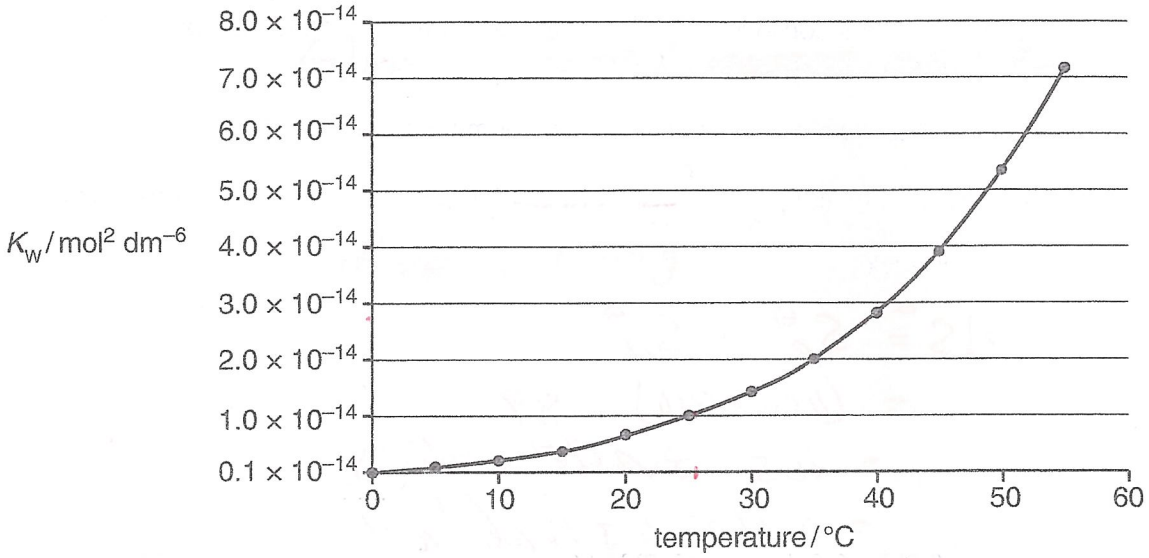


Fig. 6.1

(a) (i) Write the expression for K_w.

$K_w = [H^+][OH^-]$ [1]

(ii) Calculate the $OH^-(aq)$ concentration in an aqueous solution of hydrochloric acid with a pH of 4.37 at 25 °C.

Give your answer to **two** significant figures.

$[H^+] = 10^{-4.37}$

$= 4.27 \times 10^{-5}$

$[OH^-] = \dfrac{1 \times 10^{-14}}{4.27 \times 10^{-5}}$

$=$

OH^- concentration = 2.34×10^{-10} mol dm^{-3} [2]

(b) (i) Using **Fig. 6.1**, explain whether the dissociation of water is an exothermic or endothermic process.

ENDOTHERMIC

K_w / DISSOCIATION INCREASES WITH AN INCREASE IN TEMP.

..... [1]

(ii) Determine the pH of pure water at body temperature, 37 °C.

$K_w = 2.6 \times 10^{-14}$

$[H^+]^2 = 2.6 \times 10^{-14}$

$[H^+] = \sqrt{2.6 \times 10^{-14}}$

$= 1.6 \times 10^{-7}$

$pH = -\log [H^+] = -\log (1.6 \times 10^{-7})$

pH = 6.8 [3]

(iii) Many experimental measurements use published data, such as K_w, measured at 25 °C. Often these measurements have been taken at different temperatures, especially in experimental work carried out at body temperature.

What is the consequence of this for published scientific work?

INNACURATE AS K_w VARIES WITH TEMP

..... [1]

(c) The reverse reaction of the dissociation of water is called neutralisation.

Plan an experiment that a student could carry out to measure the enthalpy change of neutralisation.

In your answer you should explain how the enthalpy change of neutralisation could be calculated from the experimental results.

0.1M NaOH + 0.1M HCl

ADD 25cm^3 OF NaOH TO 25cm^3 OF HCl

TAKE INITIAL + FINAL TEMP.

$Q = m \times c \times \Delta T$ MOLES = $C \times V$

$\Delta H = \frac{Q/1000}{\text{MOLES}}$

[6]

(d) When dissolved in water, the enthalpy change of solution of the salt potassium fluoride, KF, is $-15\,kJ\,mol^{-1}$.

The salt rubidium fluoride, RbF, has an enthalpy change of solution in water of $-24\,kJ\,mol^{-1}$.

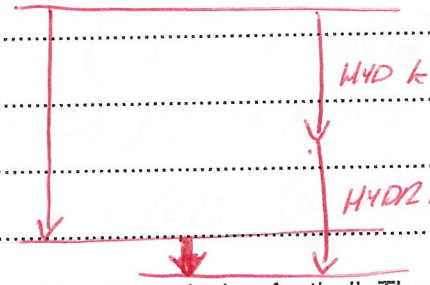
Suggest reasons for the difference between the enthalpy changes of solution of KF and RbF.

K^+ SMALLER ION

∴ LATTICE ENTHALPY WILL BE MORE (-)VE

K^+ HYDRATION ENTHALPY IS MORE (-)VE

LATTICE ENTHALPY BECOMES MORE (-)VE THAN HYDRATION ENTHALPY



[4]

(e) A student hurt his ankle whilst playing football. The physiotherapist applied a cold pack to soothe the pain.

The cold pack is made of two separated compartments, one containing ammonium nitrate crystals, NH_4NO_3, the other containing water. The pack is activated by breaking the barrier between the two compartments. The crystals dissolve spontaneously in the water causing the temperature of the pack to drop.

Explain why ammonium nitrate in the cold pack dissolves spontaneously in water even though this process is endothermic.

SOLID → aq INCREASES DISORDER

FOR ΔG = (-)VE $T\Delta S > \Delta H$

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

(+)VE ↑

∴ MORE (+)VE

[2]

[Total: 20]

7 The Dissolved Oxygen Concentration (DOC) in rivers and lakes is important for aquatic life. If the DOC falls below 5 mg dm^{-3}, most species of fish cannot survive.

Environmental chemists can determine the DOC in water using the procedure below.

- A sample of river water is shaken with aqueous Mn^{2+} and aqueous alkali. The dissolved oxygen oxidises the Mn^{2+} to Mn^{3+}, forming a pale brown precipitate of $Mn(OH)_3$.

$$O_2(aq) + 4Mn^{2+}(aq) + 8OH^-(aq) + 2H_2O(l) \longrightarrow 4Mn(OH)_3(s)$$

- The $Mn(OH)_3$ precipitate is then reacted with an excess of aqueous potassium iodide, which is oxidised to iodine, I_2.

$$2Mn(OH)_3(s) + 2I^-(aq) \longrightarrow I_2(aq) + 2Mn(OH)_2(s) + 2OH^-(aq)$$

- The iodine formed is then determined by titration with aqueous sodium thiosulfate, $Na_2S_2O_3(aq)$.

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

A 25.0 cm^3 sample of river water was analysed using the procedure above.

The titration required 24.6 cm^3 of 0.00100 mol dm^{-3} $Na_2S_2O_3(aq)$.

(a) (i) Calculate the DOC of the sample of river water, in mg dm^{-3}.

MOLES $S_2O_3^{2-}$ = $\frac{24.6 \times 0.001}{1000}$

= 2.46×10^{-5}

MOLES O_2 = $(\div 2, \times 2) \div 4$

= 6.15×10^{-6}

CONC = $\frac{\text{MOLES}}{\text{VOL}}$ = $\frac{6.15 \times 10^{-6}}{0.025}$

= 2.46×10^{-4}

CONC^{n} = $2.46 \times 10^{-4} \times 32$

= 7.872×10^{-3} g mol^{-1}

7.87

DOC = ... mg dm^{-3} [4]

(ii) Comment on whether there is enough dissolved oxygen in the river water for fish to survive.

≥ 5 : YES.

[1]

(b) The presence of nitrate(III) ions, NO_2^-, interferes with this method because NO_2^- ions can also oxidise iodide ions to iodine.

During the reaction, a colourless gas is produced with a molar mass of $30\,g\,mol^{-1}$.

(i) Predict the formula of the colourless gas.

NO

[1]

NO_2^-

(ii) Write an equation for the oxidation of aqueous iodide ions by aqueous nitrate(III) ions. Hydroxide ions are produced in this reaction.

$(I^- + NO_2^- \rightarrow OH^- + NO + I_2)$

$2I^- \rightarrow I_2 + 2e^-$

$NO_2^- \rightarrow NO \quad (\times 2)$

$2H_2O + 2NO_2^- + 2I^- \rightarrow I_2 + 2NO + 4OH^-$

[2]

[Total: 8]

END OF QUESTION PAPER