Monday 15 June 2015 – Afternoon
A2 GCE CHEMISTRY A
F325/01 Equilibria, Energetics and Elements

Candidates answer on the Question Paper.

OCR supplied materials:
• Data Sheet for Chemistry A (inserted)

Other materials required:
• Scientific calculator

Duration: 2 hours

Candidate forename

Candidate surname

Centre number

Candidate number

INSTRUCTIONS TO CANDIDATES
• The insert will be found inside this document.
• Write your name, centre number and candidate number in the boxes above. Please write clearly and in capital letters.
• Use black ink. HB pencil may be used for graphs and diagrams only.
• Answer all the questions.
• 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 page at the end of this booklet. The question number(s) must be clearly shown.
• 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.

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Turn over
Answer all the questions.

1. This question looks at properties of transition elements, ions and complexes.

(a) What is the oxidation number of Cr in the complex ion \([\text{CrOCl}_5]^2−\)?

(b) Write the equation for a reaction catalysed by a named transition element, compound or ion.

\[
\text{C}_6\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5 + \text{HCl}
\]

Catalyst: \(\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}\) [1]

(c) An octahedral complex ion \(\text{A}, \text{C}_9\text{H}_{30}\text{N}_6\text{Ni}^{3+}\), exists as two optical isomers.

In complex ion \(\text{A}, \text{Ni}^{3+}\) is bonded to three molecules of a bidentate ligand \(\text{B}\).

(i) State what is meant by a bidentate ligand.

\[\text{DONATES 2 PAIRS OF ELECTRONS TO FORM 2 DIATIVE COVALENT BONDS}\]

(ii) What is the molecular formula of the bidentate ligand \(\text{B}\)?

\[\text{(C}_9\text{H}_{30}\text{N}_6 \div 3 = ) \text{C}_3\text{H}_{10}\text{N}_2\]

(iii) Draw a possible structure for \(\text{B}\) and explain how \(\text{B}\) is able to act as a bidentate ligand.

\[
\text{CH}_2\text{CH}_2\text{CH}_2\text{N}=\text{N}\text{H}_2
\]

\[\text{EACH N HAS A LONE PAIR OF E'S TO FORM D.C. BOND}\]

(iv) What is the coordination number of complex ion \(\text{A}\)?

\[6\]
(v) Complete the 3-D diagrams of the shapes of the optical isomers of complex ion A.

You can show the bidentate ligand simply as

\[ \text{Ni} \]

You can show the bidentate ligand simply as

\[ \text{Ni} \]

\[ 3^+ \]

\[ 3^+ \]

(d) Describe the reactions of EITHER aqueous copper(II) ions OR aqueous cobalt(II) ions with:

- aqueous sodium hydroxide
- excess aqueous ammonia
- hydrochloric acid.

In your answer you should link observations with equations.

a) \( \text{Cu}^{2+} (aq) + 2\text{OH}^- (aq) \rightarrow \text{Cu(OH)}_2 (s) \) \( \checkmark \)  
   \( \text{blue ppt} \) \( \checkmark \)

b) \( [\text{Cu(H}_2\text{O)}_6]^{2+} + 4\text{NH}_3 \rightarrow [\text{Cu(NH}_3}_4]^{2+} \text{(blue soln)} \) \( \checkmark \)  
   \( \text{dark blue soln} \) \( \checkmark \)  
   \( + 4\text{H}_2\text{O} \)

c) \( [\text{Cu(H}_2\text{O)}_6]^{2+} + 4\text{H}^+ \rightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O} \) \( \checkmark \)  
   \( \text{blue soln} \) \( \checkmark \)  
   \( \text{yellow soln} \) \( \checkmark \)

[Total: 14]

Turn over
Hydrogen, H₂, reacts with nitrogen monoxide, NO, as shown below:

\[ 2\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \]

(a) The rate equation for this reaction is:

\[ \text{rate} = k[\text{H}_2(\text{g})][\text{NO}(\text{g})]^2 \]

The concentration of NO(g) is changed and a rate–concentration graph is plotted.

The chemist uses H₂(g) of concentration $2.0 \times 10^{-2} \text{mol dm}^{-3}$.

Using values from the graph, calculate the rate constant, \( k \), for this reaction.

Give your answer to two significant figures and in standard form.

Show your working.

\[ k = \frac{1}{[\text{H}_2][\text{NO}]}^2 \Rightarrow \frac{1}{[\text{H}_2][\text{NO}]} = \frac{6 \times 10^{-4}}{(2 \times 10^{-2})^2(6 \times 10^{-4})^2} \]

\[ k = 8.33 \times 10^4 \]

\[ k = 8.3 \times 10^4 \text{ units m}^{-2}\text{dm}^3\text{mol}^{-1}\text{s}^{-1} \]

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(b) A chemist investigates the effect of changing the concentration of $\text{H}_2(\text{g})$ on the initial reaction rate at two different temperatures.

The reaction is first order with respect to $\text{H}_2(\text{g})$.

(i) Using the axes below, sketch two graphs of the results.

Label the graphs as follows:
- **L** for the lower temperature
- **H** for the higher temperature.

![Graph showing initial rate vs. [H₂(g)] with L and H labels.]

*AX MUST START AT 0,0* [2]

(ii) State the effect of the higher temperature on the rate constant, $k$.

*INCREASES* $k$ [1]
(c) The reaction can also be shown as being first order with respect to H₂(g) by continuous monitoring of [H₂(g)] during the course of the reaction.

(a) Using the axes below, sketch a graph to show the results.

(b) State how you would use the graph to show this first order relationship for H₂(g).

\[ \text{[H}_2\text{(g)]} \]

\begin{align*}
\text{time} \\
\end{align*}

(b) **Constant half lives**

(d) The chemist proposes a three-step mechanism for the reaction:

\[ 2\text{H}_2\text{(g)} + 2\text{NO(g)} \rightarrow \text{N}_2\text{(g)} + 2\text{H}_2\text{O(g)} \]

(i) On the dotted line below, write the equation for step 3.

- step 1: \[ 2\text{NO} \rightarrow \text{N}_2\text{O}_2 \] fast
- step 2: \[ \text{H}_2 + \text{N}_2\text{O}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \] slow
- step 3: \[ \text{H}_2 + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{H}_2\text{O} \] fast

(ii) Explain why this mechanism is consistent with the rate equation \( \text{rate} = k[\text{H}_2\text{(g)}][\text{NO(g)}]^2 \).

\[ 2\text{NO} \rightarrow \text{N}_2\text{O}_2 \]

\[ \text{H}_2 + \text{N}_2\text{O}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \]

\[ \text{H}_2 + \text{N}_2\text{O}_2 + 2\text{NO} \rightarrow \text{NO}_2 + \text{N}_2\text{O} + \text{H}_2\text{O} \]

\[ \text{H}_2 + 2\text{NO} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \]

[Total: 11]
This question looks at two reactions involving sulfur compounds.

(a) Hydrogen reacts with carbon disulfide as shown below.

\[ 4H_2(g) + CS_2(g) \rightarrow CH_4(g) + 2H_2S(g) \]

For this reaction, \( \Delta H = -234 \text{ kJ mol}^{-1} \) and \( \Delta S = -164 \text{ JK}^{-1} \text{ mol}^{-1} \).

(i) Why does the reaction have a negative entropy change?

\( \text{Smoles of gas } \rightarrow \text{4 moles of gas} \)  
.................................................................................................................. [1]

(ii) Standard entropies are shown in the table below.

<table>
<thead>
<tr>
<th>substance</th>
<th>CS_2(g)</th>
<th>CH_4(g)</th>
<th>H_2S(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S^\circ / \text{JK}^{-1} \text{ mol}^{-1} )</td>
<td>238</td>
<td>186</td>
<td>206</td>
</tr>
</tbody>
</table>

Calculate the standard entropy for \( H_2 \).

\[ \Delta S^\circ = \sum S^\circ_\text{products} - \sum S^\circ_\text{reactants} = -164 = (238+4x) - (206 + 2 \times 186) \]

\[ x = \frac{524}{4} = 131 \]

\[ S^\circ = \text{...} \text{ JK}^{-1} \text{ mol}^{-1} \text{ [2]} \]

(iii) Explain, with a calculation, whether this reaction is feasible at 25°C.

Show your working.

\[ \Delta G = \Delta H - T \Delta S \]

\[ = -234 - (298 \times -0.164) \]

\[ = -185 \text{ kJ mol}^{-1} \]

\[ \text{REACTION IS FEASIBLE AS } \Delta G < 0 \text{ } \checkmark \]

.................................................................................................................. [3]

(iv) Explain, with a calculation, the significance of temperatures above 1154°C for this reaction.

\[ \Delta G = \Delta H - T \Delta S \]

\[ = -234 - (1427 \times -0.164) \]

\[ = 0.028 \text{ } \checkmark \]

\[ \text{At temperatures above 1154°C the } \]

\[ \text{REACTION IS NO LONGER FEASIBLE} \text{. } \checkmark \text{ [2]} \]
(b) A chemist investigated methods to improve the synthesis of sulfur trioxide from sulfur dioxide and oxygen.

\[ 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \]

The chemist:
- mixed together 1.00 mol SO₂ and 0.500 mol O₂ with a catalyst at room temperature
- compressed the gas mixture to a volume of 250 cm³
- allowed the mixture to reach equilibrium at constant temperature and without changing the total gas volume.

At equilibrium, 82.0% of the SO₂ had been converted into SO₃.

(i) Determine the concentrations of SO₂, O₂ and SO₃ present at equilibrium and calculate \( K_c \) for this reaction.

\[ \begin{align*}
\text{STAB} & : & 1.00 & & 0.500 & & 0 \\
\text{REA} & : & 0.820 & & 0.410 & & \checkmark \\
\text{EQ} & : & 0.180 & & 0.090 & & 0.820 \checkmark \\
[\text{EQ}] & : & 0.420 & & 0.360 & & 3.28 \checkmark \\
( \div 0.25) & & & & & & \\
\end{align*} \]

\[ K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 \cdot [\text{O}_2]} \]

\[ = \frac{3.28^2}{(0.420)^2 \times 0.360} \]

\[ = 57.6 \checkmark \text{ mol}^{-1} \text{ dm}^3 \]

\[ K_c = \text{............... units \text{...............} [6]} \]
(ii) Explain what would happen to the pressure as the system was allowed to reach equilibrium.

\[ \text{DECREASE} \]
\[ \text{MOVES FROM } 3 \rightarrow 2 \text{ MOLES OF GAS} \] [1]

(iii) The value of \( K_c \) for this equilibrium decreases with increasing temperature.

Predict the sign of the enthalpy change for the forward reaction. State the effect on the equilibrium yield of \( \text{SO}_3 \) of increasing the temperature at constant pressure.

\[ \Delta H: \quad (-) \text{HE} \]

Effect on \( \text{SO}_3 \) yield: \[ \text{[SO}_3\text{]} \text{DECREASES} \] [1]

(iv) The chemist repeated the experiment at the same temperature with 1.00 mol \( \text{SO}_2 \) and an excess of \( \text{O}_2 \).

The gas mixture was still compressed to a volume of 250 cm\(^3\).

State and explain, in terms of \( K_c \), how the equilibrium yield of \( \text{SO}_3 \) would be different from the yield in the first experiment.

**STATE:** \( K_c \) DOES NOT CHANGE, (ONLY \( T \) aFFECTS \( K_c \))

**EXPLAIN:** \[ \text{[O}_2\text{]} \text{WOULD BE 4X AS MUCH} \quad \Rightarrow \quad \text{EQ. \textit{SHIFTS}} \]
\[ \text{TO RHS INCREASING \textit{[SO}_3\text{]} \text{[} \]} \]
\[ \Rightarrow \text{[O}_2\text{]} \uparrow \text{ AS DOES \textit{[SO}_3\text{]} \text{, } K_c = \text{SAME} \] [3]

[Total: 19]
4 A student is supplied with 0.500 mol·dm$^{-3}$ potassium hydroxide, KOH, and 0.480 mol·dm$^{-3}$ propanoic acid, C$_2$H$_5$COOH.

The acid dissociation constant, $K_a$, for C$_2$H$_5$COOH is $1.35 \times 10^{-5}$ mol·dm$^{-3}$.

(a) C$_2$H$_5$COOH is a weak Brønsted–Lowry acid.

What is meant by a weak acid and Brønsted–Lowry acid?

(b) Calculate the pH of 0.500 mol·dm$^{-3}$ potassium hydroxide.

$$[H^+] = \frac{1 \times 10^{-14}}{0.5} = 2 \times 10^{-14} \checkmark$$

$$\text{pH} = -\log 2 \times 10^{-14}$$

$$\text{pH} = 13.7 \checkmark$$

(c) The student dilutes 25.0 cm$^3$ 0.480 mol·dm$^{-3}$ C$_2$H$_5$COOH by adding water until the total volume is 100.0 cm$^3$.

(i) Write the expression for $K_a$ for C$_2$H$_5$COOH.

$$K_a = \frac{[H^+][C_2H_5COO^-]}{[C_2H_5COOH]}$$

(ii) Calculate the pH of the diluted solution.

$$[C_2H_5COOH] = \frac{0.480}{4} = 0.120 \text{ M} \checkmark$$

$$[H^+] = \sqrt{K_a \times [C_2H_5COOH]}$$

$$= \sqrt{1.35 \times 10^{-5} \times 0.120}$$

$$= 1.27 \times 10^{-3}$$

$$\text{pH} = -\log 1.27 \times 10^{-3}$$

$$\text{pH} = 2.90 \checkmark$$

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(d) Aqueous propanoic acid, $C_2H_5COOH$, reacts with carbonates and alkalis.

(i) Write the full equation for the reaction of aqueous propanoic acid with sodium carbonate.

$$2C_2H_5COONa(aq) + Na_2CO_3(aq) \rightarrow 2C_2H_5COONa_{aq} + CO_3^{2-}(aq) + H_2O(l)$$

(ii) Write the ionic equation for the reaction of aqueous propanoic acid with aqueous potassium hydroxide.

$$H^+ + OH^- \rightarrow H_2O$$

(e) A student prepares a buffer solution containing propanoic acid $C_2H_5COOH$ and propanoate ions, $C_2H_5COO^-$. The concentrations of $C_2H_5COOH$ and $C_2H_5COO^-$ are both 1.00 mol dm$^{-3}$.

The following equilibrium is set up.

$$C_2H_5COOH(aq) \rightleftharpoons C_2H_5COO^-(aq) + H^+(aq)$$

The acid dissociation constant, $K_a$, for $C_2H_5COOH$ is $1.35 \times 10^{-5}$ mol dm$^{-3}$.

(i) Calculate the pH of this buffer solution.

Give your answer to two decimal places.

$$pH = -\log 1.35 \times 10^{-5}$$

$$pH = 4.84 \checkmark$$

(ii) A small amount of aqueous ammonia, $NH_3(aq)$, is added to the buffer solution.

Explain, in terms of equilibrium, how the buffer solution would respond to the added $NH_3(aq)$.

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$

The equilibrium moves to the right to replace $H^+$.
The student adds 6.075 g Mg to 1.00 dm³ of this buffer solution.

Calculate the pH of the new buffer solution.

Give your answer to two decimal places

\[\text{N}^{0} \text{ moles Mg} = \frac{6.075}{24.3} = 0.25 \text{ moles} \checkmark\]

\[\text{Mg} + 2\text{C}_2\text{H}_5\text{COOH} \rightarrow (\text{C}_2\text{H}_5\text{COO}^-)_2\text{Mg}^{2+} + \text{H}_2\]

\[
\begin{array}{c}
1 : 2 \text{ ratio} \\
1 : 2 \text{ ratio} \\
\end{array}
\]

\[0.25 \text{ moles Mg reacts with 0.5 moles} \rightarrow 0.5 \text{ moles} \]

\[\text{C}_2\text{H}_5\text{COOH} \rightleftharpoons \text{H}^+ + \text{C}_2\text{H}_5\text{COO}^-\]

\[
\begin{array}{c}
1 - 0.5 \\
= 0.5 \checkmark \\
1 + 0.5 \\
= 1.5 \\
\end{array}
\]

\[
[\text{H}^+] = \frac{1.35 \times 10^{-5} \times 0.5}{1.5} \rightarrow \text{pH} = -\log 4.5 \times 10^{-6} = 5.35
\]

\[\text{pH} = 5.35 \checkmark 2 \text{dp} \]

[Total: 16]
Iron(II) iodide, FeI$_2$, is formed when iron metal reacts with iodine.

(a) The table below shows enthalpy changes involving iron, iodine and iron(II) iodide.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Enthalpy change / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation of iron(II) iodide</td>
<td>$-113$</td>
</tr>
<tr>
<td>1st electron affinity of iodine</td>
<td>$-295$</td>
</tr>
<tr>
<td>1st ionisation energy of iron</td>
<td>$+759$</td>
</tr>
<tr>
<td>2nd ionisation energy of iron</td>
<td>$+1561$</td>
</tr>
<tr>
<td>Atomisation of iodine</td>
<td>$+107$</td>
</tr>
<tr>
<td>Atomisation of iron</td>
<td>$+416$</td>
</tr>
</tbody>
</table>

(i) The incomplete Born–Haber cycle below can be used to determine the lattice enthalpy of iron(II) iodide.

In the boxes, write the species present at each stage in the cycle. Include state symbols for the species.

Fe$^{2+}$(g) + 2I(g) + 2e$^-$

\[
\begin{align*}
154 & \quad \text{Fe}^{2+}(g) + 2I(g) + e^- \\
759 & \quad \text{Fe}(g) + 2I(g) \\
416 & \quad \text{Fe}(s) + 2I(g) \\
214 & \quad \text{Fe}(s) + I_2(s) \\
-113 & \quad \text{FeI}_2(s)
\end{align*}
\]

* STATE SYMBOLS + SPECIES IN EACH BOX *
(ii) Define the term lattice enthalpy.

Enthalpy change for the formation of 1 mole of a compound from its gaseous ions under standard conditions.

(iii) Calculate the lattice enthalpy of iron(III) iodide.

\[
\Delta H_{\text{le}}^\circ = \Delta H_3^\circ - (\sum \Delta H) \\
= -113 - (214 + 416 + 759 + 1561 - 590) \\
= -113 - 2360 \\
= -2473
\]

Lattice enthalpy = \(-2473\) kJ mol\(^{-1}\) [2]
(b) Some electrode potentials for ions are shown below.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>$E^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}^0$</td>
<td>$\text{Fe}(s)$</td>
<td>$-0.44\text{V}$</td>
</tr>
<tr>
<td>$\text{Fe}^{3+}(aq) + e^- \rightarrow \text{Fe}^{2+}(aq)$</td>
<td>$\text{Fe}^2+(aq)$</td>
<td>$+0.77\text{V}$</td>
</tr>
<tr>
<td>$\frac{1}{2}\text{I}_2(aq) + e^- \rightarrow \text{I}^-(aq)$</td>
<td>$\text{I}^-(aq)$</td>
<td>$+0.54\text{V}$</td>
</tr>
<tr>
<td>$\frac{1}{2}\text{Br}_2(aq) + e^- \rightarrow \text{Br}^-(aq)$</td>
<td>$\text{Br}^-(aq)$</td>
<td>$+1.09\text{V}$</td>
</tr>
<tr>
<td>$\frac{1}{2}\text{Cl}_2(aq) + e^- \rightarrow \text{Cl}^-(aq)$</td>
<td>$\text{Cl}^-(aq)$</td>
<td>$+1.36\text{V}$</td>
</tr>
</tbody>
</table>

(i) Complete the electron configurations for $\text{Fe}^{2+}$ and $\text{Br}^-$.

- $\text{Fe}^{2+}$: $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^6 \ (4s \text{ empty})$ (SQ empty)
- $\text{Br}^-$: $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^10 \ 4s^2 \ 4p^6$

(ii) Predict the products of reacting $\text{Fe}(s)$ separately with $\text{I}_2(aq)$, $\text{Br}_2(aq)$ and $\text{Cl}_2(aq)$.

- $\text{I}_2$ is more (+)VE than $-0.44$ but not $0.44$. Will react with Fe. Forms $\text{FeI}_2$.
- $\text{Br}_2$ is more (+)VE than $-0.44$ and $+0.54$. Will react with Fe $\rightarrow \text{Fe}^{2+}$, $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$.
- $\text{Cl}_2$ is more (+)VE than $-0.44$ and $+0.54$. Will react with Fe $\rightarrow \text{Fe}^{2+}$, $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$.

Compliance Data
(c) Fe$^{2+}$ ions can be used to test for NO$_3^-$ ions. In this test, aqueous iron(II) sulfate is added to a solution containing NO$_3^-$ ions, followed by slow addition of concentrated sulfuric acid. The sulfuric acid forms a layer below the aqueous solution. In the presence of NO$_3^-$ ions, a brown ring forms between the two layers.

Two reactions take place.

Reaction 1: In the acid conditions Fe$^{2+}$ ions reduce NO$_3^-$ ions to NO. Fe$^{2+}$ ions are oxidised to Fe$^{3+}$ ions. Water also forms.

Reaction 2: A ligand substitution reaction of [Fe(H$_2$O)$_6$]$^{2+}$ takes place in which one NO ligand exchanges with one water ligand. A deep brown complex ion forms as the brown ring.

Construct equations for these two reactions.

Reaction 1:

\[
4\text{H}^+ + \text{NO}_3^- + \text{Fe}^{2+} \rightarrow \text{NO} + 2\text{H}_2\text{O} + 3\text{Fe}^{3+} + \text{e}^-
\]

\[
3\text{Fe}^{2+} + 4\text{H}^+ + \text{NO}_3^- \rightarrow 3\text{Fe}^{3+} + \text{NO} + 2\text{H}_2\text{O}
\]

Species balanced.

Reaction 2:

\[
[\text{Fe(H}_2\text{O})_6]\text{NO}^{2+} + \text{NO} \rightarrow [\text{Fe(H}_2\text{O})_6\text{NO}]^{2+} + \text{H}_2\text{O}
\]

[Total: 16]
Three redox systems, C, D and E are shown in Table 6.1.

<table>
<thead>
<tr>
<th></th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Ag(NH₃)₂⁺(aq) + e⁻ ⇌ Ag(s) + 2NH₃(aq)</td>
</tr>
<tr>
<td>D</td>
<td>Ag⁺(aq) + e⁻ ⇌ Ag(s)</td>
</tr>
<tr>
<td>E</td>
<td>Ag(CN)₂⁻(aq) + e⁻ ⇌ Ag(s) + 2CN⁻(aq)</td>
</tr>
</tbody>
</table>

Table 6.1

The two cells below were set up in an experiment to compare the standard electrode potentials of redox systems C, D and E. The signs on each electrode are shown.

(a) List the three redox systems in order by adding the labels C, D and E to the table below.

<table>
<thead>
<tr>
<th>E°</th>
<th>redox system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Most negative</td>
<td>E</td>
</tr>
<tr>
<td>↑</td>
<td>C</td>
</tr>
<tr>
<td>Least negative</td>
<td>D</td>
</tr>
</tbody>
</table>

Ag⁺ / Ag more (+)ve than Ag⁺⁺ / Ag⁺⁺⁺

Ag(CN)₂⁻ / Ag⁺ + 2CN⁻ more (-)ve than Ag(NH₃)₂⁺ / Ag⁺ + 2NH₃
(b) A standard cell is set up between redox system D in Table 6.1 and a standard hydrogen half-cell. The standard cell potential of redox system D is +0.34 V.

The cell delivers a current for a length of time. The pH of the solution in the standard hydrogen half-cell decreases.

(i) What is the pH of the solution in a standard hydrogen half-cell?

\[
\text{pH} = -\log 1
\]

(ii) Explain, in terms of electrode potentials and equilibrium, why the pH of the solution in the hydrogen half-cell decreases as this cell delivers current.

**H_{\text{2}} \text{ cell is MOST (-)VE}**

\[H_2 \rightarrow 2H^+ + 2e^-\]

Eq. moves to RHS, increasing \([H^+]\)

pH decreases

(iii) Write the equation for the overall cell reaction that takes place in this cell.

\[H_2 + 2Ag^+ \rightarrow 2Ag + 2H^+\]

(c) The CN\(^-\) ion is the conjugate base of a very toxic weak acid.

In aqueous solutions of CN\(^-\) ions, an acid–base equilibrium is set up.

(i) Complete the equation for this equilibrium and label the conjugate acid–base pairs.

\[\text{CN}^- + H_2O \rightleftharpoons HCN + \text{CN}^- \]

(ii) Explain, in terms of equilibrium, why acidic conditions should **not** be used with cells containing CN\(^-\)(aq) ions.

**CN^- is removed from 1/2 cell**

**Moves Eq. (E) to RHS**
(d) Direct-ethanol fuel cells (DEFCs) are being developed in which the fuel is ethanol rather than hydrogen.

The half-equation for the reaction at the ethanol electrode of the DEFC is shown below:

\[ \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \]

(i) State one important difference between a fuel cell and a modern storage cell.

\[ \text{Constant supply of fuel and oxygen to produce electrical energy} \] \[ \text{[1]} \]

(ii) Suggest one advantage of using ethanol, rather than hydrogen, in a fuel cell for vehicles.

\[ \text{Ethanol is a liquid easier to store} \] \[ \text{[1]} \]

(iii) The overall reaction in a DEFC is the same as for the complete combustion of ethanol.

Write the equation for the overall reaction in a DEFC.

\[ \text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \] \[ \text{[1]} \]

(iv) Deduce the half-equation for the reaction at the oxygen electrode in a DEFC.

\[ \text{Redox elements in overall that are not in the } \frac{1}{2} \text{eqn given} \] \[ \text{[1]} \]

(v) Using oxidation numbers, show that oxidation and reduction take place in a DEFC.

Oxidation: \[ \text{Carbon} \rightarrow -2 \rightarrow +4 \]

Reduction: \[ \text{Oxygen} \rightarrow -2 \]

[Total: 13]
Chromite is the main ore of chromium. The chromium-containing compound in chromite is Fe(\text{CrO}_2)_2. The percentage of chromium in a sample of chromite can be determined using the method below.

**Step 1**

A 5.25g sample of chromite ore is heated with sodium peroxide, Na₂O₂.

\[
2\text{Fe(\text{CrO}_2)_2} + 7\text{Na}_2\text{O}_2 \rightarrow 2\text{NaFeO}_2 + 4\text{Na}_2\text{CrO}_4 + 2\text{Na}_2\text{O}
\]

Water is added to the resulting mixture. Na₂CrO₄ dissolves in the water forming a solution containing CrO₄²⁻ ions.

**Step 2**

The mixture from Step 1 is filtered and the filtrate is made up to 1.00 dm³ in a volumetric flask. A 25.0 cm³ sample of this alkaline solution is pipetted into a conical flask and an excess of aqueous potassium iodide is added.

- A redox reaction takes place between I⁻ ions, CrO₄²⁻ ions and H₂O.
- In this reaction 1 mol CrO₄²⁻ forms 1.5 mol I₂.

**Step 3**

The resulting mixture is titrated with 0.100 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃(aq) to estimate the I₂ present:

\[
\text{I}_2(aq) + 2\text{S}_2\text{O}_3^{2-}(aq) \rightarrow 2\text{I}^-(aq) + \text{S}_4\text{O}_6^{2-}(aq)
\]

The average titre of Na₂S₂O₃(aq) is 25.5 cm³.

(a) In Step 1 Na₂O and NaFeO₂ react with water forming an alkaline solution containing a brown precipitate. This is not a redox reaction.

\[
\text{Fe}^{3+} + \text{OH}^-
\]

Write equations for:

(a) the reaction of Na₂O with water

(b) the reaction of NaFeO₂ with water.

\[
a) \quad \text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}
\]

\[
b) \quad \text{NaFeO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + \text{NaOH}
\]
(b) Determine the percentage, by mass, of chromium in the ore.

Give your answer to one decimal place.

(c) This part refers to Step 2 of the method.

In the redox reaction between I⁻ ions, CrO₄²⁻ ions and H₂O:
- CrO₄²⁻ ions, are reduced to chromium(III) ions, Cr³⁺
- I⁻ ions are oxidised to iodine, I₂
- Construct an overall equation for the redox reaction and write half equations for the oxidation and reduction.

Overall equation:

```
3I⁻ + 4H₂O + CrO₄²⁻ → Cr³⁺ + 8OH⁻ + ½I₂
```

Half equations:

```
8I⁻ + CrO₄²⁻ + 3H₂O → Cr³⁺ + 4H₂O + 8OH⁻
```

```
4H₂O + CrO₄²⁻ → Cr³⁺ + 4H₂O + 8OH⁻
```

I⁻ → ½I₂ + e⁻

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