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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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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 $[CrOCl_5]^{2-}$?

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

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

Equation: .....

Catalyst: ..... **[1]**

(c) An octahedral complex ion **A**, $C_9H_{30}N_6Ni^{3+}$, exists as two optical isomers.

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

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

.....

.....

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

(ii) What is the molecular formula of the bidentate ligand **B**?

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

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

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..... **[2]**

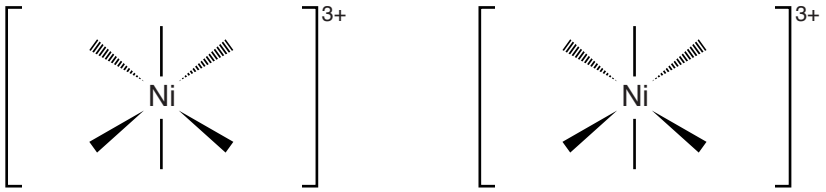
(iv) What is the coordination number of complex ion **A**?

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

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(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



[1]

(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.

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..... **[6]**

[Total: 14]

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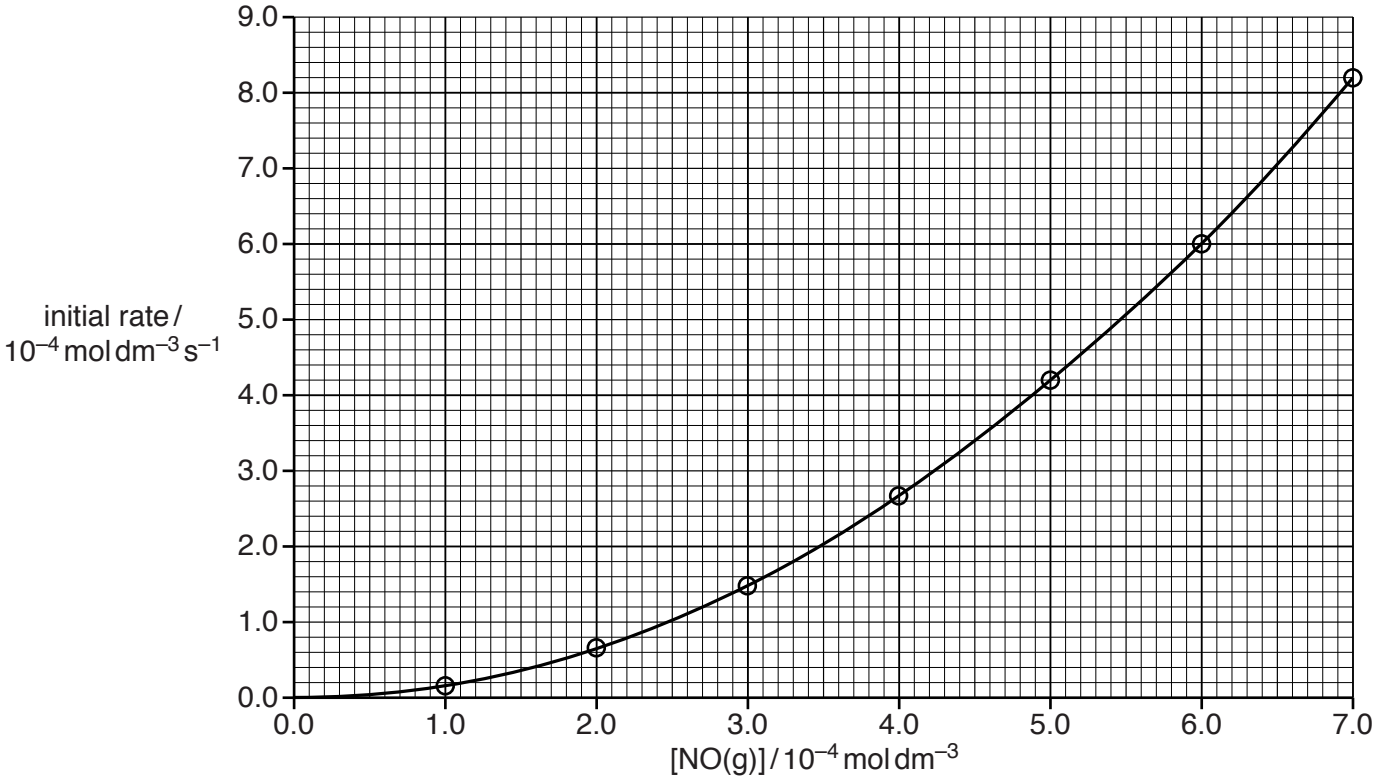
2 Hydrogen, H_2, reacts with nitrogen monoxide, NO, as shown below:

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

(a) The rate equation for this reaction is:

$$rate = k[H_2(g)][NO(g)]^2$$

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



The chemist uses $H_2(g)$ of concentration 2.0×10^{-2} 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 = ... units ..... **[4]**

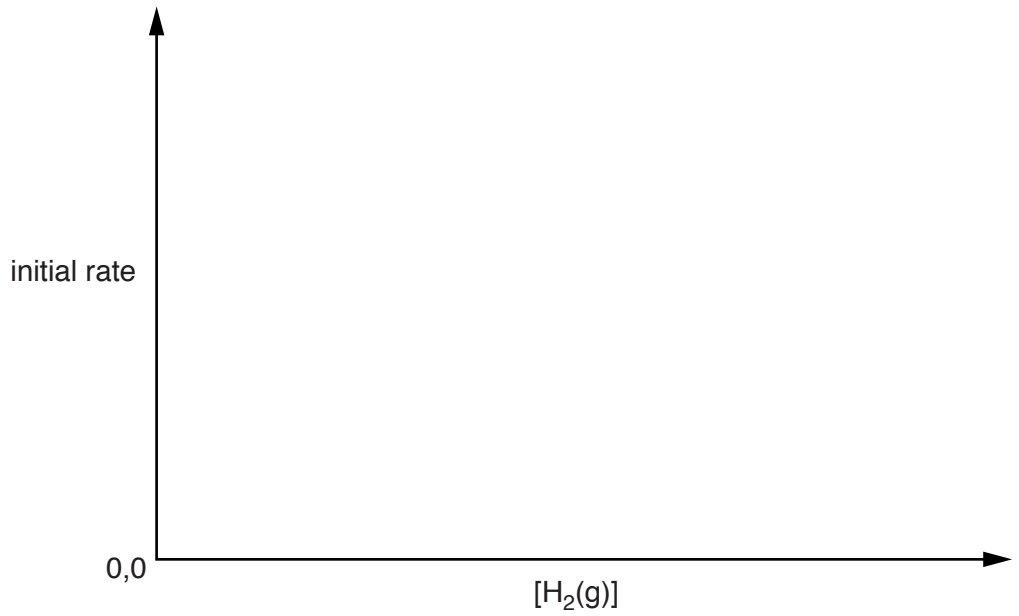
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(b) A chemist investigates the effect of changing the concentration of $H_2(g)$ on the initial reaction rate at two different temperatures.

The reaction is first order with respect to $H_2(g)$.

(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.



[2]

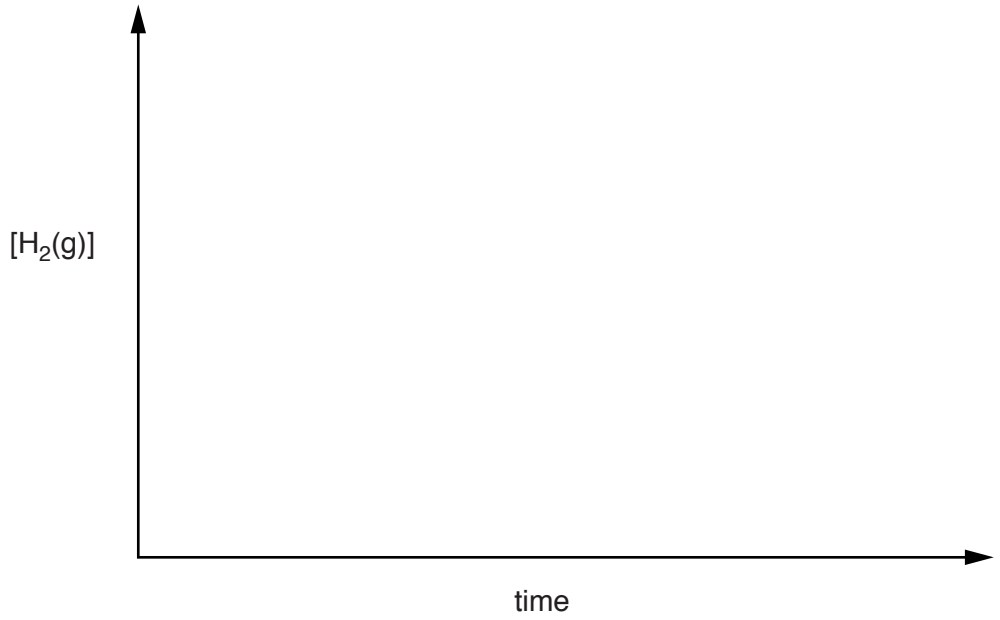
(ii) State the effect of the higher temperature on the rate constant, *k*.

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

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(c) The reaction can also be shown as being first order with respect to $H_2(g)$ by continuous monitoring of $[H_2(g)]$ during the course of the reaction.

- Using the axes below, sketch a graph to show the results.
- State how you would use the graph to show this first order relationship for $H_2(g)$.



.....

.....

..... **[2]**

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

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

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

step 1:	$2NO \longrightarrow N_2O_2$	fast
step 2:	$H_2 + N_2O_2 \longrightarrow N_2O + H_2O$	slow
step 3:	.....	fast **[1]**

(ii) Explain why this mechanism is consistent with the rate equation $rate = k[H_2(g)][NO(g)]^2$.

.....

.....

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

[Total: 11]

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3 This question looks at two reactions involving sulfur compounds.

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

$$4H_2(g) + CS_2(g) \longrightarrow CH_4(g) + 2H_2S(g)$$

For this reaction, $\Delta H = -234\,kJ\,mol^{-1}$ and $\Delta S = -164\,J\,K^{-1}\,mol^{-1}$.

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

.....

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

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

substance	**$CS_2(g)$**	**$CH_4(g)$**	**$H_2S(g)$**
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	238	186	206

Calculate the standard entropy for H_2.

$S^{\ominus}$ = ... $J\,K^{-1}\,mol^{-1}$ **[2]**

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

Show your working.

.....

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

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

.....

..... **[2]**

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(b) A chemist investigated methods to improve the synthesis of sulfur trioxide from sulfur dioxide and oxygen.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The chemist:

- mixed together 1.00 mol SO_2 and 0.500 mol O_2 with a catalyst at room temperature
- compressed the gas mixture to a volume of 250 cm^3
- allowed the mixture to reach equilibrium at constant temperature and without changing the total gas volume.

At equilibrium, 82.0% of the SO_2 had been converted into SO_3.

(i) Determine the concentrations of SO_2, O_2 and SO_3 present at equilibrium and calculate K_c for this reaction.

K_c = ... units ..... **[6]**

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(ii) Explain what would happen to the pressure as the system was allowed to reach equilibrium.

.....

.....

..... **[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 SO_3 of increasing the temperature at constant pressure.

ΔH: .....

Effect on SO_3 yield: ..... **[1]**

(iv) The chemist repeated the experiment at the same temperature with 1.00 mol SO_2 and an excess of 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 SO_3 would be different from the yield in the first experiment.

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

[Total: 19]

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4 A student is supplied with 0.500 mol dm^{-3} potassium hydroxide, KOH, and 0.480 mol dm^{-3} propanoic acid, C_2H_5COOH.

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

(a) C_2H_5COOH is a weak Brønsted–Lowry acid.

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

.....

.....

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

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

pH = ... **[2]**

(c) The student dilutes 25.0 cm^3 0.480 mol dm^{-3} C_2H_5COOH by adding water until the total volume is 100.0 cm^3.

(i) Write the expression for K_a for C_2H_5COOH.

[1]

(ii) Calculate the pH of the diluted solution.

pH = ... **[3]**

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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.

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

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

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

(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 = ... **[1]**

(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 $NH_3(aq)$.

.....

.....

.....

..... **[2]**

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(iii) The student adds 6.075 g Mg to 1.00 dm^3 of this buffer solution.

Calculate the pH of the new buffer solution.

Give your answer to **two** decimal places

pH = ... **[4]**

[Total: 16]

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5 Iron(II) iodide, FeI_2, is formed when iron metal reacts with iodine.

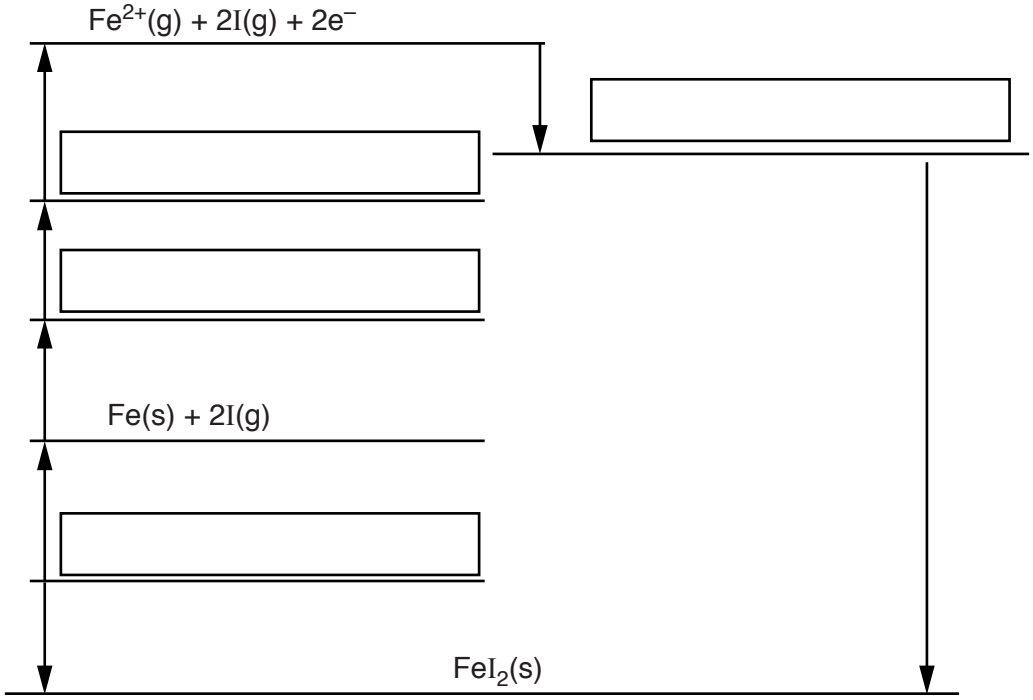
(a) The table below shows enthalpy changes involving iron, iodine and iron(II) iodide.

	Enthalpy change / kJ mol^{-1}
Formation of iron(II) iodide	–113
1st electron affinity of iodine	–295
1st ionisation energy of iron	+759
2nd ionisation energy of iron	+1561
Atomisation of iodine	+107
Atomisation of iron	+416

(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.



[4]

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(ii) Define the term *lattice enthalpy*.

.....

.....

.....

..... **[2]**

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

lattice enthalpy = ... $kJ\,mol^{-1}$ **[2]**

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(b) Some electrode potentials for ions are shown below.

$Fe^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Fe(s)$	$E^{\ominus} = -0.44\,V$
$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$	$E^{\ominus} = +0.77\,V$
$\frac{1}{2}I_2(aq) + e^-$	$\rightleftharpoons$	$I^-(aq)$	$E^{\ominus} = +0.54\,V$
$\frac{1}{2}Br_2(aq) + e^-$	$\rightleftharpoons$	$Br^-(aq)$	$E^{\ominus} = +1.09\,V$
$\frac{1}{2}Cl_2(aq) + e^-$	$\rightleftharpoons$	$Cl^-(aq)$	$E^{\ominus} = +1.36\,V$

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

Fe^{2+}: $1s^2$ .....

Br^-: $1s^2$ .....

[2]

(ii) Predict the products of reacting Fe(s) separately with $I_2(aq)$, $Br_2(aq)$ and $Cl_2(aq)$.

Explain your predictions using the electrode potential data above.

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

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(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 $[Fe(H_2O)_6]^{2+}$ 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:

.....

Reaction 2:

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

[Total: 16]

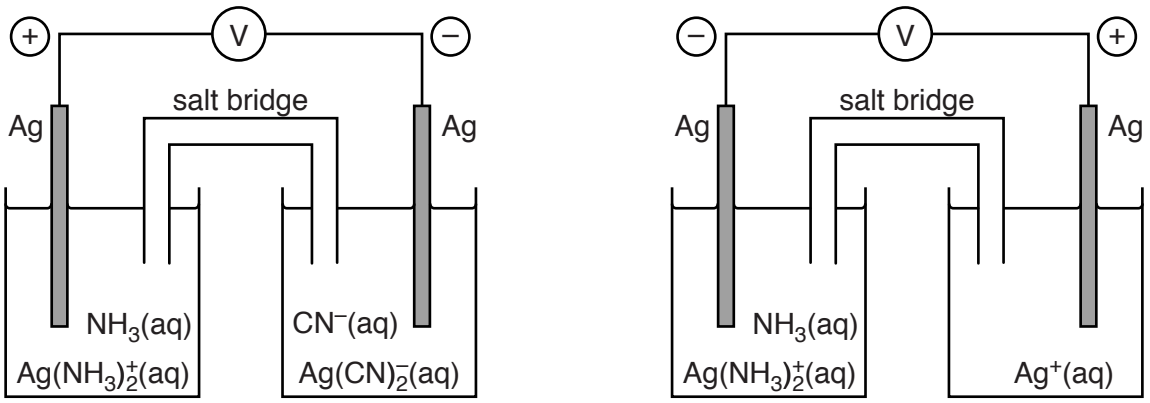
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6 Three redox systems, **C**, **D** and **E** are shown in Table 6.1.

C	$Ag(NH_3)_2^+(aq) + e^- \rightleftharpoons Ag(s) + 2NH_3(aq)$
D	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$
E	$Ag(CN)_2^-(aq) + e^- \rightleftharpoons Ag(s) + 2CN^-(aq)$

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.

$E^{\ominus}$	redox system
Most negative	
↑	
Least negative	

[1]

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(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?

pH = ... **[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.

.....

.....

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.....

..... **[2]**

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

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

(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.

CN^- + H_2O $\rightleftharpoons$ ..... + ...

....

[1]

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

.....

.....

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

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(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:

$$C_2H_5OH + 3H_2O \longrightarrow 2CO_2 + 12H^+ + 12e^-$$

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

.....

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

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

.....

..... **[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.

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

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

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

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

Oxidation: .....

.....

Reduction: .....

..... **[2]**

[Total: 13]

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Turn over for the next question

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7 Chromite is the main ore of chromium. The chromium-containing compound in chromite is $Fe(CrO_2)_2$. The percentage of chromium in a sample of chromite can be determined using the method below.

Step 1

A 5.25 g sample of chromite ore is heated with sodium peroxide, Na_2O_2.

$$2Fe(CrO_2)_2 + 7Na_2O_2 \rightarrow 2NaFeO_2 + 4Na_2CrO_4 + 2Na_2O$$

Water is added to the resulting mixture.
Na_2CrO_4 dissolves in the water forming a solution containing CrO_4^{2-} ions.

Step 2

The mixture from **Step 1** is filtered and the filtrate is made up to 1.00 dm^3 in a volumetric flask.
A 25.0 cm^3 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, CrO_4^{2-} ions and H_2O.
- In this reaction 1 mol CrO_4^{2-} forms 1.5 mol I_2.

Step 3

The resulting mixture is titrated with 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3(aq)$ to estimate the I_2 present:

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

The average titre of $Na_2S_2O_3(aq)$ is 25.5 cm^3.

(a) In **Step 1** Na_2O and $NaFeO_2$ react with water forming an alkaline solution containing a brown precipitate. This is **not** a redox reaction.

Write equations for:
- the reaction of Na_2O with water
- the reaction of $NaFeO_2$ with water.

.....

..... **[2]**

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(b) Determine the percentage, by mass, of chromium in the ore.

Give your answer to **one** decimal place.

[6]

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

In the redox reaction between I^- ions, CrO_4^{2-} ions and H_2O:

- CrO_4^{2-} ions, are reduced to chromium(III) ions, Cr^{3+}
- I^- ions are oxidised to iodine, I_2
- Construct an overall equation for the redox reaction and write half equations for the oxidation and reduction.

Overall equation:

Half equations:

[3]

[Total: 11]

END OF QUESTION PAPER

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ADDITIONAL ANSWER SPACE

If additional answer space is required, you should use the following lined page. The question number(s) must be clearly shown in the margins.

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