

Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										



General Certificate of Education
Advanced Level Examination
June 2014

Chemistry

CHEM5

Unit 5 Energetics, Redox and Inorganic Chemistry

Tuesday 17 June 2014 1.30 pm to 3.15 pm

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
3	
4	
5	
6	
7	
8	
TOTAL	

For this paper you must have:

- the Periodic Table/Data Sheet provided as an insert (enclosed)
- a ruler with millimetre measurements
- a calculator.

Time allowed

- 1 hour 45 minutes

Instructions

- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information

- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- You are expected to use a calculator, where appropriate.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
 - use good English
 - organise information clearly
 - use scientific terminology accurately.

Advice

- You are advised to spend about 75 minutes on **Section A** and about 30 minutes on **Section B**.



JUN14CHEM501

WMP/Jun14/CHEM5/E8

CHEM5

Section A

Answer all questions in the spaces provided.

- 1 (a) Write an equation for the process that has an enthalpy change equal to the electron affinity of chlorine.

[1 mark]



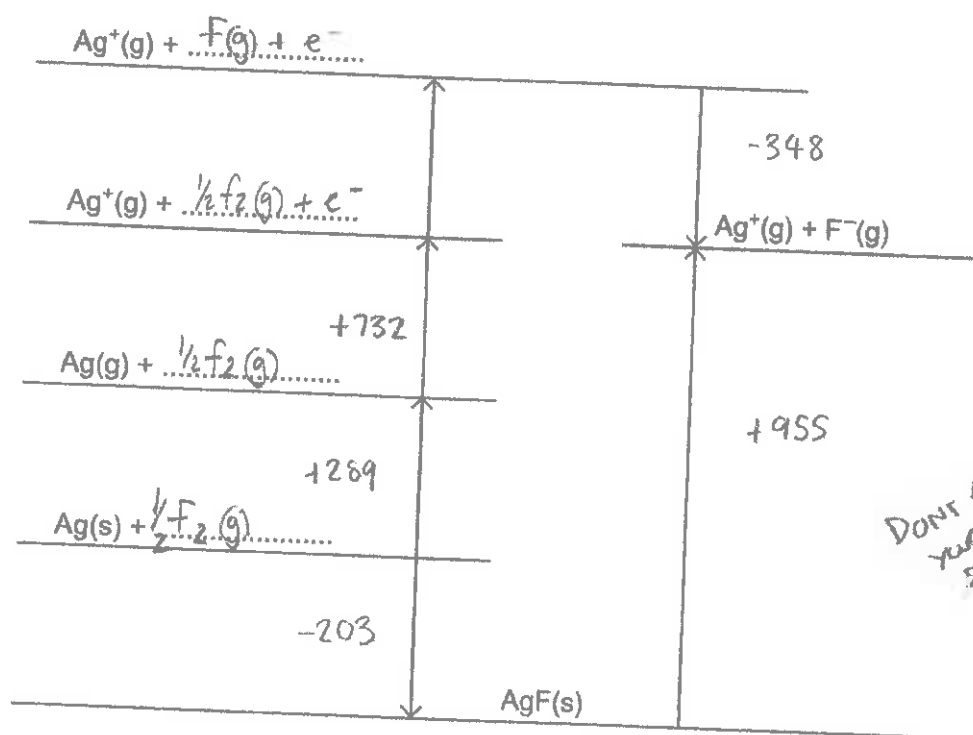
- 1 (b) In terms of electrostatic forces, suggest why the electron affinity of fluorine has a negative value.

[2 marks]

There is an attraction between the nucleus and the electron - and energy released because of this.

- 1 (c) (i) Complete the Born-Haber cycle for silver fluoride by adding the missing species on the dotted lines.

[3 marks]



- 1 (c) (ii) Use the cycle in Question 1 (c) (i) and the data in Table 1 to calculate a value, in kJ mol^{-1} , for the bond enthalpy of the fluorine-fluorine bond.

[2 marks]

Table 1

Enthalpy change	Value / kJ mol^{-1}
Enthalpy of atomisation for silver	+289
First ionisation energy for silver	+732
Electron affinity for fluorine	-348
Experimental enthalpy of lattice dissociation for silver fluoride	+955
Enthalpy of formation for silver fluoride	-203

$$203 + 289 + 732 = +1224$$

$$1303 - 1224 = +79 \text{ kJ mol}^{-1} = 1/2 \cdot$$

$$-348 + -955 = -1303$$

$$\therefore 79 \times 2 = +158 \text{ kJ mol}^{-1}$$

Question 1 continues on the next page

*There are a few
ways to calculate this
but remember left side
Must be and right (make
sure the cycle)*

Turn over ►



- 1 (d) A theoretical value for enthalpy of lattice dissociation can be calculated using a perfect ionic model.

The theoretical enthalpy of lattice dissociation for silver fluoride is $+870 \text{ kJ mol}^{-1}$.

- 1 (d) (i) Explain why the theoretical enthalpy of lattice dissociation for silver fluoride is different from the experimental value that can be calculated using a Born-Haber cycle.

[2 marks]

Silver fluoride has covalent character - but theoretical enthalpy assumes perfect ionic model - or point charges.

[Extra space]

- 1 (d) (ii) The theoretical enthalpy of lattice dissociation for silver chloride is $+770 \text{ kJ mol}^{-1}$.

Explain why this value is less than the value for silver fluoride.

[2 marks]

chloride ion is large than fluoride ion so weaker attraction for Cl^- ion to the Ag^+ ion.

[Extra space]

12



2 Table 2 shows some enthalpy change and entropy change data.

Table 2

	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{mol}^{-1}$
$\text{AgCl(s)} \longrightarrow \text{Ag}^{\text{+}}(\text{g}) + \text{Cl}^{\text{-}}(\text{g})$	+905	
$\text{AgCl(s)} \longrightarrow \text{Ag}^{\text{+}}(\text{aq}) + \text{Cl}^{\text{-}}(\text{aq})$	+77	+33
$\text{AgF(s)} \longrightarrow \text{Ag}^{\text{+}}(\text{aq}) + \text{F}^{\text{-}}(\text{aq})$	-15	to be calculated
$\text{Ag}^{\text{+}}(\text{g}) \longrightarrow \text{Ag}^{\text{+}}(\text{aq})$	-464	

2 (a) Define the term **enthalpy of hydration** of an ion.

[2 marks]

Enthalpy change when 1mol of gaseous ions form
aqueous ions.

know your
definitions!

2 (b) Use data from Table 2 to calculate a value for the enthalpy of hydration of the chloride ion.

[2 marks]

$$\Delta H_{\text{sol}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}$$

$$+77 = +905 + (-464 + ?)$$

$$+77 - 905 + 464 = -364 \text{ kJ mol}^{-1}$$

these questions are
very easy to get wrong
due to negative signs!
you should know that
2005 mark for a net
write - work from
there.

2 (c) Suggest why hydration of the chloride ion is an exothermic process.

[2 marks]

Water is polar and the chloride ion attracts the
 $\text{H}^{\delta+}$.



- 2 (d) Silver chloride is insoluble in water at room temperature.

Use data from Table 2 to calculate the temperature at which the dissolving of silver chloride in water becomes feasible.

Comment on the significance of this temperature value.

[4 marks]

Calculation of temperature $\Delta G = \Delta H - T\Delta S$

$$0 = \Delta H - T\Delta S$$

$$\frac{\Delta H}{\Delta S} = T \quad \frac{77 \times 1000}{33} = 2333 \text{ K}$$

Don't forget
to $\times 1000$ to
make sure you
are working in
the same units

Significance of temperature value *Massively above boiling temp of water!*
So water would evaporate before dissolving.

- 2 (e) When silver fluoride dissolves in water at 25 °C, the free-energy change is -9 kJ mol^{-1} .

Use this information and data from Table 2 to calculate a value, with units, for the entropy change when silver fluoride dissolves in water at 25 °C.

[3 marks]

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

$$\frac{\Delta G - \Delta H}{T} = \Delta S$$

$$\frac{-9 - (-15)}{298} = 0.0201 \times 1000 = 20.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

Make sure
your units match
your answer!
 $S = \text{J}$
 $H = \text{kJ}$

13

Turn over ▶

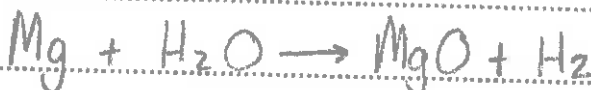


3 This question is about some Period 3 elements and their oxides.

3 (a) Describe what you would observe when, in the absence of air, magnesium is heated strongly with water vapour at temperatures above 373 K.
Write an equation for the reaction that occurs.

[3 marks]

Observations ... A white powder would be formed and a
bright white light.



Equation

3 (b) Explain why magnesium has a higher melting point than sodium.

[2 marks]

Mg^{2+} ions - higher charge than Na^+ ions.
This attracts the sea of delocalisation more strongly.

[Extra space]

3 (c) State the structure of, and bonding in, silicon dioxide.
Other than a high melting point, give two physical properties of silicon dioxide that are characteristic of its structure and bonding.

[4 marks]

Structure ... Giant Covalent

Bonding ... Covalent

Physical property 1 ... Hard

Physical property 2 ... Non conductor

Make sure you
check physical
properties - not
chemical!



- 3 (d) Give the formula of the species in a sample of solid phosphorus(V) oxide.
State the structure of, and describe fully the bonding in, this oxide.

[4 marks]

Formula P_4O_{10}

Structure Simple molecular

Bonding Covalent between atoms - weak VdW's between molecules

- 3 (e) Sulfur(IV) oxide reacts with water to form a solution containing ions.

Write an equation for this reaction.

Don't be fooled into thinking H_2SO_4 is formed. It is HSO_3^- !

[1 mark]



- 3 (f) Write an equation for the reaction between the acidic oxide, phosphorus(V) oxide, and the basic oxide, magnesium oxide.

[1 mark]



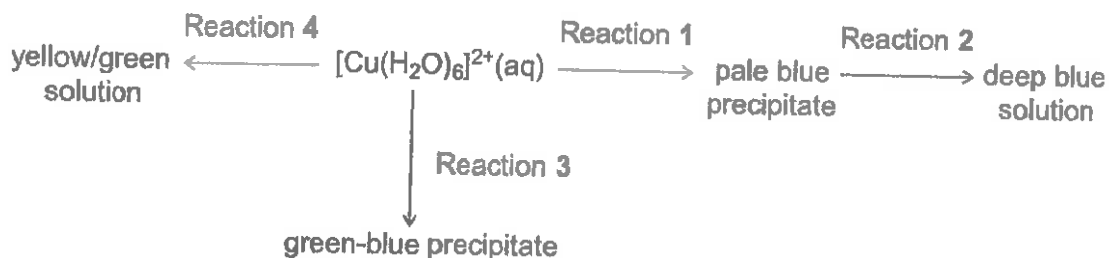
15

Turn over for the next question

Turn over ►



- 4 Consider the following reaction scheme that starts from aqueous $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions.



For each of the reactions 1 to 4, identify a suitable reagent, give the formula of the copper-containing species formed and write an equation for the reaction.

- 4 (a) Reaction 1

or NaOH

[3 marks]

Reagent Ammonia (NH_3)

Copper-containing species $\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2$

Equation $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 2\text{NH}_3 \rightarrow [\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2] + 2\text{NH}_4^+$

- 4 (b) Reaction 2

[3 marks]

Reagent Ammonia conc. (NH_3)

Copper-containing species $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$

Equation $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+} + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+} + 2\text{H}_2\text{O} + 2\text{OH}^-$

- 4 (c) Reaction 3

[3 marks]

Reagent Na_2CO_3

Copper-containing species CuCO_3

Equation $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + \text{CO}_3^{2-} \rightarrow \text{CuCO}_3 + 6\text{H}_2\text{O}$



4 (d) Reaction 4

or NaCl

[3 marks]

Reagent HCl

Copper-containing species $[\text{CuCl}_4]^{2-}$ Equation $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O}$

12

Turn over for the next question

Turn over ►



- 5 Table 3 shows some standard electrode potential data.

Table 3

	E^\ominus / V
$ZnO(s) + H_2O(l) + 2e^- \longrightarrow Zn(s) + 2OH^-(aq)$	-1.25
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	-0.44
$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$2HOCl(aq) + 2H^+(aq) + 2e^- \longrightarrow Cl_2(g) + 2H_2O(l)$	+1.64

- 5 (a) Give the conventional representation of the cell that is used to measure the standard electrode potential of iron as shown in Table 3.

[2 marks]



For this question
you need to be aware
of the hydrogen
electrode.

- 5 (b) With reference to electrons, give the meaning of the term **reducing agent**.

[1 mark]

Electron donor

- 5 (c) Identify the weakest reducing agent from the species in Table 3.

Explain how you deduced your answer.

[2 marks]

Species Cl_2

Explanation Most positive E^\ominus (or least negative).



5 (d) When HOCl acts as an oxidising agent, one of the atoms in the molecule is reduced.

5 (d) (i) Place a tick (✓) next to the atom that is reduced.

[1 mark]

Atom that is reduced	Tick (✓)
H	
O	
Cl	✓

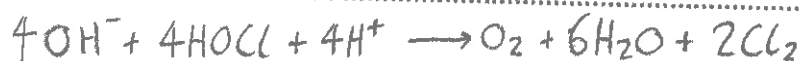
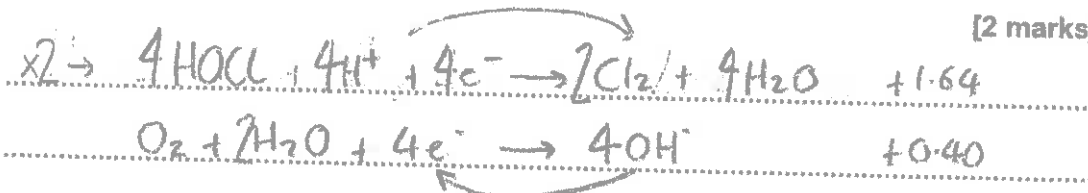
5 (d) (ii) Explain your answer to Question 5 (d) (i) in terms of the change in the oxidation state of this atom.

[1 mark]



5 (e) Using the information given in Table 3, deduce an equation for the redox reaction that would occur when hydroxide ions are added to HOCl

[2 marks]



Question 5 continues on the next page

This question was tricky as it is not instantly obvious this is what they are asking for. My only advice here is read the question carefully!

Turn over ▶



5 (f) Table 3 is repeated to help you answer this question.

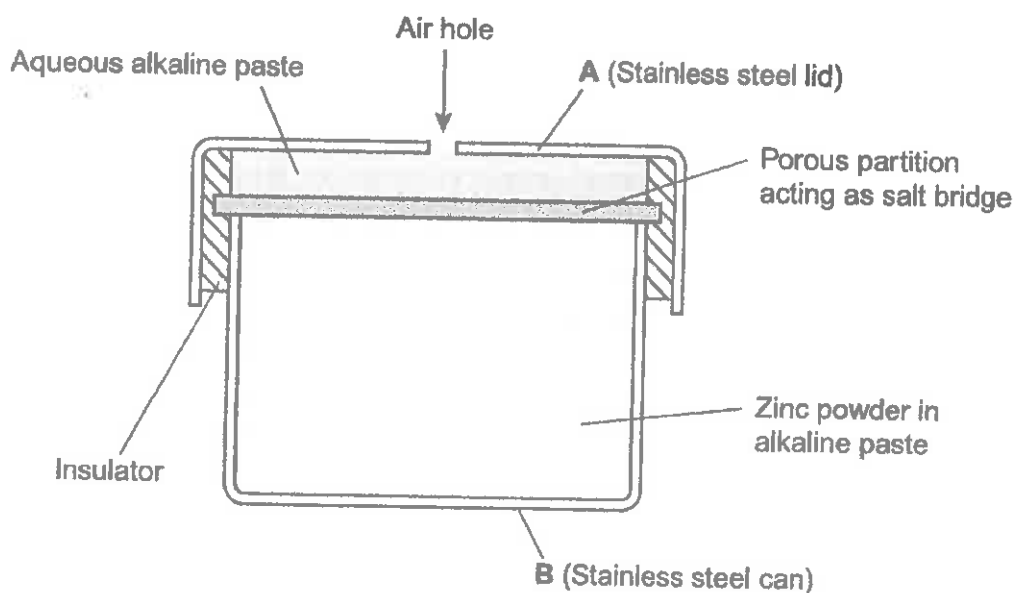
Table 3

	E°/V
$\text{ZnO(s)} + \text{H}_2\text{O(l)} + 2\text{e}^- \longrightarrow \text{Zn(s)} + 2\text{OH}^-(\text{aq})$	-1.25
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe(s)}$	-0.44
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)} + 4\text{e}^- \longrightarrow 4\text{OH}^-(\text{aq})$	+0.40
$2\text{HOCl(aq)} + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cl}_2(\text{g}) + 2\text{H}_2\text{O(l)}$	+1.64

The half-equations from Table 3 that involve zinc and oxygen are simplified versions of those that occur in hearing aid cells.

A simplified diagram of a hearing aid cell is shown in Figure 1.

Figure 1



5 (f) (i) Use data from Table 3 to calculate the e.m.f. of this cell.

[1 mark]

$$E_{\text{cell}} = R - L$$

$$E_{\text{cell}} = +0.40 - (-1.25)$$

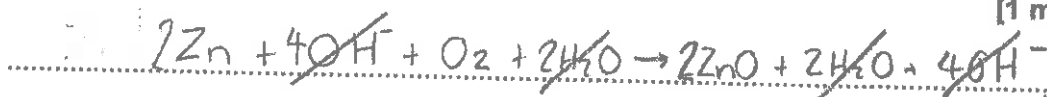
$$E_{\text{cell}} = \underline{\underline{+1.65V}}$$

Answer =



- 5 (f) (ii) Use half-equations from **Table 3** to construct an overall equation for the cell reaction.

[1 mark]



Make sure you
work out which one
is oxidised and
reduced + then cancel
out the electrons!

- 5 (f) (iii) Identify which of **A** or **B**, in **Figure 1**, is the positive electrode. Give a reason for your answer.

[2 marks]

Positive electrode A → Stainless steel lid.

Reason The O₂ has a more positive E° value and would therefore gain electrons

- 5 (f) (iv) Suggest one reason, other than cost, why this type of cell is not recharged.

[1 mark]

Cell reaction is irreversible.

You may not
know this answer
but if something can't
be recharged - common
sense dictates
answer is (2)

14

Turn over for the next question

Turn over ►



6 Hydrogen–oxygen fuel cells are used to provide electrical energy for electric motors in vehicles.

6 (a) In a hydrogen–oxygen fuel cell, a current is generated that can be used to drive an electric motor.

6 (a) (i) Deduce half-equations for the electrode reactions in a hydrogen–oxygen fuel cell.

[2 marks]



You could use
 H^+ (acid) cells
inst. red.

6 (a) (ii) Use these half-equations to explain how an electric current can be generated.

[2 marks]

Electrons are released from the hydrogen electrode and are accepted by the oxygen electrode.

6 (b) Explain why a fuel cell does not need to be recharged.

[1 mark]

The fuel is supplied continuously.

6 (c) To provide energy for a vehicle, hydrogen can be used either in a fuel cell or in an internal combustion engine.

Suggest the main advantage of using hydrogen in a fuel cell rather than in an internal combustion engine.

[1 mark]

It is much more efficient.



- 6 (d) Identify **one** major hazard associated with the use of a hydrogen–oxygen fuel cell in a vehicle.

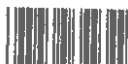
[1 mark]

Hydrogen is explosive.

7

Turn over for the next question

Turn over ►

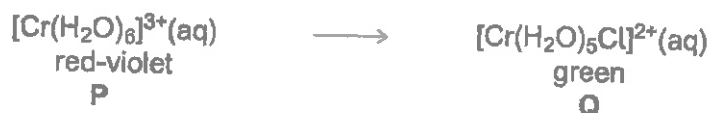


Section B

Answer all questions in the spaces provided.

7 The characteristic properties of transition metals include coloured ions, complex formation and catalytic activity.

7 (a) Consider the chromium complexes P and Q.



Explain, with reference to oxidation states and electron configurations, why the chromium ions in complexes P and Q contain the same number of d electrons. You should not consider the electrons donated by the ligands.

Explain, in terms of electrons, why the complexes are different colours. (You are **not** required to explain why the observed colours are red-violet and green.)

[6 marks]

In both P and Q chromiums oxidation state is +3, and they both have $3d^3$ electrons.

However they do have different ligands. It is these ligands that give rise to the colour differences. They cause different d electron splitting which means that different wavelengths of light is absorbed. Since different wavelengths are absorbed - different wavelengths are reflected.

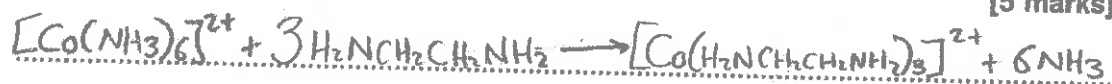
One of the most common mistakes here is confusing this with how flame tests work... About!



7 (b)

Write an equation to show how the $[\text{Co}(\text{NH}_3)_6]^{2+}(\text{aq})$ ion reacts with 1,2-diaminoethane. Explain the thermodynamic reasons why this reaction occurs.

[5 marks]



4 moles on left vs 7 moles on Right
therefore increase in disorder / entropy

As no. of and type of bonds are same then ΔH is approx. zero

ΔG is negative.

Another version of this
question is sometimes asked
involving EDTA as hexadentate
ligand be prepared.

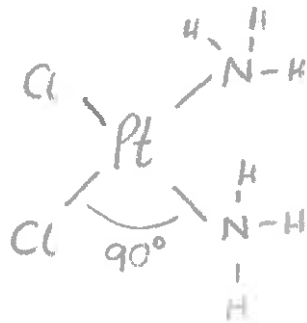
Question 7 continues on the next page

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7 (c) The toxic complex cisplatin is an effective anti-cancer drug because it reacts with the DNA in cancer cells, preventing cell division.

7 (c) (i) Draw the **displayed** structure of cisplatin.
On your structure, show the value of one of the bond angles at platinum.
State the charge, if any, on the complex.



[3 marks]

zero charge

square planar

Tricky one this - it
specifically wants
DISPLAYED formula
to show all N-H
bonds!

7 (c) (ii) When cisplatin is ingested, an initial reaction involves one of the chloride ligands being replaced by water.

Write an equation for this reaction.

Don't forget
the new ionic
charge

[1 mark]



7 (c) (iii) Suggest how the risk associated with the use of this drug can be minimised.

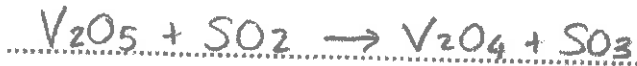
[1 mark]

Small doses.



- 7 (d) Explain, with the aid of equations, how and why vanadium(V) oxide is used in the Contact Process.

[4 marks]



Vanadium oxide is acting as a catalyst - speeding up the reaction between SO_2 and O_2 .

Very common question
Learn the reactions!

20

Turn over for the next question

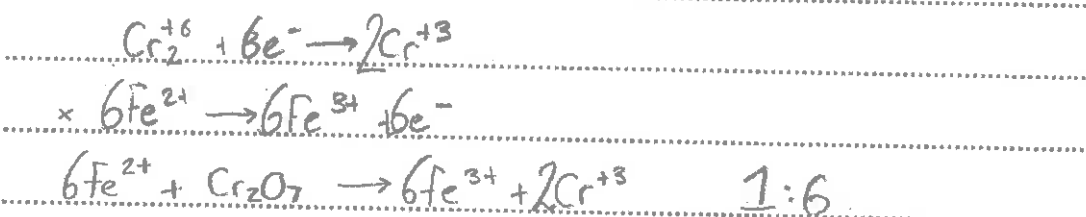
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- 8 A student carried out an experiment to find the mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in an impure sample, X.
The student recorded the mass of X. This sample was dissolved in water and made up to 250 cm^3 of solution.
The student found that, after an excess of acid had been added, 25.0 cm^3 of this solution reacted with 21.3 cm^3 of a $0.0150 \text{ mol dm}^{-3}$ solution of $\text{K}_2\text{Cr}_2\text{O}_7$
- 8 (a) Use this information to calculate a value for the mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in the sample of X.

[5 marks]

$$\frac{21.3}{1000} = 0.0213 \text{ dm}^3 \quad 0.0150 \times 0.0213 = 3.195 \times 10^{-4} \text{ moles.}$$



$$\therefore 3.195 \times 10^{-4} \times 6 = 1.917 \times 10^{-3} \text{ moles}$$

$$1.917 \times 10^{-3} \times 10 = 1.917 \times 10^{-2} \text{ moles in orig sample.}$$

Don't forget it was 250 cm³.

$$1.917 \times 10^{-2} \times 277.9 = 5.33 \text{ g}$$



- 8 (b) The student found that the calculated mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was greater than the actual mass of the sample that had been weighed out. The student realised that this could be due to the nature of the impurity.

Suggest one property of an impurity that would cause the calculated mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in X to be greater than the actual mass of X.

Explain your answer.

[2 marks]

The impurity would need to have reacted with
the dichromate - and in greater quantities for it
to be greater than the actual mass.

7

END OF QUESTIONS



There are no questions printed on this page

**DO NOT WRITE ON THIS PAGE
ANSWER IN THE SPACES PROVIDED**



