WJEC EDUQAS A-LEVEL CHEMISTRY · COMPONENT 1

CHEMISTRY



EXAM QUESTION PACK

PI2.2 CHEMISTRY OF THE D-BLOCK TRANSITION METALS

SCORE	PERCENTAGE
/63	%

STEMUP

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1.

Read the passage below and then answer the questions (a) to (e) in the spaces provided.

Copper – an essential element

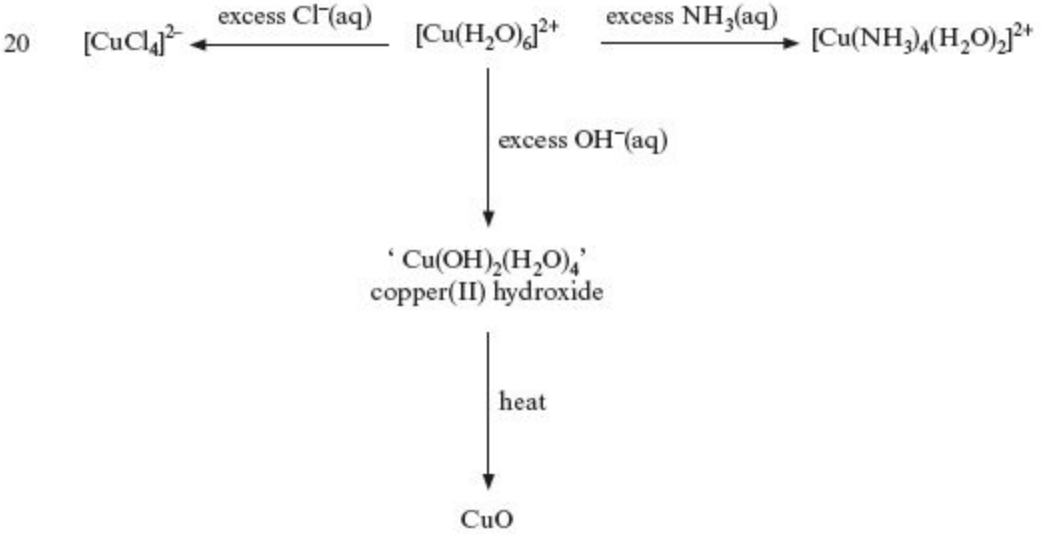
There is an ever-increasing world demand for copper and this has driven its cost upwards. This has led to the extraction of copper from sources once thought to be uneconomic. One such source of copper is the spoil heaps from old mines. The spoil heap material is crushed and then sprayed with acidified water in the presence of the bacterium *Thiobacillus ferrooxidans*. These bacteria convert any iron present to aqueous iron(III) ions, which then oxidise sulfide ions to aqueous sulfate(VI) ions, SO_4^{2-}. A solution containing copper(II) sulfate is produced that is then treated with iron to leave copper.

$$Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$$

The concentration of copper in this copper(II) sulfate solution can be found by a variety of methods, which include

- precipitating the copper and weighing it
- reacting the solution with an excess of iodide ions and titrating the liberated iodine with aqueous sodium thiosulfate
- titrating the copper(II) ions with ethylenediaminetetra-acetic acid (EDTA)
- using instrumental methods such as atomic absorption and X-ray fluorescence spectroscopy

Copper(II) sulfate continues to be a familiar and commonly used substance in schools and colleges and its reactions are typical of many transition metal compounds. For example, in aqueous solution the copper ions are present as the complex cation, $[Cu(H_2O)_6]^{2+}$. The water molecules in this complex ion can be replaced by other ligands.



Copper is a relatively unreactive metal and is easy to obtain by the smelting of its ores, as was carried out in the Bronze Age. Small quantities of many transition metals can be produced by strongly heating the oxide with aluminium or magnesium. One application of this is the reaction of aluminium with iron(III) oxide to give molten iron that can be used to weld together lengths of railway track. A similar reaction occurs when magnesium is strongly heated with copper(II) oxide.

$$Mg(s) + CuO(s) \longrightarrow Cu(l) + MgO(s) \qquad \Delta H = -431\,kJ\,mol^{-1}$$

Transition metals also have important uses as catalysts and copper can be used as an economical catalyst in a number of organic processes, for example in the production of methanal.

$$CH_3OH \xrightarrow[600\ K]{Cu} \begin{matrix} H \\ \diagdown \\ C{=}O \\ \diagup \\ H \end{matrix}$$

- End of passage -

(a) The percentage of copper in a sample from a spoil heap was found by a titration using ethylenediaminetetra-acetic acid (EDTA).
19.20 cm^3 of an EDTA solution of concentration 0.010 mol dm^{-3} reacted with 50.00 cm^3 of a solution containing copper(II) ions.
EDTA reacts with copper(II) ions in a 1:1 mole ratio.

(i) Calculate the number of moles of EDTA solution used in the titration. [1]

.....

.....

(ii) State the number of moles of copper(II) ions present in 50.00 cm^3 of the copper-containing solution. [1]

.....

(iii) Calculate the concentration of copper in the solution in **g dm^{-3}**. [2]

.....

.....

.....

(iv) The mass of the copper-containing sample was 11.56 g. All the copper in this sample was present in a solution of volume 1.00 dm^3.
Calculate the percentage of copper in the sample. [1]

.....

.....

(b) Both copper and zinc are d-block elements. Explain, using electron configurations, why copper is described as a transition metal and zinc (whose compounds contain Zn^{2+} ions) is not. [2]

(QWC) [1]

.....

.....

.....

.....

(c) The passage shows the formulae of some copper-containing species formed by ligand exchange *(line 20)*.
Complete the table below, stating the approximate shape and colour of the complex ions shown. [2]

Complex ion	Shape	Colour
$[CuCl_4]^{2-}$		
$[Cu(NH_3)_4(H_2O)_2]^{2+}$		

(d) Standard enthalpy of formation values, $\Delta H_f^{\ominus}$, can be used to calculate enthalpy changes, such as the reduction of copper(II) oxide by magnesium, described in the article *(line 27)*.
Some $\Delta H_f^{\ominus}$ values are given in the table below.

Metal oxide	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
CuO	−157
PbO	−217

State and explain how the $\Delta H_f^{\ominus}$ values for these two oxides give an indication of their relative stability. [2]

.....

.....

.....

(e) Many transition metals and their compounds act as catalysts. The article describes copper acting as a catalyst in the oxidation of methanol *(line 30)*.

(i) Give **two** reasons why transition metals and their compounds can act as catalysts. [2]

.....

.....

(ii) Give a reason, in terms of Green Chemistry, why scientists often seek new catalysts for established chemical processes. [1]

.....

.....

Total [15]

2.

Read the passage below and then answer the questions in the spaces provided.

Hydrogen Peroxide

If a non-scientist knows only one chemical formula it is most likely to be H_2O for water but how much do you know about another hydrogen oxide, hydrogen peroxide? A molecule of hydrogen peroxide has the molecular formula H_2O_2.

Most chemistry students first meet hydrogen peroxide as a colourless solution that is used to prepare oxygen. Bottles of hydrogen peroxide from a pharmacist are often labelled '20 volume'. This means that one volume of solution decomposes to give 20 volumes of oxygen gas. The equation for the decomposition is:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

$$1\,dm^3 \qquad\qquad 20\,dm^3$$

This reaction is very slow at room temperature. However the addition of a suitable catalyst increases the rate of decomposition phenomenally. Manganese(IV) oxide, potatoes and blood are all effective. Potatoes and blood both contain the enzyme catalase and one catalase molecule decomposes 50 000 molecules of H_2O_2 per second!

Is hydrogen peroxide an oxidising agent or a reducing agent?

Both in the laboratory and at home hydrogen peroxide is most commonly used as an oxidising agent (so the hydrogen peroxide itself is reduced). The half-equation is:

Reduction $\qquad H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$

Since some colouring matter is bleached by oxidation and the product of hydrogen peroxide's reduction is water, it is used as a safe bleaching agent particularly in hair treatment. A peroxide blonde is someone with almost white hair, usually as a result of treatment with hydrogen peroxide.

However, if hydrogen peroxide reacts with a more powerful oxidising agent such as potassium manganate(VII), the hydrogen peroxide will act as a reducing agent and will itself be oxidised. The half-equation is:

Oxidation $\qquad H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$

Therefore hydrogen peroxide can act as both oxidising agent and reducing agent. In fact, it can react with itself so that alternate molecules are oxidised and reduced. The overall equation is obtained by adding the half-equations for the reduction and oxidation, giving

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

which is the standard decomposition equation!

- End of passage -

(a) Using outer electrons only, draw a dot and cross diagram to show the bonding in a hydrogen peroxide molecule *(line 3)*.

[1]

(b) Use the equation for the decomposition of hydrogen peroxide *(line 8)* to calculate the concentration, in mol dm^{-3}, of aqueous hydrogen peroxide solution in a bottle of '20 volume hydrogen peroxide' at 25 °C.

[1 mol of oxygen occupies 24 dm^3 at 25 °C]

[2]

Concentration = ... mol dm^{-3}

(c) Manganese(IV) oxide *(line 10)* and potassium manganate(VII) *(lines 20-21)* are typical transition metal compounds.

(i) Give **two** reasons why transition metal compounds can act as catalysts.

[2]

(ii) Explain why transition metal complex ions appear coloured.

[4] QWC [1]

(d) In an acidic solution, hydrogen peroxide is oxidised to oxygen by potassium manganate (VII) *(lines 20-23).*

(i) Write the half-equation for the reduction of MnO_4^- to Mn^{2+} ions in acidic solution.

[1]

(ii) Use your answer to (i) and the half-equation given in *line 23* to deduce the overall equation for this reaction.

[2]

(iii) 20.0 cm^3 of an acidified solution of hydrogen peroxide required 14.80 cm^3 of a 0.020 mol dm^{-3} solution of potassium manganate(VII) for complete reaction. Calculate the concentration, in mol dm^{-3}, of the hydrogen peroxide solution.

[3]

Concentration = ... mol dm^{-3}

(e) Explain, using oxidation states, why the decomposition of hydrogen peroxide *(line 27)* can be classified as a redox reaction.

[2]

(Total 18)

3. Many industrial processes use catalysts.

Explain how a catalyst increases the rate of a chemical reaction.

[2]

State **one** example of an industrially or environmentally important heterogeneous catalyst. You should identify the reaction catalysed and name the catalyst.

[1]

(Total 3)

4. *(a)* Copper ions combine with a range of ligands to form complex ions, including $[CuCl_4]^{2-}$ and $[Cu(H_2O)_6]^{2+}$.

(i) State what is meant by a *ligand*. [1]

(ii) Draw the structures of $[CuCl_4]^{2-}$ and $[Cu(H_2O)_6]^{2+}$ ions. [2]

(iii) A solution containing $[Cu(H_2O)_6]^{2+}$ ions is blue. Explain the origin of this colour. [3]

(iv) When excess ammonia is added to a solution containing $[Cu(H_2O)_6]^{2+}$ ions, the colour of the solution changes as a new complex ion is formed. Give the formula of the new complex ion and the colour of the solution formed. [2]

(b) Phosphorus forms two chlorides, PCl_3 and PCl_5, and there is a dynamic equilibrium between these compounds in the gas phase. This is represented by the equation below.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(i) Write an expression for the equilibrium constant, K_p, for this reaction. [1]

(ii) A sealed vessel is filled with PCl_5 at a pressure of 3.0×10^5 Pa. Upon heating, the system comes to equilibrium to form a mixture that contains PCl_3 at a partial pressure of 1.3×10^5 Pa.

I. State the partial pressure of Cl_2 at equilibrium. [1]

.....

II. Calculate the value of the equilibrium constant, K_p, giving its units. [3]

K_p = ...

Units .....

III. As the temperature is increased the value of K_p increases. State what information this provides about the enthalpy change of this reaction, giving a reason for your answer. [1]

.....

.....

(c) Silicon(IV) chloride reacts with water whilst CCl_4 does not. Give the equation for the reaction of $SiCl_4$ with water and explain why the behaviour of CCl_4 and $SiCl_4$ with water is so different. [2]

.....

.....

.....

Total [16]

5.

Halogens and their compounds take part in a wide variety of reactions.

(a) Give the chemical name of a chlorine-containing compound of commercial or industrial importance. State the use made of this compound. [1]

.....

.....

(b) Hydrogen reacts with iodine in a reversible reaction.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

An equilibrium was established at 300 K, in a vessel of volume 1 dm^3, and it was found that 0.311 mol of hydrogen, 0.311 mol of iodine and 0.011 mol of hydrogen iodide were present.

(i) Write the expression for the equilibrium constant in terms of concentration, K_c. [1]

(ii) Calculate the value of K_c at 300 K. [1]

K_c = ...

(iii) What are the units of K_c, if any? [1]

.....

(iv) Equilibria of H_2, I_2 and HI were set up at 500 K and 1000 K and it was found that the numerical values of K_c were 6.25×10^{-3} and 18.5×10^{-3} respectively.

Use these data to deduce the sign of ΔH for the forward reaction. Explain your reasoning. [3]

.....

.....

.....

.....

(c) When concentrated hydrochloric acid is added to a pink aqueous solution of cobalt(II) chloride, the colour changes to blue.

Cobalt takes part in an equilibrium reaction.

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

(i) What is the oxidation state of cobalt in $[CoCl_4]^{2-}$? [1]

.....

(ii) What type of bonding is present in $[CoCl_4]^{2-}$? [1]

.....

(iii) Use the equation to identify the ions responsible for the pink and blue colours described above. Explain why the colour change occurs when concentrated hydrochloric acid is added to the pink solution. [3]

.....

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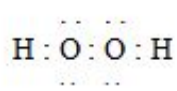
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(iv) Draw diagrams to clearly show the shape of the $[Co(H_2O)_6]^{2+}$ ion and the $[CoCl_4]^{2-}$ ion. [2]

$[Co(H_2O)_6]^{2+}$ $[CoCl_4]^{2-}$

Total [14]

2 (a)



[1]

(b) 20 dm^3 oxygen = 0.83 mol (1)

Moles H_2O_2 = 1.67 and $[H_2O_2]$ = 1.67 mol dm^{-3} (1) [2]

(c) (i) Variable oxidation states / partially filled 3d energy levels /ability to adsorb 'molecules' / form complexes (or temporary bonds) with reacting molecules
(Accept any two answers)
Do not accept 'empty / unfilled d-orbitals' [2]

(ii) 3d orbitals split by ligands (1)

Three d-orbitals have lower energy, two have higher energy (1)

Electrons absorb (visible light) energy to jump from lower level to higher level (1)

The colour is that due to the remaining / non-absorbed frequencies (1)
(Appropriate diagrams are acceptable alternatives)
[4]

QWC Legibility of text; accuracy of spelling, punctuation and grammar, clarity of meaning [1]

(d) (i) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ [1]

(ii) $5H_2O_2 + 6H^+ + 2MnO_4^- \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$ [2]

(Mark consequentially from (i) – 1 mark if formulae correct but equation not balanced properly)

(iii) Moles $MnO_4^- = \frac{0.02 \times 14.8}{1000} = 2.96 \times 10^{-4}$ (1)

Moles $H_2O_2 = 7.40 \times 10^{-4}$ (1)

Concentration $H_2O_2 = \frac{7.40 \times 10^{-4}}{0.020} = 0.037$ mol dm^{-3} (1) [3]

(e) Oxidation state of oxygen starts at –1 (in peroxide) (1)
Oxidation state in water is –2 (reduced)
oxidation state in oxygen is 0 (oxidised) (1) [2]

Total [18]

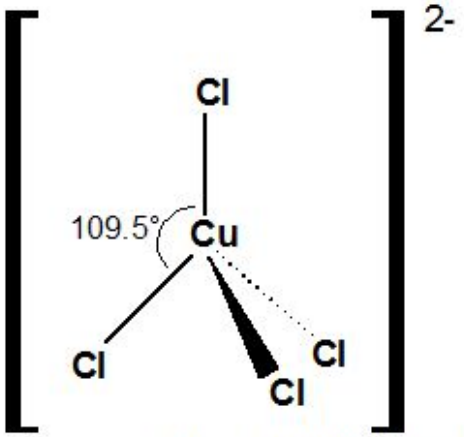
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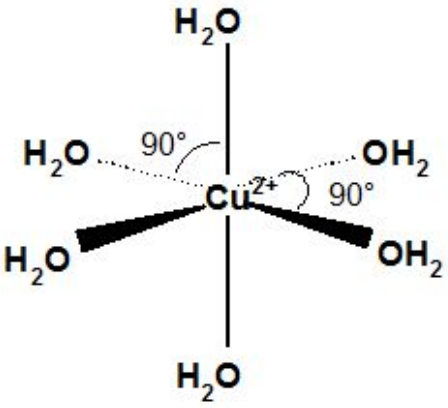
3 Provides an alternative pathway (1)
with lower activation energy / more particles have energy above E_A (1) **[2]**

any example e.g. [1]
iron for Haber process / manufacture of ammonia
vanadium(V) oxide in Contact process / manufacture of sulfuric acid
platinum / palladium / rhodium in catalytic converters / to remove toxic gases from exhaust fumes
nickel in hydrogenation of alkenes / unsaturated oils

4 (a) (i) Species with lone pair that can bond to a metal atom/ion (1) [1]

(ii) Must clearly show which atoms are bonded and the 3D structure
1 mark each (2) [2]





(iii) Ligands cause d-orbitals to split into three lower and two higher (1)
Electrons move from lower level to higher level by absorbing some frequencies (1)
Light not absorbed gives colour seen (1) [3]

(iv) $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (1) Royal blue (1) [2]

(b) (i) $K_p = \frac{P_{PCl_3}P_{Cl_2}}{P_{PCl_5}}$ do not accept if [ ] included [1]

(ii) I. 1.3×10^5 (Pa) [1]

II. $P_{PCl_5} = 3.0 \times 10^5 - 1.3 \times 10^5 = 1.7 \times 10^5$ (1) (ecf from part I)

$K_p = (1.3 \times 10^5 \times 1.3 \times 10^5) / 1.7 \times 10^5 = 9.9 \times 10^4$ (1)

Pa (1) [3]

III. Endothermic as equilibrium shifts to products when temperature increases [1]

(c) $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ OR

$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$ (1)

Silicon has available empty d-orbitals whilst carbon does not /
Silicon can expand its octet whilst carbon cannot (1) [2]

Total [16]

5 *(a)* Name of any commercially/ industrially important chlorine containing compound e.g. (sodium) chlorate(I) as bleach/ (sodium) chlorate(V) as weedkiller/ aluminium chloride as catalyst in halogenation

- do not accept CFCs **[1]**

(b) (i) $K_c = \frac{[HI]^2}{[H_2][I_2]}$ must be square brackets **[1]**

(ii) $K_c = \frac{0.11^2}{3.11^2} = 1.25 \times 10^{-3}$ follow through error (ft) **[1]**

(iii) K_c has no units ft **[1]**

(iv) when temperature increases K_c increases (1)

this means equilibrium has moved to RHS
/ increasing temperature favours endothermic reaction (1)

therefore ΔH for forward reaction is +ve (1)
(mark only awarded if marking point 2 given) **[3]**

(c) (i) +2 **[1]**

(ii) co-ordinate/ dative (covalent) **[1]**

(iii) pink is $[Co(H_2O)_6]^{2+}$ **and** blue is $[CoCl_4]^{2-}$ (1)

(ligand is) Cl^- (1)

(addition of HCl sends) equilibrium to RHS (1) **[3]**

(iv) $[Co(H_2O)_6]^{2+}$ shown as octahedral [with attempt at 3D] (1)

$[CoCl_4]^{2-}$ shown as tetrahedral/ square planar (1) **[2]**

Total [14]