

WJEC A-LEVEL CHEMISTRY • UNIT 3

CHEMISTRY



EXAM QUESTION PACK

3.2 REDOX REACTIONS

SCORE

/87

PERCENTAGE

%

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1. Potassium peroxodisulfate(VI) (persulfate) is a white crystalline compound of formula $\text{K}_2\text{S}_2\text{O}_8$. It is a powerful oxidising agent and has uses as a food additive, in hair dyes and as a nappy steriliser.

(a) Unusually for potassium compounds, it is not very soluble in water.

Temperature / °C	Solubility / g per 100 g H_2O
0	1.75
20	5.29

1 dm^3 of a saturated solution of potassium persulfate at 20°C was cooled to 0°C . Calculate the mass of solid potassium persulfate that crystallised from the solution. [2]

- (b) (i) A hot solution of potassium persulfate slowly decomposes, giving oxygen as one of the products.

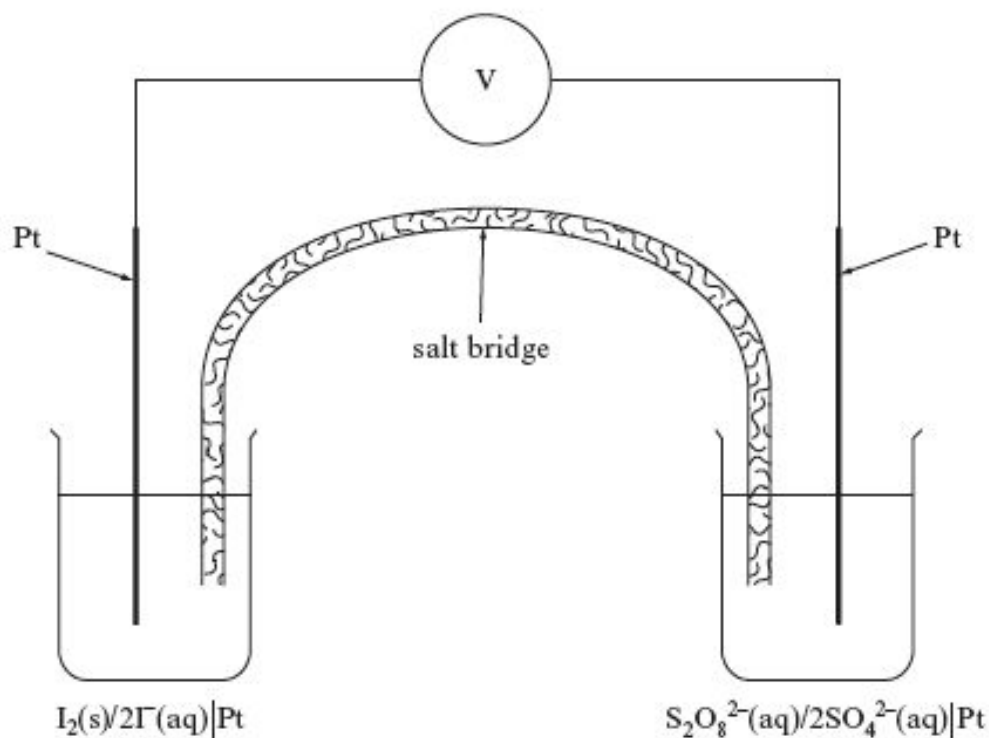


Calculate the maximum volume of oxygen gas that can be produced at 80°C when a solution containing 0.100 mol of potassium persulfate decomposes as shown above. [2]

[At 80°C 1 mol of oxygen has a volume of 29.0 dm^3]

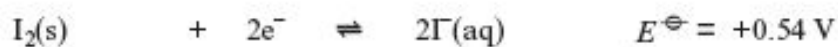
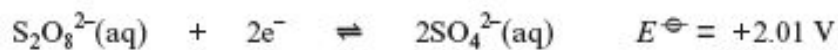
- (ii) Suggest a way that the rate of decomposition of the potassium persulfate solution described in (i) could be measured. [1]

(c) The diagram below shows a cell that uses persulfate ions in aqueous solution.



- (i) State the role of the platinum electrodes in this cell. [1]

(ii) Use the information given in the equations to state and explain the direction of electron flow in the external circuit. [2]



(d) The reaction between persulfate ions and iodide ions in aqueous solution is



In an experiment to follow the rate of this reaction, the values below were obtained.

Experiment	Initial rate / $\text{mol dm}^{-3}\text{s}^{-1}$	Initial concentration of $\text{S}_2\text{O}_8^{2-}$ / mol dm^{-3}	Initial concentration of I^- / mol dm^{-3}
1	8.64×10^{-6}	0.0400	0.0100
2	3.46×10^{-5}	0.0800	0.0200

- (i) The reaction is first order with respect to iodide ions. Use both the initial rate values and the concentrations to show that the order with respect to persulfate ions is also first order. [2]

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- (ii) Write the rate equation for this reaction and use it to calculate the value of the rate constant, k , giving its units. [3]

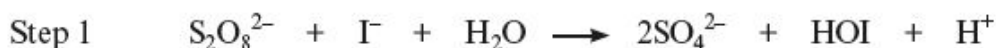
.....

.....

.....

..... Units

- (iii) It is suggested that this reaction occurs in two steps.



State, using your answer to (ii), why Step 1 is the rate-determining step. [1]

.....

.....

Total [14]

2. The leaves of the rhubarb plant are rich in ethanedioic acid (oxalic acid) which is a poisonous compound. A solution containing ethanedioate ions can be formed by boiling rhubarb leaves with water. It can be separated and samples titrated against acidified potassium manganate(VII) to find the concentration of the ethanedioate solution.

(a) Suggest how the ethanedioate solution could be separated from the rhubarb leaves.

[1]

(b) Write an ion-electron half-equation for the reduction of acidified manganate(VII) ions, MnO_4^- . [1]

(c) The ion-electron half-equation for the oxidation of ethanedioate ions is given below.



(i) Give the oxidation states for carbon at the start and end of this reaction. [1]

(ii) Write an equation for the reaction of acidified manganate(VII) ions with ethanedioate ions. [1]

(d) Give a reason why an indicator is not needed in this titration.

[1]

- (e) Four samples of 25.00 cm^3 of the ethanedioate solution were titrated against acidified potassium manganate(VII) solution of concentration $0.0200 \text{ mol dm}^{-3}$. The volumes of potassium manganate(VII) solution required for complete reaction are listed below.

	1	2	3	4
Volume of $\text{KMnO}_4(\text{aq}) / \text{cm}^3$	28.80	27.95	28.00	27.80

Use the information given to calculate the concentration of the ethanedioate solution. [4]

- (f) Heating ethanedioic acid in glycerol produces methanoic acid, HCOOH .

- (i) Write the expression for the acid dissociation constant, K_a , for methanoic acid. [1]
- (ii) The value of K_a for methanoic acid is $1.8 \times 10^{-4} \text{ mol dm}^{-3}$.
Calculate the pH of a solution of methanoic acid of concentration 0.2 mol dm^{-3} . [3]

- (iii) A mixture of methanoic acid and sodium methanoate can be used as a buffer solution. State what is meant by a *buffer solution* and explain how a mixture of methanoic acid and sodium methanoate acts as a buffer.

[3] QWC [1]

(g) Acidified potassium dichromate, $K_2Cr_2O_7$, is also an oxidising agent.

(i) Give the colour change that occurs when acidified potassium dichromate acts as an oxidising agent

[1]

(ii) When sodium hydroxide is added to a solution of potassium dichromate, a colour change occurs without a redox reaction occurring. Give the formula of the new chromium-containing ion and the colour of the solution formed.

[2]

(Total 20)

3. (a) Electrochemical cells are used as power sources in many everyday applications. To decide what to use in a cell, it is necessary to know the standard electrode potential for electrodes. This is measured using a standard hydrogen electrode as a reference standard.

Draw a labelled diagram of the apparatus you would use to measure the standard electrode potential of an Fe^{3+}/Fe^{2+} electrode. [5]

(b) Vanadium is a transition metal that can form compounds with a variety of oxidation states. Zinc however forms compounds with an oxidation state of +2 only.

(i) Why can transition elements form compounds with a variety of oxidation states? [1]

(ii) Give the electronic structure of Zn. [1]

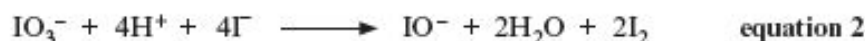
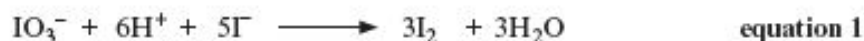
(iii) State why zinc forms Zn^{2+} . [1]

You will need the standard electrode potentials in the table below to answer part (c).

Oxidation state of vanadium at start of reaction	Reaction	$E^\ominus/V$
+5	$VO_3^-(aq) + 4H^+(aq) + e \rightleftharpoons VO^{2+}(aq) + 2H_2O(l)$	+1.00
+4	$VO^{2+}(aq) + 2H^+(aq) + e \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
+3	$V^{3+}(aq) + e \rightleftharpoons V^{2+}(aq)$	-0.26
+2	$V^{2+}(aq) + 2e \rightleftharpoons V(s)$	-1.13
	$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$	-0.76
	$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$	+0.34

- (c) Vanadium(V)(aq), as VO_3^- , is yellow and can be reduced by zinc and aqueous acid producing a series of coloured solutions until the reduction stops with the formation of a violet solution. The reducing agent involves the $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$ equilibrium.
- State the identity of the violet vanadium-containing solution produced in this reduction. Use standard electrode potentials to explain your answer. [3]
 - What is the standard potential of a cell formed from a standard $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$ electrode and a standard $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ electrode? [1]
 - Write the equilibrium equation for the change occurring at the zinc electrode showing the direction in which the reaction proceeds. [1]
 - Use Le Chatelier's principle to predict the effect on the electrode potential of the zinc electrode of increasing the concentration of $\text{Zn}^{2+}(\text{aq})$ in the electrode. Explain your answer. [2]
- (d) Halogens can also form compounds with a variety of oxidation states. Some of these including compounds of iodate(V), IO_3^- , behave as oxidising agents.

A student was investigating the reaction that occurs when iodate(V) oxidises iodide ions to produce iodine. Two possible equations were suggested.



He prepared a solution of potassium iodate(V) by dissolving 0.978 g of KIO_3 in 250 cm^3 of solution. He pipetted 25.0 cm^3 of this solution into a conical flask, added excess potassium iodide and titrated the iodine produced with 0.100 mol dm^{-3} sodium thiosulfate solution, $\text{Na}_2\text{S}_2\text{O}_3$. A volume of 27.40 cm^3 of this solution was needed to react with the iodate(V).

The equation for the reaction of thiosulfate with iodine is shown below.



- Calculate the number of moles of thiosulfate used to react with the iodine. [1]
- Deduce the number of moles of iodine present in the 25.0 cm^3 sample. [1]
- Calculate the number of moles of KIO_3 present in 250 cm^3 of the original solution and hence the number of moles present in 25.0 cm^3 . [1]
- Use your results from (ii) and (iii) to deduce which of **equation 1** and **equation 2** suggested above, correctly shows what happens when iodate(V) ions oxidise iodide ions. Show, by calculation, how you came to this conclusion. [2]

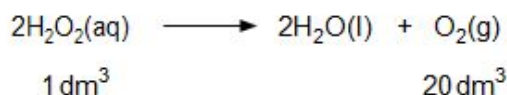
Total [20]

4. 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 .

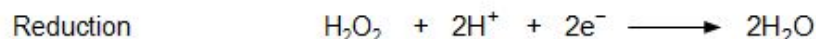
- 5 Most chemistry students first meet hydrogen peroxide as a colourless solution that is used to prepare oxygen. Bottles of hydrogen peroxide from a pharmacist are often labelled '20 volume'. This means that one volume of solution decomposes to give 20 volumes of oxygen gas. The equation for the decomposition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



- 10 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!

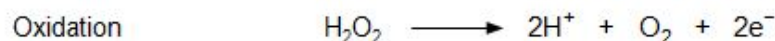
Is hydrogen peroxide an oxidising agent or a reducing agent?

- 15 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:



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.

- 20 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:



- 25 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



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 cm³ of an acidified solution of hydrogen peroxide required 14.80 cm³ 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)

6. Haematite is an ore of iron that contains Fe_2O_3 . Iron is extracted from this ore in a blast furnace.

(a) Balance the equation for the extraction of iron from Fe_2O_3 . [1]



(b) Use oxidation states to show that the reaction in (a) is a redox reaction. [2]

(c) A different oxide of iron is iron(II) oxide, FeO . The ions in this compound adopt an arrangement similar to that of sodium chloride.

(i) Give the crystal co-ordination numbers for the ions in FeO . [1]

(ii) Draw the arrangement of oxide ions around each iron ion. [1]

(d) Iron can be extracted from FeO according to the equation below.



Calculate the mass of iron that could be extracted from 20.0 kg of iron(II) oxide, FeO . [3]

(e) Carbon monoxide contains two covalent bonds and one co-ordinate bond. Explain what is meant by the terms **covalent bond** and **co-ordinate bond**, indicating the difference between them.

[2]

(f) Iron is a typical metal. Describe the bonding present in iron. Explain how it can conduct electricity and why it has a high melting temperature.

[4] QWC [1]

(Total 15)

2.

- (a) Filtration [1]
- (b) $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ [1]
- (c) (i) Carbon O.S. at start = +3; Carbon O. S. at end = +4 [1]
(ii) $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$ [1]
- (d) Colour change of manganate(VII) is used to indicate the change [1]
- (e) Volume of manganate(VII) = 27.92 cm^3 (1)
Moles manganate = $27.92 \times 0.020 / 1000 = 5.584 \times 10^{-4} \text{ mol}$ (1)
Moles oxalate = $5.584 \times 10^{-4} \times 5/2 = 1.396 \times 10^{-3} \text{ mol}$ (1)
Concentration = $1.396 \times 10^{-3} / 25 \times 10^{-3} = 0.0558 \text{ mol dm}^{-3}$ (1) [4]
- (f) (i) $K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$ [1]
(ii) $[\text{H}^+]^2 = K_a \times [\text{HCOOH}] = 1.8 \times 10^{-4} \times 0.2 = 0.36 \times 10^{-4}$ (1)
 $[\text{H}^+] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ (1)
 $\text{pH} = -\log [\text{H}^+] = 2.22$ (1) [3]
(iii) A buffer keeps the pH almost constant when **small amounts** of acid or base are added (1)
 $\text{HCOOH} \rightleftharpoons \text{HCOO}^- + \text{H}^+$ (1)
Adding acid shifts the equilibrium to the left which removes H^+ /
Adding base removes H^+ shifts equilibrium to right which replaces H^+ (1)
OR answer in terms of H^+ reacting with methanoate from sodium methanoate when acid added (1) and methanoic acid replacing H^+ when base removes H^+ (1)
MAX 3 [3]
QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter [1]
- (g) (i) Orange to green [1]
(ii) CrO_4^{2-} (1) Yellow (1) [2]

Total [20]

3.

(a) diagram with labels to show

H_2/H^+ shown in electrode (1)

platinum (in both electrodes) (1)

$\text{Fe}^{2+}(\text{aq})$ and $\text{Fe}^{3+}(\text{aq})$ (1)

high resistance voltmeter (1)

salt bridge (1)

gas at 1atm pressure, solutions of concentration 1 mol dm^{-3} , temperature 298K (1)

[any 5] [5]

(b) (i) successive ionisation energies increase gradually/ the energies of the d orbitals are similar [1]

(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} / 3d^{10} 4s^2$ [1]

(iii) after 4s electrons lost 3d is full/ stable/ d electrons ionisation energy very high [1]

(c) (i) violet solution contains V^{2+} (1)

SEP Zn^{2+}/Zn is more negative than $\text{VO}_3^-/\text{VO}^{2+}$ and $\text{VO}^{2+}/\text{V}^{3+}$ and therefore

releases electrons/ $\text{VO}_3^-/\text{VO}^{2+}$ and $\text{VO}^{2+}/\text{V}^{3+}$ are more positive than

Zn^{2+}/Zn and are stronger oxidising agents (1)

V^{2+} cannot be reduced (to V) since SEP is more negative than Zn^{2+}/Zn (1) [3]

(ii) 1.1V (ignore sign) [1]

(iii) $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^- / \text{Zn}(\text{s}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$ with some indication of direction [1]

(iv) if $\text{Zn}^{2+}(\text{aq})$ concentration increased equilibrium moves to LHS (1)

so electrode potential becomes less negative (1) [2]

(d) (i) 2.74×10^{-3} (mol) [1]

(ii) 1.37×10^{-3} (mol) [1]

(iii) $M_r \text{KIO}_3 = 214.1$

moles $\text{KIO}_3 = 0.978 / 214.1 = 4.57 \times 10^{-3}$ in 250 cm^3

4.57×10^{-4} in 25 cm^3 [1]

(iv) $1.37 \times 10^{-3} / 4.57 \times 10^{-4} = 3$ (1)

equation 1 is correct since 3 moles of iodine formed (mark awarded for reason) (1) [2]

Total [20]

3.



(b) $20 \text{ dm}^3 \text{ oxygen} = 0.83 \text{ mol}$ (1)
 $\text{Moles H}_2\text{O}_2 = 1.67$ and $[\text{H}_2\text{O}_2] = 1.67 \text{ mol dm}^{-3}$ (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]



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

(iii) $\text{Moles MnO}_4^- = \frac{0.02 \times 14.8}{1000} = 2.96 \times 10^{-4}$ (1)
 $\text{Moles H}_2\text{O}_2 = 7.40 \times 10^{-4}$ (1)
 $\text{Concentration H}_2\text{O}_2 = \frac{7.40 \times 10^{-4}}{0.020} = 0.037 \text{ mol dm}^{-3}$ (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]

4.



- (b) Oxidation state of carbon at start = +2 and at end = +4 so it has been oxidised (1)
 Oxidation state of iron at start = +3 and at end = 0 so it has been reduced (1)
 Credit 1 mark if all oxidation states are given correctly with incorrect or no reference to what has been oxidised/reduced [2]

- (c) (i) 6:6 [1]

(ii)

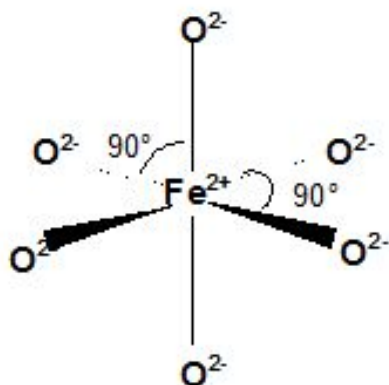


Diagram must be unambiguous, either by showing 3 dimensions, bond angles or through labelling, must identify iron and oxide as ions

[1]

- (d) Moles FeO = $20,000 \div (55.8 + 16) = 278.6$ mol (1)
 Moles Fe = moles FeO = 278.6 mol (1)
 Mass Fe = $278.6 \times 55.8 / 1000 = 15.5$ kg (1) [3]

- (e) Pair of shared electrons in both (1)
 Covalent – 1 electron from each atom **and**
 Co-ordinate – 2 electrons from same atom (1) [2]

- (f) Lattice / regular arrangement of positive ions (1)
 Sea of delocalised electrons (1)
 Electrons can move to form an electrical current (1)
 Strong forces / bonds between the delocalised electrons and the metal ions require a lot of energy to break / high temperature to overcome (1) [4]
QWC: selection of a form and style of writing appropriate to purpose and to complexity of subject matter [1]

Total [15]