WJEC Chemistry A-level

PI1.1: Redox and Standard Electrode Potentials

Practice Questions

England Specification

1.

Potassium peroxodisulfate(VI) (persulfate) is a white crystalline compound of formula $K_2S_2O_8$. 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]

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

$$2K_2S_2O_8(aq) + 2H_2O(l) \longrightarrow 4KHSO_4(aq) + O_2(g)$$

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]

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

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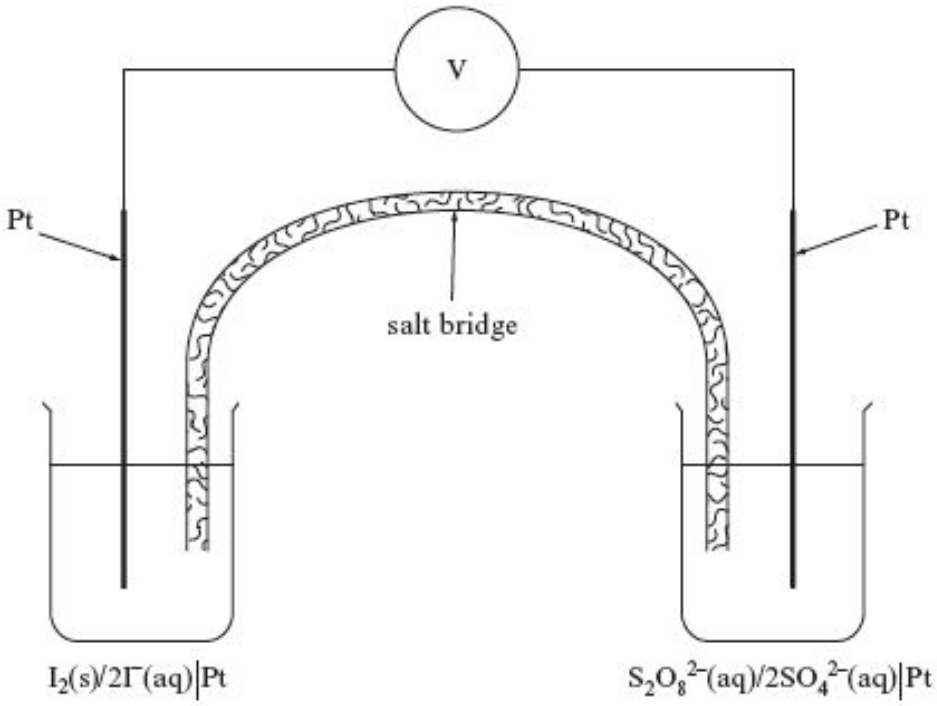
(c) The diagram below shows a cell that uses persulfate ions in aqueous solution.



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

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

$$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq) \qquad E^\ominus = +2.01\ V$$

$$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq) \qquad E^\ominus = +0.54\ V$$

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

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

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

Experiment	Initial rate / mol $dm^{-3}s^{-1}$	Initial concentration of $S_2O_8^{2-}$ / 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]

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..... *Units* .....

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

Step 1 $S_2O_8^{2-} + I^- + H_2O \longrightarrow 2SO_4^{2-} + HOI + H^+$

Step 2 $HOI + H^+ + I^- \longrightarrow H_2O + I_2$

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

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Total [14]

2. The gas oxygen, O_2, is converted into ozone, O_3, in the upper atmosphere. The equation for this process is:

$$3O_2 \longrightarrow 2O_3$$

Use oxidation states to explain why this is not a redox reaction.

[2]

(Total 2)

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 $Zn^{2+}(aq)/Zn(s)$ equilibrium.

(i) State the identity of the violet vanadium-containing solution produced in this reduction. Use standard electrode potentials to explain your answer. [3]

(ii) What is the standard potential of a cell formed from a standard $Zn^{2+}(aq)/Zn(s)$ electrode and a standard $Cu^{2+}(aq)/Cu(s)$ electrode? [1]

(iii) Write the equilibrium equation for the change occurring at the zinc electrode showing the direction in which the reaction proceeds. [1]

(iv) Use Le Chatelier's principle to predict the effect on the electrode potential of the zinc electrode of increasing the concentration of $Zn^{2+}(aq)$ 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.

$$IO_3^- + 6H^+ + 5I^- \longrightarrow 3I_2 + 3H_2O \qquad \textbf{equation 1}$$

$$IO_3^- + 4H^+ + 4I^- \longrightarrow IO^- + 2H_2O + 2I_2 \qquad \textbf{equation 2}$$

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, $Na_2S_2O_3$. 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.

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

(i) Calculate the number of moles of thiosulfate used to react with the iodine. [1]

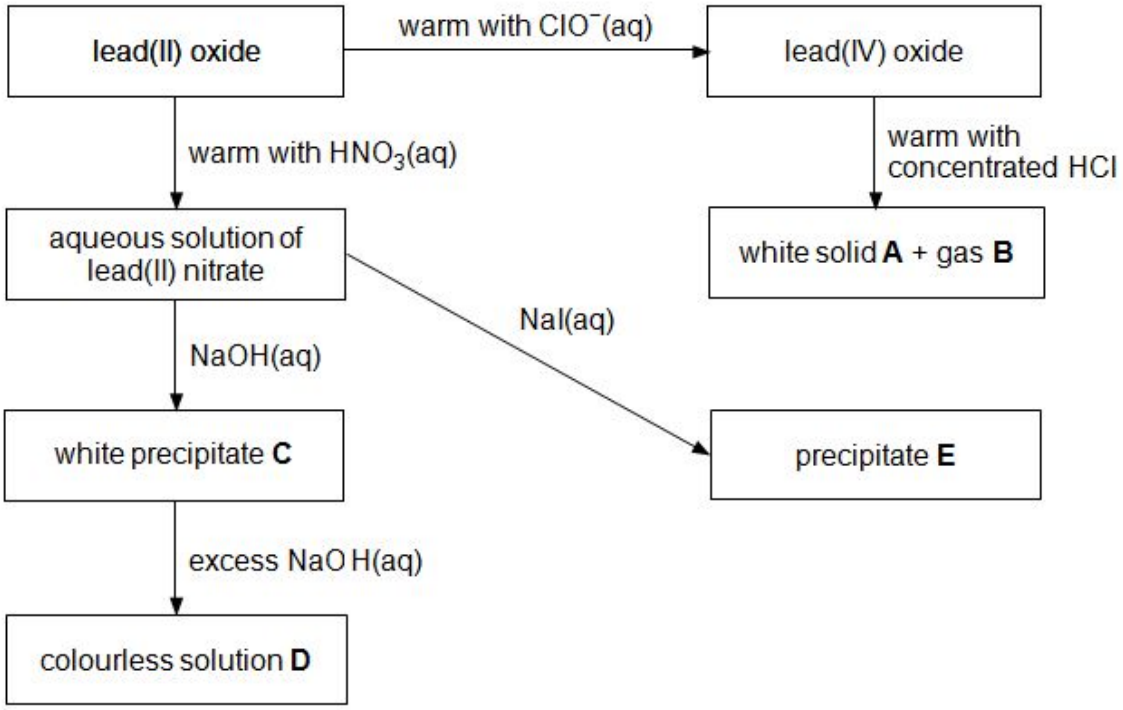
(ii) Deduce the number of moles of iodine present in the 25.0 cm^3 sample. [1]

(iii) 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]

(iv) 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. *(a)* The diagram shows some of the reactions of lead compounds.



(i) State the role of lead(IV) oxide in the reaction with concentrated hydrochloric acid.

[1]

(ii) Name white solid **A** and gas **B**.

[2]

(iii) Give the formula of the lead-containing species present in colourless solution **D**.

[1]

(iv) Give the colour of precipitate **E**.

[1]

(v) Write the equation for the formation of lead(II) nitrate from lead(II) oxide.

[1]

(b) Carbon is the first element in Group 4. Two of its allotropes are diamond and graphite. A compound that forms structures corresponding to diamond and graphite is boron nitride.

(i) Describe the structure of graphite and explain why **hexagonal** boron nitride can adopt the same structure yet have different electrical conductivity properties.

[4] QWC [1]

(ii) State **one** use for the **cubic** boron nitride structure.

[1]

(c) Another element in Group 4 is tin. At low temperatures tin exists as its grey form. At higher temperatures the white form is stable. The change can be represented by the equation:

$$Sn_{(grey)} \longrightarrow Sn_{(white)} \qquad \Delta H^{\ominus} = 1.92\,kJ\,mol^{-1}$$

The standard entropy values are $44.8\,J\,K^{-1}\,mol^{-1}$ for grey tin and $51.5\,J\,K^{-1}\,mol^{-1}$ for white tin.

(i) Calculate the minimum temperature needed to cause grey tin to change to white tin.

[3]

(ii) During Napoleon's disastrous campaign in Russia from June to December in 1812 the tin buttons on his infantry's uniforms disintegrated. Suggest a reason why this might have happened.

[1]

(d) An important technological development in recent years has been the hydrogen fuel cell. This uses electrochemical methods to get energy from hydrogen.

(i) Write the half-equations for the processes occurring at the electrodes and an equation for the overall reaction.

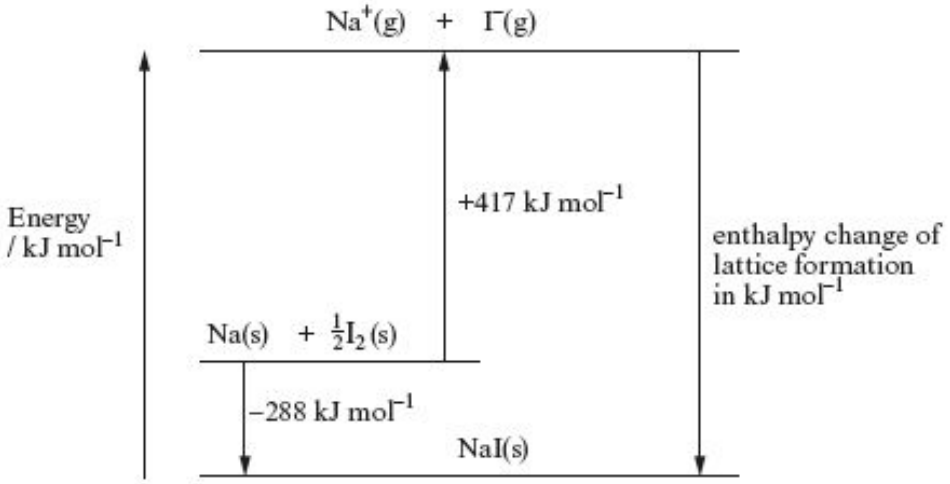
[3]

(ii) Give **one** disadvantage of using hydrogen fuel cells to power vehicles.

[1]

(Total 20)

5. *(a)* The diagram shows an outline of the Born-Haber cycle for the formation of sodium iodide (NaI) from its elements.



Use the information given to calculate the enthalpy change of lattice formation (in kJ mol^{-1}) of sodium iodide. [2]

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(b) Sodium iodide is very soluble in water at room temperature.

(i) Complete the sentence below using the relevant enthalpy terms.

For a compound to be very soluble in water the value of the enthalpy of

..... will be greater than the enthalpy of .....

[1]

(ii) Aqueous solutions of sodium iodide become yellow in the presence of oxygen due to the slow production of iodine.
One suggested reason for this is that a low concentration of hydrogen ions in the solution produces iodine according to the equation below.

$$4H^+(aq) + 4I^-(aq) + O_2(aq) \rightleftharpoons 2I_2(aq) + 2H_2O(l)$$

Use Le Chatelier's principle to suggest a reagent that you could add, apart from water, to decrease the amount of yellow iodine present. Explain your choice. [2]

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(c) Sodium chloride and sodium iodide both react with concentrated sulfuric acid to give the corresponding hydrogen halide e.g.

$$NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI$$

However, the reaction with sodium iodide continues, giving hydrogen sulfide and iodine as two of the products. This further type of reaction does not occur when sodium chloride is used in place of sodium iodide.

(i) Describe what is **seen** when solid sodium iodide is added to concentrated sulfuric acid. [2]

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(ii) The following equations show the standard electrode potentials for the Cl_2/Cl^- and I_2/I^- systems.

$$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \qquad E^\ominus = +1.36\,V$$

$$I_2 + 2e^- \rightleftharpoons 2I^- \qquad E^\ominus = +0.54\,V$$

Use these values to explain why only hydrogen iodide (represented as I^- in the equation) is able to further react with concentrated sulfuric acid in this way. [2]

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(d) The reaction of chlorine with sodium hydroxide solution gives aqueous sodium chlorate(I) as one of the chlorine-containing products.

(i) Give the equation for this reaction. [1]

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(ii) State **one** use for a solution of sodium chlorate(I). [1]

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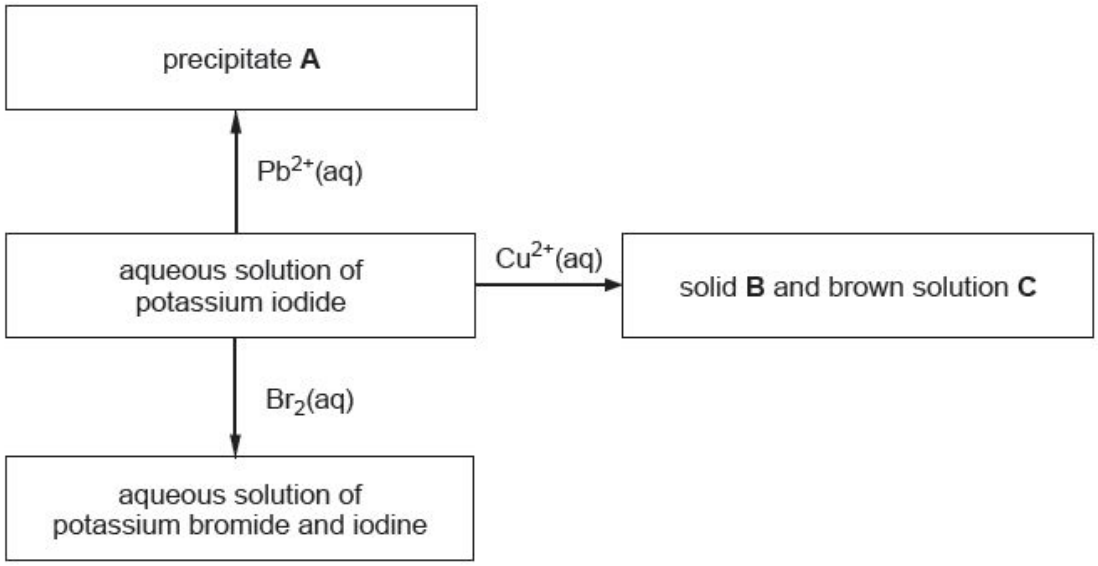
Total [11]

6. The diagram below shows some of the reactions of potassium iodide solution.



(a) Identify precipitate **A** and give its colour. [2]

(b) Write an equation for the reaction of $Cu^{2+}(aq)$ and $I^-(aq)$, clearly identifying the precipitate. [2]

(c) Bromine reacts with aqueous potassium iodide as shown above, however bromine does not react with aqueous sodium chloride. Use the standard electrode potentials below to explain these observations. [3]

QWC [1]

Half-equation	E^θ/V
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.09
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36

(d)Solid potassium iodide reacts with concentrated sulfuric acid in the same way as sodium iodide.

Describe the observations made during this reaction and identify the products formed.

[3]

(e) Hydrogen peroxide reacts with acidified potassium iodide according to the equation below.

$$2H^+ + 2I^- + H_2O_2 \longrightarrow I_2 + 2H_2O$$

(i) This reaction was studied using an iodine clock reaction. Describe the principles of how the rate of a clock reaction is determined. Experimental details are not required. [2]

(ii) The rate of this reaction was studied by a different method for a range of concentrations of $H_2O_2(aq)$ and $I^-(aq)$ and pH values. These are listed in the table below.

Experiment number	Initial concentration of $H_2O_2(aq)$ / mol dm^{-3}	Initial concentration of $I^-(aq)$ / mol dm^{-3}	pH	Initial rate / mol dm^{-3} s^{-1}
1	0.0010	0.10	1	2.8×10^{-6}
2	0.0020	0.10	1	5.6×10^{-6}
3	0.0020	0.10	2	5.6×10^{-6}
4	0.0010	0.40	1	11.2×10^{-6}

I. Some experiments were undertaken at pH 1 and some at pH 2. Give the difference in the concentrations of H^+ ions in these two solutions. [1]

II. Use the data in the table to deduce the rate equation for this reaction, giving your reasoning. [3]

III. Calculate the value of the rate constant, *k*, giving its units. [2]

IV. The reaction is repeated at a higher temperature. State how the increase in temperature affects the rate equation and rate constant. [1]

Total [20]