### HL Paper 2

Consider the following half-cell reactions and their standard electrode potentials.

$$\mathrm{Ni}^{2+}(\mathrm{aq}) + 2\mathrm{e}^{-} \rightleftharpoons \mathrm{Ni}(\mathrm{s}) \quad E^{\Theta} = -0.26 \mathrm{ V}$$
  
 $\mathrm{Al}^{3+}(\mathrm{aq}) + 3\mathrm{e}^{-} \rightleftharpoons \mathrm{Al}(\mathrm{s}) \quad E^{\Theta} = -1.66 \mathrm{ V}$ 

a. Outline two differences between an electrolytic cell and a voltaic cell.
b.i.Deduce a balanced equation for the overall reaction which will occur spontaneously when these two half-cells are connected.
b.iiDetermine the cell potential when the two half-cells are connected.

b.iiOn the cell diagram below, label the negative electrode (anode), the positive electrode (cathode) and the directions of the movement of [4] electrons and ion flow.



Consider the following equilibrium.

$$2\mathrm{SO}_2(\mathrm{g}) + \mathrm{O}_2(\mathrm{g}) \rightleftharpoons 2\mathrm{SO}_3(\mathrm{g}) \quad \Delta H^\Theta = -198 \ \mathrm{kJ \ mol}^{-1}$$

a.ii.State and explain the effect of increasing the pressure on the yield of sulfur trioxide.

a.ivState the effects of a catalyst on the forward and reverse reactions, on the position of equilibrium and on the value of  $K_c$ . [3]

b. When a mixture of 0.100 mol NO, 0.051 mol  $H_2$  and 0.100 mol  $H_2O$  were placed in a  $1.0 \text{ dm}^3$  flask at 300 K, the following equilibrium was [4] established.

established.

$$2\mathrm{NO}(\mathrm{g}) + 2\mathrm{H}_2(\mathrm{g}) \rightleftharpoons \mathrm{N}_2(\mathrm{g}) + 2\mathrm{H}_2\mathrm{O}(\mathrm{g})$$

At equilibrium, the concentration of NO was found to be  $0.062 \text{ mol dm}^{-3}$ . Determine the equilibrium constant,  $K_c$ , of the reaction at this temperature.

c.i. Outline two differences between an electrolytic cell and a voltaic cell.

[2]

[2]

[2]

[1]

C.۱	v.Electroplating is an important application o	f electrolysis. Sta	tate the composition c	of the electrodes a	nd the electrolyte used i	in the silver
	electroplating process.					

The emission spectrum of an element can be used to identify it.

a.iiiHydrogen spectral data give the frequency of $3.28 \times 10^{15} \text{ s}^{-1}$ for its convergence limit.		
Calculate the ionization energy, in J, for a single atom of hydrogen using sections 1 and 2 of the data booklet.		
a.ivCalculate the wavelength, in m, for the electron transition corresponding to the frequency in (a)(iii) using section 1 of the data	a booklet. [1]	
c.ivDeduce any change in the colour of the electrolyte during electrolysis.	[1]	
c.v.Deduce the gas formed at the anode (positive electrode) when graphite is used in place of copper.	[1]	
d. Explain why transition metals exhibit variable oxidation states in contrast to alkali metals.	[2]	
Transition metals:	7	

nunsition mo	itaio.		
Alkali metals:			

The conditions used in an electrolytic cell can determine the products formed.

A voltaic cell is constructed from two half-cells as illustrated below.



Nitrogen monoxide may be removed from industrial emissions via a reaction with ammonia as shown by the equation below.

$$4\mathrm{NH}_3(\mathrm{g})+6\mathrm{NO}(\mathrm{g})\rightarrow 5\mathrm{N}_2(\mathrm{g})+6\mathrm{H}_2\mathrm{O}(\mathrm{l})$$

- a.i. Draw an electrolytic cell illustrating the electrolysis of molten nickel(II) bromide,  $NiBr_2$ . Include in the diagram the direction of the electron flow, [5] the polarity of electrodes and state the half-equations for the product formed at each electrode.
- a.ii.Deduce the equations for the formation of the major product at the positive electrode (anode) when the following aqueous solutions are [2] electrolysed.
  - dilute sodium chloride
  - · concentrated sodium chloride

b.i. Use Table 14 of the Data Booklet to deduce the equation for the spontaneous reaction occurring in this cell.	

[1]

b.ii.Calculate the standard potential for this cell.

b.iiiState the conditions necessary for the potential of the cell to equal that calculated in part (b) (ii) using the data from Table 14. [1]

- c. Using the data below and data from Table 14 of the Data Booklet, predict and explain which metal, cadmium or chromium, may be obtained by [2] electrolysis of separate aqueous solutions of  $Cd^{2+}(aq)$  ions and  $Cr^{2+}(aq)$  ions.
- d.i. Electrolysis is used in the electroplating of metals. The same amount of current is passed through separate aqueous solutions of  $NiSO_4$ , [3]  $Sn(SO_4)_2$  and  $Cr_2(SO_4)_3$  in separate electrolytic cells for the same amount of time. State and explain which cell would deposit the greatest amount (in mol) of metal. Identify the electrode at which the metal is deposited.
- d.iiFor the  $Sn(SO_4)_2$  cell, suggest **two** factors, other than time and current, that would affect the amount of metal deposited during electroplating. [2] e.i. Deduce the oxidation number of the nitrogen in the reactants and product. [3] e.ii.Deduce the oxidation and reduction half-equations and identify the oxidizing agent for the reaction. [3]
- e.iii30.0 dm<sup>3</sup> of ammonia reacts with 30.0 dm<sup>3</sup> of nitrogen monoxide at 100 °C. Identify which gas is in excess and by how much and calculate [2] the volume of nitrogen produced.

The percentage of iron(II) ions,  $Fe^{2+}$ , in a vitamin tablet can be estimated by dissolving the tablet in dilute sulfuric acid and titrating with standard potassium manganate(VII) solution,  $KMnO_4(aq)$ . During the process iron(II) is oxidized to iron(III) and the manganate(VII) ion is reduced to the manganese(II) ion,  $Mn^{2+}(aq)$ . It was found that one tablet with a mass of 1.43 g required  $11.6 \text{ cm}^3$  of  $2.00 \times 10^{-2} \text{ mol dm}^{-3} \text{ KMnO}_4(aq)$  to reach the end-point.

a.i. State the half-equation for the oxidation of the iron(II) ions.	[1]
a.ii.State the half-equation for the reduction of the ${ m MnO}_4^-$ ions in acidic solution.	[1]
a.iiiDeduce the overall redox equation for the reaction.	[1]
b.i.Calculate the amount, in moles, of $ m MnO_4^-$ ions present in $ m 11.6~cm^3$ of $ m 2.00 imes 10^{-2}~moldm^{-3}~KMnO_4(aq).$	[1]
b.ii.Calculate the amount, in moles, of ${ m Fe}^{2+}$ ions present in the vitamin tablet.	[1]
b.iiiDetermine the percentage by mass of ${ m Fe}^{2+}$ ions present in the vitamin tablet.	[2]

Chromium is a typical transition metal with many uses.

A voltaic cell is constructed as follows. One half-cell contains a platinum electrode in a solution containing  $K_2Cr_2O_7$  and  $H_2SO_4$ . The other half-cell contains an iron electrode in a solution containing  $Fe^{2+}$  ions. The two electrodes are connected to a voltmeter and the two solutions by a salt bridge.

a.	Distinguish between the terms oxidation and reduction in terms of oxidation numbers.	[1]
b.	State the names of $Cr_2O_3$ and $CrO_3$ .	[2]
	$Cr_2O_3$ :	
	$CrO_3$ :	

c.i. Define the term oxidizing agent.

c.ii. $Cr_2O_7^{2-}(aq)$  and  $I^-(aq)$  ions react together in the **presence of acid** to form  $Cr^{3+}(aq)$  and  $IO_3^-(aq)$  ions. Deduce the balanced chemical [3] equation for this redox reaction and identify the species that acts as the oxidizing agent.

[1]

d.i. Draw a diagram of the voltaic cell, labelling the positive and negative electrodes (cathode and anode) and showing the direction of movement of [5] the electrons and ions. Deduce an equation for the reaction occurring in each of the half-cells, and the equation for the overall cell reaction.

d.iiDefine the term standard electrode potential.	[1]
d.iiiCalculate the cell potential, in V, under standard conditions, using information from Table 14 of the Data Booklet.	[1]
e.i. State <b>two</b> characteristic properties of transition elements.	[2]
e.ii.State the type of bond formed by a ligand and identify the feature that enables it to form this bond.	[2]

e.iiiExplain why the complex  $\left[ {Cr({H_2}O)_6} \right]^{3\,+}\,$  is coloured.

e.ivDraw an orbital box diagram (arrow-in-box notation) showing the electrons in the 4s and 3d sub-levels in chromium metal.

f. Chromium is often used in electroplating. State what is used as the positive electrode (anode), the negative electrode (cathode) and the
 [3] electrolyte in the chromium electroplating process.

The standard electrode potential for a half-cell made from iron metal in a solution of iron(II) ions,  $Fe^{2+}(aq)$ , has the value -0.45 V.

Consider the following table of standard electrode potentials.

	<i>E</i> <sup>●</sup> / V
$Fe^{2+}(aq) + 2e^{-} \rightleftharpoons Fe(s)$	-0.45
$\operatorname{Sn}^{2+}(\operatorname{aq}) + 2e^{-} \rightleftharpoons \operatorname{Sn}(s)$	-0.14
$H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$	0.00
$\operatorname{Sn}^{4+}(\operatorname{aq}) + 2e^{-} \rightleftharpoons \operatorname{Sn}^{2+}(\operatorname{aq})$	+0.15
$\mathrm{Fe}^{3+}(\mathrm{aq}) + \mathrm{e}^{-} \rightleftharpoons \mathrm{Fe}^{2+}(\mathrm{aq})$	+0.77
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$\frac{1}{2}$ Br <sub>2</sub> (l) + e <sup>-</sup> $\rightleftharpoons$ Br <sup>-</sup> (aq)	+1.07

From the list above:

An acidified solution of potassium dichromate is often used as an oxidizing agent in organic chemistry. During the oxidation reaction of ethanol to ethanal the dichromate ion is reduced to chromium(III) ions according to the following **unbalanced** half-equation.

$$\mathrm{Cr}_2\mathrm{O}_7^{2-}(\mathrm{aq}) + \mathrm{H^+}(\mathrm{aq}) + \mathrm{e^-} 
ightarrow \mathrm{Cr}^{3+}(\mathrm{aq}) + \mathrm{H_2O}(\mathrm{l})$$

Sodium metal can be obtained by the electrolysis of molten sodium chloride.

a.i. Define standard electrode potential.

a.ii.Explain the significance of the minus sign in $-0.45~\mathrm{V}.$	[1]
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b.i.State the species which is the strongest oxidizing agent.

b.iiDeduce which species can reduce  $Sn^{4+}(aq)$  to  $Sn^{2+}(aq)$  but will not reduce  $Sn^{2+}(aq)$  to Sn(s) under standard conditions. [1]

b.iiiDeduce which species can reduce  $\mathrm{Sn}^{2+}(\mathrm{aq})$  to Sn(s) under standard conditions.

c.i. Draw a labelled diagram of a voltaic cell made from an Fe (s) / Fe<sup>2+</sup> (aq) half-cell connected to an Ag(s) / Ag<sup>+</sup> (aq) half-cell operating under [5] standard conditions. In your diagram identify the positive electrode (cathode), the negative electrode (anode) and the direction of electron flow in the external circuit.

[3]

[1]

[2]

[1]

[1]

c.ii.Deduce the equation for the chemical reaction occurring when the cell in part (c) (i) is operating under standard conditions and calculate the		
voltage produced by the cell.		
d.i.Describe the colour change that will be observed in the reaction.	[1]	
d.iiDeduce the oxidation number of chromium in $ m Cr_2O_7^{2-}$ .	[1]	
d.iiiState the balanced half-equation for the reduction of dichromate ions to chromium(III) ions.	[1]	
d.ivDeduce the half-equation for the oxidation of ethanol to ethanal and hence the overall redox equation for the oxidation of ethanol to ethanal by	[3]	
acidified dichromate ions.		
d.vExplain why it is necessary to carry out the reaction under acidic conditions.	[1]	
d.videntify the organic product formed if excess potassium dichromate is used and the reaction is carried out under reflux.	[1]	
e.i. Explain why it is very difficult to obtain sodium from sodium chloride by any other method.	[2]	
e.ii.Explain why an aqueous solution of sodium chloride cannot be used to obtain sodium metal by electrolysis.	[2]	

A voltaic cell was set up, using the standard hydrogen electrode as a reference electrode and a standard  $Cu^{2+}(aq)/Cu(s)$  electrode.

Another voltaic cell was set up, using a  $Sn^{2+}(aq)/Sn(s)$  half-cell and a  $Cu^{2+}(aq)/Cu(s)$  half-cell under standard conditions.

Water in a beaker at a pressure of  $1.01 \times 10^5 \text{ Pa}$  and a temperature of 298 K will not spontaneously decompose. However, decomposition of water can be induced by means of electrolysis.

a.	Define oxidation in terms of oxidation number.	[1]
b.i	. Deduce the balanced chemical equation for the redox reaction of copper, Cu(s), with nitrate ions, $\mathrm{NO}^{3-}(\mathrm{aq})$ , in acid, to produce copper(II)	[2]
	ions, ${ m Cu}^{2+}({ m aq})$ , and nitrogen(IV) oxide, ${ m NO}_2({ m g}).$	
b.i	Deduce the oxidizing and reducing agents in this reaction.	[1]

Oxidizing agent:

Reducing agent:

c.i. Describe the standard hydrogen electrode including a fully labelled diagram.

c.ii.Define the term standard electrode potential,  $E^{\Theta}$ .

c.iiiDeduce a balanced chemical equation, including state symbols, for the overall reaction which will occur spontaneously when the two half-cells [2]

[3]

[1]

are connected.

d.i. Draw a fully labelled diagram of the voltaic cell, showing the positive electrode (cathode), the negative electrode (anode) and the direction of	[3]
electron movement through the external circuit.	
d.ii.Using Table 14 of the Data Booklet, calculate the cell potential, $E_{ m cell}^{\Theta}$ , in V, when the two half-cells are connected.	[1]
e.i. Deduce the sign of the standard free energy change, $\Delta G^{\Theta}$ , for any non-spontaneous reaction.	[1]
e.ii.State why dilute sulfuric acid needs to be added in order for the current to flow in the electrolytic cell.	[1]
e.iiiState why copper electrodes cannot be used in the electrolysis of water. Suggest instead suitable metallic electrodes for this electrolysis	[1]
process.	
e.ivDeduce the half-equations for the reactions occurring at the positive electrode (anode) and the negative electrode (cathode).	[2]
Positive electrode (anode):	
Negative electrode (cathode):	
e.v.Deduce the overall cell reaction, including state symbols.	[1]
e.viDraw a fully labelled diagram of the electrolytic cell, showing the positive electrode (anode) and the negative electrode (cathode).	[2]
e.viComment on what is observed at both electrodes.	[1]
f. Two electrolytic cells are connected in series (the same current passes through each cell). One cell for the electrolysis of water produces 100 cn	n [2]
$^3$ of oxygen, measured at 273 K and $1.01 imes10^5~{ m Pa}$ . The second cell contains molten lead(II) bromide, ${ m PbBr_2}$ . Determine the mass, in g, of	

a.	In acidic solution, bromate ions, BrO <sub>3</sub> <sup>-</sup> (aq), oxidize iodide ions, I <sup>-</sup> (aq).	[1]
	$BrO_3^{-}(aq) + 6H^{+}(aq) + 6e^{-} \rightleftharpoons Br^{-}(aq) + 3H_2O(I)$	
	$2I^{-}(aq) \rightleftharpoons I_{2}(s) + 2e^{-}$	
	Formulate the equation for the redox reaction.	
b.	The change in the free energy for the reaction under standard conditions, $\Delta G^{\Theta}$ , is –514 kJ at 298 K.	[2]
	Determine the value of $E^{\Theta}$ , in V, for the reaction using sections 1 and 2 of the data booklet.	
c.	Calculate the standard electrode potential, in V, for the $BrO_3^-/Br^-$ reduction half-equation using section 24 of the data booklet.	[1]

lead produced.



The standard electrode potential for  $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$  is –0.45 V. The total cell potential obtained when the cell is operating under standard conditions is 0.17 V. Cobalt is produced during the spontaneous reaction.

An electrolytic cell is made using a very dilute solution of sodium chloride.

Predict the products by giving the relevant half-equation for the reaction occurring at each electrode if the electrolyte of the cell described in part (c) was changed to:

a.i. Define the term standard electrode potential and state the meaning of the minus sign in the value of -0.45 V.	[3]
a.ii.Calculate the value for the standard electrode potential for the cobalt half-cell.	[1]
a.iiiDeduce which species acts as the oxidizing agent when the cell is operating.	[1]
a.ivDeduce the equation for the spontaneous reaction taking place when the iron half-cell is connected instead to an aluminium half-cell.	[2]
a.v.Explain the function of the salt bridge in an electrochemical cell.	[2]
b.i. $\left[\mathrm{Co(H_2O)}_6 ight]^{2+}$	[1]
b.ii. $\mathrm{Co}_2(\mathrm{SO}_4)_3$	[1]
b.iii $\left[\mathrm{CoCl}_4 ight]^{2-}$	[1]
c.i. Draw a labelled diagram of the cell. Use an arrow to show the direction of the electron flow and identify the positive and negative electrodes.	[3]
c.ii.Give the formulas of all the ions present in the solution.	[2]
c.iiiPredict the products obtained at each electrode and state the half-equation for the formation of each product.	[3]
c.ivDeduce the molar ratios of the products obtained at the two electrodes.	[1]
d.i.concentrated sodium chloride	[2]
d.ii.molten sodium bromide	[2]

 $\label{eq:constraint} \mbox{Ethanedioic acid (oxalic acid), (COOH)_2, reacts with acidified potassium permanganate solution, $KMnO_4$, according to the following equation. } \label{eq:constraint}$ 

$$5\mathrm{(COOH)}_2\mathrm{(aq)} + 2\mathrm{MnO}_4^-\mathrm{(aq)} + 6\mathrm{H}^+\mathrm{(aq)} 
ightarrow 10\mathrm{CO}_2\mathrm{(g)} + 2\mathrm{Mn}^{2+}\mathrm{(aq)} + 8\mathrm{H}_2\mathrm{O(l)}$$

The reaction is a redox reaction.

d. Deduce the half-equation involving ethanedioic acid.	[1]
e.i. The standard electrode potential for the half-equation involving ethanedioic acid is $E^{\Theta}=-0.49V$ . Using Table 14 of the Data Booklet,	[2]
calculate the standard electrode potential for the equation on page 10.	
e.ii.Explain the sign of the calculated standard electrode potential.	[1]
f. Predict the sign of $\Delta G^{\Theta}$ for this reaction.	[1]

Bromine is a member of group 7, the halogens.

Iron is a transition metal.

Freshly prepared iron(II) bromide can be electrolysed both in the liquid state and in aqueous solution.

a.i. Explain the trend in reactivity of the halogens.	[3]
a.ii.Deduce, using equations where appropriate, if bromine reacts with sodium chloride solution and with sodium iodide solution.	[2]
b.i.Describe the bonding in metals and explain their malleability.	[3]
b.iiList <b>three</b> characteristic properties of transition elements.	[2]
b.iiildentify the type of bonding between iron and cyanide in ${\left[{ m Fe}{\left({ m CN} ight)}_{6} ight]}^{3-}.$	[1]
b.ivDeduce the oxidation number of iron in ${\left[{ m Fe}({ m CN})_6 ight]}^{3-}.$	[1]
b.vDraw the abbreviated orbital diagram for an iron atom using the arrow-in-box notation to represent electrons.	[1]
b.vDraw the abbreviated orbital diagram for the iron ion in [Fe(CN) <sub>6</sub> ] <sup>3-</sup> using the arrow-in-box notation to represent electrons.	[1]
c.i. Describe, using a diagram, the essential components of an electrolytic cell.	[3]
c.ii.Describe the <b>two</b> ways in which current is conducted in an electrolytic cell.	[2]
c.iiiPredict and explain the products of electrolysis of a <b>dilute</b> iron(II) bromide solution.	[4]
c.iVidentify another product that is formed if the solution of iron(II) bromide is <b>concentrated</b> .	[1]
c.v.Explain why this other product is formed.	[1]

Bromomethane was used as a pesticide until it was found to be ozone-depleting.

a. State the equation for the reaction between methane and bromine to form bromomethane.	[1]
b.i. Explain, using equations, the complete free-radical mechanism for the reaction of methane with bromine, including necessary reaction conditions.	[4]
b.iiBromomethane reacts with aqueous sodium hydroxide. State the organic product of this reaction.	[1]
c. Explain why the rate of the reaction between iodomethane, $CH_3I$ , and NaOH(aq) is faster than the rate of the reaction between $CH_3Br$ and NaOH(aq).	[2]
d.i. Bromine can be produced by the electrolysis of <b>molten</b> sodium bromide.	[2]
Deduce the half-equation for the reaction at each electrode.	
Positive electrode (anode):	
Negative electrode (cathode):	
d.iiPredict the products formed at the electrodes during the electrolysis of concentrated aqueous sodium bromide.	[2]
Positive electrode (anode):	
Negative electrode (cathode):	
e. Bromine reacts with aqueous sodium iodide.	[1]
$\mathrm{Br_2(aq)} + 2\mathrm{NaI(aq)}  ightarrow \mathrm{I_2(aq)} + 2\mathrm{NaBr(aq)}$	
Identify the oxidizing agent in this reaction.	
f.i. Define the term standard electrode potential, $E^{\Theta}$ .	[1]
f.ii. Draw a labelled diagram for the voltaic cell in which the following reaction occurs.	[4]
$\mathrm{Mg}(\mathrm{s}) + \mathrm{Cu}^{2+}(\mathrm{aq})  o \mathrm{Mg}^{2+}(\mathrm{aq}) + \mathrm{Cu}(\mathrm{s})$	
Include in your answer the direction of electron flow and the polarity of the electrodes.	
f.iii A student measures a voltage of 2.65 V in the voltaic cell formed between magnesium and copper half-cells using a digital voltmeter.	[2]
State the random uncertainty of this value, in V, and the number of significant figures in the answer.	

Random uncertainty:

Significant figures:

f.iv.Outline how the student can reduce the random error in her results.

- g. Determine the standard enthalpy change of formation,  $\Delta H_{\rm f}^{\Theta}$ , of NaCl(s), in kJ mol<sup>-1</sup>, using a Born-Haber cycle and tables 7, 10 and 13 of the [4] data booklet. The standard enthalpy change of atomization (standard enthalpy change of sublimation),  $\Delta H_{\rm at}^{\Theta}$ , of Na(s) is +108 kJ mol<sup>-1</sup>.
- a.i. Ethanol is a primary alcohol that can be oxidized by acidified potassium dichromate(VI). Distinguish between the reaction conditions needed to [2] produce ethanal and ethanoic acid.

#### Ethanal:

Ethanoic acid:

a.ii.Determine the oxidation number of carbon in ethanol and ethanal.

#### Ethanol:

#### Ethanal:

- a.ivDeduce the overall redox equation for the reaction of ethanol to ethanal with acidified potassium dichromate(VI). [2]
- b. Ethanol can be made by reacting aqueous sodium hydroxide with bromoethane.

Explain the mechanism for this reaction, using curly arrows to represent the movement of electron pairs.

c.i. Determine the orders of reaction of the reactants and the overall rate expression for the reaction between 2-bromobutane and aqueous sodium [2]

hydroxide using the data in the table.

Experiment	[NaOH] / mol dm <sup>−3</sup>	$[C_4H_9Br] / moldm^{-3}$	Rate / mol dm <sup>-3</sup> s <sup>-1</sup>
1	1.00	1.00	1.66 × 10 <sup>-3</sup>
2	0.50	1.00	8.31 × 10 <sup>-4</sup>
3	0.25	0.25	1.02 × 10 <sup>-4</sup>
4	1.00	0.50	8.29 × 10 <sup>-4</sup>

c.ii.Determine the rate constant, k, with its units, using the data from experiment 3.

c.iiildentify the molecularity of the rate-determining step in this reaction.

d.i.2-bromobutane exists as optical isomers.

State the essential feature of optical isomers.

d.ii2-bromobutane exists as optical isomers.

[2]

[1]

[4]

[2]

[1] [1]

[2]

Outline how a polarimeter can distinguish between these isomers.

- f. Describe the formation of  $\sigma$  and  $\pi$  bonds in an alkene.
- g. The two most abundant isotopes of bromine have the mass numbers 79 and 81.

Calculate the relative abundance of <sup>79</sup>Br using table 5 of the data booklet, assuming the abundance of the other isotopes is negligible.

Oxidation and reduction can be defined in terms of electron transfer or oxidation numbers.

A reactivity series can be experimentally determined by adding the metals W, X, Y and Z to solutions of these metal ions. The following reactions were observed:

$$egin{aligned} & \mathrm{W}^{2+}(\mathrm{aq}) + \mathrm{X}(\mathrm{s}) o \mathrm{W}(\mathrm{s}) + \mathrm{X}^{2+}(\mathrm{aq}) \ & \mathrm{Y}(\mathrm{s}) + \mathrm{W}^{2+}(\mathrm{aq}) o \mathrm{Y}^{2+}(\mathrm{aq}) + \mathrm{W}(\mathrm{s}) \ & \mathrm{Z}^{2+}(\mathrm{aq}) + \mathrm{W}(\mathrm{s}) o \mathrm{Z}(\mathrm{s}) + \mathrm{W}^{2+}(\mathrm{aq}) \ & \mathrm{Y}(\mathrm{s}) + \mathrm{X}^{2+}(\mathrm{aq}) o \mathrm{Y}^{2+}(\mathrm{aq}) + \mathrm{X}(\mathrm{s}) \end{aligned}$$

A student carries out the electrolysis of aqueous potassium iodide, KI, using inert electrodes.

Three electrolytic cells were set up in series (one cell after the other), as shown below.

All of the solutions had a concentration of  $1.00 \ {
m mol} \ {
m dm}^{-3}$ .



- a. Alcohols with the molecular formula  $C_4H_9OH$  occur as four structural isomers. Three of the isomers can be oxidized with acidified potassium [9] dichromate solution to form compounds with the molecular formula  $C_4H_8O$ .
  - (i) Deduce the half-equation for the oxidation of the alcohol  $C_4H_9OH.$
  - (ii) Deduce the overall equation for the redox reaction.

[2]

[2]

(iii) Two of the isomers with the molecular formula  $C_4H_9OH$  can be oxidized further to form compounds with the molecular formula  $C_4H_8O_2$ . Deduce the structural formulas of these two isomers.

(iv) One isomer cannot be oxidized by acidified potassium dichromate solution.

Deduce its structural formula, state its name and identify it as a primary, secondary or tertiary alcohol.

Name:

Alcohol:

(v) All isomers of the alcohol  $C_4H_9OH$  undergo complete combustion. State an equation for the complete combustion of  $C_4H_9OH$ .

b. (i) Deduce the order of reactivity of these four metals, from the least to the most reactive.

(ii) A voltaic cell is made by connecting a half-cell of X in  $XCl_2(aq)$  to a half-cell of Z in  $ZCl_2(aq)$ . Deduce the overall equation for the reaction taking place when the cell is operating.

(iii) The standard electrode potential for  $Z^{2+}(aq) + 2e^- \rightleftharpoons Z(s)$  is +0.20 V. State which species is oxidized when this half-cell is connected to a standard hydrogen electrode.

(iv) Describe the standard hydrogen electrode including a fully labelled diagram.

c. (i) State the half-equation for the reaction that occurs at each electrode.

Positive electrode (anode):

Negative electrode (cathode):

- (ii) Suggest, giving a reason, what would happen if the electrodes were changed to aluminium.
- d. (i) Determine the mass of copper produced at one of the electrodes in cell 2 if the tin electrode in cell 1 decreased in mass by 0.034 g. [6]

(ii) Compare the colour and the pH of the solutions in cells 2 and 3 after the current has been flowing for one hour.

[4]

[6]

(iii) Explain your answer given for part (d) (ii).

Colour:

pH:

Magnesium is the eighth most abundant element in the earth's crust. The successive ionization energies of the element are shown below.



Magnesium can be produced from the electrolysis of molten magnesium chloride, MgCl<sub>2</sub>.

The lattice enthalpy of magnesium chloride can be calculated from the Born-Haber cycle shown below.



a.	(i)	Define the term <i>first ionization energy</i> and state the equation for the first ionization of magnesium.	[8]
	(ii)	Explain the general increase in successive ionization energies of the element.	
	(iii)	Explain the large increase between the tenth and eleventh ionization energies.	
b.	(i)	Explain how molten magnesium chloride conducts an electric current.	[5]
	(ii)	Identify the electrode where oxidation occurs during electrolysis of molten magnesium chloride and state an equation for the half-reaction.	
	(iii)	Explain why magnesium is not formed during the electrolysis of aqueous magnesium chloride solution.	
c.	(i)	Identify the enthalpy changes labelled by I and V in the cycle.	[10]
	(ii) mag	Use the ionization energies given in the cycle above and further data from the Data Booklet to calculate a value for the lattice enthalpy of nesium chloride.	
	(iii) theo	The theoretically calculated value for the lattice enthalpy of magnesium chloride is +2326 kJ. Explain the difference between the retically calculated value and the experimental value.	
	(iv) lattic	The experimental lattice enthalpy of magnesium oxide is given in Table 13 of the Data Booklet. Explain why magnesium oxide has a highe ce enthalpy than magnesium chloride.	r

- d. (i) State whether aqueous solutions of magnesium oxide and magnesium chloride are acidic, alkaline or neutral.
  - (ii) State an equation for the reaction between magnesium oxide and water.

In acidic solution, ions containing titanium can react according to the half-equation below.

$${
m TiO}^{2+}({
m aq})+2{
m H}^+({
m aq})+{
m e}^-
ightarrow{
m Ti}^{3+}({
m aq})+{
m H}_2{
m O}({
m l}) \quad E^\Theta=-0.06~{
m V}$$

In the diagram below, A and B are inert electrodes and, in the aqueous solutions, all ions have a concentration of  $1 \text{ mol} \, dm^{-3}$ .



Sodium, silicon and sulfur are elements in period 3 of the periodic table that all form oxides.

Although carbon and silicon both belong to group 4 of the periodic table, carbon dioxide and silicon dioxide are different in many ways.

[1]

[2]

a. Define the term standard electrode potential,  $E^{\Theta}.$ 

Initial oxidation number	Final oxidation number	Oxidized / reduced

- b.ii.Considering the above equilibrium, predict, giving a reason, how adding more acid would affect the strength of the TiO<sup>2+</sup> ion as an oxidizing [2] agent.
- c. In the two experiments below, predict whether a reaction would occur and deduce an equation for any reaction that takes place. Refer to Table [3] 14 of the Data Booklet if necessary.

KI(aq) is added to a solution containing  $Ti^{3+}(\mathrm{aq})$  ions:

Zn (s) is added to a solution containing  ${\rm TiO}^{2+}({\rm aq})$  and  ${\rm H}^+({\rm aq})$  ions:

d.i. Using Table 14 of the Data Booklet, state the balanced half-equation for the reaction that occurs at electrode A and whether it involves [2]

oxidation or reduction.

d.ii.Calculate the cell potential in V.

d.iiiOn the diagram above label with an arrow

- the direction of electron flow in the wire
- the direction in which the positive ions flow in the salt bridge.
- e.i. Compare the properties of the three oxides by completing the table below.

	Na <sub>2</sub> O	SiO <sub>2</sub>	SO <sub>2</sub>
Bonding type			
Standard state			
Effect on pH of water			

e.ii.Sulfur dioxide is a significant contributor to acid deposition. Identify a major, man-made source of this pollutant.

e.iiiAs well as the oxide above, sodium forms a peroxide that contains the peroxide ion,  $\mathrm{O}_2^{2-}$ . Draw the Lewis (electron dot) structure of the

peroxide ion.

[3]

[1]

[1]

[1] [2]

- f.i. Describe the differences in the hybridization of these group 4 elements and the precise nature of the bonds that they form with the oxygen [3] atoms.
- f.ii. Xenon, although a noble gas, forms an oxide, XeO<sub>2</sub>, that has a structure related to that of SiO<sub>2</sub>. Compare the geometry around the silicon [3] atoms in  $SiO_2$  with the geometry around the xenon atoms in  $XeO_2$ , using the valence shell electron pair repulsion (VSEPR) theory.

Millerite, a nickel sulfide mineral, is an important source of nickel. The first step in extracting nickel is to roast the ore in air.

The reaction for the formation of liquid tetracarbonylnickel is shown below:

$$Ni(s) + 4CO(g) \rightarrow Ni(CO)_4(l)$$

- a. Formulate an equation for the oxidation of nickel(II) sulfide to nickel(II) oxide.
- b. The nickel obtained from another ore, nickeliferous limonite, is contaminated with iron. Both nickel and iron react with carbon monoxide gas to [1] form gaseous complexes, tetracarbonylnickel,  $Ni(CO)_4(g)$ , and pentacarbonyliron,  $Fe(CO)_5(g)$ . Suggest why the nickel can be separated from the iron successfully using carbon monoxide.
- c.i. Calculate the standard entropy change,  $\Delta S^{\theta}$ , of the reaction, in  $\mathrm{J\,K^{-1}}$ , using the values given.

	S <sup>e</sup> / J K <sup>-1</sup> mol <sup>-1</sup>
Ni(s)	29.9
CO(g)	197.6
$Ni(CO)_4(l)$	313.4

c.ii.Calculate a value for  $\Delta H^{\theta}$  in kJ.

	∆H <sup>⊕</sup> <sub>f</sub> / kJ mol <sup>-1</sup>
CO(g)	-110.5
$Ni(CO)_4(l)$	-633.0

c.iiiUse your answers to (c)(i) and (c)(ii), to determine the temperature, in °C, at which the decomposition of liquid tetracarbonylnickel to nickel and [3] carbon monoxide becomes favourable.

(If you did not get answers to (c)(i) and (c)(ii), use -500 J K<sup>-1</sup> and -200 kJ respectively but these are not the correct answers.)

d. Suggest why experiments involving tetracarbonylnickel are very hazardous.

Consider the following half-cell reactions and their standard electrode potentials.

[1]

[2]

[1]

[1]

	E <sup>e</sup> / V
$Mn^{2^+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.18
$Ni^{2^+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.26
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54

a.	Deduce a balanced equation for the overall reaction when the standard nickel and iodine half-cells are connected.	[1]
b.	Predict, giving a reason, the direction of movement of electrons when the standard nickel and manganese half-cells are connected.	[2]
c.	Calculate the cell potential, in V, when the standard iodine and manganese half-cells are connected.	[1]
d.	Identify the best reducing agent in the table above.	[1]

e. State and explain the products of electrolysis of a concentrated aqueous solution of sodium chloride using inert electrodes. Your answer should [4] include half-equations for the reaction at each electrode.

Positive electrode (anode):	
Negative electrode (cathode):	

Magnesium, a reactive metal found in many common minerals, is also an essential nutrient for both plants and animals.

Successive ionization energies of magnesium are given in the table below.

	First	Second	Third
Energy required / kJ mol <sup>-1</sup>	738	1450	7730

Magnesium metal is mainly used as a component in lightweight alloys, particularly in combination with aluminium and titanium.

Magnesium is usually produced by the electrolysis of molten magnesium chloride.

a. Define the term *first ionization energy*.

[2]

- (ii) Explain why the third ionization energy is much greater than the second ionization energy.
- c. Although magnesium is usually found as  $Mg^{2+}$  in its compounds, it is possible to use the Born-Haber cycle to investigate the possibility of [3]

```
Mg^{+} being able to form stable compounds.
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Use the ionization energy data from part (b), along with the other data provided below, to determine the enthalpy change of formation of MgCl(s). Assume that, because  $Mg^+$  would be similar in size to  $Na^+$ , MgCl would have a similar lattice enthalpy to NaCl.

Enthalpy of atomization of Mg  $+146 \text{ kJ mol}^{-1}$ Bond enthalpy in Cl<sub>2</sub>  $+243 \text{ kJ mol}^{-1}$ Electron affinity of Cl  $+349 \text{ kJ mol}^{-1}$ Lattice enthalpy of NaCl  $+790 \text{ kJ mol}^{-1}$ 

d. Consider the lattice enthalpies of MgF<sub>2</sub>, MgCl<sub>2</sub> and CaCl<sub>2</sub>. List these from the most endothermic to the least endothermic and explain your [3] order.

 $Most \ endothermic \rightarrow Least \ endothermic$ 

e. Magnesium hydroxide,  $Mg(OH)_2$ , is only sparingly soluble in water and the equilibrium below exists when excess solid is in contact with a saturated solution. [2]

$$\mathrm{Mg(OH)}_2(\mathrm{s}) \rightleftharpoons \mathrm{Mg}^{2+}(\mathrm{aq}) + 2\mathrm{OH}^{-}(\mathrm{aq})$$

[4]

[7]

Outline how the solubility of magnesium hydroxide will vary with pH.

- f. (i) Describe the bonding present in magnesium metal.
  - (ii) Suggest why magnesium is harder than sodium.
  - (iii) Outline why alloys are generally less malleable than their component metals.
- g. (i) Draw a labelled diagram of a suitable apparatus for the electrolysis.
  - (ii) State equations for the reactions that take place at the electrodes.

Negative electrode (cathode) reaction:

Positive electrode (anode) reaction:

(iii) When dilute aqueous magnesium chloride is used as the electrolyte, the reactions at both electrodes are different. State equations for the reactions that occur in aqueous solution.

Negative electrode (cathode) reaction:

Positive electrode (anode) reaction:

(iv) Outline why magnesium metal is not produced in the electrolysis of aqueous magnesium chloride.

Bleaches in which chlorine is the active ingredient are the most common, although some environmental groups have concerns about their use.

In aqueous chlorine the equilibrium below produces chloric(I) acid (hypochlorous acid), HOCI, the active bleach.

$$\mathrm{Cl}_2(\mathrm{aq}) + \mathrm{H}_2\mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{HOCl}(\mathrm{aq}) + \mathrm{H}^+(\mathrm{aq}) + \mathrm{Cl}^-(\mathrm{aq})$$

Aqueous sodium chlorate(I), NaOCI, the most common active ingredient in chlorine based bleaches, oxidizes coloured materials to colourless products while being reduced to the chloride ion. It will also oxidize sulfur dioxide to the sulfate ion.

The standard electrode potential for the reduction of the chlorate(V) ion to the chloride ion is +1.49 V.

a. (i)	Describe the colour change that occurs when aqueous chlorine is added to aqueous sodium bromide.	[3]
(ii)	Outline, with the help of a chemical equation, why this reaction occurs.	
b.i.Ch	loric(I) acid is a weak acid, but hydrochloric acid is a strong acid. Outline how this is indicated in the equation above.	[1]
b.ii.Sta	ate a balanced equation for the reaction of chloric(I) acid with water.	[1]
b.iiiOu	tline, in terms of the equilibrium in aqueous chlorine, why it is dangerous to use an acidic toilet cleaner in combination with this kind of	[2]
ble	ach.	
b.ivSu	ggest why a covalent molecule, such as chloric(I) acid, is readily soluble in water.	[2]
b.v.Par	rtial neutralization of chloric(I) acid creates a buffer solution. Given that the $\mathrm{p}K_{\mathrm{a}}$ of chloric(I) acid is 7.53, determine the pH of a solution that	[4]
has	$ m s \ [HOCl] = 0.100 \ mol \ dm^{-3} \ and \ [ClO^-] = 0.0500 \ mol \ dm^{-3}.$	
b.vDe	scribe, using HIn to represent the indicator in its acid form, why an indicator changes colour when excess alkali is added.	[3]
c. (i)	Deduce a balanced equation for the reaction between the chlorate(I) ion and sulfur dioxide from the appropriate half-equations.	[6]

(ii) State the initial and final oxidation numbers of both chlorine and sulfur in the final equation.

Element	Initial oxidation number	Final oxidation number
Chlorine		
Sulfur		

d. (i) Define the term standard electrode potential.

(ii) Referring to Table 14 of the Data Booklet, deduce, giving a reason, whether the oxidation of the chromium(III) ion to the dichromate(VI) ion by the chlorate(V) ion is energetically feasible.

Iron rusts in the presence of oxygen and water. Rusting is a redox process involving several steps that produces hydrated iron(III) oxide,

#### $Fe_2O_3 \bullet nH_2O$ , as the final product.

The half-equations involved for the first step of rusting are given below.

 $\begin{array}{ll} \mbox{Half-equation 1:} & Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \\ \mbox{Half-equation 2:} & O_2(aq) + 4e^- + 2H_2O(l) \rightarrow 4OH^-(aq) \end{array}$ 

- a. (i) Identify whether half-equation 1 represents oxidation or reduction, giving a reason for your answer.
  - (ii) Identify the oxidation number of each atom in the three species in half-equation 2.

 $O_2(aq) + 4e^- + 2H_2O(1) \rightarrow 4OH^-(aq)$ 

- (iii) Deduce the overall redox equation for the first step of rusting by combining half-equations 1 and 2.
- (iv) Identify the reducing agent in the redox equation in part (iii).
- b. The oxygen in half-equation 2 is atmospheric oxygen that is found dissolved in water in very small concentrations. Explain, in terms of [2] intermolecular forces, why oxygen is not very soluble in water.
- c. State the relationship between the electron arrangement of an element and its group and period in the periodic table.
- d. Transition metals and their compounds often catalyse reactions. The catalyzed decomposition of hydrogen peroxide by CuO is an example. [2]
   State two other examples of catalyzed reactions giving the transition metal or its compound acting as catalyst.
- e. (i) State a chemical equation for the partial dissociation of water into ions, including state symbols.
  - (ii) The dissociation of water into ions is reversible. State the expression for the ionic product constant of water.

[3]

[5]

[2]

[6]

(iii) The ionic product constant of water was measured at three different temperatures.

Temperature / K	K <sub>w</sub>
298	$1.00 \times 10^{-14}$
313	$2.92 \times 10^{-14}$
373	$5.13 \times 10^{-13}$

Deduce whether the ionization of water is exothermic or endothermic, giving your reason.

- (iv) Use the data in part (iii) to determine the pH of water at 373 K, correct to **two** decimal places.
- f. (i) An aqueous solution of sodium chloride is electrolysed using inert electrodes. Explain which product is obtained at the positive electrode [5]
   (anode) if the concentration of sodium chloride is high.

(ii) State the half-equations occurring at the electrodes during the electrolysis of the concentrated aqueous solution of sodium chloride.

Negative electrode (cathode):

Positive electrode (anode):

g. Describe how electrolysis can be used to electroplate a bracelet with a layer of silver metal. Include the choice of electrodes and electrolyte [3]
 needed in your description.

Chromium is a transition metal with many uses.

A voltaic cell is constructed as follows. One half-cell contains a chromium electrode immersed in a solution containing  $Cr^{3+}(aq)$  ions. The other half-cell contains a copper electrode immersed in a solution containing  $Cu^{2+}(aq)$  ions. The two electrodes are connected to a voltmeter and the two solutions by a salt bridge.



a.i. Draw an orbital diagram (using the arrow-in-box notation) showing the electrons in the 4s and 3d sub-levels in chromium metal.	[1]
a.ii.Outline the nature of the metallic bonding present in chromium.	[1]
a.iiiExplain why chromium metal is malleable.	[1]
b.i.State the name of $\mathrm{Cr}_2\mathrm{O}_3.$	[1]
b.iiDescribe the ionic bonding present in $ m Cr_2O_3$ and how the ions are formed.	[2]
b.iiiSuggest why solid ${ m Cr}_2{ m O}_3$ does <b>not</b> conduct electricity.	[1]
c.i. Chromium forms the complex ion $[\mathrm{Cr}(\mathrm{NH}_3)_4\mathrm{Cl}_2]^+.$	[1]
Deduce the oxidation number of chromium in this complex.	
c.ii.Chromium forms the complex ion $[\mathrm{Cr}(\mathrm{NH}_3)_4\mathrm{Cl}_2]^+.$	[2]
Describe the nature of the ligand-chromium ion bonds in terms of acid-base theory.	
c.iiiChromium forms the complex ion $[\mathrm{Cr}(\mathrm{NH}_3)_4\mathrm{Cl}_2]^+.$	[4]
Explain why $\left[\mathrm{Cr}(\mathrm{NH}_3)_4\mathrm{Cl}_2 ight]^+$ is coloured.	
c.ivChromium forms the complex ion $[\mathrm{Cr}(\mathrm{NH}_3)_4\mathrm{Cl}_2]^+.$	[2]
Draw the structures of <b>two</b> possible isomers of this complex ion.	
d.i. The dichromate ion, $Cr_2O_7^{2-}(aq)$ , and the iodide ion, $I^-(aq)$ , react together in the presence of an acid to form $Cr^{3+}(aq)$ and $IO_3^-(aq)$ ions.	[2]

Deduce the half-equation for the reaction of  $I^-$  to  $IO_3^-$  and the overall equation for this reaction.

Half-equation:

### Overall equation:

 $\label{eq:constraint} d.ii Explain in terms of oxidation numbers whether iodine is oxidized or reduced in part (d) (i).$ 

[1]

e.ii.Calculate the cell potential, in V, under standard conditions, for this voltaic cell, using table 14 of the data booklet and $E^{\Theta}_{Cr^{3+}/Cr} = -0.74 \text{ V}.$	[1]
e.iiiPredict the balanced equation for the spontaneous reaction which will produce a current in this voltaic cell.	[1]
e.iv/dentify the negative and the positive electrodes in this cell.	[1]
e.v.Predict the direction of movement of electrons in the external circuit.	[1]
e.viState the directions in which the negative ions (anions) and the positive ions (cations) flow in the salt bridge.	[1]

Magnesium is a group 2 metal which exists as a number of isotopes and forms many compounds.

- c. Magnesium ions produce no emission or absorption lines in the visible region of the electromagnetic spectrum. Suggest why most magnesium [1]
   compounds tested in a school laboratory show traces of yellow in the flame.
- d. (i) Explain the convergence of lines in a hydrogen emission spectrum.

(ii) State what can be determined from the frequency of the convergence limit.

i. Magnesium chloride can be electrolysed.

(i) Deduce the half-equations for the reactions at each electrode when **molten** magnesium chloride is electrolysed, showing the state symbols of the products. The melting points of magnesium and magnesium chloride are 922K and 987K respectively.

Anode (positive electrode): Cathode (negative electrode):

(ii) Identify the type of reaction occurring at the cathode (negative electrode).

(iii) State the products when a very **dilute** aqueous solution of magnesium chloride is electrolysed.

Anode (positive electrode):	
Cathode (negative electrode):	

j. Standard electrode potentials are measured relative to the standard hydrogen electrode. Describe a standard hydrogen electrode.

k. A magnesium half-cell, Mg(s)/Mg<sup>2+</sup>(aq), can be connected to a copper half-cell, Cu(s)/Cu<sup>2+</sup>(aq).

(i) Formulate an equation for the spontaneous reaction that occurs when the circuit is completed.

[2]

[5]

- (ii) Determine the standard cell potential, in V, for the cell. Refer to section 24 of the data booklet.
- (iii) Predict, giving a reason, the change in cell potential when the concentration of copper ions increases.

#### The diagram shows an incomplete voltaic cell with a light bulb in the circuit.



- a. Identify the missing component of the cell and its function.
- b. Deduce the half-equations for the reaction at each electrode when current flows.

Positive electrode (cathode): Negative electrode (anode):

c.	Annotate the diagram with the location and direction of electron movement when current flows.	[1]
d.	Calculate the cell potential, in V, using section 24 of the data booklet.	[1]
e.	Determine the loss in mass of one electrode if the mass of the other electrode increases by 0.10 g.	[2]

Vanadium has a number of different oxidation states.

Electrode potentials for the reactions of vanadium and other species are shown below.

$V^{3^+}(aq) + e^- \rightleftharpoons V^{2^+}(aq)$	-0.26∨
$VO^{2+}(aq) + 2H^{+}(aq) + e^{-} \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34 V
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.0V
	I
$Zn^{2^+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76∨
$Pb^{2^+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.13V
$SO_4^{2^-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	+0.17V
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80V
$\frac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$	+1.36V

[2]

#### a. Determine the oxidation state of vanadium in each of the following species.

V <sub>2</sub> O <sub>5</sub> :		
VO <sup>2+</sup> :		

b.i.Identify, from the table, a non-vanadium species that can reduce VO <sup>2+</sup> (aq) to V <sup>3+</sup> (aq) but no further.	[1]
b.iiJdentify, from the table, a non-vanadium species that could convert ${ m VO}_2^+({ m aq})$ to V <sup>2+</sup> (aq).	[1]
c.i. Formulate an equation for the reaction between $VO^{2+}(aq)$ and $V^{2+}(aq)$ in acidic solution to form $V^{3+}(aq)$ .	[1]

c.ii.Comment on the spontaneity of this reaction by calculating a value for  $\Delta G^{\theta}$  using the data given in (b) and in section 1 of the data booklet. [3]

Phosphine (IUPAC name phosphane) is a hydride of phosphorus, with the formula PH<sub>3</sub>.

a. (i) Draw a Lewis (electron dot) structure of phosphine.	

- (ii) State the hybridization of the phosphorus atom in phosphine.
- (iii) Deduce, giving your reason, whether phosphine would act as a Lewis acid, a Lewis base, or neither.
- (iv) Outline whether you expect the bonds in phosphine to be polar or non-polar, giving a brief reason.
- (v) Phosphine has a much greater molar mass than ammonia. Explain why phosphine has a significantly lower boiling point than ammonia.
- (vi) Ammonia acts as a weak Brønsted-Lowry base when dissolved in water.

### $NH_{3}(aq) + H_{2}O(l) \rightleftharpoons NH_{4}^{+}(aq) + OH^{-}(aq)$

Outline what is meant by the terms "weak" and "Brønsted-Lowry base".

Weak:

Brønsted-Lowry base:

hydroxide. The equation for the reaction is:

# $\mathsf{P}_4(\mathsf{s}) + 3\mathsf{OH}^{-}(\mathsf{aq}) + 3\mathsf{H}_2\mathsf{O}(\mathsf{l}) \rightarrow \mathsf{PH}_3(\mathsf{g}) + 3\mathsf{H}_2\mathsf{PO}_2^{-}(\mathsf{aq})$

(i) The first reagent is written as P<sub>4</sub>, not 4P. Describe the difference between P<sub>4</sub> and 4P.

(ii) The ion  $H_2PO_2^-$  is amphiprotic. Outline what is meant by amphiprotic, giving the formulas of **both** species it is converted to when it behaves in this manner.

(iii) State the oxidation state of phosphorus in  $P_4$  and  $H_2PO_2^-$ .

P<sub>4</sub>:

 $H_2PO_2^-$ :

(iv) Oxidation is now defined in terms of change of oxidation number. Explore how earlier definitions of oxidation and reduction may have led to conflicting answers for the conversion of  $P_4$  to  $H_2PO_2^-$  and the way in which the use of oxidation numbers has resolved this.

c. 2.478 g of white phosphorus was used to make phosphine according to the equation:

## $\mathsf{P}_4(\mathsf{s}) + 3\mathsf{OH}^-(\mathsf{aq}) + 3\mathsf{H}_2\mathsf{O}(\mathsf{l}) \rightarrow \mathsf{PH}_3(\mathsf{g}) + 3\mathsf{H}_2\mathsf{PO}_2^-(\mathsf{aq})$

(i) Calculate the amount, in mol, of white phosphorus used.

(ii) This phosphorus was reacted with 100.0 cm<sup>3</sup> of 5.00 mol dm<sup>-3</sup> aqueous sodium hydroxide. Deduce, showing your working, which was the limiting reagent.

- (iii) Determine the excess amount, in mol, of the other reagent.
- (iv) Determine the volume of phosphine, measured in cm<sup>3</sup> at standard temperature and pressure, that was produced.
- d. Impurities cause phosphine to ignite spontaneously in air to form an oxide of phosphorus and water.

(i) 200.0 g of air was heated by the energy from the complete combustion of 1.00 mol phosphine. Calculate the temperature rise using section 1 of the data booklet and the data below.

Standard enthalpy of combustion of phosphine,  $\Delta H_c^{\ominus} = -750 \text{ kJ mol}^{-1}$ 

Specific heat capacity of air = 1.00Jg<sup>-1</sup>K<sup>-1</sup>=1.00kJkg<sup>-1</sup>K<sup>-1</sup>

(ii) The oxide formed in the reaction with air contains 43.6% phosphorus by mass. Determine the empirical formula of the oxide, showing your method.

(iii) The molar mass of the oxide is approximately  $285 \text{ g mol}^{-1}$ . Determine the molecular formula of the oxide.

(iv) State the equation for the reaction of this oxide of phosphorus with water.

(v) Suggest why oxides of phosphorus are not major contributors to acid deposition.

(vi) The levels of sulfur dioxide, a major contributor to acid deposition, can be minimized by either pre-combustion and post-combustion methods. Outline **one** technique of each method.

Pre-combustion:

Post-combustion:

[4]

[8]