

**Chemistry**  
**Higher level**  
**Paper 2**

Thursday 12 May 2016 (morning)

Candidate session number

2 hours 15 minutes

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**Instructions to candidates**

- Write your session number in the boxes above.
- Do not open this examination paper until instructed to do so.
- Answer all questions.
- Write your answers in the boxes provided.
- A calculator is required for this paper.
- A clean copy of the **Chemistry data booklet** is required for this paper.
- The maximum mark for this examination paper is **[95 marks]**.



Answer **all** questions. Write your answers in the boxes provided.

1. Phosphine (IUPAC name phosphane) is a hydride of phosphorus, with the formula  $\text{PH}_3$ .

(a) (i) Draw a Lewis (electron dot) structure of phosphine. [1]

(ii) State the hybridization of the phosphorus atom in phosphine. [1]

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(iii) Deduce, giving your reason, whether phosphine would act as a Lewis acid, a Lewis base, or neither. [1]

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(iv) Outline whether you expect the bonds in phosphine to be polar or non-polar, giving a brief reason. [1]

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**(Question 1 continued)**

- (v) Phosphine has a much greater molar mass than ammonia. Explain why phosphine has a significantly lower boiling point than ammonia. [2]

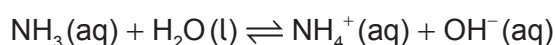
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- (vi) Ammonia acts as a weak Brønsted–Lowry base when dissolved in water.



- Outline what is meant by the terms “weak” and “Brønsted–Lowry base”. [2]

Weak:

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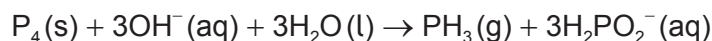
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Brønsted–Lowry base:

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- (b) Phosphine is usually prepared by heating white phosphorus, one of the allotropes of phosphorus, with concentrated aqueous sodium hydroxide. The equation for the reaction is:



- (i) The first reagent is written as  $\text{P}_4$ , not  $4\text{P}$ . Describe the difference between  $\text{P}_4$  and  $4\text{P}$ . [1]

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**(Question 1 continued)**

- (ii) The ion  $\text{H}_2\text{PO}_2^-$  is amphiprotic. Outline what is meant by amphiprotic, giving the formulas of **both** species it is converted to when it behaves in this manner. [2]

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- (iii) State the oxidation state of phosphorus in  $\text{P}_4$  and  $\text{H}_2\text{PO}_2^-$ . [2]

$\text{P}_4$ :  
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 $\text{H}_2\text{PO}_2^-$ :  
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- (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  $\text{P}_4$  to  $\text{H}_2\text{PO}_2^-$  and the way in which the use of oxidation numbers has resolved this. [3]

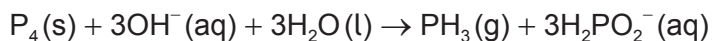
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**(Question 1 continued)**

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



(i) Calculate the amount, in mol, of white phosphorus used. [1]

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(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. [1]

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(iii) Determine the excess amount, in mol, of the other reagent. [1]

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(iv) Determine the volume of phosphine, measured in cm<sup>3</sup> at standard temperature and pressure, that was produced. [1]

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**(Question 1 continued)**

(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. [1]

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

Specific heat capacity of air =  $1.00 \text{ J g}^{-1} \text{ K}^{-1} = 1.00 \text{ kJ kg}^{-1} \text{ K}^{-1}$

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(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. [3]

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

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**(Question 1 continued)**

(iv) State the equation for the reaction of this oxide of phosphorus with water. [1]

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(v) Suggest why oxides of phosphorus are not major contributors to acid deposition. [1]

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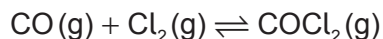
(vi) The levels of sulfur dioxide, a major contributor to acid deposition, can be minimized by either pre-combustion and post-combustion methods. Outline **one** technique of each method. [2]

Pre-combustion:  
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Post-combustion:  
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2. Phosgene,  $\text{COCl}_2$ , is usually produced by the reaction between carbon monoxide and chlorine according to the equation:



- (a) (i) Deduce the equilibrium constant expression,  $K_c$ , for this reaction. [1]

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- (ii) At exactly  $600^\circ\text{C}$  the value of the equilibrium constant is 0.200. Calculate the standard Gibbs free energy change,  $\Delta G^\ominus$ , for the reaction, in kJ, using sections 1 and 2 of the data booklet. State your answer to **three** significant figures. [3]

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- (iii) The standard enthalpy change of formation of phosgene,  $\Delta H_f^\ominus$ , is  $-220.1 \text{ kJ mol}^{-1}$ . Determine the standard enthalpy change,  $\Delta H^\ominus$ , for the forward reaction of the equilibrium, in kJ, using section 12 of the data booklet. [2]

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**(Question 2 continued)**

- (iv) Calculate the standard entropy change,  $\Delta S^\ominus$ , in  $\text{JK}^{-1}$ , for the forward reaction at  $25^\circ\text{C}$ , using your answers to (a) (ii) and (a) (iii).  
 (If you did not obtain an answer to (a) (ii) and/or (a) (iii) use values of  $+20.0\text{ kJ}$  and  $-120.0\text{ kJ}$  respectively, although these are not the correct answers.) [2]

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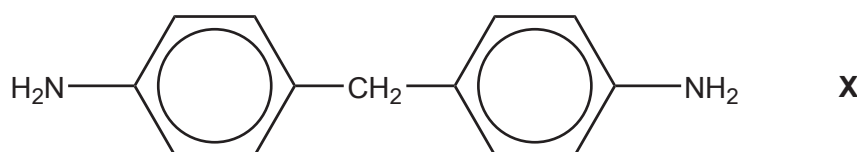
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- (b) One important industrial use of phosgene is the production of polyurethanes. Phosgene is reacted with diamine **X**, derived from phenylamine.



- (i) Classify diamine **X** as a primary, secondary or tertiary amine. [1]

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- (ii) Phenylamine,  $\text{C}_6\text{H}_5\text{NH}_2$ , is produced by the reduction of nitrobenzene,  $\text{C}_6\text{H}_5\text{NO}_2$ . Suggest how this conversion can be carried out. [2]

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**(Question 2 continued)**

- (iii) Nitrobenzene can be obtained by nitrating benzene using a mixture of concentrated nitric and sulfuric acids. Formulate the equation for the equilibrium established when these two acids are mixed. [1]

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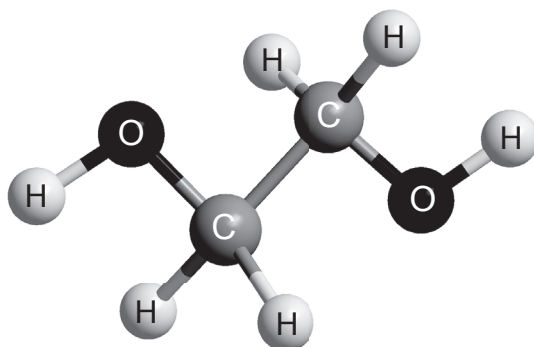
- (iv) Deduce the mechanism for the nitration of benzene, using curly arrows to indicate the movement of electron pairs. [4]

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(Question 2 continued)

- (c) The other monomer used in the production of polyurethane is compound **Z** shown below.



- (i) State the name, applying IUPAC rules, of compound **Z** and the class of compounds to which it belongs.

[2]

Name:

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Class:

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- (ii) Deduce the number of signals you would expect to find in the  $^1\text{H}$  NMR spectrum of compound **Z**, giving your reasons.

[1]

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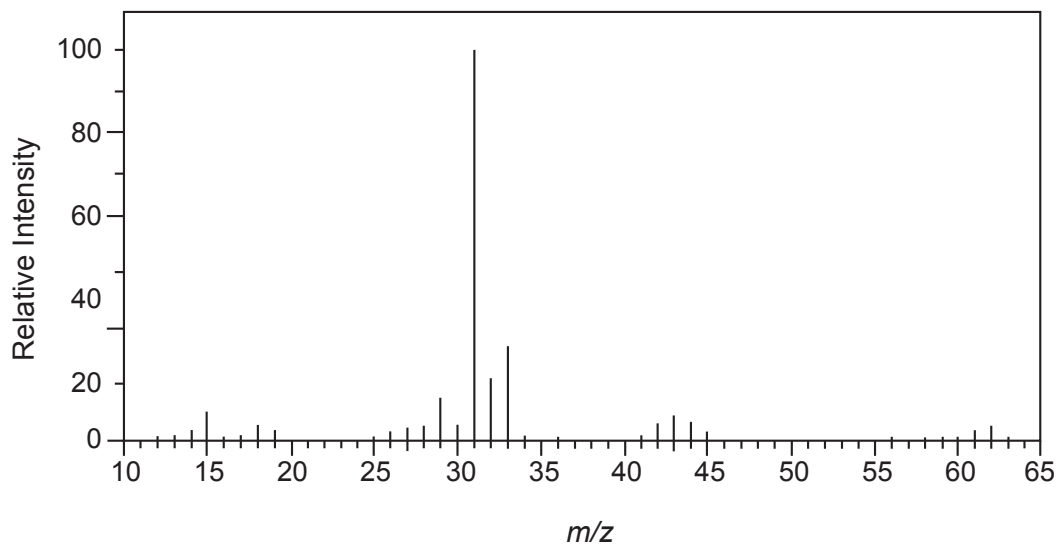
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**(Question 2 continued)**

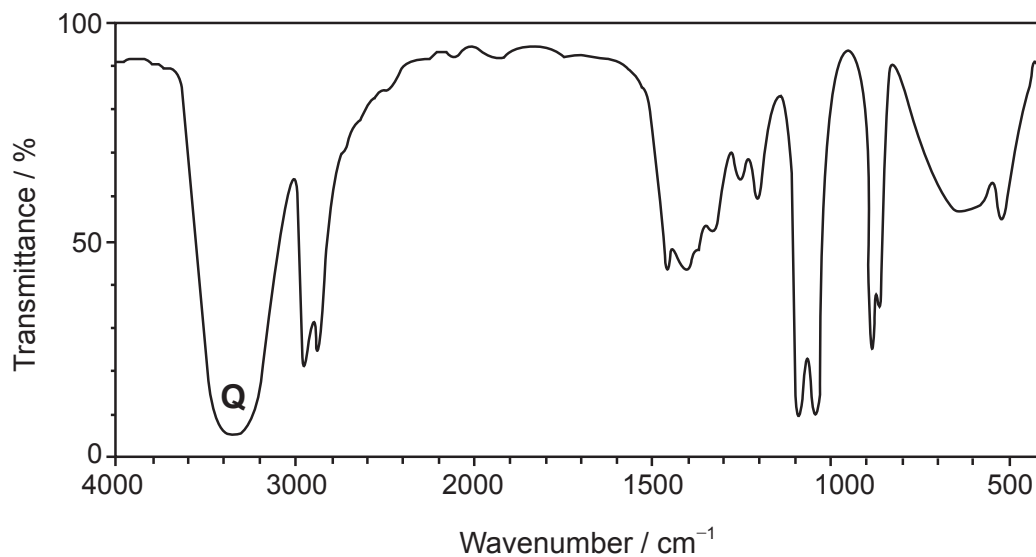
The mass spectrum and infrared (IR) spectrum of compound **Z** are shown below:

Mass spectrum



[Source: <http://sdbs.db.aist.go.jp>]

IR spectrum



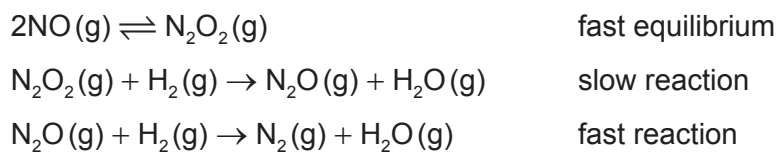
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3. The reaction between hydrogen and nitrogen monoxide is thought to proceed by the mechanism shown below.



(a) (i) State the equation for the overall reaction. [1]

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(ii) Deduce the rate expression consistent with this mechanism. [1]

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(iii) Explain how you would attempt to confirm this rate expression, giving the results you would expect. [3]

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**(Question 3 continued)**

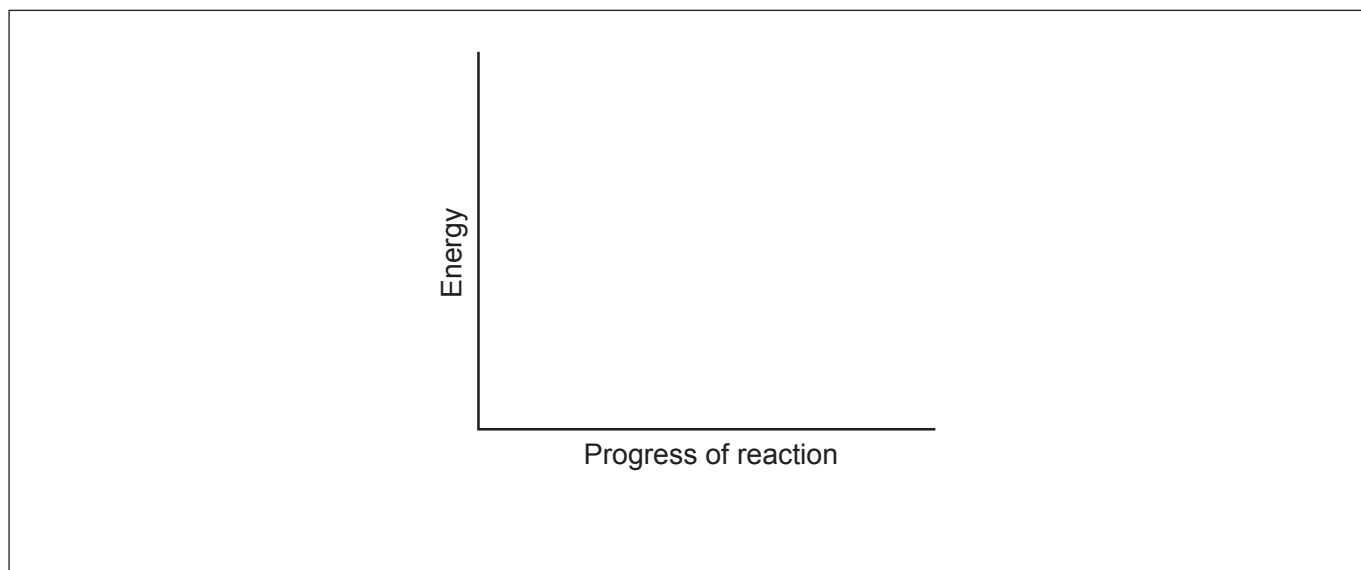
- (iv) State, giving your reason, whether confirmation of the rate expression would prove that the mechanism given is correct. [1]

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- (v) Suggest how the rate of this reaction could be measured experimentally. [1]

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- (b) The enthalpy change for the reaction between nitrogen monoxide and hydrogen is  $-664 \text{ kJ}$  and its activation energy is  $63 \text{ kJ}$ .



- (i) Sketch the potential energy profile for the overall reaction, using the axes given, indicating both the enthalpy of reaction and activation energy. [2]

- (ii) This reaction is normally carried out using a catalyst. Draw a dotted line labelled "Catalysed" on the diagram above to indicate the effect of the catalyst. [1]

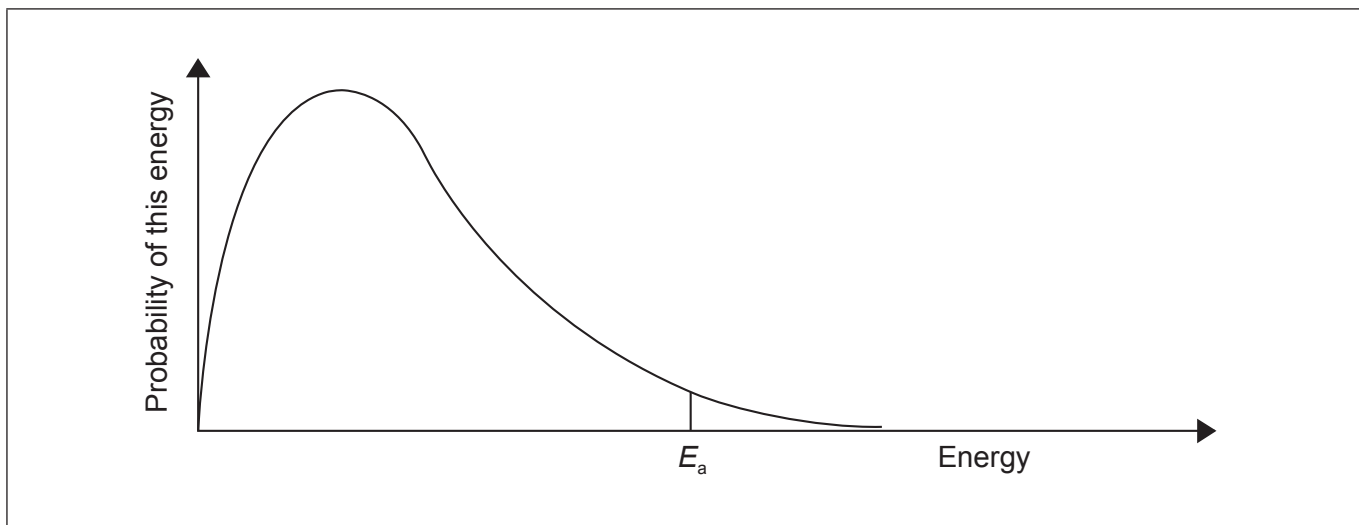
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(Question 3 continued)

- (iii) Sketch and label a second Maxwell–Boltzmann energy distribution curve representing the same system but at a higher temperature,  $T_{\text{higher}}$ .

[1]



- (iv) Explain why an increase in temperature increases the rate of this reaction.

[2]

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(Question 3 continued)

- (c) One of the intermediates in the reaction between nitrogen monoxide and hydrogen is dinitrogen monoxide,  $N_2O$ . This can be represented by the resonance structures below:



- (i) Analyse the bonding in dinitrogen monoxide in terms of  $\sigma$ -bonds and  $\pi$ -bonds. [3]

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- (ii) State what is meant by resonance. [1]

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4. Tin(II) chloride is a white solid that is commonly used as a reducing agent.

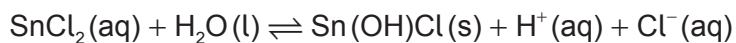
(a) (i) State why you would expect tin(II) chloride to have a similar lattice enthalpy to strontium chloride, using section 9 of the data booklet. [1]

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(ii) Calculate the molar enthalpy change when strontium chloride is dissolved in water, using sections 18 and 20 of the data booklet. [2]

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(iii) Tin(II) chloride reacts with water to precipitate the insoluble basic chloride, Sn(OH)Cl.



Suggest why tin(II) chloride is usually dissolved in dilute hydrochloric acid. [1]

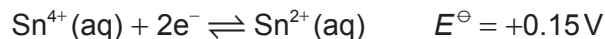
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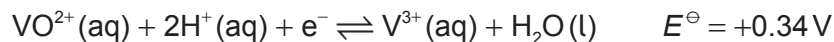


(Question 4 continued)

(b) Tin can also exist in the +4 oxidation state.



Vanadium can be reduced from an oxidation state of +4 to +3 according to the equation:



(i) Calculate the cell potential,  $E^{\ominus}$ , and the standard free energy,  $\Delta G^{\ominus}$ , change for the reaction between the  $\text{VO}^{2+}$  and  $\text{Sn}^{2+}$  ions, using sections 1 and 2 of the data booklet. [2]

$E^{\ominus}$ :

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.....

$\Delta G^{\ominus}$ :

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(ii) Deduce, giving your reason, whether a reaction between  $\text{Sn}^{2+}(\text{aq})$  and  $\text{VO}^{2+}(\text{aq})$  would be spontaneous. [1]

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(c) Outline, giving the **full** electron configuration of the vanadium atom, what is meant by the term transition metal. [2]

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**(Question 4 continued)**

(d) In an aqueous solution of vanadium(III) chloride, the vanadium exists as  $[V(H_2O)_6]^{3+}$ ,  $[VCl(H_2O)_5]^{2+}$  or  $[VCl_2(H_2O)_4]^+$  depending on the concentration of chloride ions in the solution.

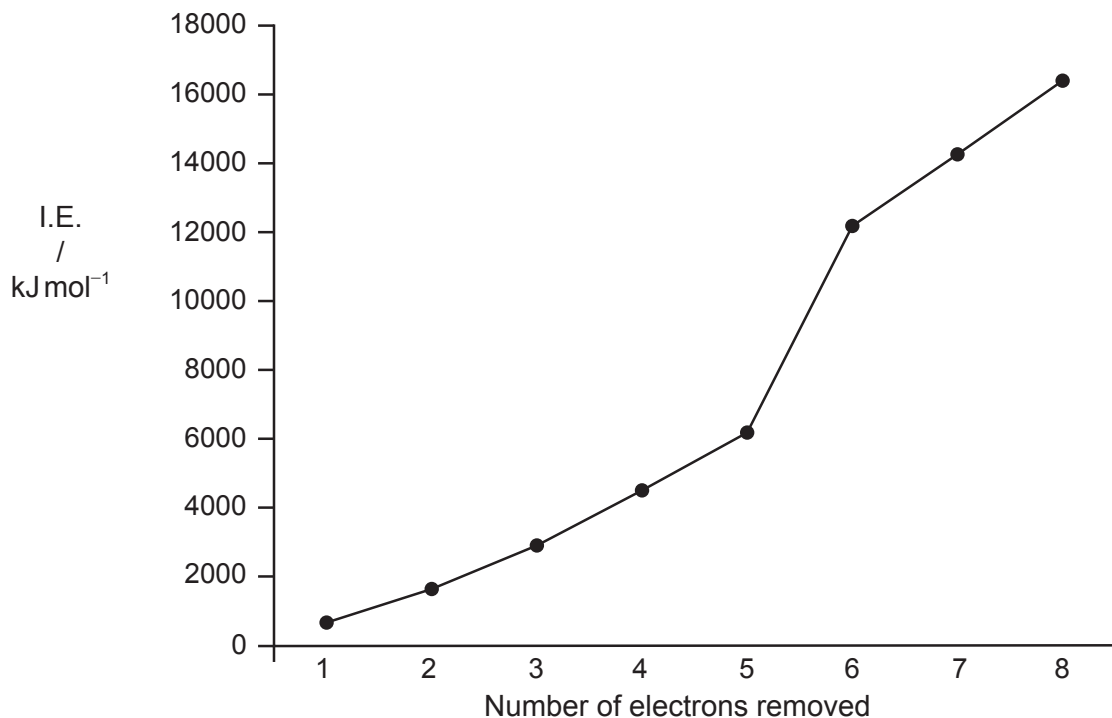
(i) Describe how  $Cl^-$  and  $H_2O$  bond to the vanadium ion. [1]

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(ii) Outline what would happen to the wavelength at which the vanadium complex ions would absorb light as the water molecules are gradually replaced by chloride ions, using section 15 of the data booklet. [2]

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(e) Eight successive ionisation energies of vanadium are shown in the graph below:



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**(Question 4 continued)**

- (i) State the sub-levels from which each of the first four electrons are lost. [1]

First: . . . . Second: . . . . Third: . . . . Fourth: . . . .

- (ii) Outline why there is an increase in ionization energy from electron 3 to electron 5. [1]

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- (iii) Explain why there is a large increase in the ionization energy between electrons 5 and 6. [3]

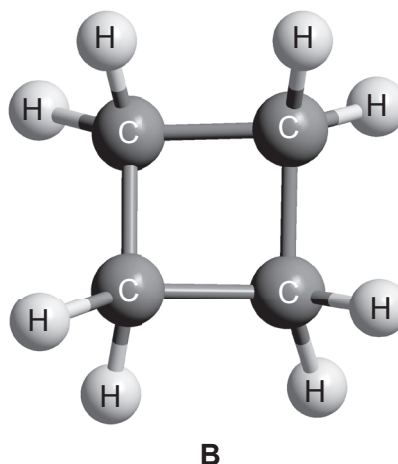
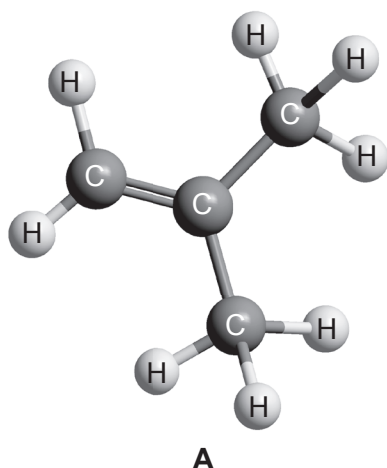
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- (iv) Vanadium is comprised almost entirely of  $^{51}\text{V}$ . State the number of neutrons an atom of  $^{51}\text{V}$  has in its nucleus. [1]

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5. Compound **A** and compound **B** are hydrocarbons.



- (a) (i) State the term that is used to describe molecules that are related to each other in the same way as compound **A** and compound **B**. [1]

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- (ii) Suggest a chemical test to distinguish between compound **A** and compound **B**, giving the observation you would expect for each. [2]

Test:

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Observation with **A**:

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Observation with **B**:

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**(Question 5 continued)**

- (b) Outline how you could use the IR spectra of compounds **A** and **B** and section 26 of the data booklet to identify them.

[1]

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- (c) Two signals occur in the  $^1\text{H}$  NMR spectrum of compound **A**. Deduce their expected chemical shift and their splitting pattern, using section 27 of the data booklet.

[2]

Signal	1	2
Chemical shift / ppm	.....	.....
Splitting pattern	.....	.....



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Answers written on this page  
will not be marked.



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