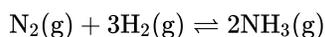


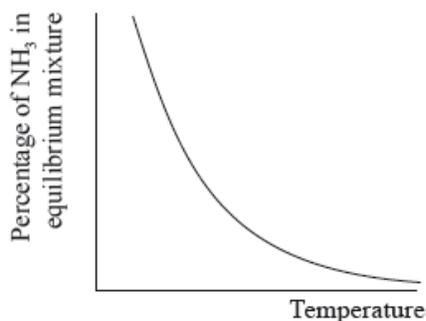
HL Paper 2

The Haber process enables the large-scale production of ammonia needed to make fertilizers.

The equation for the Haber process is given below.



The percentage of ammonia in the equilibrium mixture varies with temperature.



Ammonia can be converted into nitric acid, $\text{HNO}_3(\text{aq})$, and hydrocyanic acid, $\text{HCN}(\text{aq})$. The $\text{p}K_{\text{a}}$ of hydrocyanic acid is 9.21.

A student decided to investigate the reactions of the two acids with separate samples of 0.20 mol dm^{-3} sodium hydroxide solution.

- a. (i) Use the graph to deduce whether the forward reaction is exothermic or endothermic and explain your choice. [9]
- (ii) State and explain the effect of increasing the pressure on the yield of ammonia.
- (iii) Deduce the equilibrium constant expression, K_{c} , for the reaction.
- (iv) A mixture of 1.00 mol N_2 and 3.00 mol H_2 was placed in a 1.0 dm^3 flask at $400 \text{ }^\circ\text{C}$. When the system was allowed to reach equilibrium, the concentration of was found to be $0.062 \text{ mol dm}^{-3}$. Determine the equilibrium constant, K_{c} , of the reaction at this temperature.
- (v) Iron is used as a catalyst in the Haber process. State the effect of a catalyst on the value of K_{c} .
- b. (i) Distinguish between the terms *strong* and *weak acid* and state the equations used to show the dissociation of each acid in aqueous solution. [9]
- (ii) Deduce the expression for the ionization constant, K_{a} , of hydrocyanic acid and calculate its value from the $\text{p}K_{\text{a}}$ value given.
- (iii) Use your answer from part (b) (ii) to calculate the $[\text{H}^+]$ and the pH of an aqueous solution of hydrocyanic acid of concentration $0.108 \text{ mol dm}^{-3}$. State **one** assumption made in arriving at your answer.
- c. A small piece of magnesium ribbon is added to solutions of nitric and hydrocyanic acid of the same concentration at the same temperature. [2]
- Describe **two** observations that would allow you to distinguish between the two acids.
- d. (i) Calculate the volume of the sodium hydroxide solution required to react exactly with a 15.0 cm^3 solution of 0.10 mol dm^{-3} nitric acid. [3]
- (ii) The following hypothesis was suggested by the student: "Since hydrocyanic acid is a weak acid it will react with a smaller volume of the 0.20 mol dm^{-3} sodium hydroxide solution." Comment on whether or not this is a valid hypothesis.
- (iii) Use Table 16 of the Data Booklet to identify a suitable indicator for the titration of sodium hydroxide and hydrocyanic acid.

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), HOCl, the active bleach.



Aqueous sodium chlorate(I), NaOCl, 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. Chloric(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. State a balanced equation for the reaction of chloric(I) acid with water. [1]

b.iii. Outline, in terms of the equilibrium in aqueous chlorine, why it is dangerous to use an acidic toilet cleaner in combination with this kind of bleach. [2]

b.iv. Suggest why a covalent molecule, such as chloric(I) acid, is readily soluble in water. [2]

b.v. Partial neutralization of chloric(I) acid creates a buffer solution. Given that the $\text{p}K_{\text{a}}$ of chloric(I) acid is 7.53, determine the pH of a solution that has $[\text{HOCl}] = 0.100 \text{ mol dm}^{-3}$ and $[\text{ClO}^-] = 0.0500 \text{ mol dm}^{-3}$. [4]

b.v. Describe, 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]

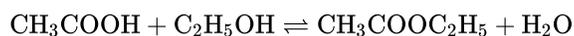
(ii) State the initial and final oxidation numbers of both chlorine and sulfur in the final equation.

Element	Initial oxidation number	Final oxidation number
Chlorine		
Sulfur		

d. (i) Define the term *standard electrode potential*. [3]

- (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.

A class studied the equilibrium established when ethanoic acid and ethanol react together in the presence of a strong acid, using propanone as an inert solvent. The equation is given below.



One group made the following **initial mixture**:

Liquid	Volume / cm^3
Ethanoic acid	5.00 ± 0.05
Ethanol	5.00 ± 0.05
6.00 mol dm^{-3} aqueous hydrochloric acid	1.00 ± 0.02
Propanone	39.0 ± 0.5

After one week, a $5.00 \pm 0.05 \text{ cm}^3$ sample of the final equilibrium mixture was pipetted out and titrated with $0.200 \text{ mol dm}^{-3}$ aqueous sodium hydroxide to determine the amount of ethanoic acid remaining. The following titration results were obtained:

Titration number	1	2	3
Initial reading / $\text{cm}^3 \pm 0.05$	1.20	0.60	14.60
Final reading / $\text{cm}^3 \pm 0.05$	28.80	26.50	40.70
Titre / cm^3	27.60	25.90	26.10

- a. The density of ethanoic acid is 1.05 g cm^{-3} . Determine the amount, in mol, of ethanoic acid present in the initial mixture. [3]
- b. The concentration of ethanoic acid can be calculated as $1.748 \text{ mol dm}^{-3}$. Determine the percentage uncertainty of this value. (Neglect any uncertainty in the density and the molar mass.) [3]
- c.i. Calculate the absolute uncertainty of the titre for Titration 1 (27.60 cm^3). [1]
- c.ii. Suggest the average volume of alkali, required to neutralize the 5.00 cm^3 sample, that the student should use. [1]
- c.iii. 3.00 cm^3 of the $0.200 \text{ mol dm}^{-3}$ aqueous sodium hydroxide reacted with the hydrochloric acid present in the 5.00 cm^3 sample. Determine the concentration of ethanoic acid in the final equilibrium mixture. [2]
- c.iv. Deduce the equilibrium constant expression for the reaction. [1]
- c.v. The other concentrations in the equilibrium mixture were calculated as follows: [1]

Compound	$\text{C}_2\text{H}_5\text{OH}$	$\text{CH}_3\text{COOC}_2\text{H}_5$	H_2O
Concentration / mol dm^{-3}	0.884	0.828	1.80

Use these data, along with your answer to part (iii), to determine the value of the equilibrium constant. (If you did not obtain an answer to part (iii), assume the concentrations of ethanol and ethanoic acid are equal, although this is not the case.)

- d. Outline how you could establish that the system had reached equilibrium at the end of one week. [1]
- e. Outline why changing the temperature has only a very small effect on the value of the equilibrium constant for this equilibrium. [1]
- f. Outline how adding some ethyl ethanoate to the initial mixture would affect the amount of ethanoic acid converted to product. [2]
- g. Propanone is used as the solvent because one compound involved in the equilibrium is insoluble in water. Identify this compound and explain why it is insoluble in water. [2]
- h. Suggest **one** other reason why using water as a solvent would make the experiment less successful. [1]

When nitrogen gas and hydrogen gas are allowed to react in a closed container the following equilibrium is established.



- a.i. Outline **two** characteristics of a reversible reaction in a state of dynamic equilibrium. [2]
- a.ii. Predict, with a reason, how each of the following changes affects the position of equilibrium. [2]

The volume of the container is increased.

Ammonia is removed from the equilibrium mixture.

- a.iii. Define the term *activation energy*, E_a . [1]
- b. Ammonia is manufactured by the Haber process in which iron is used as a catalyst. [2]
- Explain the effect of a catalyst on the rate of reaction.
- c. Typical conditions used in the Haber process are 500 °C and 200 atm, resulting in approximately 15% yield of ammonia. [3]
- (i) Explain why a temperature lower than 500 °C is **not** used.

(ii) Outline why a pressure higher than 200 atm is **not** often used.

- d.i. Deduce the equilibrium constant expression, K_c , for the reaction on page 10. [1]
- d.ii. When 1.00 mol of nitrogen and 3.00 mol of hydrogen were allowed to reach equilibrium in a 1.00 dm³ container at a temperature of 500 °C and a pressure of 1000 atm, the equilibrium mixture contained 1.46 mol of ammonia. [2]
- Calculate the value of K_c at 500 °C.

e.i. Define the term *base* according to the Lewis theory.

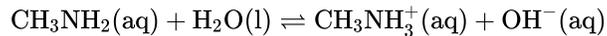
[1]

e.ii. Define the term *weak base* according to the Brønsted–Lowry theory.

[1]

e.iii. Deduce the formulas of conjugate acid–base pairs in the reaction below.

[2]



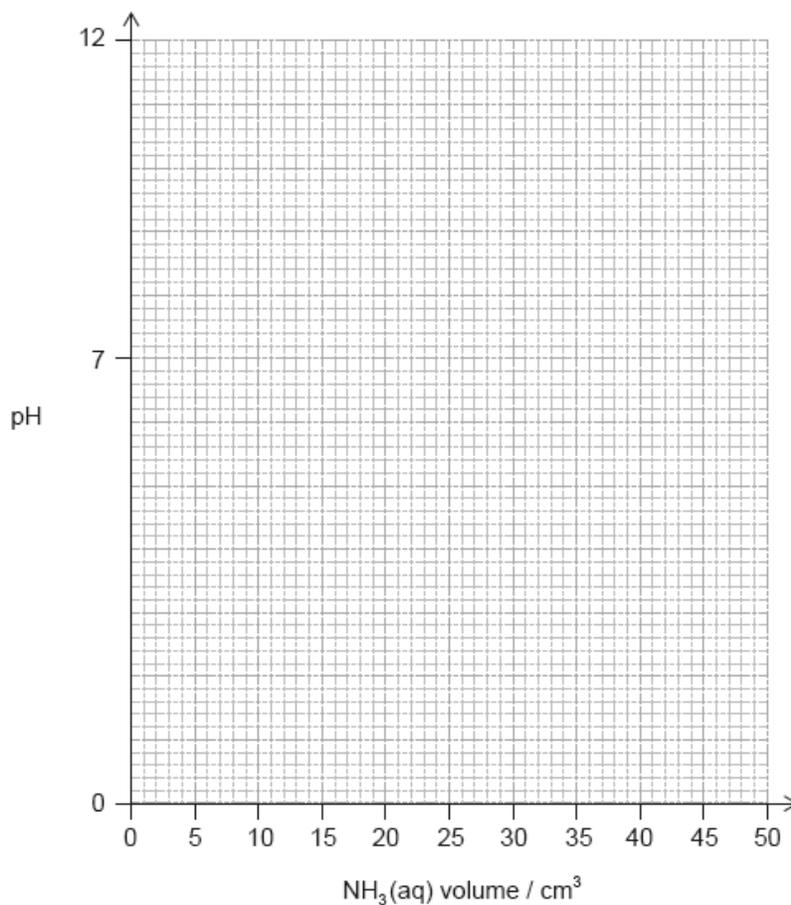
Acid	Conjugate base
.....
.....

f. Determine the pH of a $0.100 \text{ mol dm}^{-3}$ solution of ammonia, $\text{NH}_3(\text{aq})$, using tables 2 and 15 of the data booklet.

[4]

g. (i) Sketch the pH titration curve obtained when 50.0 cm^3 of $0.100 \text{ mol dm}^{-3} \text{NH}_3(\text{aq})$ is added to 25.0 cm^3 of $0.100 \text{ mol dm}^{-3} \text{HCl}(\text{aq})$.

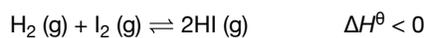
[4]



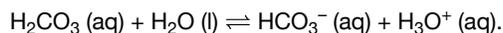
(ii) Identify an indicator from table 16 of the data booklet that could be used for this titration.

Many reactions are in a state of equilibrium.

The following reaction was allowed to reach equilibrium at 761 K.



The pH of 0.010 mol dm⁻³ carbonic acid, H₂CO₃ (aq), is 4.17 at 25 °C.



a.i. State the equilibrium constant expression, K_c , for this reaction.

[1]

a.ii. The following equilibrium concentrations in mol dm⁻³ were obtained at 761 K.

[1]

[H ₂ (g)]	[I ₂ (g)]	[HI(g)]
8.72×10^{-4}	2.72×10^{-3}	1.04×10^{-2}

Calculate the value of the equilibrium constant at 761 K.

a.iii. Determine the value of ΔG^\ominus , in kJ, for the above reaction at 761 K using section 1 of the data booklet.

[1]

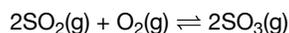
c.i. Calculate [H₃O⁺] in the solution and the dissociation constant, K_a , of the acid at 25 °C.

[3]

c.ii. Calculate K_b for HCO₃⁻ acting as a base.

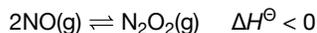
[1]

A mixture of 1.00 mol SO₂(g), 2.00 mol O₂(g) and 1.00 mol SO₃(g) is placed in a 1.00 dm³ container and allowed to reach equilibrium.



c.i. Nitrogen oxide is in equilibrium with dinitrogen dioxide.

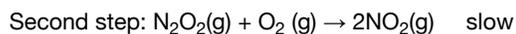
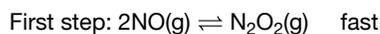
[1]



Deduce, giving a reason, the effect of increasing the temperature on the concentration of N₂O₂.

c.ii. A two-step mechanism is proposed for the formation of NO₂(g) from NO(g) that involves an exothermic equilibrium process.

[2]



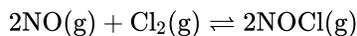
Deduce the rate expression for the mechanism.

d. The rate constant for a reaction doubles when the temperature is increased from 25.0 °C to 35 °C.

[2]

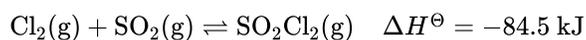
Calculate the activation energy, E_a , in kJ mol⁻¹ for the reaction using section 1 and 2 of the data booklet.

Consider the following reaction studied at 263 K.



It was found that the forward reaction is first order with respect to Cl₂ and second order with respect to NO. The reverse reaction is second order with respect to NOCl.

Consider the following equilibrium reaction.



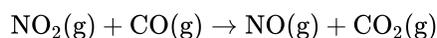
In a 1.00 dm³ closed container, at 375 °C, 8.60 × 10⁻³ mol of SO₂ and 8.60 × 10⁻³ mol of Cl₂ were introduced. At equilibrium, 7.65 × 10⁻⁴ mol of SO₂Cl₂ was formed.

a.i. State the rate expression for the forward reaction. [1]

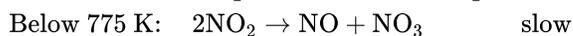
a.ii. Predict the effect on the rate of the forward reaction and on the rate constant if the concentration of NO is halved. [2]

a.iii. 1.0 mol of Cl₂ and 1.0 mol of NO are mixed in a closed container at constant temperature. Sketch a graph to show how the concentration of NO and NOCl change with time until after equilibrium has been reached. Identify the point on the graph where equilibrium is established. [4]

b. Consider the following reaction. [2]



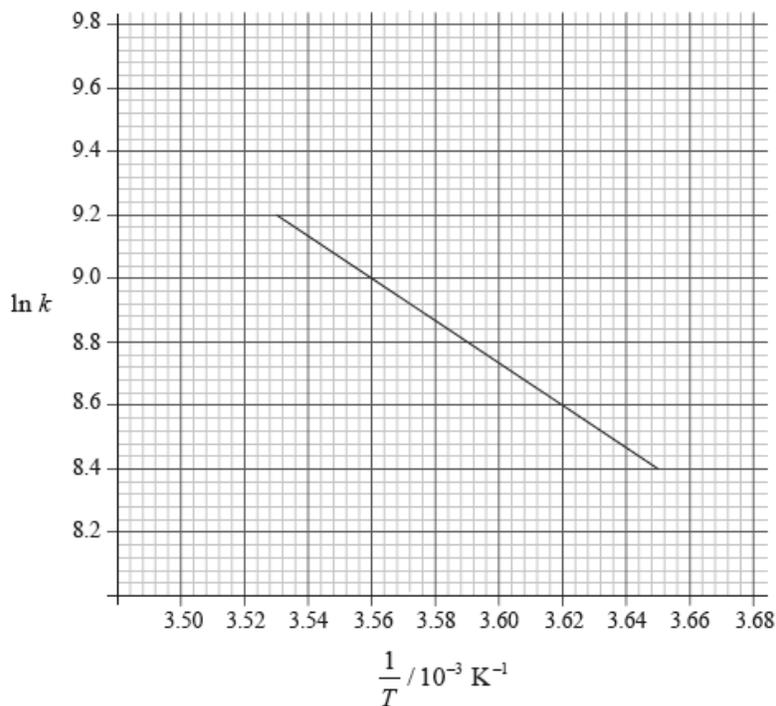
Possible reaction mechanisms are:



Based on the mechanisms, deduce the rate expressions above and below 775 K.

c. State **two** situations when the rate of a chemical reaction is equal to the rate constant. [2]

d. Consider the following graph of $\ln k$ against $\frac{1}{T}$ for the first order decomposition of N₂O₄ into NO₂. Determine the activation energy in kJ mol⁻¹ for this reaction. [2]



e.i. Deduce the equilibrium constant expression, K_c , for the reaction. [1]

e.ii. Determine the value of the equilibrium constant, K_c . [3]

e.iii. If the temperature of the reaction is changed to 300 °C, predict, stating a reason in each case, whether the equilibrium concentration of SO₂Cl₂ and the value of K_c will increase or decrease. [3]

e.iv. If the volume of the container is changed to 1.50 dm^3 , predict, stating a reason in each case, how this will affect the equilibrium concentration of SO_2Cl_2 and the value of K_c . [3]

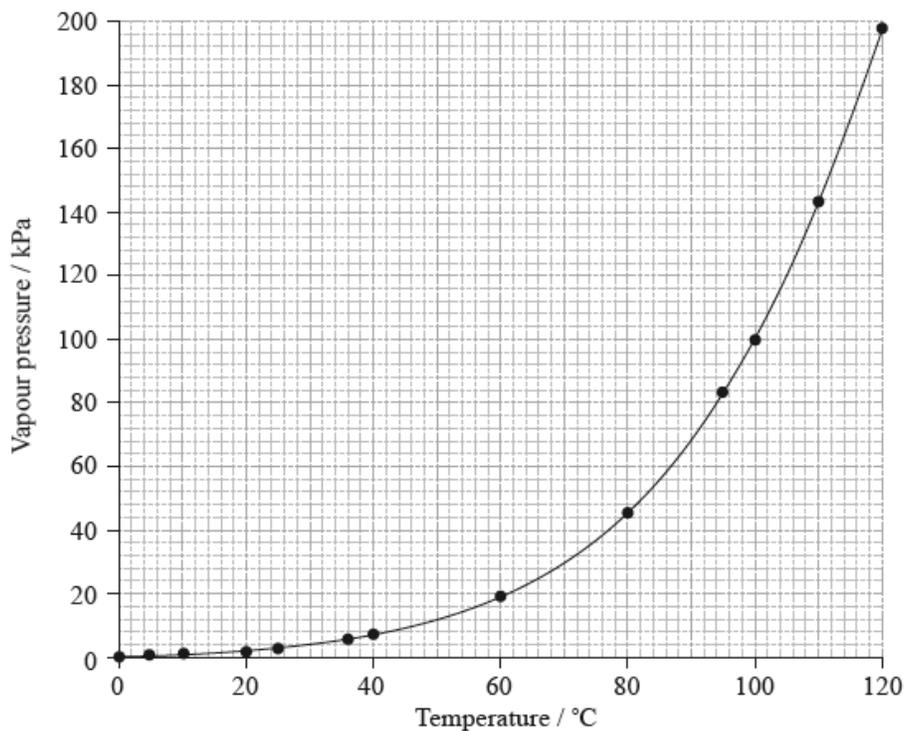
e.v. Suggest, stating a reason, how the addition of a catalyst at constant pressure and temperature will affect the equilibrium concentration of SO_2Cl_2 . [2]

Hydrogen gas reacts with iodine gas to form hydrogen iodide gas. A 2.00 dm^3 flask was filled with $1.50 \times 10^{-2} \text{ mol}$ of hydrogen and $1.50 \times 10^{-2} \text{ mol}$ of iodine at a temperature, T . The equilibrium constant, K_c , has a value of 53.0 at this temperature.

a.i. Deduce the equilibrium constant expression, K_c , for the formation of $\text{HI}(\text{g})$. [1]

a.ii. Determine the equilibrium concentrations, in mol dm^{-3} , of hydrogen, iodine and hydrogen iodide. [4]

The vapour pressure of water changes with temperature according to the graph below.



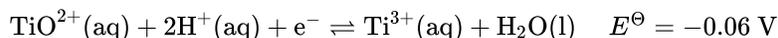
a. A liquid boils when its vapour pressure equals atmospheric pressure. Determine the boiling point of water on a mountaintop on a day when the atmospheric pressure is 60.0 kPa. [1]

b. Sketch another curve on the axes above to show how the vapour pressure of a liquid that has weaker intermolecular forces than water, such as bromine, changes with temperature. [1]

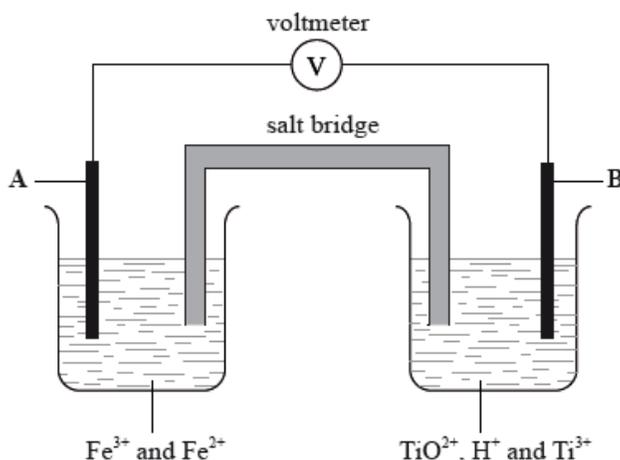
c. (i) A sample of liquid bromine was left in a closed conical (Erlenmeyer) flask at 298 K and allowed to reach a state of equilibrium. State an observation that indicates that equilibrium was reached. [3]

(ii) The temperature of the closed flask was increased and the system was allowed to reach a new equilibrium. Compare the equilibrium formed at the new temperature with the equilibrium at the original temperature on the molecular level.

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



In the diagram below, **A** and **B** are inert electrodes and, in the aqueous solutions, all ions have a concentration of 1 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.

a. Define the term *standard electrode potential*, E^{\ominus} . [1]

b.i.State the initial and final oxidation numbers of titanium and hence deduce whether it is oxidized or reduced in this change. [2]

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^{2+} ion as an oxidizing agent. [2]

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 14 of the Data Booklet if necessary. [3]

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

Zn (s) is added to a solution containing $\text{TiO}^{2+}(\text{aq})$ and $\text{H}^+(\text{aq})$ 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 oxidation or reduction. [2]

d.ii. Calculate the cell potential in V. [1]

d.iii. On the diagram above label with an arrow [1]

- 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. [3]

	Na_2O	SiO_2	SO_2
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. [1]

e.iii. As well as the oxide above, sodium forms a peroxide that contains the peroxide ion, O_2^{2-} . Draw the Lewis (electron dot) structure of the peroxide ion. [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 atoms. [3]

f.ii. Xenon, although a noble gas, forms an oxide, XeO_2 , that has a structure related to that of SiO_2 . Compare the geometry around the silicon atoms in SiO_2 with the geometry around the xenon atoms in XeO_2 , using the valence shell electron pair repulsion (VSEPR) theory. [3]

An equilibrium exists between nitrosyl chloride, NOCl, nitrogen oxide, NO, and chlorine, Cl_2 .



20.0 cm³ of hexane, C₆H₁₄, and 20.0 cm³ of pentan-1-ol, C₅H₁₁OH, were placed separately into two closed containers at 298 K and allowed to reach equilibrium.

Ammonia is a weak base.

a. (i) Deduce the equilibrium constant expression for this reaction. [7]

(ii) Explain the effect on the position of equilibrium and the value of K_c when pressure is decreased and temperature is kept constant.

(iii) 2.00 mol of NOCl was placed in a 1.00 dm³ container and allowed to reach equilibrium at 298 K. At equilibrium, 0.200 mol of NO was present. Determine the equilibrium concentrations of NOCl and Cl₂, and hence calculate the value of K_c at this temperature.

(iv) The value of K_c is 1.60×10^{-5} at 318 K. State and explain whether the forward reaction is exothermic or endothermic.

b. (i) Compare the two liquids in terms of their boiling points, enthalpies of vaporization and vapour pressures. [4]

(ii) Explain your answer given for part (b)(i).

c.i. Calculate the pH of a 1.50 mol dm⁻³ solution of ammonia at 298 K to two decimal places, using Table 15 of the Data Booklet. [2]

c.ii. A buffer solution is made using 25.0 cm³ of 0.500 mol dm⁻³ hydrochloric acid, HCl (aq), and 20.0 cm³ of 1.50 mol dm⁻³ ammonia solution, NH₃(aq). [2]

Describe the meaning of the term *buffer solution*.

c.iii. Determine the pH of the buffer solution at 298 K. [4]

c.iv. A 1.50 mol dm⁻³ solution of ammonia is added to 25.0 cm³ of a 0.500 mol dm⁻³ hydrochloric acid solution in a titration experiment. [1]

Calculate the total volume of the solution at the equivalence point.

c.v. Calculate the pH of the solution at the equivalence point, using Table 15 of the Data Booklet. [4]

c.vi. Identify a suitable indicator for this titration, using Table 16 of the Data Booklet. [1]

The rate of reaction is an important factor in industrial processes such as the Contact process to make sulfur trioxide, $\text{SO}_3(\text{g})$.

a. Define the term *rate of reaction*. [1]

b. Describe the collision theory. [3]

c.i. The Contact process involves this homogeneous equilibrium: [2]



State and explain how increasing the pressure of the reaction mixture affects the yield of SO_3 .

c.ii. The Contact process involves this homogeneous equilibrium: [4]



2.00 mol of $\text{SO}_2(\text{g})$ are mixed with 3.00 mol of $\text{O}_2(\text{g})$ in a 1.00 dm^3 container until equilibrium is reached. At equilibrium there are 0.80 mol of $\text{SO}_3(\text{g})$.

Determine the equilibrium constant (K_c) assuming all gases are at the same temperature and pressure.

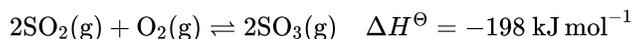
c.iii. The Contact process involves this homogeneous equilibrium: [1]



State the effect of increasing temperature on the value of K_c for this reaction.

d. Outline the economic importance of using a catalyst in the Contact process. [2]

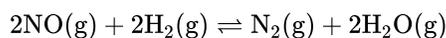
Consider the following equilibrium.



a.ii. State and explain the effect of increasing the pressure on the yield of sulfur trioxide. [2]

a.iv. State 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 dm^3 flask at 300 K, the following equilibrium was established. [4]



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.

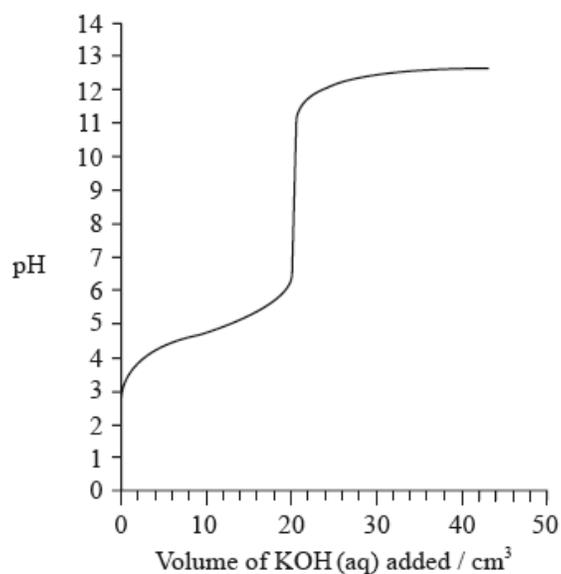
c.i. Outline **two** differences between an electrolytic cell and a voltaic cell. [2]

c.v. Electroplating is an important application of electrolysis. State the composition of the electrodes and the electrolyte used in the silver electroplating process. [3]

a.i. Define the terms *acid* and *base* according to the Brønsted-Lowry theory. Distinguish between a weak base and a strong base. State **one** example of a weak base. [3]

a.ii. Weak acids in the environment may cause damage. Identify a weak acid in the environment **and** outline **one** of its effects. [2]

a.iii. The graph below indicates the pH change during the titration of 20.0 cm³ of 0.100 mol dm⁻³ of CH₃COOH(aq) with 0.100 mol dm⁻³ KOH(aq). From the graph, identify the volume of KOH(aq) and the pH at the equivalence point. [2]



a.iv. Explain how the graph could be used to determine the pK_a of ethanoic acid **and** determine the pK_a value for these data. [2]

a.v. Sketch a graph, similar to the graph on the previous page, to indicate the change in pH during a titration of 25.0 cm³ of 0.100 mol dm⁻³ HNO₃(aq) with 0.100 mol dm⁻³ KOH(aq). On your graph, clearly indicate the starting pH value, the equivalence point, the pH at the equivalence point and the final pH reached. [4]

b.i. Describe how an indicator works. [3]

b.ii. Using Table 16 of the Data Booklet, identify the most appropriate indicator for the titration of ethanoic acid with potassium hydroxide. Explain your choice. [2]

d. Determine the pH of the solution resulting when 100 cm³ of 0.50 mol dm⁻³ HCl(aq) is mixed with 200 cm³ of 0.10 mol dm⁻³ NaOH(aq). [5]

The periodic table shows the relationship between electron configuration and the properties of elements and is a valuable tool for making predictions in chemistry.

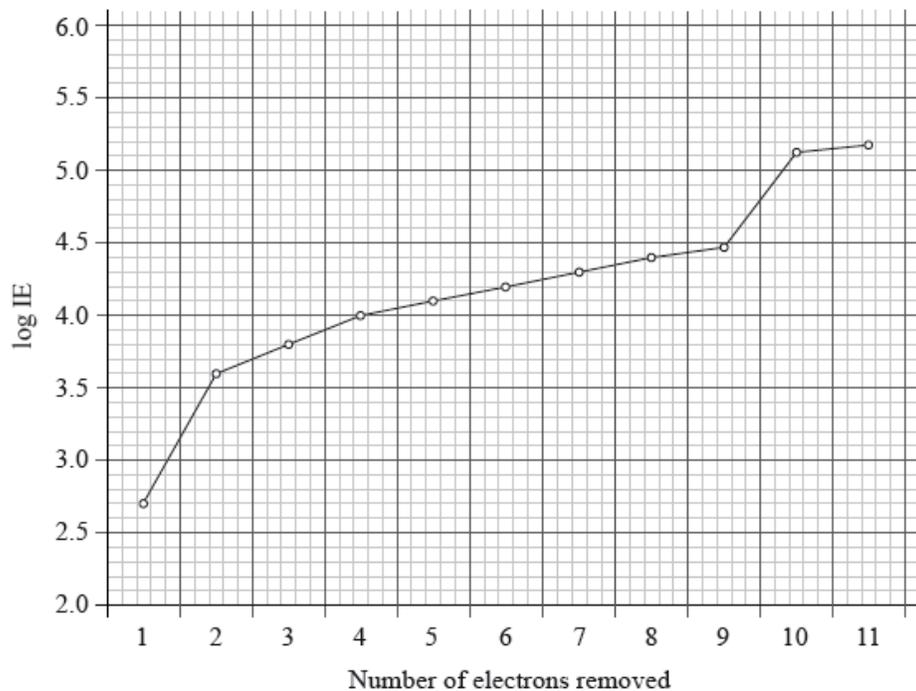
The ten elements in the first-row d-block have characteristic properties and many uses.

b.i. Define the term *electronegativity*. [2]

c. (i) Outline **two** reasons why a sodium ion has a smaller radius than a sodium atom. [4]

(ii) Explain why the ionic radius of P^{3-} is **greater** than the ionic radius of Si^{4+} .

d. The graph below represents the successive ionization energies of sodium. The vertical axis plots log (ionization energy) instead of ionization energy to allow the data to be represented without using an unreasonably long vertical axis. [4]



State the full electron configuration of sodium and explain how the successive ionization energy data for sodium are related to its electron configuration.

e. (i) Explain why the first ionization energy of aluminium is **lower** than the first ionization energy of magnesium. [4]

(ii) Explain why the first ionization energy of sulfur is **lower** than the first ionization energy of phosphorus.

f.i. State and explain the type of reaction that takes place between Fe^{3+} and H_2O to form $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ in terms of acid-base theories. [2]

f.ii. Explain why $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is coloured. [3]

f.iii. Outline the economic significance of the use of a catalyst in the Haber process which is an exothermic reaction. [2]

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^{-1}	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]
- b. (i) Explain why the second ionization energy is greater than the first ionization energy. [4]

(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 Mg^+ being able to form stable compounds. [3]

Use the ionization energy data from part (b), along with the other data provided below, to determine the enthalpy change of formation of $\text{MgCl}(\text{s})$. 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_2 $+243 \text{ kJ mol}^{-1}$

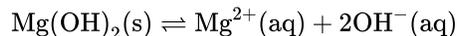
Electron affinity of Cl $+349 \text{ kJ mol}^{-1}$

Lattice enthalpy of NaCl $+790 \text{ kJ mol}^{-1}$

- d. Consider the lattice enthalpies of MgF_2 , MgCl_2 and CaCl_2 . List these from the most endothermic to the least endothermic and explain your order. [3]

Most endothermic \rightarrow Least endothermic

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



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

- f. (i) Describe the bonding present in magnesium metal. [4]

(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. [7]

(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.

Water is an important substance that is abundant on the Earth's surface.

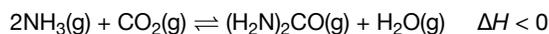
Buffer solutions resist small changes in pH. A phosphate buffer can be made by dissolving NaH_2PO_4 and Na_2HPO_4 in water, in which NaH_2PO_4 produces the acidic ion and Na_2HPO_4 produces the conjugate base ion.

A 0.10 mol dm^{-3} ammonia solution is placed in a flask and titrated with a 0.10 mol dm^{-3} hydrochloric acid solution.

- a. (i) State the expression for the ionic product constant of water, K_w . [7]
- (ii) Explain why even a very acidic aqueous solution still has some OH^- ions present in it.
- (iii) State and explain the effect of increasing temperature on the value of K_w given that the ionization of water is an endothermic process.
- (iv) State and explain the effect of increasing temperature on the pH of water.
- b. (i) Deduce the acid and conjugate base ions that make up the phosphate buffer and state the ionic equation that represents the phosphate buffer. [7]
- (ii) Describe how the phosphate buffer minimizes the effect of the addition of a strong base, OH^- (aq), to the buffer. Illustrate your answer with an ionic equation.
- (iii) Describe how the phosphate buffer minimizes the effect of the addition of a strong acid, H^+ (aq), to the buffer. Illustrate your answer with an ionic equation.
- c. (i) Explain why the pH of the ammonia solution is less than 13. [11]
- (ii) Estimate the pH at the equivalence point for the titration of hydrochloric acid with ammonia and explain your reasoning.
- (iii) State the equation for the reaction of ammonia with water and write the K_b expression for NH_3 (aq).
- (iv) When half the ammonia has been neutralized (the half-equivalence point), the pH of the solution is 9.25. Deduce the relationship between $[\text{NH}_3]$ and $[\text{NH}_4^+]$ at the half-equivalence point.
- (v) Determine $\text{p}K_b$ and K_b for ammonia based on the pH at the half-equivalence point.
- (vi) Describe the significance of the half-equivalence point in terms of its effectiveness as a buffer.

Urea, $(\text{H}_2\text{N})_2\text{CO}$, is excreted by mammals and can be used as a fertilizer.

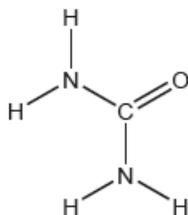
Urea can also be made by the direct combination of ammonia and carbon dioxide gases.



a.i. Calculate the percentage by mass of nitrogen in urea to two decimal places using section 6 of the data booklet. [2]

a.ii. Suggest how the percentage of nitrogen affects the cost of transport of fertilizers giving a reason. [1]

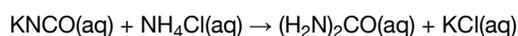
b. The structural formula of urea is shown. [3]



Predict the electron domain and molecular geometries at the nitrogen and carbon atoms, applying the VSEPR theory.

	Electron domain geometry	Molecular geometry
Nitrogen
Carbon	trigonal planar

c. Urea can be made by reacting potassium cyanate, KNCO , with ammonium chloride, NH_4Cl . [2]



Determine the maximum mass of urea that could be formed from 50.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ potassium cyanate solution.

d.i. State the equilibrium constant expression, K_c . [1]

d.ii. Predict, with a reason, the effect on the equilibrium constant, K_c , when the temperature is increased. [1]

d.iii. Determine an approximate order of magnitude for K_c , using sections 1 and 2 of the data booklet. Assume ΔG^\ominus for the forward reaction is approximately $+50 \text{ kJ}$ at 298 K . [2]

e.i. Suggest one reason why urea is a solid and ammonia a gas at room temperature. [1]

e.ii. Sketch two different hydrogen bonding interactions between ammonia and water. [2]

f. The combustion of urea produces water, carbon dioxide and nitrogen. [2]

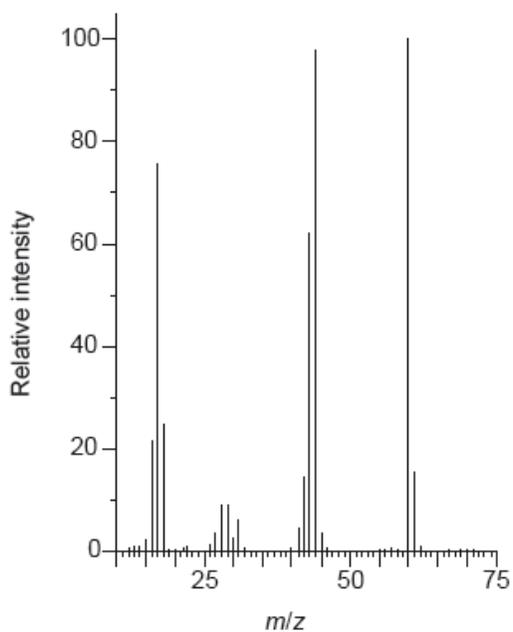
Formulate a balanced equation for the reaction.

g. Calculate the maximum volume of CO_2 , in cm^3 , produced at STP by the combustion of 0.600 g of urea, using sections 2 and 6 of the data booklet. [1]

h. Describe the bond formation when urea acts as a ligand in a transition metal complex ion. [2]

i. The C–N bonds in urea are shorter than might be expected for a single C–N bond. Suggest, in terms of electrons, how this could occur. [1]

j. The mass spectrum of urea is shown below. [2]

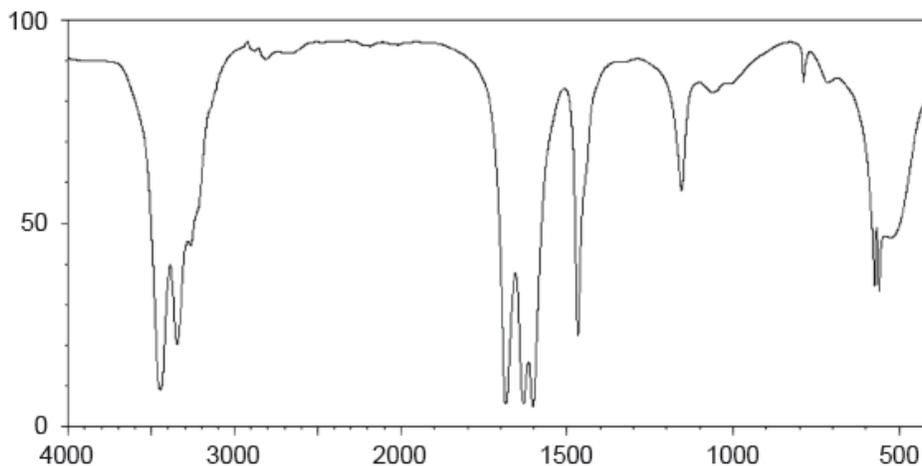


[Source: <http://sdfs.db.aist.go.jp>]

Identify the species responsible for the peaks at $m/z = 60$ and 44.

60:
44:

k. The IR spectrum of urea is shown below. [2]



[Source: sdfs.db.aist.go.jp]

Identify the bonds causing the absorptions at 3450 cm^{-1} and 1700 cm^{-1} using section 26 of the data booklet.

3450 cm⁻¹:

.....

1700 cm⁻¹:

.....

- i.i. Predict the number of signals in the ¹H NMR spectrum of urea. [1]
- i.ii. Predict the splitting pattern of the ¹H NMR spectrum of urea. [1]
- i.iii. Outline why TMS (tetramethylsilane) may be added to the sample to carry out ¹H NMR spectroscopy and why it is particularly suited to this role. [2]

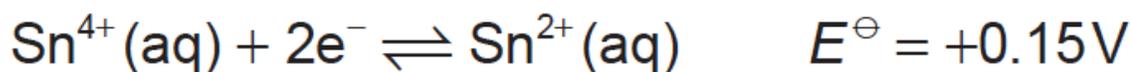
Tin(II) chloride is a white solid that is commonly used as a reducing agent.

- 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. [4]
- (ii) Calculate the molar enthalpy change when strontium chloride is dissolved in water, using sections 18 and 20 of the data booklet.
- (iii) Tin(II) chloride reacts with water to precipitate the insoluble basic chloride, Sn(OH)Cl.

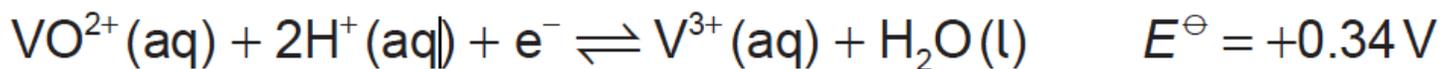


Suggest why tin(II) chloride is usually dissolved in dilute hydrochloric acid.

- b. Tin can also exist in the +4 oxidation state. [3]



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, ΔG^\ominus , change for the reaction between the VO^{2+} and Sn^{2+} ions, using sections 1 and 2 of the data booklet.

E^\ominus :

ΔG^\ominus :

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

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

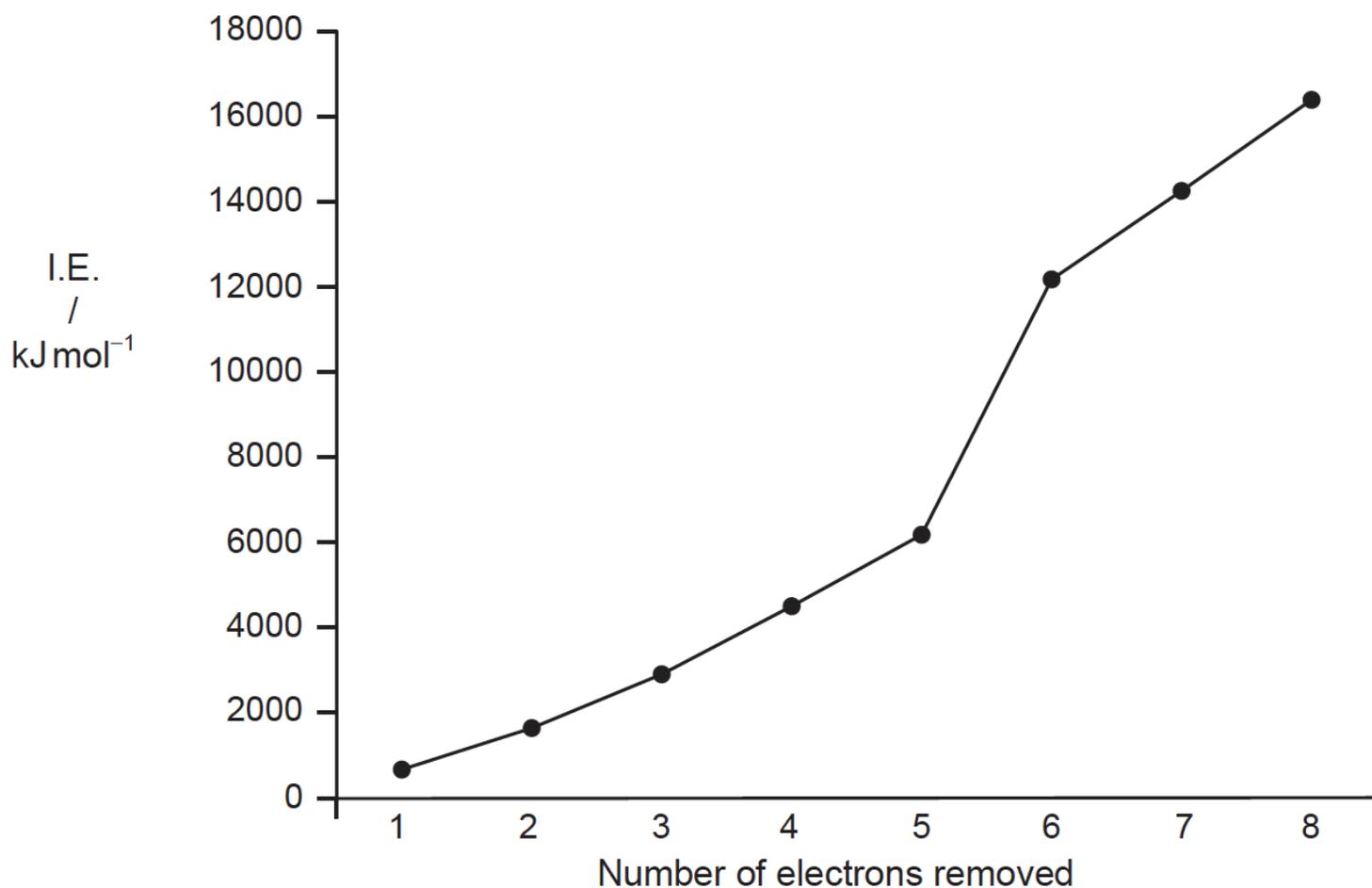
- d. In an aqueous solution of vanadium(III) chloride, the vanadium exists as $[\text{V}(\text{H}_2\text{O})_6]^{3+}$, $[\text{VCl}(\text{H}_2\text{O})_5]^{2+}$ or $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ depending on the concentration of chloride ions in the solution. [3]

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

(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.

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

[6]



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

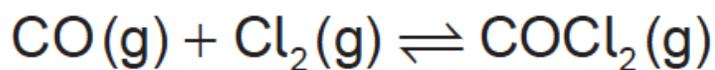
First: Second: Third: Fourth:

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

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

(iv) Vanadium is comprised almost entirely of ⁵¹V. State the number of neutrons an atom of ⁵¹V has in its nucleus.

Phosgene, COCl₂, 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.

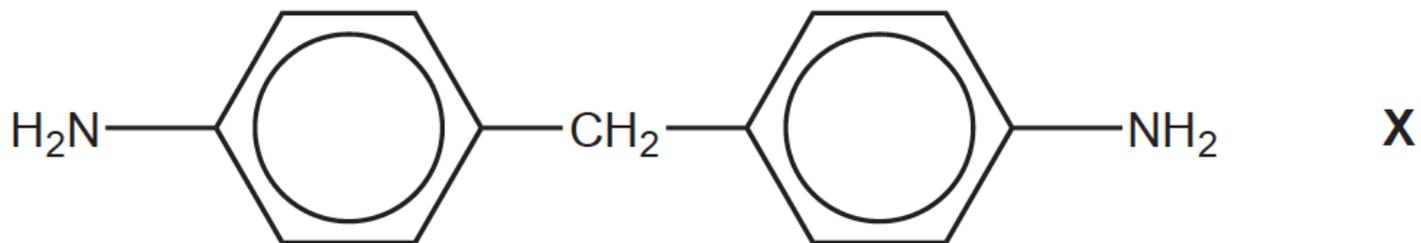
[8]

(ii) At exactly 600°C the value of the equilibrium constant is 0.200. Calculate the standard Gibbs free energy change, ΔG^\ominus , for the reaction, in kJ, using sections 1 and 2 of the data booklet. State your answer to **three** significant figures.

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

(iv) Calculate the standard entropy change, ΔS^\ominus , in JK^{-1} , for the forward reaction at 25°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 kJ respectively, although these are not the correct answers.)

b. One important industrial use of phosgene is the production of polyurethanes. Phosgene is reacted with diamine **X**, derived from phenylamine. [8]



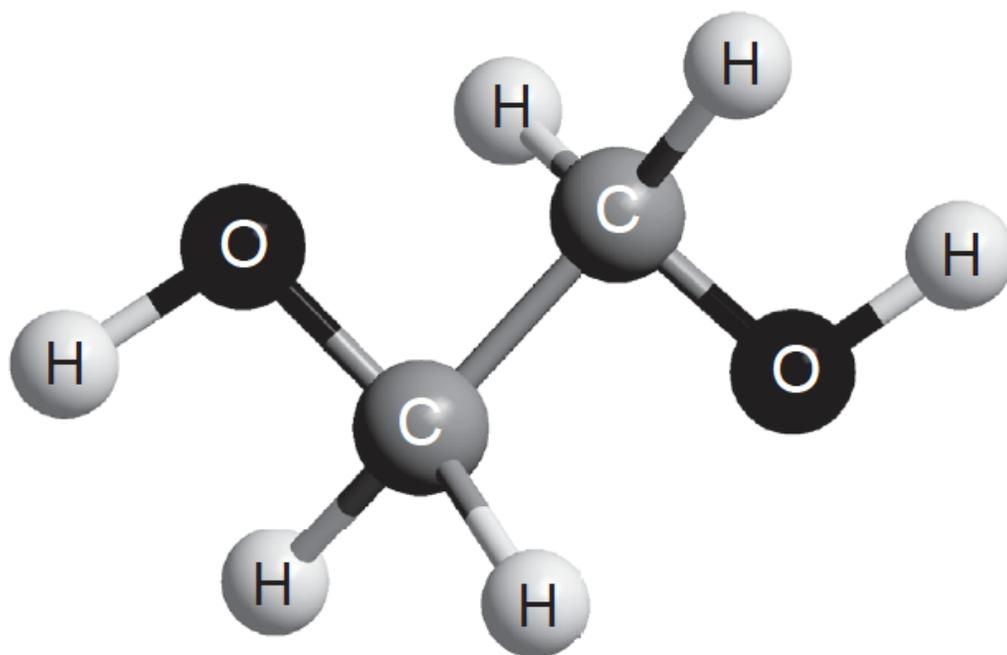
(i) Classify diamine **X** as a primary, secondary or tertiary amine.

(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.

(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.

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

c. The other monomer used in the production of polyurethane is compound **Z** shown below. [5]



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

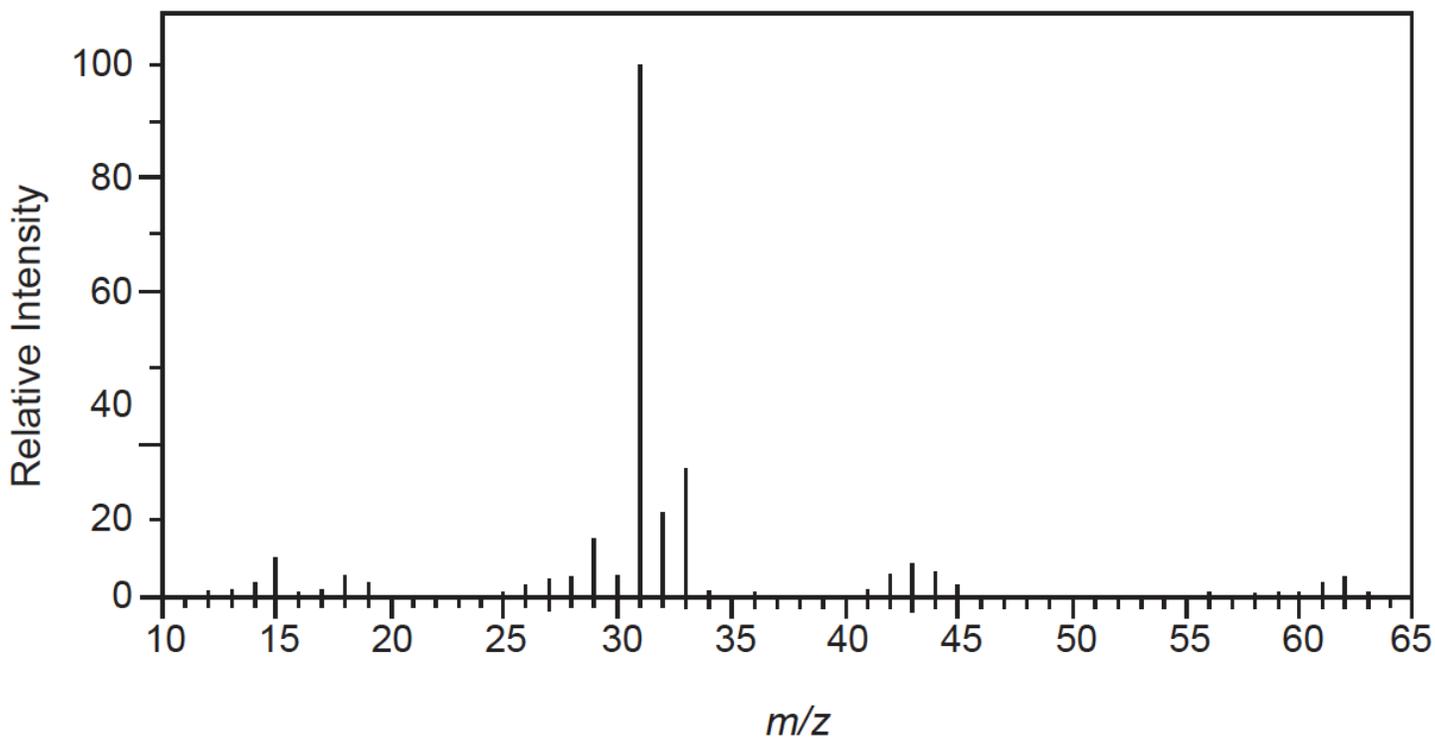
Name:

Class:

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

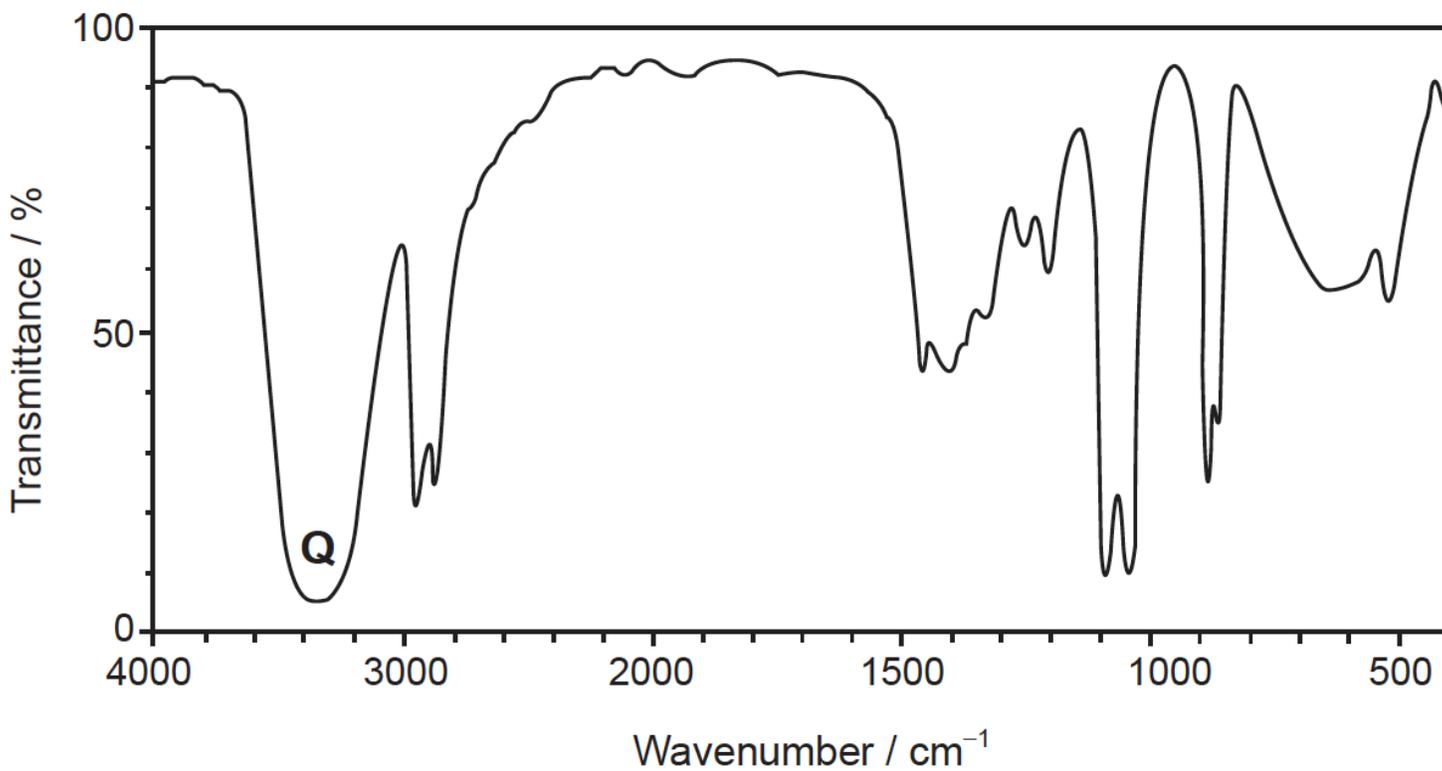
The mass spectrum and infrared (IR) spectrum of compound **Z** are shown below:

Mass spectrum



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

IR spectrum



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

(iii) Identify the species causing the large peak at $m/z=31$ in the mass spectrum.

(iv) Identify the bond that produces the peak labelled **Q** on the IR spectrum, using section 26 of the data booklet.

d. Phenylamine can act as a weak base. Calculate the pH of a $0.0100 \text{ mol dm}^{-3}$ solution of phenylamine at 298K using section 21 of the data booklet. [4]
