PEARSON EDEXCEL IAL CHEMISTRY · YCH11

CHEMISTRY



EXAM QUESTION PACK

UNIT 4: CHEMICAL EQUILIBRIA

SCORE	PERCENTAGE
/174	%

STEMUP

These questions belong to Pearson Edexcel, not to us.

The examination questions, mark schemes and examiner comments in this pack were written and published by Pearson Edexcel. They are past assessment materials, reproduced here so that students can revise from them.

What we do not own

STEMUP is not affiliated with Pearson Edexcel and does not own, and makes no claim to own, any of the question, mark scheme or examiner report material in this pack. Pearson Edexcel has not endorsed, approved or been involved in the production of it. Pearson Edexcel and the qualification titles used here belong to their respective owners and appear for identification only.

Where to find the originals

Pearson Edexcel publishes its past papers, mark schemes and examiner reports free of charge. Always check the current specification at qualifications.pearson.com before you revise, because content and wording can change between series.

If you hold the rights to any material in this pack and would like it amended or removed, contact admin@stemup.co.uk and we will act on it.

Q1.

This question is about ammonia and ammonium chloride.

(a) Ammonia is produced by reacting nitrogen and hydrogen as shown.

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$$

(i) Write the expression for the equilibrium constant, K_p.

(1)

(ii) An equilibrium was established by mixing nitrogen and hydrogen in a 1 : 3 ratio by volume, at a temperature of 450 °C and pressure of 200 atm.
The equilibrium mixture contained 28 % of ammonia by volume.

Complete the table.

(3)

Substance	Mole fraction	Partial pressure / atm
N_2		
H_2		
NH_3	0.28	56

(iii) Calculate the equilibrium constant.

Give your answer to an appropriate number of significant figures and include units, if required.

(3)

(iv) When the temperature was reduced to 400 °C at the same pressure, the equilibrium mixture contained 36 % of ammonia.

Explain what can be deduced about this reaction from this information.

(2)

.....

.....

.....

.....

.....

.....

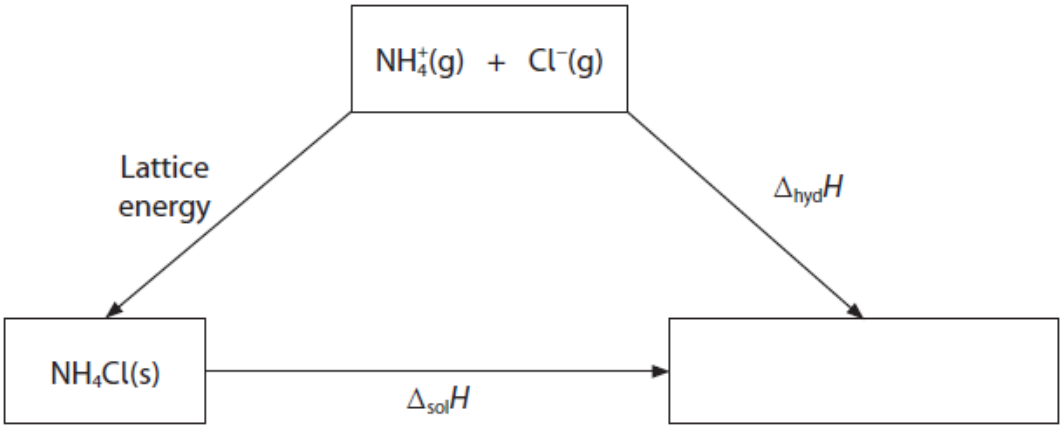
(b) Ammonium chloride can be produced by reacting ammonia with hydrogen chloride.

Ammonium chloride is a white solid that is very soluble in water.

Hess's Law can be used to calculate the enthalpy of solution of ammonium chloride, using hydration enthalpies and lattice energy.

(i) Complete the Hess cycle by filling in the empty box.

(1)



(ii) Complete the expression for the enthalpy change of solution using the hydration enthalpies and lattice energy.

(1)

$\Delta_{sol}H$ =

(iii) Calculate the enthalpy change of solution, using your expression in (b)(ii) and these data.

Enthalpy change of hydration of NH_4^+ = −307 kJ mol^{-1}

Enthalpy change of hydration of Cl^- = −378 kJ mol^{-1}

Lattice energy of NH_4Cl = −705 kJ mol^{-1}

(2)

(iv) A student suggested that the enthalpy change of solution of ammonium bromide would be of a similar magnitude to the enthalpy change of solution of ammonium chloride.

Comment on this suggestion in terms of the hydration enthalpies and lattice energies of these two compounds.

(3)

.....

.....

.....

.....

.....

.....

.....

.....

(c) Write an **ionic** equation to show why aqueous solutions of ammonium chloride are acidic. State symbols are not required.

(1)

(Total for question = 17 marks)

Q2.

Ammonia is manufactured in the Haber Process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

In this process, pressures between 100 atm and 300 atm and temperatures between 675 K and 725 K are usually used.

(a) (i) Calculate $\Delta S^{\ominus}_{system}$ for this reaction at 298 K.
Include a sign and units with your answer.

[Standard molar entropy, $S^{\ominus}$, for 1 mol of each gas, in J K^{-1} mol^{-1}:
$N_2 = 191.6$ $H_2 = 130.6$ $NH_3 = 192.3$]

(2)

(ii) Explain, using ideas about disorder, whether the sign of your answer to (a)(i) is as expected.

(2)

.....

.....

.....

.....

.....

(iii) At 700 K, the enthalpy change for this reaction is $\Delta H = -110.2$ kJ mol^{-1}.

Calculate the entropy change of the surroundings, $\Delta S_{surroundings}$, at 700 K. Include a sign and units in your answer.

(2)

(iv) At 700 K, the total entropy change, $\Delta S_{total} = -78.7\,J\,K^{-1}\,mol^{-1}$.

Calculate ΔS_{system} for this reaction at 700 K. Include a sign and units in your answer.

(1)

*(v) Explain **one** advantage and **one** disadvantage of using a temperature higher than 700 K in the Haber process.

Consider the effect of an increase in temperature on the rate of reaction, on the values of $\Delta S_{surroundings}$ and ΔS_{total} and on the equilibrium constant.

(6)

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(b) (i) Write the expression for the equilibrium constant, K_p , for the reaction in the Haber Process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(1)

(ii) A mixture of nitrogen, hydrogen and ammonia is at equilibrium at 255 atm and 700 K. The partial pressure of nitrogen is 25 atm and that of hydrogen is 150 atm.

Calculate the equilibrium constant, K_p , for the formation of ammonia, at 700 K. Include units in your answer.

(3)

(iii) The pressure of the system is doubled at constant temperature.

Explain the effect of this on the yield of ammonia by considering the change in the K_p expression and hence the position of equilibrium.

(3)

.....

.....

.....

.....

.....

.....

.....

.....

(Total for question = 20 marks)

Q3.

Equal amounts of W and X are mixed and allowed to reach equilibrium.

$$W + X \rightleftharpoons Y + Z$$

The value of the equilibrium constant is $K_c = 4.85$. At equilibrium, the mixture will contain

☒ **A** almost all Y and Z

☒ **B** almost all W and X

☒ **C** W, X, Y and Z but there is less Y and Z than W and X

☒ **D** W, X, Y and Z but there is more Y and Z than W and X

(Total for question = 1 mark)

Q4.

A student carried out an experiment to determine the equilibrium constant for the reaction to form ethyl ethanoate from ethanol and ethanoic acid.

$$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

Different amounts of each substance were added to conical flasks, each containing 2.0 cm^3 of 1.0 mol dm^{-3} hydrochloric acid.

Conical flask	Volume added / cm^3				
	HCl (aq)	H_2O (l)	CH_3COOH (l)	$CH_3COOCH_2CH_3$ (l)	CH_3CH_2OH (l)
1	2.0	1.0	0	2.0	0
2	2.0	0	5.0	0	5.0
3	2.0	0	4.0	0	3.0
4	2.0	0	0	3.0	0

The flasks were then stoppered and left for a week to reach equilibrium.

Each mixture was then titrated with 1.0 mol dm^{-3} sodium hydroxide.

(a) In which flask(s) was the equilibrium approached from the right-hand side of the equation?

(1)

☒ **A** flask 1 only

☒ **B** flask 4 only

☒ **C** flasks 1 and 4 only

☒ **D** flasks 2 and 3 only

(b) Which of these statements explains why it is possible to titrate the reaction mixture directly to find the equilibrium concentrations?

(1)

☒ **A** the equilibrium reaction is slow

☒ **B** the sodium hydroxide quickly hydrolyses the ester

☒ **C** all the reactant concentrations remain constant during the titration

☒ **D** a buffer solution forms in the reaction

(Total for question = 2 marks)

Q5.

For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

The reaction shown is at equilibrium. The forward reaction is endothermic.

$$C(s) + CO_2(g) \leftrightarrow 2CO(g)$$

(a) Which will **increase** when the temperature is lowered?

(1)

☒ **A** the mole fraction of carbon dioxide

☒ **B** the partial pressure of carbon monoxide

☒ **C** the rate of the backward reaction

☒ **D** the value of K_p for the forward reaction

(b) At 680 °C and 1 atm, 52.6 % of the molecules in the gas mixture are carbon monoxide. What is the partial pressure of carbon dioxide, in atmospheres?

(1)

☒ **A** 0.237

☒ **B** 0.263

☒ **C** 0.474

☒ **D** 0.526

(Total for question = 2 marks)

Q6.

For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

The equation for the precipitation of lead(II) chloride is shown.

$$Pb^{2+}(aq) + 2Cl^{-}(aq) \leftrightarrow PbCl_2(s)$$

What are the units of the equilibrium constant, K_c?

☒ **A** $dm^9\ mol^{-3}$

☒ **B** $dm^6\ mol^{-2}$

☒ **C** $mol^2\ dm^{-6}$

☒ **D** $mol^3\ dm^{-9}$

(Total for question = 1 mark)

Q7.

Ethanol may be manufactured by the hydration of ethene.

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g) \qquad \Delta H^{\ominus} = -45.3\ kJ\ mol^{-1}$$

(a) In a laboratory investigation of this reaction, 1.00 mol of ethene was mixed with 1.00 mol of steam at 150 °C. At equilibrium, when the total pressure of the system was 50.0 atm, 0.450 mol of ethanol had formed.

(i) Give the expression for the equilibrium constant, K_p, for the reaction.

(1)

(ii) Calculate the equilibrium constant, K_p, for the hydration of ethene at 150 °C.

Include units with your answer.

(5)

(b) The manufacture of ethanol is carried out at 230 °C and 70 atm; the overall conversion into ethanol is 95 %.

Comment on these conditions in relation to their effect on the equilibrium and the overall yield of ethanol.

(3)

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(Total for question = 9 marks)

Q8.

Answer the questions with a cross in the boxes you think are correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

The water gas reaction is used in the manufacture of hydrogen.

$$C(s) + H_2O(g) \leftrightarrow CO(g) + H_2(g) \qquad \Delta H^{\ominus} = +131.2 \text{ kJ mol}^{-1}$$

(a) What is the equilibrium constant, K_c, for this reaction?

(1)

☒ **A** $K_c = [CO][H_2]$

☒ **B** $K_c = \dfrac{[CO][H_2]}{[C]}$

☒ **C** $K_c = \dfrac{[CO][H_2]}{[H_2O]}$

☒ **D** $K_c = \dfrac{[CO][H_2]}{[H_2O][C]}$

(b) What happens to the equilibrium constants of the forward and reverse reactions when the temperature is **increased**?

(1)

	K_c of forward reaction	K_c of reverse reaction
☒ **A**	increases	increases
☒ **B**	increases	decreases
☒ **C**	decreases	increases
☒ **D**	decreases	decreases

(Total for question = 2 marks)

Q9.

Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

The equation for the equilibrium decomposition of hydrogen iodide into hydrogen and iodine can be written in two ways.

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ Equilibrium constant = K_c

or

$HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$ Equilibrium constant = K_c'

What is the expression linking the two equilibrium constants?

☒ **A** $K_c = (K_c')^2$

☒ **B** $K_c = K_c'$

☒ **C** $K_c = 2(K_c')$

☒ **D** $K_c = \sqrt{K_c'}$

(Total for question = 1 mark)

Q10.

Esters are used in flavourings and perfumes.
They can be made by reactions involving alcohols.

(a) A flask containing a mixture of 0.200 mol of ethanoic acid and 0.150 mol of ethanol was left at 25 °C, in the presence of a catalyst, until equilibrium had been established.

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

The ethanoic acid present in the equilibrium mixture required 34.8 cm^3 of a 2.50 mol dm^{-3} solution of sodium hydroxide for complete neutralisation.

(i) Calculate the value of the equilibrium constant, K_c, for this reaction at 25 °C.

(4)

(ii) The enthalpy change for this reaction is small.

Explain, by reference to the type and number of bonds being broken and made, how this might have been predicted.

(2)

.....

.....

.....

.....

.....

(b) An ester which smells of raspberries can be formed by either of two different reactions.

Reaction **1**

$$HCOOH + (CH_3)_2CHCH_2OH \overset{\text{catalyst}}{\rightleftharpoons} HCOOCH_2CH(CH_3)_2 + H_2O$$

Reaction **2**

$$HCOCl + (CH_3)_2CHCH_2OH \rightarrow HCOOCH_2CH(CH_3)_2 + HCl$$

(i) **Name** the carboxylic acid, alcohol and catalyst used in Reaction **1**.

(2)

HCOOH ..... catalyst .....

$(CH_3)_2CHCH_2OH$ .....

(ii) Explain **one** advantage and **one** disadvantage of using Reaction **2** rather than Reaction **1**.

(4)

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(Total for question = 12 marks)

Q11.

This question is about halides.

(a) Silicon tetrachloride, $SiCl_4$, is used in the manufacture of optical fibres. It can be made by the reaction of silicon carbide, SiC, with hydrogen chloride using a catalyst of nickel(II) chloride.

$SiC(s) + 4HCl(g) \rightarrow SiCl_4(l) + CH_4(g)$ $\Delta H = -631.3\,kJ\,mol^{-1}$

The standard molar entropies $S^{\ominus}$, of the substances are shown in the table.

Substance	SiC(s)	HCl(g)	$SiCl_4(l)$	$CH_4(g)$
$S^{\ominus}/JK^{-1}\,mol^{-1}$	+16.5	+186.8	+239.7	+186.2

(i) Calculate the total entropy change, ΔS_{total}, for this reaction, at 298 K, using the information given.

Include a sign and units in your answer which should be given to an appropriate number of significant figures.

(5)

(ii) In industry, the reaction is carried out at 700 °C.

By considering entropy and other relevant factors, justify the use of this temperature.

(3)

.....

.....

.....

.....

.....

.....

.....

.....

(iii) Use your answer from (a)(i) to calculate the equilibrium constant for the reaction at 298 K.

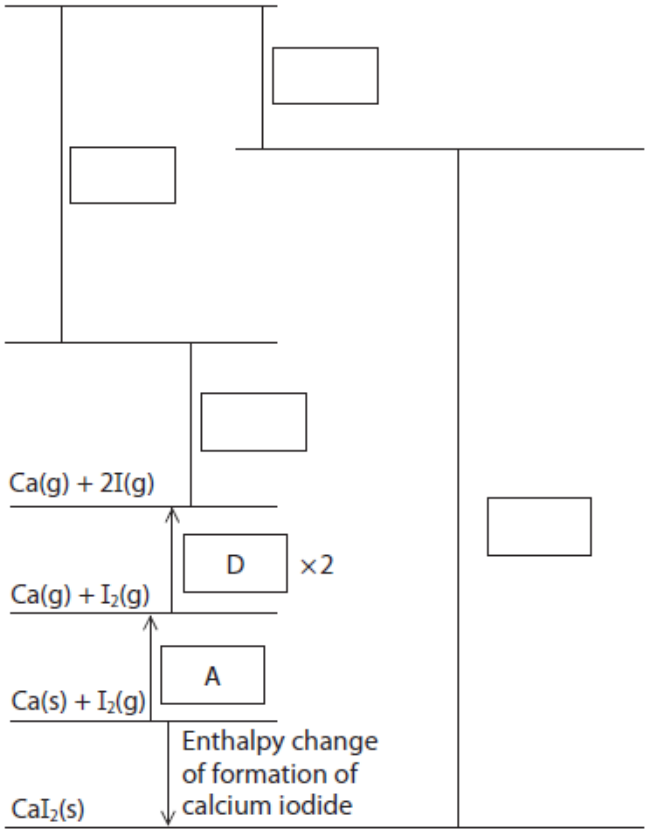
(2)

(b) The following data can be used in a Born-Haber cycle for calcium iodide, CaI_2.

Letter	Energy change	Value / kJ mol^{-1}
A	Enthalpy change of atomisation of calcium	+178.2
B	First ionisation energy of calcium	+590
C	Second ionisation energy of calcium	+1145
D	Enthalpy change of atomisation of iodine ($\frac{1}{2}I_2(s) \rightarrow I(g)$)	+106.8
E	Electron affinity of iodine	−295.4
F	Lattice energy of calcium iodide	−2074

(i) Complete the Born-Haber cycle by adding letters in the boxes for the energy changes, relevant species on the blank lines and arrowheads to show the direction of each energy change.

(3)



(ii) Use the data to calculate the value for the enthalpy change of formation of calcium iodide.

(2)

(iii) The value for the lattice energy of calcium iodide determined experimentally by using the Born-Haber cycle differs significantly from the theoretical calculated value.

Explain why the Born-Haber and the theoretical values for the lattice energies are similar for calcium fluoride but significantly different for calcium iodide.

(4)

.....

.....

.....

.....

.....

.....

.....

.....

(c) The electron affinity of iodine is –295.4 kJ mol^{-1}.

Explain how the electron affinity of chlorine differs from that of iodine.

(3)

.....

.....

.....

.....

.....

.....

.....

.....

(Total for question = 22 marks)

Mark Scheme

Q1.

Question Number	Answer	Additional Guidance	Mark
(a)(i)	$K_p = \frac{p_2NH_3}{pN_2\ p^3H_2}$	Allow round or no brackets Allow upper case Allow pp/PP Allow $p(NH_3)_2$ $p\,NH_{32}$ etc Ignore units even if incorrect Do not award square brackets	(1)

Question Number	Answer	Additional Guidance	Mark
(a)(ii)	• mole fraction of N_2 (1) • mole fraction of H_2 (1) • both partial pressures (1)	Example of completed table Substance / Mole fraction / Partial pressure/atm N_2 / 0.18 / 36 H_2 / 0.54 / 108 NH_3 / 0.28 / 56 TE for M3 on calculated mole fractions multiplied by 200	(3)

Question Number	Answer	Additional Guidance	Mark
(a)(iii)	An answer that makes reference to the following points: • correct use of K_p expression (1) • correct answer **and** 1 or 2 SF (1) • correct units (1)	Example of calculation $56^2 \div (108^3 \times 36)$ 7 or 6.9×10^{-5} / 0.00007 or 0.000069 Allow 3SF 6.92×10^{-5} /0.0000692 Do not award 7.0×10^{-5} / 0.000070 atm^{-2} Allow TE from (a)(i) and (a)(ii) If mole fractions are used for the calculation max score 1 for the correct answer **and** 1-3 SF Correct answer with or without working scores 3	(3)

Question Number	Answer	Additional Guidance	Mark
(a)(iv)	An answer that makes reference to the following points: • the (forward) reaction is/ must be exothermic **(1)** • (more ammonia shows that) the equilibrium has moved/shifted to the right **OR** (more ammonia shows that) a new K_p is established which is larger **(1)**	Allow reverse argument Allow favours forward reaction/shifts to the product side Allow K_p increases/eqm constant increases Ignore just 'more ammonia produced' or 'yield increases'	**(2)**

Question Number	Answer	Additional Guidance	Mark
(b)(i)	• $NH_4^+(aq) + Cl^-(aq)$	Do not award $NH_4^+Cl^-(aq)$ Do not award $NH_4Cl(aq)$ Do not award any other state symbols	**(1)**

Question Number	Answer	Additional Guidance	Mark
(b)(ii)	• $\Delta_{sol}H = \Delta_{hyd}H$ – Lattice Energy or $\Delta_{sol}H = -$ Lattice Energy + $\Delta_{hyd}H$	Allow LE for Lattice Energy Allow $\Delta_{sol}H = -$ Lattice Energy + hydration enthalpies Allow $\Delta_{sol}H = -$ Lattice Energy + hydration enthalpies Allow ΔH_{hyd} etc Ignore standard signs	**(1)**

Question Number	Answer	Additional Guidance	Mark
(b)(iii)	• enthalpy change of hydration of ammonium chloride **(1)** • enthalpy change of solution **(1)**	Example of calculation $-307 + (-378) = -685$ (kJ mol^{-1}) Allow (kJ mol$^-$) $705 + (-685) = (+)20$ (kJ mol^{-1}) Allow TE on arithmetical errors Do not award use of incorrect expression Correct answer with or without working scores 2 Units are not required but if wrong penalise only once.	**(2)**

STEMUP.CO.UK

Question Number	Answer	Additional Guidance	Mark
(b)(iv)	An explanation that makes reference to three of the following points • M1 the bromide (ion) is larger than the chloride (ion) **(1)** And any 2 of the following • M2 hydration enthalpy of the bromide ion less exothermic/less negative (than the chloride) **(1)** • M3 lattice energy of ammonium bromide would be less exothermic/less negative (than ammonium chloride) **(1)** • M4 the enthalpy of solutions depends on the values of both hydration and lattice energies (so the enthalpies of solution should be similar) **(1)**	Allow bromine ion larger than the chlorine ion Do not award larger atomic radius Allow smaller/lower Allow hydration enthalpy of bromine would be less exothermic/less negative (than the chlorine) Allow hydration enthalpy of ammonium bromide would be less exothermic/less negative (than ammonium chloride) Allow smaller/lower Accept because we don't know the magnitude of the reduction in hydration and lattice energies it is not possible to assess the overall effect Allow reverse arguments for MP1, MP2 and MP3 Ignore any reference to reactivity, polarisation and charge density	(3)

Question Number	Answer	Additional Guidance	Mark
(c)	• $NH_4^+ + H_2O \longrightarrow NH_3 + H_3O^+$	Accept $NH_4^+ \longrightarrow NH_3 + H^+$ Allow eqm sign Ignore $NH_4Cl \longrightarrow NH_4^+ + Cl^-$ Ignore $NH_4Cl + aq \longrightarrow NH_4^+ + Cl^-$ Ignore state symbols even if incorrect Do not award $NH_4Cl + aq \longrightarrow NH_3 + HCl$ Do not award $NH_4Cl \longrightarrow NH_3 + HCl$ Do not award $NH_4Cl \longrightarrow NH_3 + H^+ + Cl^-$ Do not award $NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$	(1)

Q2.

Question Number	Answer	Additional guidance	Mark
(a)(i)	• Gives expression for $\Delta S^{\ominus}_{system}$ **(1)** • Calculation of value of $\Delta S^{\ominus}_{system}$ **(1)**	Example of calculation $\Delta S^{\ominus}_{system}$ = (2 x 192.3) – 191.6 – (3 x 130.6) = **–198.8** / **–199** (J K^{-1} mol^{-1}) Ignore SF except 1 SF but award –200 (2 SF) Award –0.198.8 / –0.199 / –0.20 kJ K^{-1} mol^{-1} but units **must** be given Allow kJ mol^{-1} K^{-1} Do not award incorrect units Correct answer with no working scores (2) A positive version of the acceptable answer scores (1) –0.2 kJ K^{-1} mol^{-1} scores (1) Allow TE on an incorrect expression which contains either (2 x 192.3) or (3 x 130.6)	**(2)**

Question Number	Answer	Additional guidance	Mark
(a)(ii)	An explanation that makes reference to the following points: (Yes because….) • Disorder / number of ways of distributing energy quanta decreases **(1)** • As number of molecules / moles / particles (of gas) decreases **(1)**	Allow just "entropy decreases" Do not award just '$\Delta S^{\ominus}_{system}$ is negative' Allow 4 moles gives 2 moles / 4 molecules gives 2 molecules Do not award 2 molecules gives 1 molecule Allow TE on positive result in (a)(i), but must state **answer is unexpected**. Ignore no changes of states If (a)(i) is positive and no statement about expectation is made max (1) Positive answer expected scores (0)	**(2)**

Question Number	Answer	Additional guidance	Mark
(a)(iii)	• Use of $\Delta S_{surroundings} = -\Delta H/T$ **(1)** • Calculates $\Delta S_{surroundings}$ **(1)**	Example of calculation: $\Delta S_{surroundings}$ = -(-110.2 x 1000) ÷ 700 = (+) 157.4 / 157 (J K^{-1} mol^{-1}) OR = (+) 0.1574 / 0.157 kJ K^{-1} mol^{-1} Allow TE on incorrect equation with recognisable error, e.g. transfer error of value for ΔH or use of incorrect temperature. Do not award incorrect units Ignore SF except 1 SF Correct answer with no working scores (2) Correct value with negative sign scores (1)	**(2)**

Question Number	Answer	Additional guidance	Mark
(a)(iv)	• Finds ΔS_{system}	Example of calculation ($\Delta S_{system} = \Delta S_{total} - \Delta S_{surroundings}$) = (-78.7 - 157.4)) = -236.1 / -236 (J K^{-1} mol^{-1}) OR = -0.2361 / -0.236 (kJ K^{-1} mol^{-1}) Allow -235.7 if $\Delta S_{surroundings}$ = 157 J K^{-1} mol^{-1} -238.7 if $\Delta S_{surroundings}$ = 160 J K^{-1} mol^{-1} TE from (a)(iii) Ignore SF except 1 SF	**(1)**

Question Number	Answer	Additional guidance	Mark
(a)(v)	This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning. Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning. The following table shows how the marks should be awarded for indicative content. Number of indicative marking points seen in answer / Number of marks awarded for indicative marking points 6 / 4 5–4 / 3 3–2 / 2 1 / 1 0 / 0 The following table shows how the marks should be awarded for structure and lines of reasoning. Number of marks awarded for structure of answer and sustained line of reasoning Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout. / 2 Answer is partially structured with some linkages and lines of reasoning. / 1 Answer has no linkages between points and is unstructured. / 0 **Indicative content** • Rate of reaction is higher / faster • More ammonia produced in a given time • At higher temperature ΔS_{surr} is less positive / decreases / smaller • ΔS_{total} more negative / less positive • K_p decreases • equilibrium position moves further left / in the endothermic direction / in reverse direction / gives lower yield of ammonia / makes reaction less feasible	Guidance on how the mark scheme should be applied: The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning). If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages). In general it would be expected that 5 or 6 indicative points would get 2 reasoning marks, and 3 or 4 indicative points would get 1 mark for reasoning, and 0, 1 or 2 indicative points would score zero marks for reasoning. If there is any incorrect Chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded, do not deduct mark(s). Ignore comments about ΔS_{system} ALLOW reaches equilibrium faster Higher energy cost as an alternative but not just higher cost without justification. ALLOW $-\Delta H/T$ for ΔS_{surr} Ignore decreases / smaller ALLOW K_c or K	(6)

Question Number	Answer	Additional guidance	Mark
(b)(i)	• Correct expression for K_p	$K_p = \frac{pp(NH_3)^2}{pp(N_2)\ pp(H_2)^3}$ Other formats are acceptable but must have a p or pp. Accept capital P Do not award use of square brackets, e.g. $[N_2]$	(1)

Question Number	Answer	Additional guidance	Mark
(b)(ii)	• Calculates partial pressure of ammonia (1) • Calculates value of K_p (1) • States units (1)	Example of calculation $ppNH_3 = (255 - 25 - 150) = 80$ (atm) $K_p = ((80)^2 / (25)(150)^3) = (7.5851852 \times 10^{-5})$ $= 7.5852 \times 10^{-5}$ Ignore SF except 1 SF TE on incorrect $ppNH_3$ and on equation in (i) atm^{-2} TE for units on incorrect equation in (i)	(3)

Question Number	Answer	Additional guidance	Mark
(b)(iii)	An explanation that makes reference to the following points: • (K_p) remains the same (1) • Fraction / quotient / Q / Q_p / apparent value of K_p decreases in value (when pressure increases) (1) • so equilibrium shifts to right hand side (to return K_p to its original value / to keep K_p constant) (1)	Allow partial pressures of denominator / N_2 and H_2 increases more than the numerator / NH_3 Ignore use of Le Chatelier's Principle Must be linked to Q_p returning to the value of K_p not as a result of Le Chatelier's Principle Allow produces more ammonia (so K_p is constant / returns to original value)	(3)

Q3.

Question Number	Answer	Mark
	The only correct answer is **D** (W, X, Y and Z but there is more Y and Z than W and X) *A is incorrect as this requires in a very large value for K_c* *B is incorrect as this will result in a very small value for K_c, < 1* *C is incorrect as this will result in a small value for K_c < 1*	1

Q4.

Question Number	Answer	Mark
(a)	The only correct answer is **C** (flasks 1 and 4 only) *A is incorrect as flask 4 also contains only substances from the right-hand side of the equilibrium (HCl(aq) includes some water)* *B is incorrect as flask 1 also contains only substances from the right-hand side of the equilibrium* *D is incorrect as flasks 2 and 3 do not contain any ester*	1

Question Number	Answer	Mark
(b)	The only correct answer is **A** (the equilibrium reaction is slow) *B is incorrect as rapid hydrolysis would affect the position of the equilibrium* *C is incorrect as the acid is neutralized* *D is incorrect as although a buffer may form it does not affect the position of the ester equilibrium*	1

Q5.

Question Number	Correct Answer	Mark
(a)	**The only correct answer is A** (the mole fraction of carbon dioxide) ***B*** *is incorrect because the equilibrium will move to the left hand side so this will decrease* ***C*** *is not correct because the rate of both reactions will decrease at lower temperature* ***D*** *is incorrect because the equilibrium will move to the left hand side so this will decrease*	(1)

Question Number	Correct Answer	Mark
(b)	**The only correct answer is C** (0.474) ***A*** *is incorrect because this answer divides the mole fraction of carbon dioxide by 2* ***B*** *is incorrect because this answer divides the mole fraction of carbon monoxide by 2* ***D*** *is incorrect because this is the partial pressure of carbon monoxide*	(1)

Q6.

Question Number	Correct Answer	Mark
	The only correct answer is A ($dm^9\ mol^{-3}$) ***B*** *is incorrect because the units of concentration should be raised to the power of -3 not -2* ***C*** *is incorrect because the units should be the reciprocal of concentration raised to the power of -3 not -2* ***D*** *is incorrect because the units should be the reciprocal of concentration raised to the power of -3 not -2*	(1)

Q7.

Question number	Answer	Additional guidance	Mark
(a)(i)	• $K_p = \frac{p(C_2H_5OH)}{p(C_2H_4) \times p(H_2O)}$	Allow p_x etc; upper case P / pp Do not award square brackets Do not award omission of 'p' Ignore correct state symbols Ignore omission of times sign	1

Question number	Answer	Additional guidance	Mark
(a)(ii)	• calculation of moles at equilibrium (1) • calculation of mole fractions at equilibrium (1) • calculation of partial pressures at equilibrium (1) • substitution of values into equation (1) • calculation of K_p **and** units of atm^{-1} (1)	Example of calculation $K_p = \frac{14.516}{17.742^2}$ $= 0.046116 / 4.6116 \times 10^{-2}\ atm^{-1}$ TE on expression in (a)(i) and at each stage Ignore SF except 1 SF Correct answer with some working scores (5)	5

	C_2H_4	H_2O	C_2H_5OH
Initial mol	1.00	1.00	0
Equil^m mol	0.55	0.55	0.45
Mole Fraction	$\frac{0.55}{1.55} = 0.3548$	$\frac{0.55}{1.55}$	$\frac{0.45}{1.55} = 0.2903$
Partial Pressure	$\frac{50 \times 0.55}{1.55}$	$\frac{50 \times 0.55}{1.55}$	$\frac{50 \times 0.45}{1.55}$
Partial Pressure values	17.742	17.742	14.516

Question number	Answer	Additional guidance	Mark
(b)	An answer that makes reference to the following • high pressure favours the formation of ethanol **and** because 2 mol (gas) form 1 mol (1) • high temperature lowers the formation of ethanol **and** because the (forward) reaction is exothermic (1) • high temperature is needed because otherwise the rate of reaction is too slow **Or** unconverted reactants can be recycled to increase the overall yield (1)	Allow reverse arguments Accept increases yield (of ethanol) Allow reaction shifts to the right Allow fewer moles on RHS Do not award change in pressure changes K_p Accept decreases yield (of ethanol) Allow reaction shifts to the left Accepts because the back reaction is endothermic M1 & M2 both first statements without explanation scores 1 out of 2 Ignore just 'increasing / high temperature increases rate'	3

Q8.

Question number	Answer	Mark
(a)	**The only correct answer is C** $\left(K_c = \frac{[CO][H_2]}{[H_2O]} \right)$ *A is incorrect because the concentration of steam has been omitted* *B is incorrect because the concentration of steam has been omitted and carbon is not in the gas phase* *D is incorrect because carbon is not in the gas phase*	(1)

Question number	Answer	Mark
(b)	**The only correct answer is B** (increases, decreases) *A is incorrect because the reverse reaction is exothermic so K_c decreases* *C is incorrect because the forward reaction is endothermic so K_c increases and the reverse reaction is exothermic so K_c decreases* *D is incorrect because the forward reaction is endothermic so K_c increases*	(1)

Q9.

Question Number	Answer	Mark
	The only correct answer is A ($K_c = (K_c')^2$) *B is incorrect because this is not true as K_c' must be squared* *C is incorrect because this is not true as K_c' must be squared not multiplied by 2* *D is incorrect because this is not true as K_c' must be squared not square rooted*	(1)

Q10.

Question Number	Answer	Additional Guidance	Mark
(a)(i)	• calculates moles of acid present in the mixture **(1)** • calculates moles of ester and water present in the mixture **(1)** • calculates moles of ethanol present in the mixture **(1)** • expression for K_c and final answer	Example calculation mol of acid = mol of NaOH = $\frac{34.8}{1000}$ x 2.50 = 0.087 (mol) mol of ester = mol of water = 0.2 – 0.087 = 0.113(mol) mol of ethanol = 0.150 – 0.113 = 0.037 If the expression for Kc is incorrect, e.g. no water, allow TE on M1-3 for example not calculating moles of water as well as ester $K_c = \frac{0.113/V \times 0.113/V}{0.087/V \times 0.037/V}$ = 3.9668 / 4.0 (no units) OR $K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$ = 3.9668 / 4.0 **and** statement that volumes cancel Do not penalise lack of square brackets in equilibrium expression Assumption that 0.087 is moles of acid used gives moles ethanol = 0.063 moles ester = water = 0.087 Kc = 1.0632 scores max (3) Calculation of acid moles at equilibrium larger than acid moles at the start can score M4 only If no other mark is scored Award (1) for calculation of 0.087(mol) however it is used, Ignore SF	**(4)**

Question Number	Answer	Additional Guidance	Mark
(a)(ii)	An answer that makes reference to the following points: • same type of / similar bonds being broken and made **(1)** • same number of each type of bond being broken and made **(1)**	Allow O-H and C-O bonds being broken and made Allow the same bond being broken and made Allow C-OH Ignore C-O-H and COH Ignore CO without the bond shown Award 2 marks for a complete list of the bonds being broken and made e.g. Bonds broken and made are 1 x C-O and 1 x O-H scores 2 Allow ester link as C-O If no other mark is scored award 1 mark for 1 O-H bond is broken and made Or 1 C-O bond is broken and made If no other mark is scored allow the energy required to break the bonds is similar to the energy released making the bonds for (1)	**(2)**

Question Number	Answer	Additional Guidance	Mark
(b)(i)	• methanoic acid • (concentrated) sulfuric acid • 2-methylpropan-1-ol	All three correct scores (2) Any two correct scores (1) Allow hydrochloric acid / H_2SO_4 / HCl Ignore H^+ Ignore (aq) after formulae Ignore hydrogen chloride in words Allow methylpropan-1-ol Allow 2-methyl-1-propanol Allow methyl-1-propanol Do not award 2-methylpropanol	**(2)**

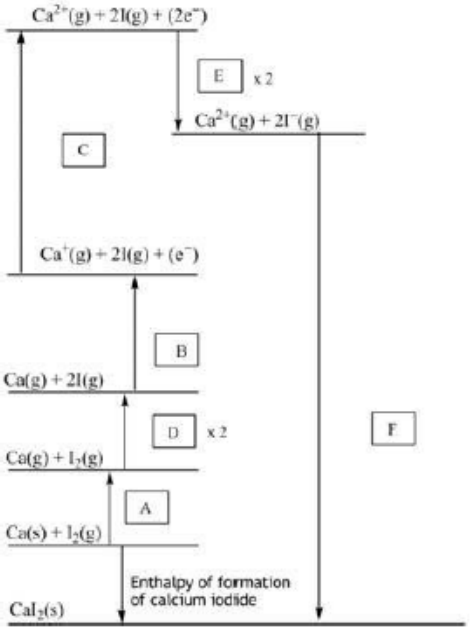
Question Number	Answer	Additional Guidance	Mark
(b)(ii)	Any one advantage: • no heat required / works at room temperature **(1)** • so reduces energy cost **(1)** or • no catalyst required **(1)** • reducing product purification costs / making purification easier / no need to recover catalyst **(1)** or • reaction is not an equilibrium / reaction goes to completion **(1)** • so produces a higher yield **(1)** Any one disadvantage: • hydrogen chloride produced is acidic / corrosive **(1)** • corrosion resistant plant/equipment required (which is more expensive) **(1)** or • HCl is toxic **(1)** • use a fume cupboard / clean exhaust gases / capture the gas (for sale)	• Accept the reaction is (much) faster • so no energy required Ignore just lower cost Ignore more product Allow reactants are not wasted Ignore reference to atom economy	**(4)**

Q11.

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)(i)	**M1** Expression for ΔS_{system} (1) **M2** Value for ΔS_{system} (1) **M3** Expression for $\Delta S_{surroundings}$ (1) **M4** Value for $\Delta S_{surroundings}$ (1) **M5** Value for ΔS_{total} to 2 or 3 SF and units (1)	Example of calculation: (186.2 + 239.7) – (16.5 + (4 x 186.8)) —337.8 (J K^{-1} mol^{-1}) $\Delta S_{surroundings} = -\frac{\Delta H}{T} = -(-631.3 \times 10^3) / 298$ = (+) 2118.5 (J K^{-1} mol^{-1}) / (+)2.1185 (kJ K^{-1} mol^{-1}) (= 2118.5 + (– 337.8) = (+)1780.7 = (+)1780 / (+)1800 J K^{-1} mol^{-1} (+)1.78 / (+)1.80 kJ K^{-1} mol^{-1} Allow TE at each stage Correct answer with no working scores 5 (+)2340 J K^{-1} mol^{-1} scores 4 (1 x 186.8) (+) 2460 J K^{-1} mol^{-1} scores 3 (react-prod)	5

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)(ii)	An answer that makes reference to: • A higher temperature would result in a less positive / lower $\Delta S_{surroundings}$ (ΔS_{system} is relatively unaffected by temperature) (1) • So ΔS_{total} is less positive / lower, which makes reaction less feasible /reduces yield (1) COMMENT: For M1 and M2 allow correct calculation of ΔS_{total} (at 973K) >0 to show that the reaction is feasible. • but high temperature is used to increase rate (1)	Ignore references to Le Chatelier for M1 and M2. Allow A higher temperature would result in a an insignificant change in $\Delta S_{surroundings}$ as its value is so large (ΔS_{system} is relatively unaffected by temperature) So ΔS_{total} is unchanged (in sign), which means feasibility of reaction is unchanged Ignore less easily / readily Standalone mark	3

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)(iii)	Recall of expression for K (1) Rearrangement of expression and calculation of ln K and value for K (1) **Allow TE from (a)(i) but no TE if incorrect expression given in M1.**	Example of calculation: $\Delta S_{total} = R \ln K$ ln $K = \Delta S_{total} / R$ = 1780.7 / 8.31 = 214.1998 1.15440 x 10^{93} Allow any answer between 1.06 x 10^{93} and 1.18 x 10^{94} Ignore any units; Ignore SF Correct answer with no working scores 2	2

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(i)	Arrows upwards for first and second ionisation energies for calcium and correct labels, B and C in boxes (1) Downward arrows for electron affinity and lattice enthalpy and correct labels E x 2 and F in boxes (1) Correct species including state symbols on horizontal lines (1)  	Only penalise lack of arrow once in M1 and M2. If electrons are included, they must be correct but allow e for e^-	3

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(ii)	Correct expression (1) Evaluation (1)	Example of calculation: [(178.2 + 590 + 1145+ (106.8 x 2) – (295.4 x 2)] – 2074 = —538 (kJ mol^{-1}) If E x 2 penalised in b(i), allow use of 1 x 295.4 as TE. In this case only -242.6(kJ mol^{-1}) scores 2 However, if E x 2 not penalised in b(i) then penalise failure to multiply by 2 once only in b(ii) -349.4(kJ mol^{-1}) scores 1 (misses both x 2) -242.6(kJ mol^{-1}) scores 1 (misses 2 x 295.4) -644.8 (kJ mol^{-1}) scores 1 (misses 2 x 106.8) +538 (kJ mol^{-1}) scores 1 (expression wrong way round) ignore SF except 1 SF	2

Question Number	Acceptable Answers	Additional Guidance	Marks
(b)(iii)	Bonding in calcium fluoride is (virtually) 100% ionic (1) Whereas bonding in calcium iodide has a degree of covalency / somecovalent character (1) Then any **2** from these 3 marking points The calcium **ion** is polarizing (1) The fluoride (ion) is small so not easily polarised / electron cloud not soeasily distorted (1) the iodide (ion) is larger and so is easily polarised / electron cloud iseasily distorted (1)	 Allow Iodide / I^- has some covalent character Penalise the use of fluorine and iodine once only	4

Question Number	Acceptable Answers	Additional Guidance	Mark
(c)	**M1** More exothermic / more negative / greater in magnitude (1) **M2** As (the atomic radius of) chlorine is smaller / less shielding between nucleus and electron (to be gained) / chlorine has fewer shells (of electrons) (1) **M3** Stronger attraction (between nucleus and electron to be gained) (1)	Ignore larger / less / higher Allow 'more energy released' Do not award chloride for chlorine Allow chlorine is more electronegative than iodine Allow reverse argumentfor M2 and M3	3

Q1.

Answer the question with a cross in the box you think is correct ☒ . If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒ .

The total entropy change, ΔS_{total} , of a reaction at 298 K is -85.0 J K^{-1} mol^{-1}.

What is the value of the equilibrium constant for this reaction at 298 K?

[R = 8.31 J mol^{-1} K^{-1}]

☒ **A** 3.61×10^{-5}

☒ **B** 9.07×10^{-1}

☒ **C** 9.66×10^{-1}

☒ **D** 2.77×10^{4}

(Total for question = 1 mark)

Q2.

Calcium oxide is manufactured by heating limestone at 1000 °C for 30 minutes.

The equation for the reaction is:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \qquad \Delta_r H = +178\,kJ\,mol^{-1}$$

(a) The numerical value of the equilibrium constant for this reaction is increased by:

(1)

☒ **A** allowing the carbon dioxide to escape

☒ **B** increasing the heating time

☒ **C** increasing the temperature

☒ **D** reducing the pressure

(b) Which is the correct expression for the equilibrium constant, K_c, for this reaction?

(1)

☒ **A** $K_c = [CO_2]$

☒ **B** $K_c = \frac{1}{[CO_2]}$

☒ **C** $K_c = \frac{[CaCO_3]}{[CaO][CO_2]}$

☒ **D** $K_c = \frac{[CaO][CO_2]}{[CaCO_3]}$

(Total for question = 2 marks)

Q3.

For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

At 25 °C, the pH of pure water is 7.00 and at 100 °C, the pH of pure water is 6.14. What can be deduced from this information?

	Enthalpy change of dissociation of water	Concentration of hydrogen ions
☒ **A**	endothermic	higher at 100 °C than at 25 °C
☒ **B**	endothermic	lower at 100 °C than at 25 °C
☒ **C**	exothermic	higher at 100 °C than at 25 °C
☒ **D**	exothermic	lower at 100 °C than at 25 °C

(Total for question = 1 mark)

Q4.

Iodine was dissolved in an organic solvent, trichloromethane, and the resulting solution added to an equal volume of deionised water. The mixture was then shaken, producing two immiscible solutions: iodine in water and iodine in trichloromethane.

At equilibrium, the equation for the reaction can be written as:

$$I_2(\text{trichloromethane}) \rightleftharpoons I_2(aq)$$

(a) What is the expression for this equilibrium constant, K_c?

(1)

☒ **A** $K_c = \dfrac{[I_2(\text{trichloromethane})]}{[I_2(aq)]}$

☒ **B** $K_c = \dfrac{(I_2(aq))}{(I_2(\text{trichloromethane}))}$

☒ **C** $K_c = \dfrac{I_2(aq)}{I_2(\text{trichloromethane})}$

☒ **D** $K_c = \dfrac{[I_2(aq)]}{[I_2(\text{trichloromethane})]}$

(b) Which statement describes what is happening at equilibrium?

(1)

☒ **A** iodine molecules move from the water to the trichloromethane layer only

☒ **B** iodine molecules move from the trichloromethane to the water layer only

☒ **C** iodine molecules move from the water to the trichloromethane and from the trichloromethane to the water layer.

☒ **D** there is no movement of individual iodine molecules

(Total for question = 2 marks)

Q5.

The reversible reaction between hydrogen chloride and oxygen produces water **vapour** and chlorine.

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g) \qquad \Delta H = -114 \text{ kJ mol}^{-1}$$

(a) Explain what effect, if any, each of the following changes has on the yield of chlorine at equilibrium **and** on the equilibrium constant, K_p .

(i) An increase in the total pressure

(3)

.....

.....

.....

.....

.....

.....

.....

(ii) An increase in the temperature

(2)

.....

.....

.....

.....

.....

(iii) The use of a catalyst

(2)

.....

.....

.....

.....

.....

(b) 0.850 mol of hydrogen chloride was mixed with 0.600 mol of oxygen and allowed to reach equilibrium in a closed flask.
At equilibrium the total pressure was 1.50 atm and there was 0.250 mol of chlorine in the flask.

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$$

(i) Complete the table.

(3)

Substance	Initial amount / mol	Equilibrium amount / mol	Mole fraction at equilibrium
HCl	0.850		
O_2	0.600		
H_2O	0		
Cl_2	0	0.250	0.189
Total moles at equilibrium =			

(ii) Write the expression for the equilibrium constant, K_p .

(1)

(iii) Use your answers to (b)(i) and (b)(ii) to calculate the value for K_p. Give your answer to an appropriate number of significant figures, and include units.

(3)

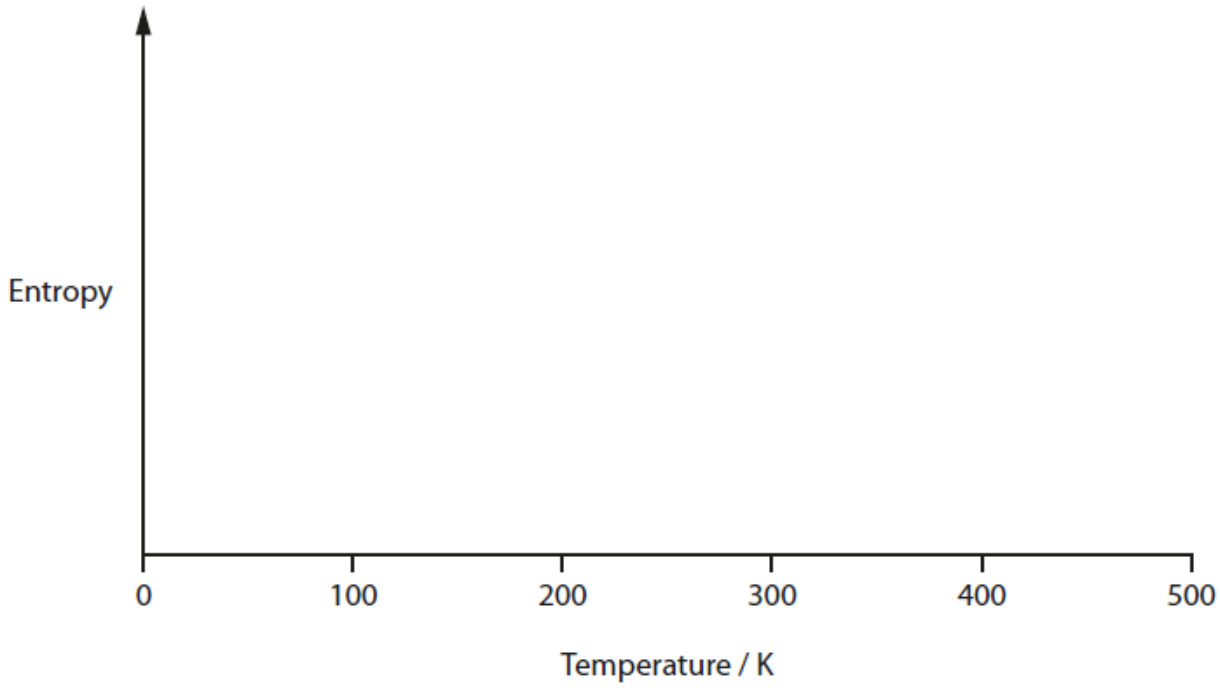
(iv) Use your answer to (b)(iii) to calculate a value for the total entropy change of the reaction, ΔS_{total}.

(2)

(c) Draw a sketch of entropy against temperature for water to illustrate the entropy changes as temperature increases, including when water changes state.

A scale is not required for the vertical axis

(3)



(Total for question = 19 marks)

Q6.

This question is about sulfuric acid and its salts.

(a) The manufacture of sulfuric acid involves the equilibrium

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta_r H = -197 \text{ kJ mol}^{-1}$$

(i) A catalyst of vanadium(V) oxide is used in this reaction.

State the effect, if any, of the catalyst on the value of the equilibrium constant, K_p .

(1)

.....

.....

(ii) The temperature used for this reaction in industry is 700 K.

Explain, in terms of the equilibrium constant and the equilibrium position, the effect of an increase in temperature on the equilibrium yield of sulfur trioxide.

(2)

.....

.....

.....

.....

.....

.....

(iii) Write the expression for the equilibrium constant, K_p , for this equilibrium. State symbols are not required.

(1)

(iv) A mixture of 2.00 mol of sulfur dioxide and 1.00 mol of oxygen is allowed to reach equilibrium at 5.00 atm pressure.
1.60 mol of sulfur trioxide is formed.

Calculate the value of K_p.
Include units and give your answer to an appropriate number of significant figures.

(4)

(b) Sulfur trioxide is used to produce sulfuric acid.

(i) Commercial concentrated sulfuric acid contains 98.5 % H_2SO_4 and 1.5 % water by mass.
The density of concentrated sulfuric acid is 1800 g dm^{-3}.

Calculate the concentration of this sulfuric acid in mol dm^{-3}.

(2)

(ii) The pH of a 0.10 mol dm^{-3} solution of sulfuric acid at 25 °C is 0.97.

Calculate the concentration of hydrogen ions, in mol dm^{-3}, in this solution.

(1)

(iii) In an aqueous solution of sulfuric acid, the following equilibria exist.

$H_2SO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4^-(aq)$ $\quad K_a$ very large

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$ $\quad K_a = 0.012\ mol\ dm^{-3}$

Explain, in terms of these equilibria, why the concentration of hydrogen ions in a 0.10 mol dm^{-3} solution of sulfuric acid is **not** 0.20 mol dm^{-3}. No calculation is required.

(2)

.....

.....

.....

.....

.....

.....

(c) A buffer solution is made from HSO_4^- and SO_4^{2-} ions.

(i) Write two ionic equations involving HSO_4^- and SO_4^{2-} ions to show how this solution acts as a buffer.
State symbols are not required.

(2)

(ii) A buffer solution is formed by mixing

25.0 cm^3 of a solution that is 0.150 mol dm^{-3} with respect to SO_4^{2-} ions with
75.0 cm^3 of a solution that is 0.100 mol dm^{-3} with respect to HSO_4^- ions.

Calculate the pH of this buffer solution.

[K_a for HSO_4^- ions = 0.012 mol dm^{-3}]

(5)

(Total for question = 20 marks)

Q7.

The equation for the formation of ammonia in the Haber Process is shown

$$\tfrac{1}{2}N_2(g) + 1\tfrac{1}{2}H_2(g) \rightleftharpoons NH_3(g)$$

(a) At 298 K the standard entropy change of the system, $\Delta S^{\ominus}_{system} = -98\,J\,K^{-1}\,mol^{-1}$.

Calculate the standard entropy of one mole of ammonia.

Use the value of $\Delta S^{\ominus}_{system}$ and the data in the table.

Substance	Standard molar entropy, $S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$
N_2	192
H_2	131

(2)

(b) The value of the total entropy change, ΔS_{total}, varies with temperature.

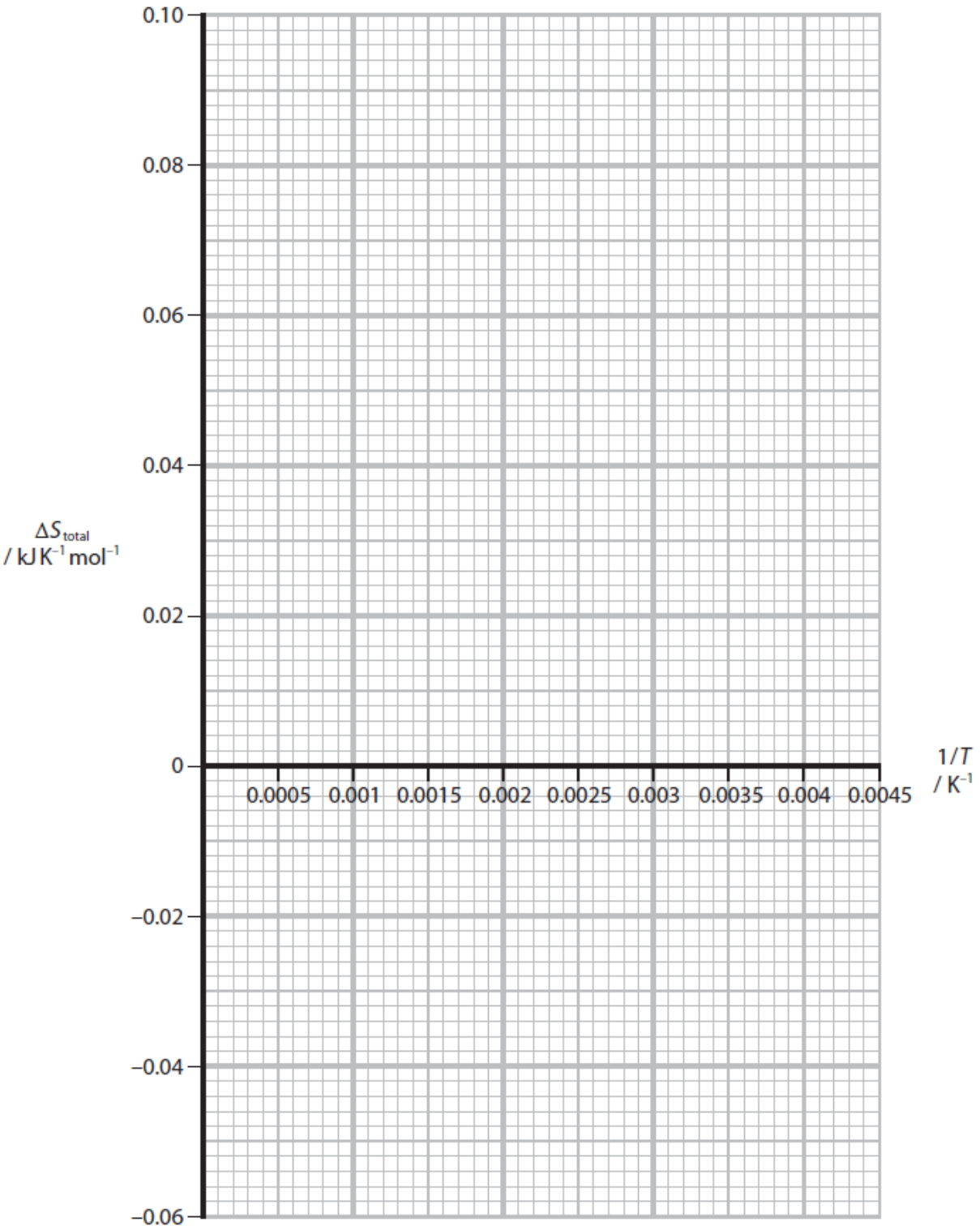
Data for the value of ΔS_{total} at different temperatures but at standard pressure of 100 kPa are given for this reaction.

Temperature / K	$1/T$ / K^{-1}	ΔS_{total} / $kJ\,K^{-1}\,mol^{-1}$
250	4.00×10^{-3}	8.27×10^{-2}
375	2.67×10^{-3}	2.25×10^{-2}
500	2.00×10^{-3}	-0.764×10^{-2}
625	1.60×10^{-3}	-2.57×10^{-2}
750	1.33×10^{-3}	-3.77×10^{-2}

Plot a graph of ΔS_{total} against $1/T$ on the grid.

Include a line of best fit.

(2)



(c) The relationship between ΔS_{total} and $1/T$ can be found by combining the two equations:

$\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$

and $\Delta S_{surroundings} = -\Delta H/T$

to give

$\Delta S_{total} = -\Delta H/T + \Delta S_{system}$

(i) Determine the gradient of the line plotted in (b), including units in your answer.

(1)

(ii) Identify the thermodynamic quantity that can be obtained from this gradient.

(1)

.....

(iii) Determine the temperature at which the reaction ceases to be thermodynamically feasible at a pressure of 100 kPa.

(1)

.....

(d) The industrial synthesis of ammonia

$$\tfrac{1}{2}N_2(g) + 1\tfrac{1}{2}H_2(g) \rightleftharpoons NH_3(g)$$

is carried out at pressures of about 20 000 kPa and temperatures between 700K and 750K. These temperatures are higher than the answer to (c)(iii).

(i) State the relationship between the total entropy, ΔS_{total}, and the equilibrium constant, K.

(1)

.....

(ii) Calculate the value of the equilibrium constant K at 750K.

[ΔS_{total} at 750K = –37.7 J K^{-1} mol^{-1}]

(2)

(iii) Explain why ΔS_{total} decreases with an increase in temperature.

(3)

.....

.....

.....

.....

.....

.....

.....

.....

.....

(iv) State how the Haber Process is made economically feasible at 750 K even though the total entropy change is negative.

(1)

.....

.....

.....

(e) Ammonia from the Haber Process reacts with acids.

With phosphoric acid, H_3PO_4, a number of products are formed in solution.
One of these is the fertiliser diammonium hydrogenphosphate.

(i) Write an equation for the production of this fertiliser.

State symbols are not required.

(2)

(ii) Write an **ionic** equation to show that ammonium ions are acidic in aqueous solution.

State symbols are not required.

(1)

(iii) A solution containing both ammonia and ammonium ions acts as a buffer.

Explain, using a relevant ionic equation, the effect of adding a small amount of acid to this buffer.

(3)

.....

.....

.....

.....

.....

.....

.....

.....

.....

(Total for question = 20 marks)

Q8.

This question is about the thermodynamics of the reaction:

$$N_2O_4(g) \rightarrow 2NO_2(g) \qquad \Delta H = +57.2\,kJ\,mol^{-1}.$$

Compound	Standard molar entropy at 298 K, $S^{\ominus}$ / J K^{-1} mol^{-1}	Standard molar enthalpy of formation at 298 K, $\Delta_f H^{\ominus}$ / kJ mol^{-1}	Colour
NO_2	+240.0	+33.2	brown
N_2O_4	+304.2		colourless

(a) Calculate the entropy change for the reaction, using the information in the table.

Include a sign and units in your answer.

(2)

(b) Calculate the enthalpy change of formation, $\Delta_f H$, of N_2O_4 (g) at 298 K, using the information in the table and the enthalpy change of the reaction.

Include a sign and units in your answer.

(2)

(c) Calculate the entropy change of the surroundings, $\Delta S_{surroundings}$, at 298 K.

Give your answer to an appropriate number of significant figures.
Include a sign and units in your answer.

(3)

(d) (i) Use your answers to parts (a) and (c) to calculate the total entropy change, ΔS_{total}, for this reaction at 298 K.

(1)

(ii) This reaction can also be written as an equilibrium:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Calculate the temperature at which ΔS_{total} is zero for this equilibrium.

(2)

(e) (i) Write the expression for the equilibrium constant, K_p, for this reaction, including the units, if any.

(2)

(ii) In an experiment, 10 mol of N_2O_4(g) was placed in a closed container at 50 °C. At equilibrium, 27% of the N_2O_4(g) had dissociated, and the pressure in the container was 4.0 atm.

Calculate the value of K_p at 50 °C.

(4)

(iii) The total pressure is doubled to 8.0 atm.

State the effect on K_p.

(1)

.....

.....

(iv) The total pressure is doubled to 8.0 atm at constant temperature.

Explain the change in the percentage dissociation of $N_2O_4(g)$ by considering the effect on the partial pressures of $NO_2(g)$ and $N_2O_4(g)$.

(3)

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(Total for question = 20 marks)

Mark Scheme

Q1.

Question Number	Answer	Mark
	The only correct answer is A (3.61×10^{-5}) ***B** is not correct because R and ΔS_{total} are the wrong way up* ***C** is not correct because the temperature should not be included* ***D** is not correct because the negative sign for ΔS_{total} has been omitted*	(1)

Q2.

Question number	Answer	Mark
(a)	C increase the temperature	1

Question number	Answer	Mark
(b)	A $[CO_2]$	1

Q3.

Question Number	Correct Answer	Mark
	The only correct answer is A (the dissociation of water is endothermic, so the concentration of hydrogen ions is higher at 100°C than it is at 25°C) ***B** is incorrect because at higher temperatures more hydrogen ions are present* ***C** is incorrect because the dissociation of water is endothermic* ***D** is incorrect because the dissociation of water is endothermic*	(1)

Q4.

Question number	Answer	Mark
(a)	$K_c = \frac{[I_2(aq)]}{[I_2(\text{trichloromethane})]}$ D	1

Question number	Answer	Mark
(b)	C iodine molecules move from the water to the trichloromethane and from the trichloromethane to the water layer	1

Q5.

Q	Acceptable Answers	Additional Guidance	Mark
(a)(i)	When the pressure is increased • equilibrium moves to RHS and yield (of chlorine) increases **(1)** • as fewer gas molecules on the RHS (5:4) **(1)** • K_p remains constant **(1)**	Marking points are independent Allow 'backward reaction favoured so yield (of chlorine) increases' If numbers are given they must be correct Allow 'change in pressure has no effect on value for K_p'	3

Q	Acceptable Answers	Additional Guidance	Mark
(a)(ii)	When the temperature increases • equilibrium moves to LHS as (forward) reaction is exothermic **(1)** • K_p decreases and so yield (of chlorine) decreases **(1)**	Marking points are independent Allow reaction moves in endothermic direction	2

Q	Acceptable Answers	Additional Guidance	Mark
(a)(iii)	When a catalyst is used • rate of backward and forward reactions increases by same amount **(1)** • so K_p **and** yield (of chlorine) is unchanged **(1)**		2

Q	Acceptable Answers	Additional Guidance	Mark
(b)(i)			3

Substance	Initial amount / mol	Equilibrium amount / mol	Mole fraction at equilibrium
HCl	0.850	**0.350**	**0.26415**
O_2	0.600	**0.475**	**0.35849**
H_2O	0	**0.250**	**0.18868**
Cl_2	0	0.250	0.189
Total moles at equilibrium = **1.325**			

All values correct scores (3)

M1 1 correct equilibrium amount **(1)**

M2 other 2 correct equilibrium amounts **(1)**

M3 Consequential total moles and mol fraction **(1)**

For mole fractions allow
e.g. 0.350 ○1.325

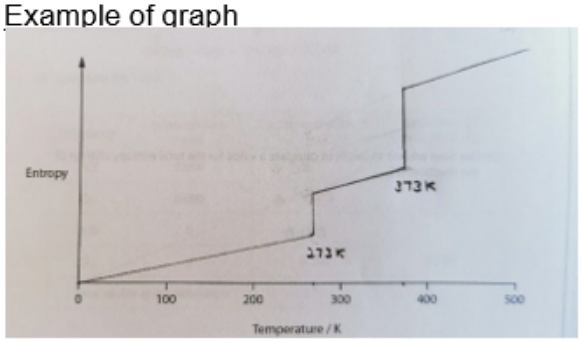
allow correct rounding

Ignore SF except 1 SF

Q	Acceptable Answers	Additional Guidance	Mark
(b)(ii)	$K_p = p(H_2O)^2\, p(Cl_2)^2 \circ p(HCl)^4\, p(O_2)$	Ignore parentheses Do not award square brackets	1

Q	Acceptable Answers	Additional Guidance	Mark
(b)(iii)	• mole fractions converted to partial pressure **(1)** • final value for K_p given to 2 or 3SF **(1)** • correct units given **(1)**	Example of calculation allow TE from 20b(i) **substance** / **pp** HCl / 0.39623 O_2 / 0.53774 H_2O / 0.28302 Cl_2 / 0.28302 Allow e.g. for pp(HCl) ; 0.26415 x 1.5 $\frac{(0.28302)^2(0.28302)^2}{(0.39623)^4(0.53770)}$ = 0.48407 (Note = 0.48408 if no rounding) = 0.48 / 0.484 No TE for M2 for incorrect expression Check final answer if close, and allow if correct rounding used in working atm^{-1} allow TE for M3 from incorrect expression in (b)(ii)	3

Q	Acceptable Answers	Additional Guidance	Mark
(b)(iv)	• recall of expression for ΔS_{total} **(1)** • calculation of ΔS_{total} **(1)**	$\Delta S_{total} = R \ln K$ = 8.31 x – 0.726 = – 6.033 ($J\ K^{-1}\ mol^{-1}$) Allow TE / rounded value from (iii) No TE for M2 from incorrect expression Ignore SF except 1 SF Ignore units even if incorrect NOTE ΔS_{total} = – 6.0289 if no rounding from (b)(iii) ΔS_{total} = – 6.0993 if 0.48 used from b(iii)	2

Q	Acceptable Answers	Additional guidance	Mark
(c)	• general shape of increase from left to right **(1)** **ALLOW** straight line • two vertical stages for melting and boiling **(1)** • include the use of 273K for melting and 373K for boiling temperature either by labelling or position on x axis **(1)**	Allow horizontal sections allowed between phase changes for M1 M3 is independent of M2, providing a line is drawn Example of graph  	3
			(Total for Question = 19 marks)

Q6.

Question Number	Answer	Additional Guidance	Mark
(a)(i)	• no effect / none / nothing / no change	Ignore references to rate	(1)

Question Number	Answer	Additional Guidance	Mark
(a)(ii)	An explanation that makes reference to the following points: • (equilibrium) yield (of sulfur trioxide / SO_3 / product) decreases • the equilibrium constant / K_p / K_c / K decreases (as temperature increases) (1) **and** because the (forward / right) reaction is exothermic / releases heat (energy) / ΔH is negative (1)	Allow less sulfur trioxide / SO_3 / product forms Ignore equilibrium position shifts to the left Ignore more reactants formed Allow the equilibrium constant / K_p / K_c / K decreases (as temperature increases) **and** because the reverse / backward / left reaction is endothermic / absorbs heat (energy) Allow K decreases because $\Delta S_{surroundings}$ / ΔS_{total} decreases / becomes less positive (as temperature increases and assuming ΔS_{system} is constant) Ignore reference to rate	(2)

STEMUP.CO.UK

Question Number	Answer	Additional Guidance	Mark
(a)(iii)	• expression for K_p	Example of expression for K_p: $K_p = \frac{p(SO_3(g))^2}{p(SO_2(g))^2 \text{ (x) } p(O_2(g))}$ Allow *P* / *PP* / *pp* etc for partial pressure and this can be inside the brackets Allow e.g. p^2SO_3 Ignore missing (g) / brackets around formulae Do not award square brackets	(1)

Question Number	Answer	Additional Guidance	Mark
(a)(iv)	• calculation of eqm moles (1) • calculation or expressions for 3 partial pressures (1) • substitution of values into K_p expression (1) • calculation of K_p **and** answer to 2 / 3 SF **and** units (1)	Example of calculation: |	SO_2	O_2	SO_3
Initial mol	2.00	1.00	-
Eqm mol	2.00 – 1.60 = 0.40	1.00 – 0.80 = 0.20	1.60
Total mol at eqm	0.40 + 0.20 + 1.60 = 2.20		
Partial pressure /atm	$\frac{0.40 \times 5.00}{2.20}$ = 0.90909	$\frac{0.20 \times 5.00}{2.20}$ = 0.45455	$\frac{1.60 \times 5.00}{2.20}$ = 3.6364	 TE for partial pressures on eqm moles $K_p = \frac{3.6364^2}{0.90909^2 \times 0.45455}$ $= 35.2 / 35 \text{ atm}^{-1}$ TE on expression for K_p in (a)(iii) Allow answer from previous correct rounding to 2 or more SF e.g. 0.91 0.45 and 3.6 gives 34.8 Penalise incorrect rounding once only e.g. 0.909 to 0.9 Allow fractions in working but not in final answer Allow atm^- for units but do not allow any other units Allow correct units written in (a)(iii) if not written here Correct answer to 2 or 3 SF with units and no working scores (4)	(4)

Question Number	Answer	Additional Guidance	Mark
(b)(i)	• calculation of mass of H_2SO_4 in 1 dm^3 (1) • calculation of concentration of acid (1)	Example of calculation: mass of H_2SO_4 in 1 dm^3 concentrated acid = 0.985 x 1800 = 1773 (g) concentration of acid = $\frac{1773}{(2 \times 1.0) + 32.1 + (4 \times 16.0)}$ = 18.073 / 18.07 / 18.1 / 18 (mol dm^{-3}) TE on mass of H_2SO_4 in 1 dm^3 Allow 98 for molar mass of H_2SO_4 giving 18.092 / 18.09 / 18.1 / 18 (mol dm^{-3}) Correct answer to 3 or more SF with no working scores (2) Do not award (2) for 18 unless 0.985 has been used in calculation	(2)

Question Number	Answer	Additional Guidance	Mark
(b)(ii)	• calculation of $[H^+(aq)]$ / $[H_3O^+(aq)]$	Example of calculation: $[H^+(aq)] / [H_3O^+(aq)] = 10^{-0.97}$ = 0.10715 / 0.1072 / 0.107 / 0.11 (mol dm^{-3}) Ignore SF except 1 SF Ignore incorrect units Correct answer with no working scores (1) Do not award 0.1 / 0.10 / 0.214	(1)

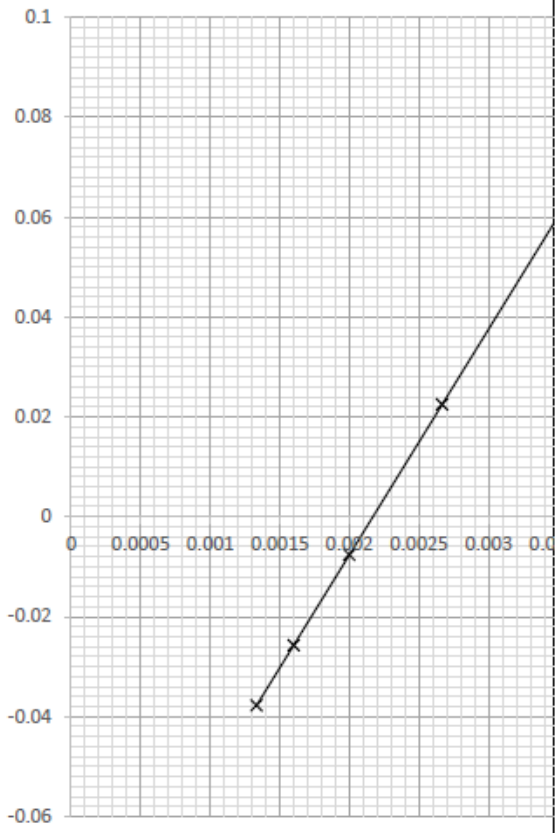
Question Number	Answer	Additional Guidance	Mark
(b)(iii)	An explanation that makes reference to the following points: **First equilibrium** • the first ionisation of sulfuric acid is complete **or** the equilibrium position of the first equation lies very far to the right (1) **Second equilibrium** • so $[H_3O^+(aq)]$ (from the second equilibrium) is very small (1)	Allow $[H^+(aq)]$ for $[H_3O^+(aq)]$ Ignore missing state symbols Allow high $[H_3O^+(aq)]$ from first equilibrium Allow acid fully dissociates in first equilibrium Ignore just acid fully dissociates Allow second equilibrium shifts to the left Allow second dissociation is suppressed / further dissociation is prevented	(2)

Question Number	Answer	Additional Guidance	Mark
(c)(i)	• $HSO_4^- + OH^- \rightarrow SO_4^{2-} + H_2O$ (1) • $SO_4^{2-} + H^+ \rightarrow HSO_4^-$ or $SO_4^{2-} + H_3O^+ \rightarrow HSO_4^- + H_2O$ (1)	Allow equations in either order Allow ⇌ provided equations written in directions shown Ignore state symbols even if incorrect Penalise non-ionic equations once only e.g. using HCl and NaOH Allow $HSO_4^- \rightarrow SO_4^{2-} + H^+$ and $H^+ + OH^- \rightarrow H_2O$ for M1	(2)

Question Number	Answer	Additional Guidance	Mark
(c)(ii)	• calculation of the concentration of SO_4^{2-} ions (1) • calculation of the concentration of HSO_4^- ions (1) • expression for K_a (1) • re-arrangement of expression and calculation of $[H^+]$ (1) • calculation of pH (1)	Example of calculation: $[SO_4^{2-}] = \frac{25.0 \times 0.150}{1000} \times \frac{1000}{100}$ $= 0.0375$ (mol dm^{-3}) Allow mol $SO_4^{2-} = 0.00375 / 3.75 \times 10^{-3}$ (mol) $[HSO_4^-] = \frac{75.0 \times 0.100}{1000} \times \frac{1000}{100}$ $= 0.075$ (mol dm^{-3}) Allow mol $HSO_4^- = 0.0075 / 7.5 \times 10^{-3}$ (mol) Do not award this mark if subtraction then done $K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} / 0.012 = \frac{[H^+] \times 0.0375}{0.075}$ Allow mol substituted into correct expression $[H^+] = \frac{K_a[HSO_4^-]}{[SO_4^{2-}]} = \frac{0.012 \times 0.075}{0.0375}$ $= 0.024$ (mol dm^{-3}) TE on expression, $[SO_4^{2-}]$ and $[HSO_4^-]$ or mol $pH = -\log[H^+] = -\log 0.024$ $=1.6198 / 1.620 / 1.62 / 1.6$ TE on $[H^+]$ Ignore SF except 1 SF Correct answer without working scores (5) Allow alternative methods	(5)

Q7.

Question Number	Answer	Additional Guidance	Mark
(a)	• states or uses equation **(1)** • calculate $S^{\ominus}_{products}$ **(1)**	$\Delta S^{\ominus}_{system} = S^{\ominus}_{products} - S^{\ominus}_{reactants}$ $-98.0 = S^{\ominus}_{products} - ((0.5 \times 192) + (1.5 \times 131))$ $S^{\ominus}_{products} = 292.5 - 98$ $S^{\ominus}_{products}$ = (+)194.5 / 195 ($J\ K^{-1}\ mol^{-1}$) If units are given they must be correct Allow TE on incorrect $S^{\ominus}_{reactants}$ Comment Correct answer with no working scores (2) $S^{\ominus}_{products}$ = 63.5 scores max (1) $S^{\ominus}_{products}$ = 225 scores max (1)	**(2)**

Question Number	Answer	Additional Guidance	Mark
(b)	• 5 points plotted on the graph to within one square **(1)** • straight line of best fit passing through all points **(1)**		**(2)**

Question Number	Answer	Additional Guidance	Mark
(c)(i)	An answer that makes reference to the following points: • uses the line or points from the data to calculate the gradient **and** units	Example of calculation Gradient = $\frac{8.27 \times 10^{-2} - -0.76 \times 10^{-2}}{4.00 \times 10^{-3} - 2.00 \times 10^{-3}}$ = 45.15 kJ mol^{-1} Allow an answer between 42.0 – 48.0 Ignore SF except 1 SF	**(1)**

Question Number	Answer	Additional Guidance	Mark
(c)(ii)	An answer that makes reference to the following points: • enthalpy change of reaction / $\Delta_r H$ (of the Haber process)	 Allow $-\Delta_r H$ Allow enthalpy change / ΔH / $-\Delta H$	**(1)**

Question Number	Answer	Additional Guidance	Mark
(c)(iii)	An answer that makes reference to the following points: • value of T found either by reading from the graph the value of T when $\Delta S_{total} = 0$ or by calculation	 460 (K) Allow an answer between 440 - 480 $= \frac{\text{answer to (c)(i)}}{98}$ $= \frac{45150}{98} = 460.71$ / 460 (K) Or $= \frac{-\text{answer to (b)}}{-98}$ $= \frac{-45150}{-98} = 460.71$ / 460 (K) ALLOW TE on graph or on answer to (c)(i)	**(1)**

Question Number	Answer	Additional Guidance	Mark
(d)(i)	• total entropy, $\Delta S = R\ln K$ or $\ln K = \Delta S / R$ or $K = e^{\frac{\Delta S}{R}}$		**(1)**

Question Number	Answer	Additional Guidance	Mark
(d)(ii)	• calculation of ln K **(1)** • evaluation of K **(1)**	Example of calculation $-37.7 = 8.31 \times \ln K$ $\ln K = -4.5367$ $K = 0.01071 / 1.071 \times 10^{-2}$ Final answer with no working scores (2) Allow TE on M1 to M2 No TE on incorrect expression Ignore units Ignore SF except 1 SF	**(2)**

Question Number	Answer	Additional Guidance	Mark
(d)(iii)	An answer that makes reference to the following points: Either • (ΔS_{total} decreases because) ΔS_{system} (and ΔH) do not change with temperature (significantly) **(1)** • therefore $\Delta S_{surroundings}$ must decrease (so that (ΔS_{total} decreases) **(1)** • this is because $\Delta S_{surroundings} = -\Delta H/T$ (so as T increases $-\Delta H/T$ becomes less positive because ΔH is exothermic) **(1)** Or • the reaction is exothermic **and** so increasing temperature shits the equilibrium to the left / towards the reactants **(1)** • the value of K decreases • because ΔS_{total} is proportional to K / $S_{total} = R \ln K$ the value of ΔS_{total} decreases	Allow more negative / less positive Accept the backward reaction is favoured	**(3)**

Question Number	Answer	Additional Guidance	Mark
(d)(iv)	• overall conversion to ammonia is increased by recycling unused reactants	Allow remove the ammonia from the equilibrium / as it is formed Ignore references to catalysts, temperature and pressure	**(1)**

Question Number	Answer		Additional Guidance	Mark
(e)(i)	• formula of diammonium hydrogenphosphate • balanced equation	**(1)** **(1)**	$(NH_4)_2HPO_4$ $2NH_3 + H_3PO_4 \rightarrow (NH_4)_2HPO_4$ Allow multiples Allow ions for the product Allow for M2 $NH_3 + H_3PO_4 \rightarrow (NH_4)H_2PO_4$ Allow ions for the product No other TE Ignore state symbols even if incorrect	**(2)**

Question Number	Answer	Additional Guidance	Mark
(e)(ii)	• $NH_4^+ = NH_3 + H^+$ OR • $NH_4^+ + H_2O = NH_3 + H_3O^+$	Allow $\rightarrow$ instead of $\rightleftharpoons$ Do not award reactions reversed Allow $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ Allow $\rightleftharpoons$ instead of $\rightarrow$ Ignore state symbols even if incorrect	**(1)**

Question Number	Answer	Additional Guidance	Mark
(e)(iii)	An answer that makes reference to the following points: • the mixture contains a large amount/ (large) reservoir of **both** ammonium ions and ammonia / of NH_4^+ and NH_3 **(1)** **Either** • added H^+ reacts with ammonia to form ammonium ions / $H^+ + NH_3 \rightleftharpoons NH_4^+$ **Or** • added H^+ combines with OH^- ions in water to form water / $H^+ + OH^- \rightarrow H_2O$ **And** ammonia reacts with water to produce OH^- ions / $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ **(1)** • ratio of ammonium ions to ammonia hardly changes **(1)**	Do not award incorrect formulae such as NH_3^- in M1 and M2 but allow TE in M3 Ignore comments about acid / base in relation to NH_4^+ / NH_3 unless defined Allow $\rightarrow$ instead of $\rightleftharpoons$ Allow H_3O^+ Allow $\rightarrow$ instead of $\rightleftharpoons$ This marking point must include at least one ionic equation Allow remains constant Allow pH is unchanged / changes very little because added H^+ removed **and** change in concentration of NH_3 **and** NH_4^+ is small	**(3)**

Q8.

Question number	Answer	Additional guidance	Mark
(a)	• use of $\Delta S_{system} = \Delta S_{products} - \Delta S_{reactants}$ (1) • correct value with sign and units (1)	Example of calculation: $\Delta S_{system} = (2 \times 240.0) - 304.2$ $= +175.8 \text{ J K}^{-1} \text{ mol}^{-1}$ Correct answer with no working scores 2 Allow 3 SF	**2**

Question number	Answer	Additional guidance	Mark
(b)	• use of $\Delta_r H = 2 \times \Delta_f H(NO_2) - \Delta_f H(N_2O_4)$ (1) • correct value with sign and units (1)	Example of calculation: $\Delta_r H = (2 \times 33.2) - \Delta_f H(N_2O_4) = 57.2$ $\Delta_f H(N_2O_4) = +9.2$ kJ mol^{-1} Correct answer with no working scores 2	2

Question number	Answer	Additional guidance	Mark
(c)	• use of $\Delta S_{surroundings} = -\Delta H/T$ (1) • correct value (1) • answer to 3 SF with correct sign and correct units (1)	Example of calculation: $-(57.2 \times 1000/298)$ $= (-)191.(946)$ -192 J K^{-1} mol^{-1} Allow -0.192 kJ K^{-1} mol^{-1} for M2 and M3 Correct answer to 3 SF with no working scores 3	3

Question number	Answer	Additional guidance	Mark
(d)(i)	• $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ • $\Delta S_{total} = +175.8 + (-191.9) = -16(.1)$ (J mol^{-1} K^{-1})	Allow TE from 23a and 23c Allow answers in kJ mol^{-1} K^{-1}	1

Question number	Answer	Additional guidance	Mark
(d)(ii)	• correct expression (1) • correct evaluation (1)	Example of expression and calculation: $\Delta H = T\Delta S_{system}$ or $T = \Delta H/\Delta S_{system}$ or $\Delta S_{system} = \Delta H/T$ or $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = 0$ $T = 57.2 \times 1000/175.8 = 325.37$ $= 325$ K/52 °C	2

Question number	Answer	Additional guidance	Mark
(e)(i)	• correct expression for K_p (1) • units of pressure (1)	$K_p = (p_{NO_2})^2/p_{N_2O_4}$ Do not award any square brackets atm	2

Question number	Answer		Additional guidance	Mark
(e)(ii)	• moles of N_2O_4 **and** NO_2 at eqm	(1)	Example of calculation: (mol)N_2O_4 = 7.3, (mol)NO_2 = 5.4.	4
	• total number of moles **and** mole fractions calculated	(1)	Total moles = 12.7 Mole fraction N_2O_4 = 0.575 Mole fraction NO_2 = 0.425 Allow TE from M1	
	• converted to partial pressure	(1)	P N_2O_4 = 2.30 (answers to M2 × 4) NO_2 = 1.70 Allow TE from M2	
	• calculation of K_p	(1)	K_p = 1.26 (atm) Allow TE from M3 Ignore SF except 1 SF	

Question number	Answer	Additional guidance	Mark
(e)(iii)	• no effect on (the value of) K_p		1

Question number	Answer		Additional guidance	Mark
(e)(iv)	• double pressure (effect of squaring) increases numerator more than denominator	(1)		3
	• (but K_p must remain constant therefore) mole fraction of N_2O_4 must increase (relative to mole fraction of NO_2)	(1)		
	• (therefore) % dissociation of N_2O_4 decreases	(1)		