PEARSON EDEXCEL IAL CHEMISTRY · YCH11

CHEMISTRY



EXAM QUESTION PACK

UNIT 4: ENTROPY

SCORE	PERCENTAGE
/164	%

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Q1.

Which of these changes has the largest **increase** in the entropy of the system?

☒ **A** $H_2O(s) \rightarrow H_2O(l)$

☒ **B** $Hg(l) \rightarrow Hg(g)$

☒ **C** $H_2O(l) + HCl(g) \rightarrow H_3O^+(aq) + Cl^-(aq)$

☒ **D** C(graphite) → C(diamond)

(Total for question = 1 mark)

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)

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(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)

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(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)

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(Total for question = 20 marks)

Q3.

This question is about some compounds of bromine.

(a) Potassium bromate(V) decomposes to form potassium bromide and oxygen.

$$2KBrO_3(s) \rightarrow 2KBr(s) + 3O_2(g) \qquad \Delta_r H^{\ominus} = -67.2\,kJ\,mol^{-1}$$

The standard molar entropies of these substances are given in the table.

Substance	$KBrO_3(s)$	$KBr(s)$	$O_2(g)$
$S^{\ominus}/JK^{-1}mol^{-1}$	149.2	95.9	205.0

Calculate the total entropy change, ΔS_{total}, for this reaction at 298 K.

(5)

(b) Bromide ions react with bromate(V) ions in acidic solution.

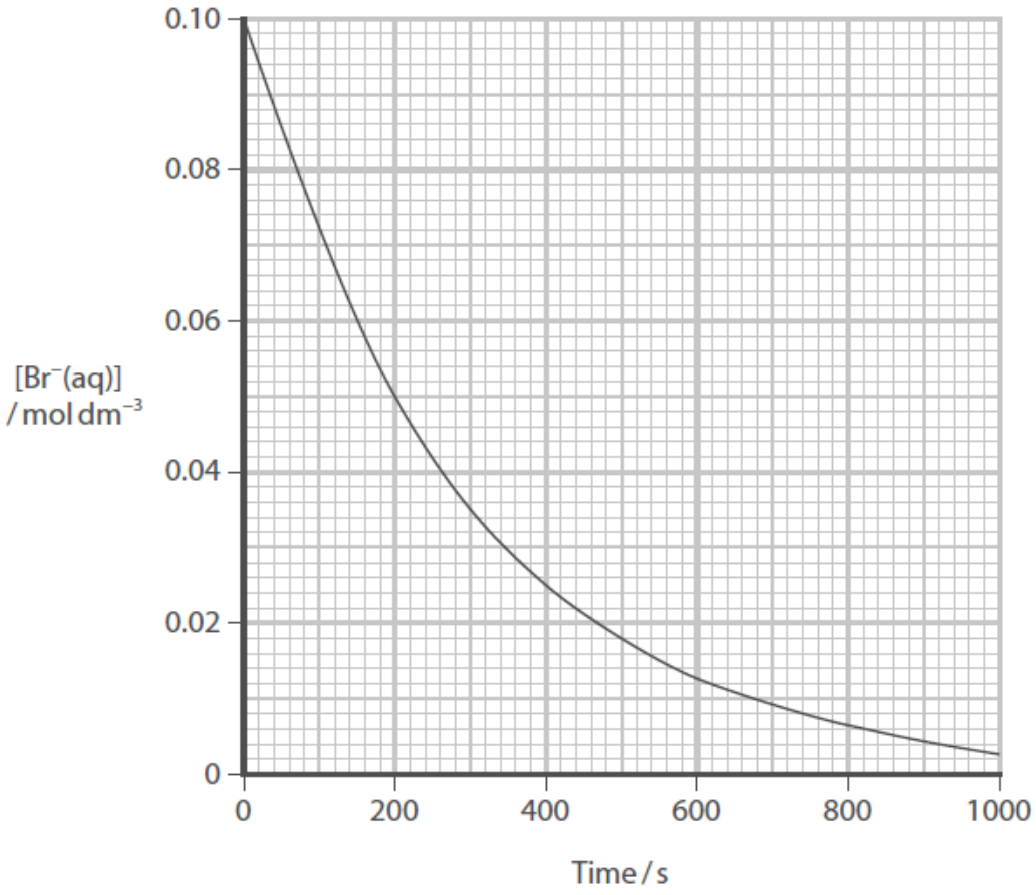
$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

Two experiments are carried out.

(i) **Experiment 1**

The concentration of Br^- ions is determined at different times.
The concentrations of BrO_3^- ions and H^+ ions are in large excess and effectively constant.

The graph of concentration of Br^- ions against time is shown.



Determine the order of the reaction with respect to bromide ions.
Show your working on the graph.

(3)

(ii) **Experiment 2**

The initial concentrations of BrO_3^- ions and H^+ ions are changed and the initial rate of reaction is determined.
The initial concentration of Br^- ions is constant and in large excess.

Run	$[BrO_3^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.1	0.1	3.6×10^{-3}
2	0.2	0.1	7.2×10^{-3}
3	0.3	0.2	4.3×10^{-2}

Determine the order of reaction with respect to BrO_3^- ions and to H^+ ions.

You must explain your working.

(3)

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(iii) Give the overall rate equation for this reaction.
Include the units for the rate constant.

(2)

(c) The rate constant for the reaction between bromoalkane and cyanide ions is determined at five different temperatures.

The results are given in the table.

Temperature (T) / K	1/Temperature ($1/T$) / K^{-1}	Rate constant (k) / s^{-1}	ln k
300	3.33×10^{-3}	3.72×10^{-5}	−10.20
310	3.23×10^{-3}	1.34×10^{-4}	−8.92
320	3.13×10^{-3}	5.48×10^{-4}	−7.51
330	3.03×10^{-3}	2.01×10^{-3}	−6.21
340	2.93×10^{-3}	7.23×10^{-3}	−4.93

Plot a graph of ln k against $1/T$ and use it to determine the activation energy, E_a .

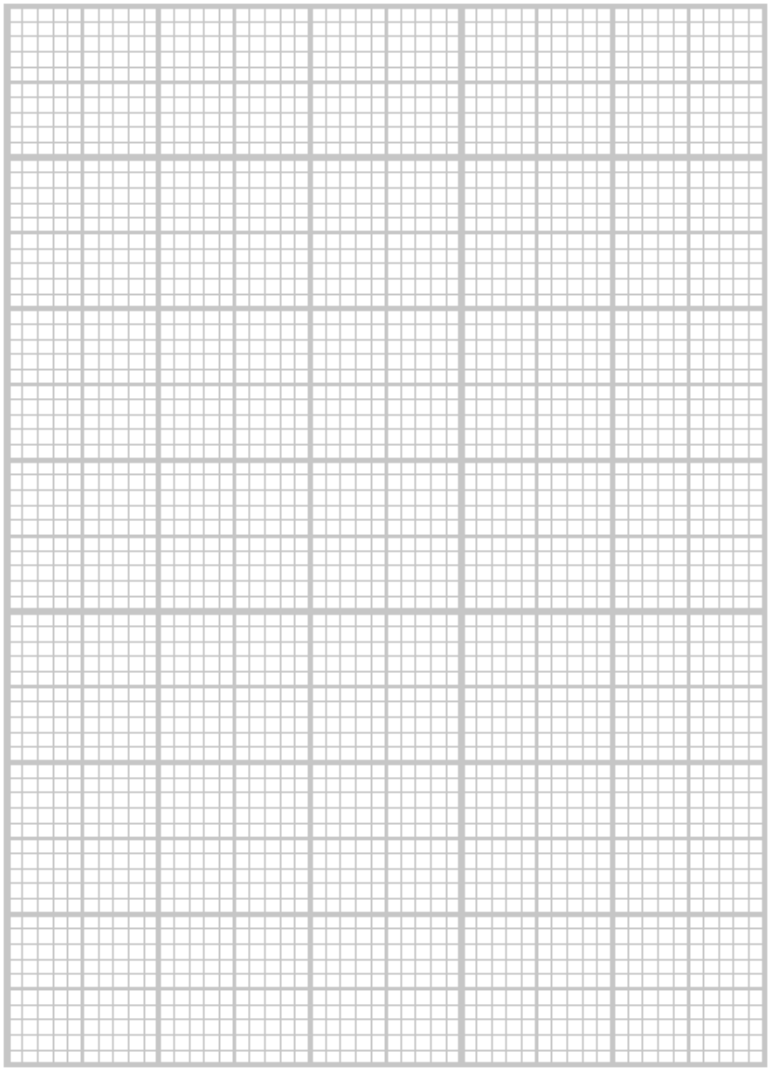
Include the sign and units of the gradient and the activation energy.

(7)

The Arrhenius equation can be expressed as

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant}$$

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



(Total for question = 20 marks)

Q4.

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 decomposition of calcium carbonate is an important reaction in the manufacture of cement.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad \Delta H^{\ominus} = +178 \text{ kJ mol}^{-1}$$

What are the signs of the entropy change of the system, ΔS_{system}, and of the entropy change of the surroundings, $\Delta S_{surroundings}$?

		Sign of ΔS_{system}	Sign of $\Delta S_{surroundings}$
☒	**A**	positive	positive
☒	**B**	positive	negative
☒	**C**	negative	positive
☒	**D**	negative	negative

(Total for question = 1 mark)

Q5.

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 entropy change of the surroundings, $\Delta S_{surroundings}$, and the entropy change of the system, ΔS_{system} , for four different reactions are given.

Reaction	$\Delta S_{surroundings}$ / J K^{-1} mol^{-1}	ΔS_{system} / J K^{-1} mol^{-1}
P	+245	+34
Q	+350	−276
R	−482	+65
S	−563	−128

Which of these is thermodynamically feasible?

☒ **A** reaction **P** only

☒ **B** reactions **P** and **Q** only

☒ **C** reaction **R** only

☒ **D** reactions **R** and **S** only

(Total for question = 1 mark)

Q6.

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 an exothermic reaction is shown.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Which of these is true?

☒ **A** ΔH is positive

☒ **B** $\Delta S_{surroundings}$ is positive

☒ **C** ΔS_{system} is negative

☒ **D** ΔS_{total} is negative

Use this space for any rough working. Anything you write in this space will gain no credit.

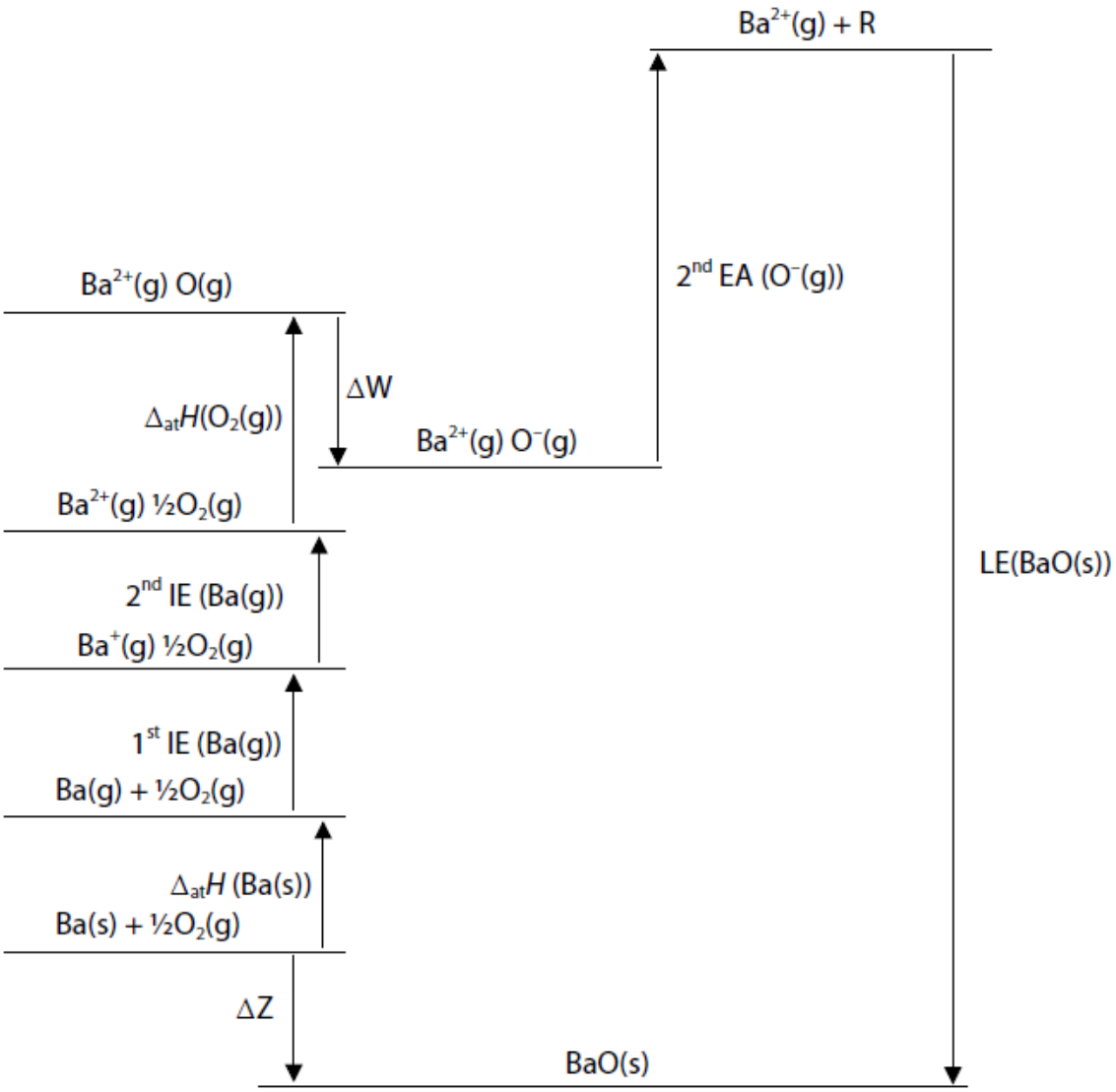
(Total for question = 1 mark)

Q7.

Barium oxide is an ionic compound that reacts with water to form barium hydroxide.

(a) A Born-Haber cycle for barium oxide, BaO, is shown.

Some of the detail is missing. The letters **R**, **W** and **Z** represent some missing information.



(i) Identify the missing detail represented by the following letters.

(2)

R .....

W .....

(ii) Use the following data to calculate a value for the quantity ΔZ shown on the Born-Haber cycle.

Include a sign and units in your answer.

(3)

Energy quantity	Enthalpy change / kJ mol^{-1}
Enthalpy change of atomisation of barium, $\Delta_{at}H$(Ba(s))	+180.0
Enthalpy change of atomisation of oxygen, $\Delta_{at}H$ (½O_2(g))	+249.2
First ionisation energy of barium, lst IE (Ba(g))	+503.0
Second ionisation energy of barium, 2nd IE (Ba(g))	+965.0
ΔW	–141.1
Second electron affinity of oxygen, 2nd EA (O^-(g))	+798.0
Lattice energy barium oxide, $\Delta_{LE}H$(BaO(s))	–3054.0

(iii) The table gives some information about the lattice energies of barium oxide and magnesium iodide and shows the % difference between the theoretical and experimental values.

	Lattice energy / kJ mol^{-1}		
	Experimental	Theoretical	% difference
BaO(s)	–3054	–3029	0.8
MgI_2(s)	–2327	–1944	16.5

Explain why there is closer agreement for barium oxide than for magnesium iodide.

(3)

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(b) The table gives some information about Group 2 ions, M^{2+}, and their hydroxides.

Formula of hydroxide	Lattice energy / kJ mol^{-1}	$\Delta_{sol}H$ / kJ mol^{-1}	Solubility / mol per 100 g	Ion	$\Delta_{hyd}HN^{2+}$ / kJ mol^{-1}
$Mg(OH)_2$	–3000	+150	2.0×10^{-5}	Mg^{2+}	–1930
$Ca(OH)_2$	–2640	+140	1.6×10^{-4}	Ca^{2+}	–1580
$Sr(OH)_2$	–2475	+105	3.3×10^{-4}	Sr^{2+}	–1450
$Ba(OH)_2$	–2230		2.4×10^{-4}	Ba^{2+}	–1360

(i) Calculate the enthalpy change of solution, $\Delta_{sol}H$, of $Ba(OH)_2$ using a fully-labelled Hess's cycle.

[The hydration enthalpy of the hydroxide ion, OH^- = –460 kJ mol^{-1}.]

(4)

(ii) Explain why strontium hydroxide is slightly soluble in water, even though the enthalpy change of solution is endothermic.

(2)

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(Total for question = 14 marks)

Q8.

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 ☒ .

Which of these gases would have the greatest standard molar entropy?

☒ **A** NH_3

☒ **B** H_2

☒ **C** N_2

☒ **D** SO_2

(Total for question = 1 mark)

Q9.

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.

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

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)

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

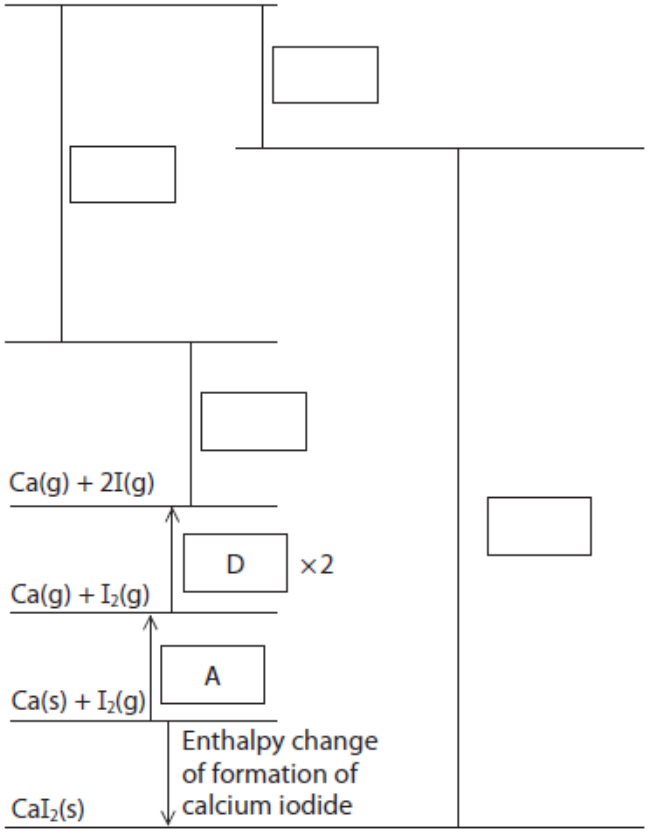
(2)

(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)

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(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)

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(Total for question = 22 marks)

Q10.

This question is about oxides of iron.

(a) The equation for the reduction of iron(III) oxide by carbon is shown.

$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$$

Some data relating to this reaction are shown.

Substance	Fe_2O_3	C	Fe	CO
$\Delta_f H^{\ominus}$ / kJ mol^{-1}	−824.2	0	0	−110.5
$S^{\ominus}$ / J K^{-1} mol^{-1}	87.4	5.7	27.3	197.6

(i) Calculate the standard enthalpy change, $\Delta_r H^{\ominus}$, for the reduction of iron(III) oxide by carbon.

(2)

(ii) Calculate the entropy change, ΔS_{system}, for this reaction.

(3)

(iii) Calculate the temperature at which this reaction becomes feasible, using your answers from (a)(i) and (a)(ii).

(3)

(b) The equation for the reduction of iron(III) oxide by carbon monoxide is shown.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta H^{\ominus} = -24.8 \text{ kJ mol}^{-1}$$

The entropy change, $\Delta S^{\ominus}_{system}$, for this reaction is +15.2 J mol^{-1} K^{-1}.

(i) Explain why the reaction should be feasible at any temperature.

(2)

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(ii) Explain how an increase in temperature would affect $\Delta S^{\ominus}_{total}$ total of this reaction. No calculation is required.

(3)

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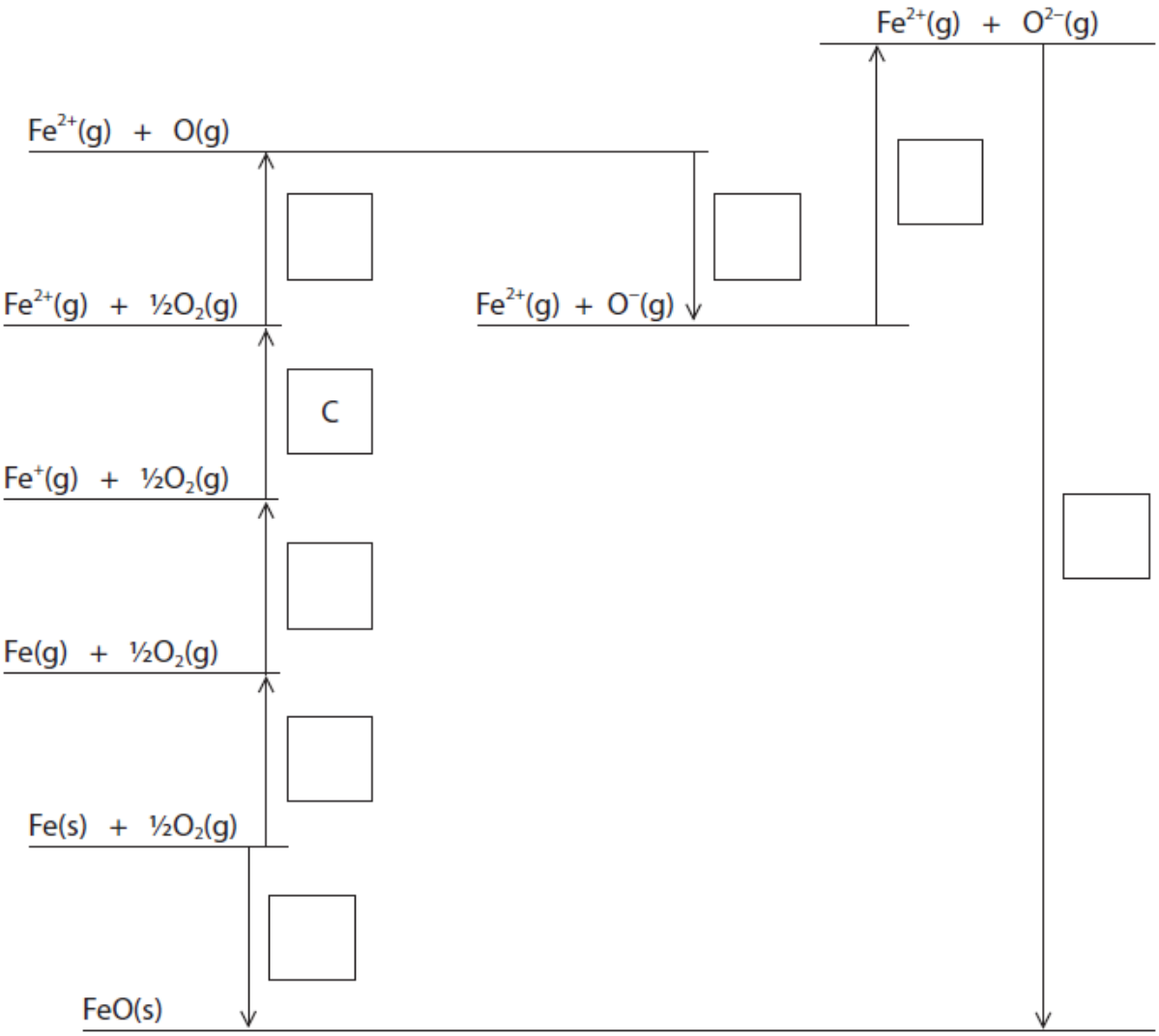
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(c) Iron also forms iron(II) oxide. The data in the table can be used to construct a Born-Haber cycle for iron(II) oxide, FeO.

Letter	Enthalpy change	Value /kJ mol^{-1}
A	Enthalpy change of atomisation of iron	+416
B	First ionisation energy of iron	+759
C	Second ionisation energy of iron	
D	Enthalpy change of formation of iron(II) oxide	−272
E	First electron affinity of oxygen	−141
F	Second electron affinity of oxygen	+798
G	Lattice energy of iron(II) oxide	−3920
H	Enthalpy change of atomisation of oxygen ($\frac{1}{2}O_2(g) \rightarrow O(g)$)	+249

(i) Complete the Born-Haber cycle by putting letters in the boxes to label the energy changes.

(3)



(ii) Calculate the value for second ionisation energy of iron, C.

(2)

(iii) Suggest why the second electron affinity of oxygen is positive.

(2)

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(Total for question = 20 marks)

Mark Scheme

Q1.

Question Number	Answer	Mark
	The only correct answer is **B** ($Hg(l) \rightarrow Hg(g)$) *A is incorrect as the increase in disorder from (s) to (l) is less than that from (l) to (g)* *C is incorrect as there is a decrease in disorder as the gaseous ion is hydrated* *D is incorrect as there is no significant change in number of particles or state.*	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: $\Delta S_{surroundings} = -(-110.2 \times 1000) \div 700$ $= (+)\ 157.4 / 157\ (J\ K^{-1}\ mol^{-1})$ 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.	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.	(6)

	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	If there is any incorrect Chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded, do not deduct mark(s).	
	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	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	

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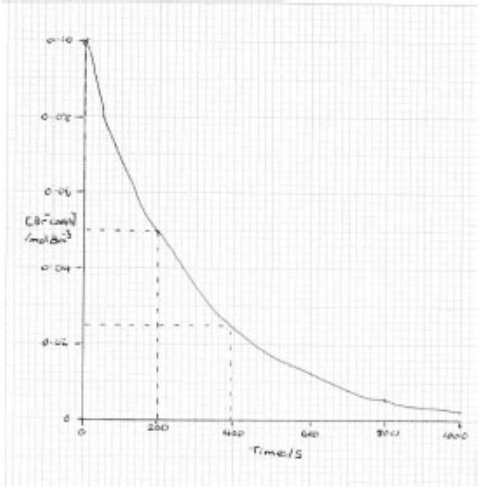
Question Number	Answer	Additional guidance	Mark
(b)(i)	• Correct expression for K_p	$K_p = \frac{pp(NH_3)^2}{pp(N_2)\ pp(H_2)^3}$ Other formats are acceptable but must have a p or pp. Accept capital P Do not award use of square brackets, e.g. $[N_2]$	(1)

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.

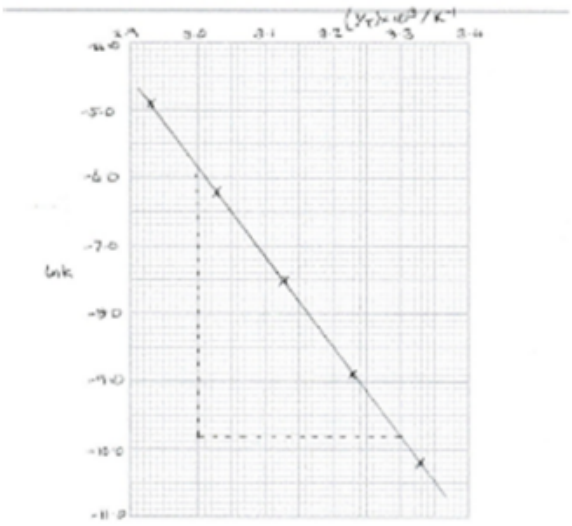
Question Number	Ans	Additional Guidance	Mark
(a)	• substitution of values into expression for ΔS_{system} (1) • calculation of ΔS_{system} (1) • substitution of values into expression for $\Delta S_{surroundings}$ (1) • calculation of $\Delta S_{surroundings}$ (1) • calculation of ΔS_{total} (1)	Example of calculation: $\Delta S_{system} = (2 \times 95.9) + (3 \times 205.0) - (2 \times 149.2)$ Allow 191.8 + 615.0 – 298.4 / 806.8 – 298.4 $\Delta S_{system} = (+)508.4$ (J K^{-1} mol^{-1}) $\Delta S_{surroundings} = -\frac{(-67.2)}{298}$ $\Delta S_{surroundings} = (+)0.2255$ (kJ K^{-1} mol^{-1}) or $(+)225.5$ (J K^{-1} mol^{-1}) $\Delta S_{total} = 508.4 + 225.5 = (+)733.9$ (J K^{-1} mol^{-1}) or $(+)0.7339$ (kJ K^{-1} mol^{-1}) TE on calculated values for ΔS_{system} and $\Delta S_{surroundings}$ Do not award ΔS_{system} added to $\Delta S_{surroundings}$ in different units e.g. 508.4 + 0.2255 = 508.6255 Ignore SF except 1 SF Units are not needed. Units in any order e.g. J mol^{-1} K^{-1} Penalise incorrect / incomplete units in ΔS_{total} but allow: e.g. J / mol/ K or J/mol.K mol^{-} and K^{-} in otherwise correct units Correct answer with no working scores (5)	(5)

Question Number	Answer	Additional Guidance	Mark
(b)(i)	• working for at least one half-life shown on graph (1) • values of two half-lives (1) • first order **and** because the half-lives are constant / the same / similar (1)	Example of half-lives:  half-lives may be written or clearly shown on graph first half-life = 200 s **and** second half-life = 200 s ± 20 s Allow 2nd half-life = 400 – 200 = 200 s Stand alone mark Do not award zero order / second order	(3)

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Question Number	Answer	Additional Guidance	Mark
(b)(ii)	An explanation that makes reference to the following points: • first order with respect to BrO_3^- ions **and** because in runs 1 and 2 as $[BrO_3^-]$ doubles (and $[H^+]$ is constant) the rate doubles (1) • in runs 1 and 3, as $[BrO_3^-]$ triples rate should triple (to 1.08×10^{-2}) and $[H^+]$ also doubles and rate increases by a factor of 4 (1) • so reaction is second order with respect to H^+ ions (1)	In M1 and M2, the working may be shown in the table Allow implied runs e.g. as $[BrO_3^-]$ doubles (and $[H^+]$ is constant), the rate doubles Allow correct alternative explanations using runs 2 and 3 and others e.g. $[BrO_3^-]$ triples, $[H^+]$ doubles and rate x 12 Do not award just $[H^+]$ doubles and rate x 4 with no mention of bromate ions Stand alone mark	(3)

Question Number	Answer	Additional Guidance	Mark
(b)(iii)	• rate equation (1) • units of k (1)	rate = $k[Br^-(aq)][BrO_3^-(aq)][H^+(aq)]^2$ TE on orders in (a)(i) and (ii) Allow species in any order / R for rate / K for k Ignore missing state symbols If no order given in (a)(i), allow rate equation with Br^- included or omitted $dm^9\ mol^{-3}\ s^{-1}$ Allow these in any order Allow $dm^9\ mol^{-3}\ s^-$ TE on rate equation	(2)

Question Number	Answer	Additional Guidance	Mark
(c)		Example of graph:  Example of gradient: $\frac{-9.8-(-5.85)}{3.3 \times 10^{-3} - 3.0 \times 10^{-3}} = -13167$ K	(7)

Question Number	Answer	Additional Guidance	Mark
(c)	• axes correct way around **and** suitable scale **(1)**	Points / line must cover at least half the grid in both directions ln *k* values must become more negative down the axis with negative signs shown Allow horizontal axis shown at bottom of graph	
	• both axes labelled **and** units for x axis **(1)**	y axis: ln k with no units on y axis **and** x axis: 0.0033 etc with (1/T) / K^{-1} **or** 3.3 etc with (1/T) / 10^{-3} K^{-1} **or** 3.3 x 10^{-3} etc with (1/T) / K^{-1} **or** 3.3 etc with (1/T) x 10^{3} / K^{-1} Brackets are not needed around 1/T	
	• all points plotted correctly **and** best-fit straight line **(1)**	Allow ± ½ square Allow line covering points provided it is straight Ignore extrapolation in either direction	
	• calculation of gradient **(1)**	This may be shown on the graph Allow gradient in the range (−)12800 to (−)13800 Allow gradient calculated from data in the table If gradient not evaluated, allow correct working	
	• sign and units of gradient **(1)**	Negative sign **and** units K Allow 1/K^{-1} for units Allow −12.8 to −13.8 kK for M4 and M5	
	• calculation of activation energy **(1)**	E_a = 13167 x 8.31 / 1000 = 109.418 Expected range 106 to 115 **or** 13167 x 8.31 = 109418 TE on gradient	
	• sign and corresponding units of activation energy **(1)**	+ 109.418 kJ mol^{-1} or +109418 J mol^{-1} Allow kJ mol^{-} or J mol^{-} Ignore missing + but do not award − sign Penalise 1 SF for gradient and E_a value once only	

Q4.

Question number	Answer	Mark
	The only correct answer is B (positive, negative) *A* *is incorrect because endothermic reactions have negative* $\Delta S_{surroundings}$ *C* *is incorrect because when there are more gas molecules in the products than the reactants* ΔS_{system} *is positive and endothermic reactions have negative* $\Delta S_{surroundings}$ *D* *is incorrect because when there are more gas molecules in the products than the reactants* ΔS_{system} *is positive*	(1)

Q5.

Question Number	Answer	Mark
	The only correct answer is B (reactions **P** and **Q** only) *A is not correct because both reactions* ***P*** *and* ***Q*** *have a positive value for* ΔS_{total} *C is not correct because reaction* ***R*** *has a negative value for* ΔS_{total} *so is not feasible* *D is not correct because both reactions* ***R*** *and* ***S*** *have a negative value for* ΔS_{total} *so are not feasible*	(1)

Q6.

Question Number	Answer	Mark
	The only correct answer is B ($\Delta S_{surroundings}$ is positive) *A is incorrect because* ΔH *is negative for an exothermic reaction* *C is incorrect because* ΔS_{system} *is positive as a gas is being formed* *D is incorrect because as both* ΔS_{system} *and* $\Delta S_{surroundings}$ *are positive so* ΔS_{total} *will be positive*	(1)

Q7.

Question number	Answer		Additional guidance	Mark
(a)(i)	• R = O^{2-}(g)	(1)		2
	• W = first electron affinity O(g)	(1)	Allow alternative ways to express electron affinity, e.g. EA State required Do not allow O_2/O^-	

Question number	Answer		Additional guidance	Mark
(a)(ii)			Example of calculation:	3
	• correct application of cycle	(1)	$\Delta_f H$ (BaO(s)) = $\Delta_{at} H$(Ba(s))+$\Delta_{at} H$(½O_2(g))+ I^{st} IE (Ba)(g) +2^{nd} IE (Ba(g))+2^{nd} EA (O(g))+1^{st} EA (O(g)) +$\Delta_{LE} H$ (BaO(s)) or Correct numbers = 180.0+249.2+503+965+798−141.1−3054	
	• correct value	(1)	(−)499.9/(−)500 (kJ mol^{-1})	
	• correct sign and units	(1)	Allow TE from incorrect application of cycle Allow TE for incorrect numbers Correct answer with no working scores 3	

Question number	Answer		Additional guidance	Mark
(a)(iii)	• ionic radius of Ba^{2+} >> ionic radius of Mg^{2+}/(have) lower charge density **and** Ba^{2+} (ions are) less polarising/(have) lower charge density	(1)	Allow reverse argument	3
	• iodide ions/I^- are large **and** their electron clouds are easily distorted/polarised (by Group 2 cations) or oxide ions/O^{2-} are small(er) **and** their electron clouds are less easily distorted/polarised	(1) (1)		
	• more distortion/covalency leads to greater difference between theoretical and experimental values			

Question number	Answer		Additional guidance	Mark
(b)(i)			Do not allow energy profile or energy level diagrams	4
	• all arrows in the correct direction	(1)	Species at each corner must be approximately correct	
	• correct formulae at each corner and enthalpies of hydration, and solution and LE correctly identified	(1)	Allow missing minor detail: brackets, position of subscripts, etc. but not absence of subscripts	
	• correct expression or correct substitution of values	(1)	Example of calculation: $\Delta_{sol}H = (\Delta_{hyd}H\ (Ba^{2+}) + 2\Delta_{hyd}H(OH^-)) -$ LE $(Ba(OH)_2)$ or $= (-1360 + (2 \times -460)) - (-2230)$	
	• correct evaluation	(1)	$= -50$ (kJ mol^{-1}) Allow TE from their cycle if $\Delta_{hyd}H(OH^-)$ is not doubled	

Question number	Answer		Additional guidance	Mark
b(ii)	• entropy (change) of system/ΔS_{system}/$\Delta S_{dissolving}$ is large and positive (and outweighs negative $\Delta S_{surroundings}$ ($-\Delta H/T$))	(1) (1)		2
	• overall entropy change/ΔS_{total} is positive or			
	• use of $\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$	(1)		
	• $\Delta S_{total} = \Delta S_{surroundings} + (-\Delta H/T)$	(1)	Allow use of ΔG	

Q8.

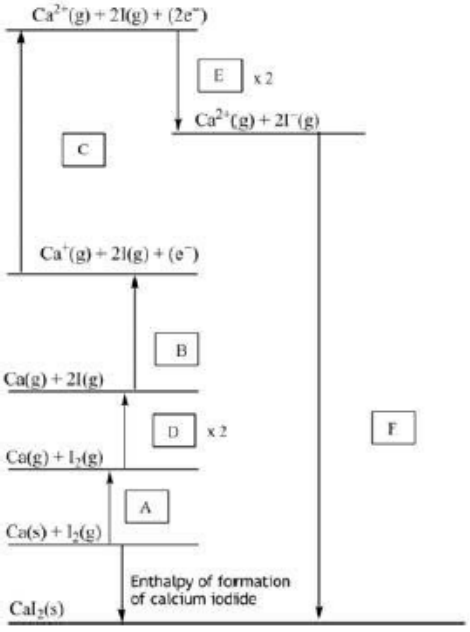
Q	Correct Answer	Mark
	The only correct answer is D (SO_2) ***A*** *is incorrect as although it has four atoms, it has ten electrons* ***B*** *is incorrect as it has two atoms and two electrons* ***C*** *is incorrect as it has two atoms and only fourteen electrons*	1

Q9.

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: $\Delta S_{total} = R \ln K$ $\ln K = \Delta S_{total} / R = 1780.7 / 8.31$ $= 214.1998$ 1.15440×10^{93} Allow any answer between 1.06×10^{93} and 1.18×10^{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

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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

Q10.

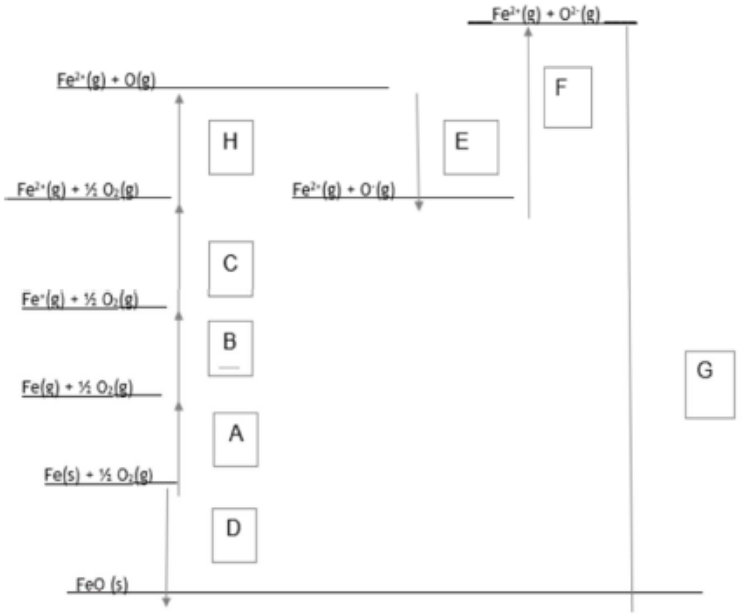
Question Number	Answer	Additional Guidance	Mark
(a)(i)	• correct use of enthalpy data **(1)** • correct enthalpy change **(1)**	Example of calculation $-(-824.2)+(3\times-110.5)$ $=(+)492.7$ (kJ mol^{-1}) Correct answer with or without working scores 2 The following score 1 for a single error: (+) 713.7 (kJ mol^{-1}) not x3 −492.7 (kJ mol^{-1}) signs reversed Allow 3SF Penalise wrong units once only in (a)(i) and (ii)	**(2)**

Question Number	Answer	Additional Guidance	Mark
(a)(ii)	• $\sum S$ products **(1)** • $\sum S$ reactants **(1)** • $\Delta S_{system} = \sum S$ products $- \sum S$ reactants **(1)**	Example of calculation S = products (2 x 27.3) + (3 x 197.6) = 647.4 (J K^{-1} mol^{-1}) S = reactants 87.4 + (3 x 5.7) = 104.5 (J K^{-1} mol^{-1}) ΔS_{system} = 647.4 − 104.5 = (+)542.9 (J K^{-1} mol^{-1}) Correct answer with no working scores 3 Allow TE for M3	**(3)**

Question Number	Answer	Additional Guidance	Mark
(a)(iii)	• use of $\Delta S_{surroundings} = -\frac{\Delta H}{T}$ **(1)** • at equilibrium $\Delta S_{total} = 0$ **(1)** $= \Delta S_{surroundings} + \Delta S_{system}$ • calculation of temperature **(1)**	Example of calculation $\Delta S_{surroundings} = -(+492.7) \times 1000/T$ $0 = -492.7 \times 1000/T + 542.9$ ≥ 907.53(K) 0.90753 scores 2 (not x 1000) Ignore SF TE on (a)(i) and (a)(ii) Correct answer based on ai and aii without working scores 3 Allow use of $\Delta G = \Delta H - T\Delta S_{system}$	**(3)**

Question Number	Answer	Additional Guidance	Mark
(b)(i)	An answer that makes reference to the following points: • $\Delta S_{surroundings}$ **and** ΔS_{system} are positive **(1)** • so ΔS_{total} will always be positive (so reaction will be feasible) **(1)** **OR** Using $\Delta G = \Delta H - T\Delta S_{system}$ • Allow ΔH is negative **and** ΔS_{system} is positive **(1)** • so ΔG will always be negative (so reaction will be feasible) **(1)**	Allow ΔH is negative/reaction exothermic **and** ΔS_{system} is positive M2 **dependent** on M1 M2 **dependent** on M1	**(2)**

Question Number	Answer	Additional Guidance	Mark
(b)(ii)	An answer that makes reference to the following points: • at a higher temperature $\Delta S_{surroundings}$ will decrease **(1)** • ΔS_{system} does not change (significantly) **(1)** • so ΔS_{total} will decrease/become less positive **(1)**	Ignore reference to $\Delta S_{total} = R\ln K$	**(3)**

Question Number	Answer	Additional Guidance	Mark
(c)(i)	 All 7 correct 3 marks 4–6 correct 2 marks 2–3 correct 1 mark	Allow values instead of letters	**(3)**

Question Number	Answer	Additional Guidance	Mark
(c)(ii)	• correct expression **(1)** • correct calculation **(1)**	Example of calculation − 759 – 416 – 272 + 3920 – 798 + 141 − 249 = (+)1567 (kJ mol^{-1}) Allow 3SF Correct answer with or without working scores 2 marks Allow 1 mark for one mistake	**(2)**

Question Number	Answer	Additional Guidance	Mark
(c)(iii)	• the electron is being added to a negative ion **(1)** • and so there is repulsion (so energy is required) **(1)**	This can be shown by an equation Allow repulsion between the electrons	**(2)**

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 standard enthalpy change of solution of potassium chloride, KCl, is +17 kJ mol^{-1}.

The solubility of potassium chloride in water at 298 K is 359 g dm^{-3}.

Which of these explains the solubility of potassium chloride in water?

☒ **A** the hydration enthalpy of K^+ and the lattice energy of KCl are exothermic

☒ **B** the hydration enthalpy of K^+ and the lattice energy of KCl are endothermic

☒ **C** the total entropy change when KCl dissolves is positive

☒ **D** the total entropy change when KCl dissolves is negative

(Total for question = 1 mark)

Q2.

The mechanism for the rapid decomposition of hydrogen peroxide, H_2O_2, in the presence of iodide ions, is:

$$H_2O_2 + I^- \rightarrow IO^- + H_2O \qquad \text{equation 1}$$

$$H_2O_2 + IO^- \rightarrow I^- + H_2O + O_2 \qquad \text{equation 2}$$

(a) Write the overall equation for the reaction and hence state the role of the iodide ions.

(2)

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(b) In further experiments, a student calculated the rate constant for the decomposition of hydrogen peroxide at two different temperatures.

Temperature/ °C	Rate constant (k) / $dm^3\ mol^{-1}\ s^{-1}$
22.0	4.90×10^{-4}
47.0	2.92×10^{-3}

The rate constant (k) is related to the temperature, T, (in Kelvin) by the following equation:

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad R = 8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$$

Use the data in the table to calculate the activation energy, E_a, for the reaction by a non-graphical method.
Give your answer in kJ mol^{-1} and to an appropriate number of significant figures.
Include a sign in your answer.

(4)

(c) If acid conditions are used, the decomposition of hydrogen peroxide proceeds by a different mechanism. The equation for this reaction is:

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

This reaction is first order with respect to both iodide ions and hydrogen peroxide.

The progress of this reaction is usually followed by adding a fixed quantity of sodium thiosulfate solution and a little starch solution to the reaction mixture, then timing the appearance of a blue-black colour. This is known as a clock reaction.

(i) Explain the formation of the blue-black colour and why its appearance is delayed.

(3)

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(ii) Although the oxidation of thiosulfate ions ($S_2O_3^{2-}$) by hydrogen peroxide is thermodynamically favourable, it does not take place in this clock reaction.
Suggest a reason for this.

(1)

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(Total for question = 10 marks)

Q3.

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 ☒.

Ammonium nitrate is very soluble in water.

$$NH_4NO_3(s) + aq \rightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H^{\ominus} = +25.8 \text{ kJ mol}^{-1}$$

What is the best explanation for this?

☒ **A** all ammonium salts are soluble in water

☒ **B** the activation energy of the reaction is very low

☒ **C** the enthalpies of hydration of the ions are very exothermic

☒ **D** the entropy change of the system, ΔS_{system}, is positive

(Total for question = 1 mark)

Q4.

The standard enthalpy change of solution for ammonium nitrate, NH_4NO_3 , is +25.7 kJ mol^{-1}.

(a) Calculate the value for the standard entropy change in the surroundings, $\Delta S^{\ominus}_{surroundings}$, when ammonium nitrate dissolves in water at 298 K. Include a sign and units with your answer.

(2)

(b) Explain what can be deduced from your answer in (a) about the sign and the value of the standard entropy change in the system, $\Delta S^{\ominus}_{system}$, when NH_4NO_3 dissolves.

(3)

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(Total for question = 5 marks)

Q5.

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 ☒ .

What is the standard entropy change of the system, in J K^{-1} mol^{-1}, for the reaction between nitrogen and hydrogen to form ammonia?

$$N_2 + 3H_2 \rightarrow 2NH_3$$

	Standard molar entropy / J K^{-1} mol^{-1}
H_2	130.6
N_2	191.6
NH_3	192.3

☒ **A** –198.8

☒ **B** –129.9

☒ **C** +129.9

☒ **D** +198.8

(Total for question = 1 mark)

Q6.

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 ☒ .

Which of these has the **highest** standard molar entropy at 298 K and 1 atm pressure?

☒ **A** carbon dioxide, CO_2

☒ **B** copper, Cu

☒ **C** ethanol, C_2H_5OH

☒ **D** hydrogen, H_2

(Total for question = 1 mark)

Q7.

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 standard molar entropy, $S^{\ominus}$, of a substance

☒ **A** is not affected by changes of state or changes in temperature

☒ **B** only changes when the temperature changes

☒ **C** only changes when the substance changes state

☒ **D** changes when the temperature changes and when the substance changes state

(Total for question = 1 mark)

Q8.

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 ☒.

In which series does the standard molar entropy of the compounds increase?

☒ **A** $CaO(s) < H_2O(l) < CO_2(g) < SO_2(g)$

☒ **B** $CaO(s) < H_2O(l) < SO_2(g) < CO_2(g)$

☒ **C** $SO_2(g) < CO_2(g) < H_2O(l) < CaO(s)$

☒ **D** $CO_2(g) < SO_2(g) < H_2O(l) < CaO(s)$

(Total for question = 1 mark)

Q9.

Which substance has the highest standard molar entropy?

(1)

☒ **A** ethane(g)

☒ **B** water(s)

☒ **C** water(l)

☒ **D** water(g)

(Total for question = 1 mark)

Q10.

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

$$½N_2(g) + 1½H_2(g) \rightleftharpoons NH_3(g)$$

(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, $S^{\ominus}$ / $JK^{-1}mol^{-1}$
N_2	192
H_2	131

(2)

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

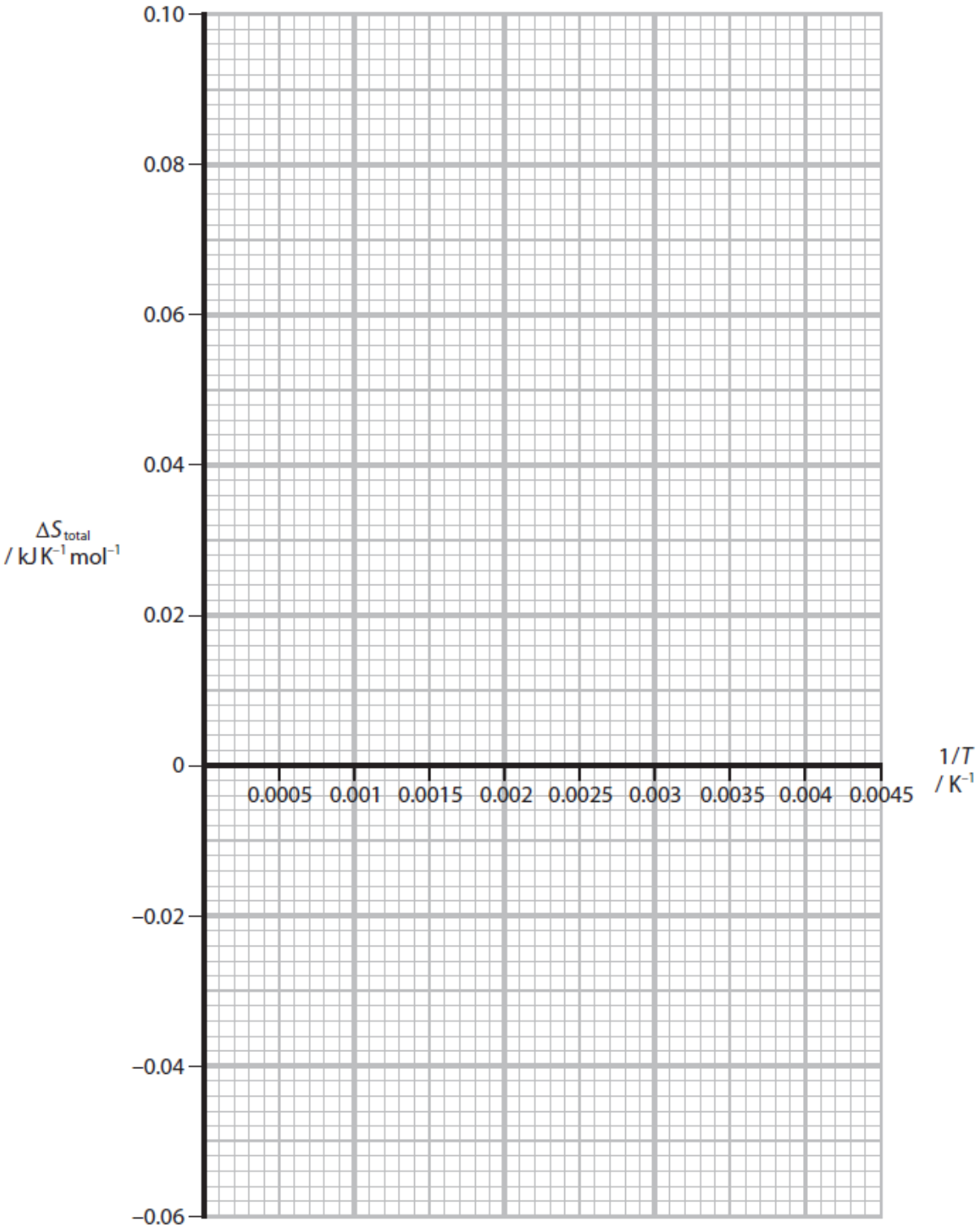
Data for the value of ΔS_{total} at different temperatures but at standard pressure of 100 kPa are given for this reaction.

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)

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

(1)

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(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)

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(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)

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

(1)

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(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)

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(Total for question = 20 marks)

Q11.

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)

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(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)

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(Total for question = 20 marks)

Q12.

The element sulfur can exist in two solid, interchangeable, structural forms known as rhombic sulfur and monoclinic sulfur.

$$S(s, \text{rhombic}) \rightleftharpoons S(s, \text{monoclinic}) \qquad \Delta S_{total} = -0.307\,J\,K^{-1}\,mol^{-1}$$

The value of ΔS_{total} is for the forward reaction. What can be concluded from this information?

(1)

☒ **A** monoclinic sulfur will change quickly into rhombic sulfur

☒ **B** rhombic sulfur could change into monoclinic sulfur but nothing can be deduced about the rate

☒ **C** there can be no change of structural form as they are both solids

☒ **D** monoclinic sulfur could change into rhombic sulfur but nothing can be deduced about the rate

(Total for question = 1 mark)

Mark Scheme

Q1.

Question Number	Answer	Mark
	The only correct answer is C (the total entropy when KCl dissolves is positive) *A is not correct because the enthalpy change of hydration for all ions and lattice energy for all ionic compounds are exothermic so this does not explain why KCl is soluble* *B is not correct because the enthalpy change of hydration for all ions and lattice energy for all ionic compounds are exothermic* *D is not correct because the total entropy must be positive for a spontaneous reaction*	(1)

Q2.

Question number	Answer	Additional guidance	Mark
(a)	• $2H_2O_2 \rightarrow 2H_2O + O_2$ (1) • iodide ions act as a catalyst (as they don't appear in the overall equation) (1)	Ignore state symbols even if incorrect	2

Question number	Answer	Additional guidance	Mark
(b)	• converts both temperatures from °C to K (1) • correct subtraction (1) • substitute numbers in equation correctly (1) • correct value of E_a (1)	Example of calculation: 22.0 °C = 295.0 K 47.0 °C = 320.0 K $\ln\left(\frac{K_1}{K_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ $\ln\left(\frac{4.90\times10^{-4}}{1.07\times10^{-3}}\right) = -\frac{E_a}{8.31}\left(\frac{1}{295} - \frac{1}{320}\right)$ (+)56.(0) (kJ mol^{-1}) Sign and final answer to 2 or 3 SF Incorrect units loses MP4 Correct answer with no working scores 4	4

Question number	Answer	Additional guidance	Mark
(c)(i)	An explanation that makes reference to the following points: • (blue-black colour is) product of starch-iodine reaction (1) • the iodine produced reacts (rapidly) with the thiosulfate ions (to reform iodide ions) (1) • when all of the thiosulfate has reacted, the blue-black colour appears. (1)		3

Question number	Answer	Additional guidance	Mark
(c)(ii)	• the reaction (between thiosulfate and hydrogen peroxide) is slow	Allow reaction has high E_a	1

Q3.

Question number	Answer	Mark
	The only correct answer is D (the entropy change of the system, ΔS_{system}, is positive) *A* *is incorrect because this is a statement not an explanation* *B* *is incorrect because activation energy affects rate not direction of change* *C* *is incorrect because the overall enthalpy of reaction is still endothermic*	(1)

Q4.

Q	Acceptable Answers	Additional Guidance	Mark
(a)	• correct expression for $\Delta S_{surroundings}$ **(1)** • correct evaluation **and** correct units **and** correct sign **(1)**	Example of calculation $-\Delta H \circ T = -25.7 \circ 298$ -0.086242 kJ K^{-1} mol^{-1} / -86.242 J K^{-1} mol^{-1} Ignore SF except 1 SF Correct answer with no working scores (2) Allow TE in M2 for use of $\Delta H \circ T$ Comment Mark value first – if correct, with units and sign award 2 marks For units allow kJ K^{-} mol^{-} / J K^{-} mol^{-}	**2**

Q	Acceptable Answers	Additional Guidance	Mark
(b)	An explanation that makes reference to: • ΔS_{system} must be positive **(1)** • ΔS_{system} > 86.24 J mol^{-1} / answer to (a) **(1)** • (as compound does dissolve) ΔS_{total} is > 0 / positive **(1)**	Allow 'ΔS_{system} is more positive' Allow $T\Delta S_{system}$ is greater in magnitude / more negative than ΔH ΔG is negative If answer to (a) is positive , then M1 and M2 will be • ΔS_{system} could be positive or negative • ΔS_{system} smaller in magnitude than answer to (a) / $T\Delta S_{system}$ is greater than ΔH	**3**
			(Total for Question = 5 marks)

Q5.

Q	Correct Answer	Mark
	The only correct answer is A (– 198.8) ***B*** *is incorrect as number of moles of* NH_3 *and* H_2 *have not been considered* ***C*** *is incorrect as number of moles of* NH_3 *and* H_2 *have not been considered and the expression to find the standard entropy of the system is the wrong way round* ***D*** *is incorrect as expression to find the standard entropy of the system is the wrong way round*	1

Q6.

Question Number	Answer	Mark
	The only correct answer is A (carbon dioxide, CO_2) ***B*** *is not correct because copper is a solid at 298 K and 1 atm pressure so has the lowest entropy* ***C*** *is not correct because ethanol is a liquid at 298 K and 1 atm pressure and has a lower entropy than a gas* ***D*** *is not correct because hydrogen is also a gas at 298 K and 1 atm pressure, but its molecules are smaller than carbon dioxide molecules*	(1)

Q7.

Question number	Answer	Mark
	The only correct answer is D(changes when the temperature changes and when the substance changes state) ***A*** *is incorrect because standard molar entropy is affected by change of state and change in temperature* ***B*** *is incorrect because standard molar entropy is affected by change of state* ***C*** *is incorrect because standard molar entropy is affected change in temperature*	(1)

Q8.

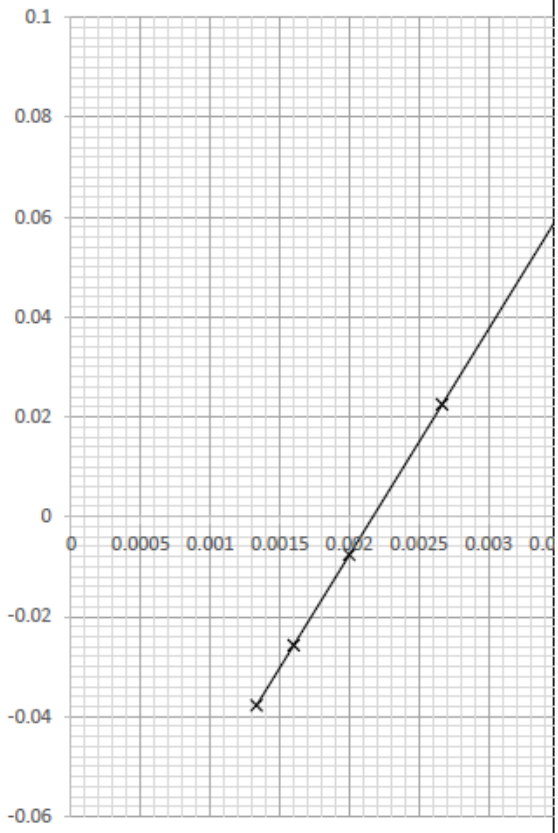
Question Number	Answer	Mark
	The only correct answer is A ($CaO(s) < H_2O(l) < CO_2(g) < SO_2(g)$) ***B*** *is not correct because* $SO_2(g)$ *has a greater standard molar entropy than* $CO_2(g)$ ***C*** *is not correct because* $SO_2(g)$ *has the greatest standard molar entropy* ***D*** *is not correct because* $SO_2(g)$ *has the greatest standard molar entropy*	(1)

Q9.

Question number	Answer	Mark
	A ethane(g)	1

Q10.

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)**

Q11.

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)		

Q12.

Question number	Answer	Mark
	D monoclinic sulfur could change into rhombic sulfur but nothing can be deduced about the rate	1