1. The reaction between solid barium hydroxide and solid ammonium chloride can be represented by the equation below.

$$Ba(OH)_2(s) + 2NH_4Cl(s) \rightarrow BaCl_2(s) + 2NH_3(g) + 2H_2O(l) \qquad \Delta H^\ominus = +51.1\ \text{kJ mol}^{-1}$$

The standard entropies, at 298 K, for the reactants and products are:

$S^\ominus[Ba(OH)_2(s)] = +99.7\ \text{J mol}^{-1}\text{K}^{-1}$

$S^\ominus[NH_4Cl(s)] = +94.6\ \text{J mol}^{-1}\text{K}^{-1}$

$S^\ominus[BaCl_2(s)] = +123.7\ \text{J mol}^{-1}\text{K}^{-1}$

$S^\ominus[NH_3(g)] = +192.3\ \text{J mol}^{-1}\text{K}^{-1}$

$S^\ominus[H_2O(l)] = +69.9\ \text{J mol}^{-1}\text{K}^{-1}$

(a) Why is the standard entropy of ammonia more positive than the standard entropy of barium chloride?

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(1)

(b) Use the values given to calculate the standard entropy change, $\Delta S^\ominus_{\text{system}}$, for this reaction. Include the sign and units in your answer.

(2)

(c) Calculate the standard entropy change of the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$, at 298 K for this reaction.

(2)

(d) Use your answers to (b) and (c) to show that this reaction is feasible at 298 K.

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(1)

(e) Calculate the minimum temperature, in kelvin, at which the reaction is spontaneous.

(2)

(Total 8 marks)

2. Thermochemical data, at 298 K, for the equilibrium between zinc carbonate, zinc oxide and carbon dioxide is shown below.

$$ZnCO_3(s) \rightleftharpoons ZnO(s) + CO_2(g) \qquad \Delta H^\ominus = +71.0 \text{ kJ mol}^{-1}$$

$$S^\ominus[ZnO(s)] = +43.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^\ominus[ZnCO_3(s)] = +82.4 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^\ominus[CO_2(g)] = +213.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

(a) (i) Suggest reasons for the differences between the three standard entropies.

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(2)

(ii) Calculate the entropy change for the system, $\Delta S^\ominus_{system}$, for this reaction. Include the sign and units in your answer.

(2)

(b) Calculate the entropy change for the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$, at 298 K, showing your method clearly.

(2)

(c) (i) Calculate the total entropy change for this reaction, $\Delta S^{\ominus}_{\text{total}}$, at 298 K.

(1)

(ii) What does the result of your calculation in (c)(i) indicate about the natural direction of this reaction at 298 K?

Justify your answer.

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(1)

(d) (i) Write an expression for the equilibrium constant, K_p, for this reaction.

(1)

(ii) State how you would alter ONE condition to increase the yield of carbon dioxide from this equilibrium reaction.

Justify your answer.

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(2)
(Total 11 marks)

3. When dinitrogen tetroxide, N_2O_4, dissociates, the following equilibrium is established.

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

(a) State a property which could be measured to follow the progress of this reversible reaction.

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(1)

(b) Write an expression for the equilibrium constant, K_c, for this reaction.

(1)

(c) When a sample of 0.0370 moles of gaseous dinitrogen tetroxide is allowed to dissociate at 25 °C in a container of volume 1 dm^3, 0.0310 moles of $N_2O_4(g)$ remain in the equilibrium mixture.

Complete the table below, and use the data to calculate K_c for the reaction. Include a unit in your answer.

	N_2O_4	NO_2
Number of moles at start	0.0370	0
Number of moles in 1 dm^3 at equilibrium	0.0310	

K_c calculation:

(3)

(d) The reaction was repeated at a higher pressure, maintaining the temperature at 25 °C.

(i) How does this increase in pressure affect the amount of nitrogen dioxide, $NO_2(g)$, in the equilibrium mixture?

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(1)

(ii) How does this increase in pressure affect the value of K_c?

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(1)

(e) The reaction was repeated at the original pressure, but the temperature was increased to 75 °C. The value of K_c was approximately twenty times greater.

How does this information show that the reaction is endothermic?

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(1)

(f) Predict the sign of ΔS_{system} for the reaction, giving a reason for your answer.

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(2)

(g) Write the equation for the relationship between $\Delta S_{\text{surroundings}}$ and ΔH for the reaction.

(1)

(h) The magnitude of ΔS_{system} for the reaction is greater than the magnitude of $\Delta S_{\text{surroundings}}$. Explain why this must be the case.

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(2)
(Total 13 marks)

4. The equation below shows a possible reaction for producing methanol.

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l) \qquad \Delta H^\ominus = -129\ \text{kJ mol}^{-1}$$

(a) The entropy of one mole of each substance in the equation, measured at 298 K, is shown below.

Substance	$S^\ominus$ /J mol^{-1} K^{-1}
$CO(g)$	197.6
$H_2(g)$	130.6
$CH_3OH(l)$	239.7

(i) Suggest why methanol has the highest entropy value of the three substances.

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.... **(1)**

(ii) Calculate the entropy change of the system, $\Delta S^\ominus_{system}$, for this reaction.

(2)

(iii) Is the sign of $\Delta S^\ominus_{system}$ as expected? Give a reason for your answer.

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.... **(1)**

(iv) Calculate the entropy change of the surroundings $\Delta S^{\ominus}_{surroundings}$, at 298 K.

(2)

(v) Show, by calculation, whether it is possible for this reaction to occur spontaneously at 298 K.

(2)

(b) When methanol is produced in industry, this reaction is carried out at 400 °C and 200 atmospheres pressure, in the presence of a catalyst of chromium oxide mixed with zinc oxide. Under these conditions methanol vapour forms and the reaction reaches equilibrium. Assume that the reaction is still exothermic under these conditions.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

(i) Suggest reasons for the choice of temperature and pressure.

Temperature ....

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Pressure ....

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(3)

(ii) The catalyst used in this reaction is **heterogeneous**. Explain this term.

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(1)

(iii) Write an expression for the equilibrium constant in terms of pressure, K_p, for this reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

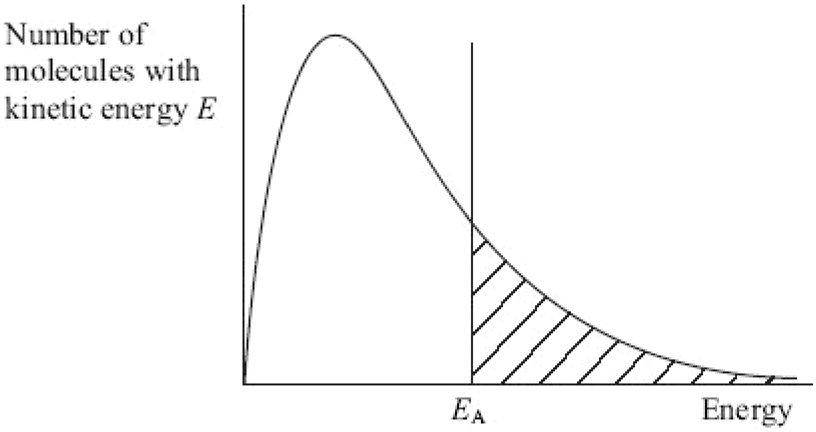
(1)

(iv) In the equilibrium mixture at 200 atmospheres pressure, the partial pressure of carbon monoxide is 55 atmospheres and the partial pressure of hydrogen is 20 atmospheres.

Calculate the partial pressure of methanol in the mixture and hence the value of the equilibrium constant, K_p. Include a unit in your answer.

(2)

(c) The diagram below shows the distribution of energy in a sample of gas molecules in a reaction when no catalyst is present. The activation energy for the reaction is E_A.



(i) What does the shaded area on the graph represent?

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(1)

(ii) Draw a line on the graph, labelled $\boldsymbol{E}_C$, to show the activation energy of the catalysed reaction.

(1)
(Total 17 marks)

5. The reaction between nitrogen and hydrogen can be used to produce ammonia.

$$N_2(g) + 3H^2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\ominus = -\,92.2 \text{ kJ mol}^{-1}$$

Standard entropies are given below

$S^\ominus$ [N_2(g)] = +191.6 J mol^{-1} K^{-1}

$S^\ominus$ [H_2(g)] = +130.6 J mol^{-1} K^{-1}

$S^\ominus$ [NH_3(g)] = +192.3 J mol^{-1} K^{-1}

(a) Calculate the entropy change of the system, $\Delta S^{\ominus}_{\text{system}}$, for this reaction. Include a sign and units in your answer.

(2)

(b) Calculate the entropy change of the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$, at 298 K. Include a sign and units in your answer.

(2)

(c) (i) Calculate the total entropy change, $\Delta S^{\ominus}_{\text{total}}$, at 298 K. Include a sign and units in your answer.

(1)

(ii) Is this reaction feasible at 298 K? Justify your answer.

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(1)

(d) In industry the reaction is carried out at about 700 K using an iron catalyst and high pressures.

(i) The yield of ammonia produced at equilibrium is less at 700 K than at 298 K, if the pressure remains constant. In terms of entropy, explain why this happens.

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(1)

(ii) Higher pressures increase the yield of ammonia at equilibrium. Suggest a reason why pressures greater than 300 atmospheres are **not** routinely used.

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(1)

(iii) Iron is a heterogeneous catalyst. Explain what is meant by **heterogeneous**.

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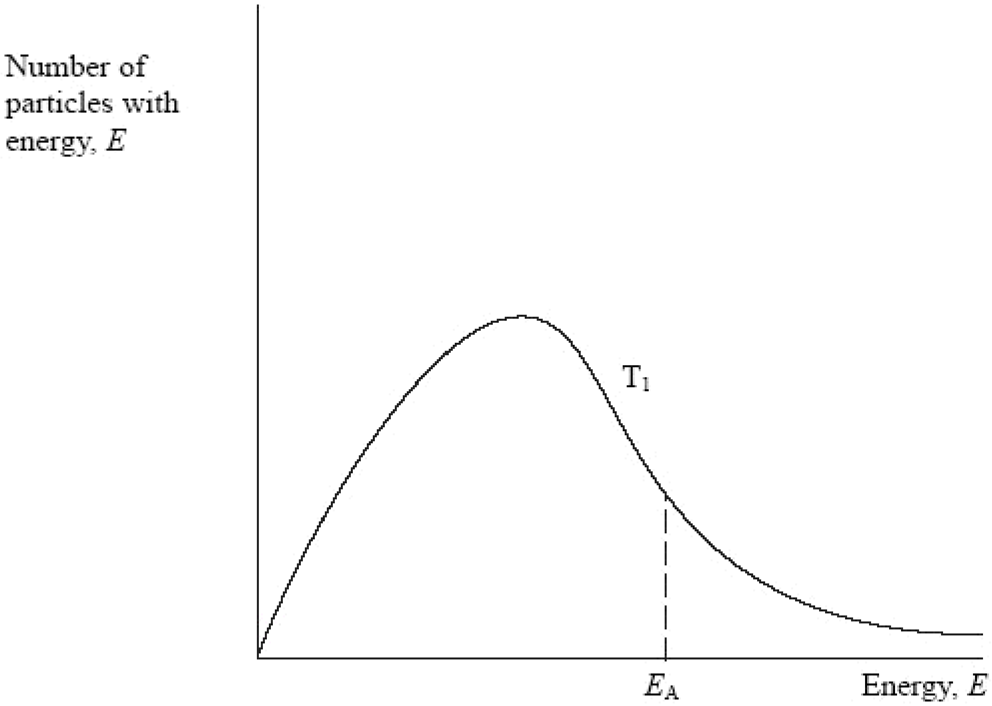
(1)
(Total 9 marks)

6. (a) The distribution of the energy of particles in a gas at temperature T1 is shown below.



(i) On the diagram above, draw the distribution of energy of particles at a **lower** temperature, T2.

(2)

(ii) Use the diagram to explain why the rate of a reaction increases with an increase in temperature.

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(3)

(iii) Explain fully why a catalyst increases the rate of a reaction.

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(2)

(b) The fermentation of glucose is an exothermic reaction and is catalysed by enzymes in yeast.

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

The reaction is slow at room temperature.

(i) Describe, with the aid of a diagram, an experiment you could do to follow the progress of this reaction at different temperatures.

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(4)

(ii) Would you expect ΔS_{system} to be positive or negative for this reaction? Justify your answer with TWO pieces of evidence.

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(2)

(iii) Deduce the sign of $\Delta S_{\text{surroundings}}$. Show your reasoning.

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(2)

(Total 15 marks)

7. In the first stage of an industrial process for purifying nickel, carbon monoxide is passed over impure nickel at 323 K. Gaseous nickel tetracarbonyl, $Ni(CO)_4$, is formed.

$$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g) \qquad \Delta H^\ominus = -191 \text{ kJ mol}^{-1}$$

(a) (i) Calculate $\Delta S^\ominus_{system}$ for this reaction given the following standard entropy values.

Substance	$S^\ominus$ /J mol^{-1} K^{-1}
$Ni(s)$	+29.9
$CO(g)$	+197.6
$Ni(CO)_4(g)$	+313.4

Include a sign and units in your answer.

(2)

(ii) Refer to the equation above and comment on the sign of your answer.

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(1)

(iii) Calculate $\Delta S^\ominus_{surroundings}$ at 323 K. Include a sign and units in your answer.

(2)

(iv) Deduce the direction of this reaction at 323 K. Justify your answer.

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(1)

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

(1)

(ii) 100 moles of gaseous carbon monoxide is mixed with excess solid nickel at 323 K in a vessel kept at 1.00 atmosphere pressure. At equilibrium, 1.00 mole of the carbon monoxide has reacted.

Complete the table below and then calculate the value of K_p at this temperature. Include the units of K_p in your answer.

Substance	Moles at start	Moles at equilibrium	Partial pressure, p_{eq} /atm
$Ni(CO)_4$	0		
CO	100	99.0	

(4)

(iii) As K_p has such a small value, suggest THREE ways in which this industrial process could be improved to increase profitability. Justify each of your suggestions.

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(3)

(c) The second stage of this process is to recover the nickel from the nickel tetracarbonyl, $Ni(CO)_4$. By considering your calculations of the entropy changes, suggest how this could be done. Justify your suggestion.

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(2)
(Total 16 marks)

8. One step in the manufacture of nitric acid is the reaction between nitrogen(II) oxide and oxygen to form nitrogen(IV) oxide.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = -114 \text{ kJ mol}^{-1}$$

(a) (i) Use the equation to suggest the sign of ΔS_{system} for the forward reaction. Justify your answer.

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(2)

(ii) What is the sign of $\Delta S_{\text{surroundings}}$ for the forward reaction? Justify your answer.

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(2)

(b) (i) Write the expression for K_p for this reaction.
What are the units of K_p in this reaction?

Units ....

(2)

(ii) Suggest how the temperature and pressure could be altered to make nitrogen(IV) oxide more economically. Justify your suggestions by considering both yield and rate.

Temperature

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Pressure

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(4)

(c) (i) What property would allow you to follow the progress of this reaction? Justify your answer.

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(2)

(ii) In a series of experiments, the following results were obtained.

Experiment	[NO(g)] /mol dm^{-3}	[O_2(g)] /mol dm^{-3}	Initial rate /mol dm^{-3} s^{-1}
1	1.0×10^{-3}	1.0×10^{-3}	8.0×10^{-6}
2	2.0×10^{-3}	1.0×10^{-3}	3.2×10^{-5}
3	2.0×10^{-3}	2.0×10^{-3}	6.4×10^{-5}

- What is the order of the reaction with respect to NO(g)? Justify your answer.

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(2)

- What is the order of the reaction with respect to O_2(g)?

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(1)

(iii) What is the rate equation for this reaction?

(1)

(iv) What is the overall order for this reaction?

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(1)

(v) Calculate the rate constant, *k*, for this reaction. Include units with your answer.

(2)

(d) Suggest why this reaction takes place quickly at room temperature and pressure.

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(1)
(Total 20 marks)

9. This question is about the reaction between calcium carbonate and hydrochloric acid.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

One method of studying the kinetics of this reaction is to measure the volume of carbon dioxide given off at various timed intervals when using an excess of calcium carbonate.

(a) Suggest TWO other methods for following this reaction. Explain your choices.

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(2)

(b) Suggest why the volume of carbon dioxide given off in the first few seconds of the reaction is an unreliable measure of the initial rate of the reaction.

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(1)

(c) In an experiment, the following results were obtained.

Time / s	Volume of CO_2 V_t/cm^3	$(V_{final} – V_t)$ / cm^3
5	3	85
35	42	46
65	62	26
95	72	
125	79	
155	84	
185	87	

(i) What was the final volume, V_{final}?

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(1)

(ii) Complete the table.

(1)

(iii) To what is $(V_{final} – V_t)$ proportional?

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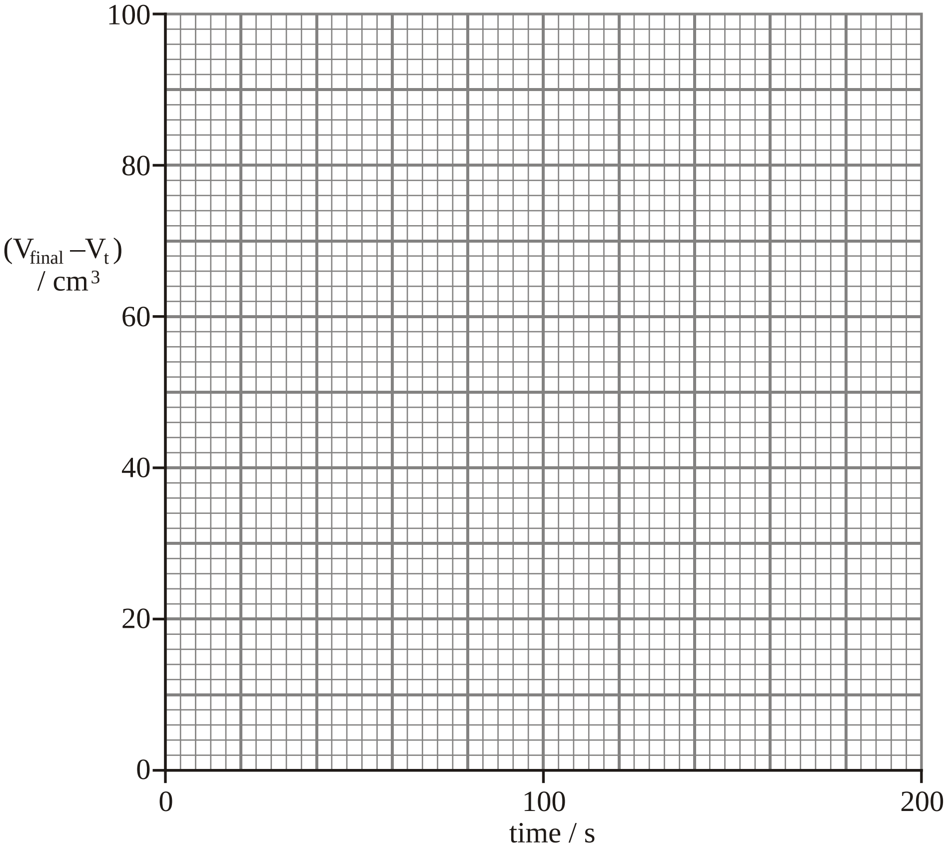
(1)

(iv) Plot these results on the grid below.



(2)

(v) On your graph measure and record THREE successive half-lives. Deduce the order of the reaction. Justify your answer.

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(3)

(vi) Give the rate equation for this reaction.

(1)

(vii) What are the units of the rate constant?

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(1)

(d) What would you expect the signs of ΔS_{system} and ΔS_{total} to be for the reaction between calcium carbonate and hydrochloric acid? Justify your answers.

ΔS_{system} ....

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ΔS_{total} ....

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(4)
(Total 17 marks)

10. When barium nitrate is heated it decomposes as follows:

$$Ba(NO_3)_2(s) \rightarrow BaO(s) + 2NO_2(g) + ½O_2(g) \qquad \Delta H = +505.0 \text{ kJ mol}^{-1}$$

(a) Use the following data when answering this part of the question.

Substance	Standard entropy, $S^\ominus$ / J mol^{-1} K^{-1}
Ba(NO3)$_2$(s)	+ 213.8
BaO(s)	+ 70.4
NO_2(g)	+ 240.0
O_2(g)	+ 205.0

(i) Explain why:

- $S^\ominus$ [NO_2(g)] is greater than $S^\ominus$ [BaO(s)]

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- $S^\ominus$ [$Ba(NO_3)_2$(s)] is greater than $S^\ominus$ [BaO(s)].

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(2)

(ii) Calculate the entropy change of the system, $\Delta S^\ominus_{system}$, for this reaction. Include a sign and units in your answer.

(2)

(b) Calculate the entropy change of the surroundings, $\Delta S^\ominus_{surroundings}$, for the reaction at 298 K. Include a sign and units in your answer.

(2)

(c) Calculate $\Delta S^\ominus_{total}$, and explain the significance of the sign for this value.

....

(2)

(d) Calculate the minimum temperature at which the decomposition of barium nitrate should occur.

You can assume that ΔH and ΔS_{system} are **not** affected by a change in temperature.

(2)
(Total 10 marks)

11. Ammonia can be oxidised to form nitrogen(II) oxide and water according to the equation

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g) \qquad \Delta H^\ominus = -905.6 \text{ kJ mol}^{-1}.$$

In industry, the reaction is carried out at 1123 K with a platinum/rhodium catalyst.

The standard entropy of one mole of each substance in the equation, measured at 298 K, is shown in the table below.

Substance	$S^\ominus$/ J mol^{-1} K^{-1}
NH_3 (g)	+192.3
O_2 (g)	+205.0
NO (g)	+210.7
H_2O (g)	+188.7

(a) (i) Use the values given to calculate the standard entropy change of the system, $\Delta S^\ominus_{\text{system}}$, for this reaction. Include the sign and units in your final answer.

(2)

(ii) Is the sign for your value for $\Delta S^\ominus_{\text{system}}$ what you expected? Justify your answer.

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(1)

(iii) Calculate the entropy change of the surroundings, $\Delta S_{\text{surroundings}}$, at 1123 K for this reaction. Include the sign and units in your final answer.

(2)

(iv) Calculate the total entropy change, ΔS_{total}, for this reaction at 1123 K. Include the sign and units in your final answer. You may assume that ΔS_{system} is unchanged at high temperatures.

(1)

(v) What does your answer to (iv) tell you about the extent of the reaction at 1123 K? Justify your answer.

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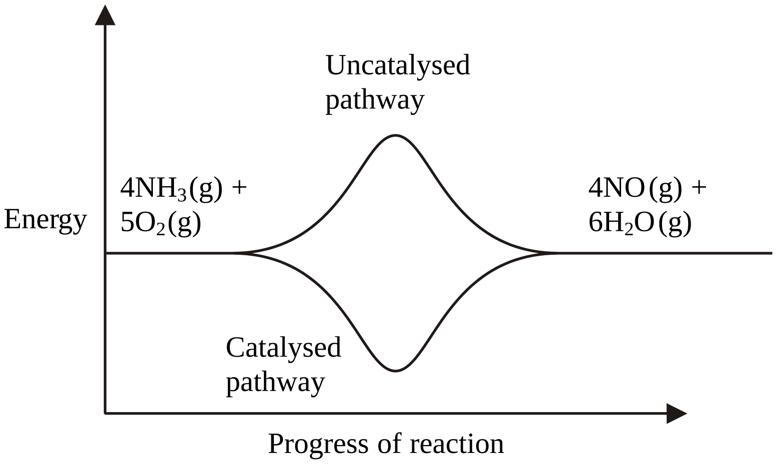
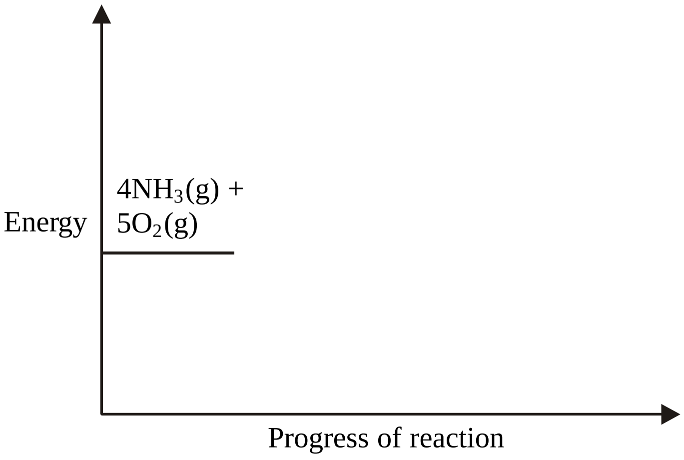
(1)

(vi) An energy profile was proposed to illustrate the effect of the catalyst on this reaction. The proposal has two errors. Draw a corrected version on the axes below.

Proposal



Corrected version



(2)

(b) The oxidation of nitrogen(II) oxide leads to the following equilibrium

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The number of moles of each gas in a reaction mixture at equilibrium, at a pressure of 1.5atm, was found to be

Substance	Number of moles at equilibrium
NO (g)	0.025
O_2 (g)	0.025
NO_2 (g)	4.95

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

(1)

(ii) Calculate the mole fraction of each gas and hence the value of the equilibrium constant, K_p, for this mixture. Include units, if required, in your answer.

(4)

(iii) What does your answer to (ii) tell you about the position of the equilibrium? Justify your answer.

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(1)

(iv) If the total pressure of the reaction mixture was increased, describe what would happen to the value of the equilibrium constant, K_p, and the partial pressure of $NO_2(g)$. In each case justify your answer.

Equilibrium constant, K_p.

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....

Partial pressure of $NO_2(g)$.

....

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(2)
(Total 17 marks)

12. This question is about the reaction between barium hydroxide and ammonium chloride:

$$Ba(OH)_2(s) + 2NH_4Cl(s) \rightarrow BaCl_2.2H_2O(s) + 2NH_3(g) \qquad \Delta H = +21.2 \text{ kJ mol}^{-1}$$

(a) Standard entropies of the reactants and products are shown below:

Substance	Standard entropy, $S^\ominus$ / J mol^{-1} K^{-1}
$Ba(OH)_2(s)$	+ 99.7
$NH_4Cl(s)$	+ 94.6
$BaCl_2.2H_2O(s)$	+202.9
$NH_3(g)$	+192.3

Calculate the standard entropy change for the system, $\Delta S^\ominus_{system}$, for this reaction. Include a sign and units in your answer.

(2)

(b) Calculate the entropy change for the surroundings, $\Delta S^\ominus_{surroundings}$, at 298 K. Give your answer to **3** significant figures and include a sign and units in your answer.

(2)

(c) (i) Use your answers to (a) and (b) to explain why this reaction is spontaneous at 298 K.

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(1)

(ii) When these two solids are mixed together in a beaker, no reaction is observed. What explanation can be given for this, in view of the fact that the process is spontaneous?

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(1)

(iii) Apart from heating the mixture, suggest what might be done to encourage the reaction to take place. Explain why your suggestion is likely to work.

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(2)

(Total 8 marks)

13. The equation below shows the equilibrium existing between nitrogen, oxygen and nitrogen monoxide.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

The equilibrium constant, K_p, at 298 K is 5.0×10^{-31}

(a) (i) Write an expression for the equilibrium constant, K_p, in terms of the partial pressures of the three gases.

(1)

(ii) Why does the value for K_p have no units?

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....

(1)

(b) An equilibrium mixture of these three gases was found to contain nitrogen, at a partial pressure of 0.87 atm, and oxygen, at a partial pressure of 0.23 atm.

(i) Calculate the partial pressure exerted by the nitrogen monoxide.

(2)

(ii) Deduce the value of the total pressure of the equilibrium mixture of gases.

(1)

(iii) Assuming that the total pressure on the mixture of gases is doubled, what, if any, would be the effect on the

- partial pressure of nitrogen monoxide

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- equilibrium constant, K_p?

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(2)

(c) Inside a car engine, air (a mixture of nitrogen and oxygen) is drawn in and, under the high temperatures operating, the value of K_p increases dramatically.

This increase is also accompanied by an increase in the value of ΔS_{total}. Typical values of K_p and ΔS_{total} are shown in the table below.

Temperature / K	K_p	ΔS_{total} / J mol^{-1} K^{-1}
298	5.0×10^{-31}	–580
1500	1.0×10^{-5}	– 96

Although the value of ΔS_{system} is unlikely to alter very much, the value for $\Delta S_{surroundings}$ will change significantly.

(i) At a temperature of 1500 K, ΔS_{total} is negative.

Does this mean that the reaction between nitrogen and oxygen cannot occur at this temperature? Explain your reasoning.

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(1)

(ii) Why is the value for ΔS_{system} for this equilibrium approximately constant when the temperature rises above 298 K?

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(1)

(iii) What is the sign of $\Delta S_{\text{surroundings}}$ for an **endothermic** reaction? Justify your answer.

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(1)

(iv) Explain why an endothermic reaction results in an increase in the value of ΔS_{total} as the temperature increases.

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(1)

(d) A student used the value for K_p at 1500 K to calculate the partial pressure of nitrogen monoxide inside a working car engine.

Why might the actual partial pressure be lower than the calculated answer?

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(1)
(Total 12 marks)

14. Phosphorus(V) chloride dissociates as follows:

$$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g) \qquad \Delta H^\ominus = +\,123.8\ \text{kJ mol}^{-1}$$

Substance	Standard entropy, $S^\ominus$ / J mol^{-1} K^{-1}
$PCl_5(s)$	+ 166.5
$PCl_3(l)$	+ 217.1
$Cl_2(g)$	+ 165.0

(a) (i) Explain why the entropy of solid phosphorus(V) chloride, PCl_5, is smaller than the entropy of liquid phosphorus(III) chloride, PCl_3?

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(1)

(ii) Calculate $\Delta S^\ominus_{system}$ for the forward reaction. Include a sign in your answer.

(1)

(iii) Is the sign of $\Delta S^\ominus_{system}$ as you would expect? Fully justify your answer.

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(2)

(b) Calculate $\Delta S^{\ominus}_{\text{surroundings}}$ for the forward reaction at 298 K. Include a sign and units in your answer.

(2)

(c) (i) Use your answers to calculate $\Delta S^{\ominus}_{\text{total}}$ for the forward reaction at 298 K. Include a sign in your answer.

(1)

(ii) Comment on the position of equilibrium at 298 K.

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(1)

(d) In an experiment to investigate this equilibrium, 41.7 g of phosphorus(V) chloride (molar mass 208.5 g mol^{-1}) was heated in a closed vessel at 150 °C until equilibrium was established. The final pressure was found to be 4.32 atm and 0.15 moles of phosphorus(V) chloride remained. At this temperature all of the reactants and products are gaseous.

(i) Give the expression for the equilibrium constant, K_p, and its units at this temperature.

(2)

(ii) Complete the table

Substance	Moles at start	Moles at equilibrium	Partial pressure at equilibrium, p_{eq} /atm
$PCl_5(g)$		0.15	
$PCl_3(g)$	0		
$Cl_2(g)$	0		
Total number of moles at equilibrium			

(3)

(iii) Calculate K_p.

(1)

(iv) How would you expect the value of K_p to change, if at all, if the following changes were made? Justify each of your answers.

A Only 20.85 g of phosphorus(V) chloride had been used.

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B The temperature had been increased to 250 °C.

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(2)
(Total 16 marks)

15. This question refers to the following reaction at 298 K:

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

	S /J mol^{-1} K^{-1}
$N_2O_4(g)$	304.2
$NO_2(g)$	240.0

(a) Calculate ΔS_{system}, in J mol^{-1} K^{-1}, for this reaction.

A –175.8

B +175.8

C –64.2

D +64.2

(1)

(b) Calculate $\Delta S_{surroundings}$, in J mol^{-1} K^{-1}, for this reaction at 298 K.

A –192

B +192

C –0.192

D +0.192

(1)
(Total 2 marks)

16. This question is about the reaction of magnesium with hydrochloric acid which takes place rapidly at room temperature.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g) \qquad \Delta H = -467 \text{ kJ mol}^{-1}$$

(a) Rewrite the equation omitting spectator ions.

(1)

(b) Suggest the sign of the following entropy changes for this reaction. Justify each of your answers.

(i) ΔS_{system}

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(2)

(ii) $\Delta S_{\text{surroundings}}$

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(2)

(iii) ΔS_{total}

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(1)

(c) A student carried out this experiment at five different temperatures in order to calculate the activation energy of the reaction. The student's laboratory record is shown below.

Method

Clean a strip of magnesium weighing 0.100 g with sand paper. Measure the temperature of 20 cm^3 of 1.00 mol dm^{-3} hydrochloric acid in a 100 cm^3 beaker. Add the magnesium ribbon, stir continuously, and time how long it takes for the magnesium to disappear. Repeat the experiment at four other temperatures.

Assumption*: the initial rate of reaction is proportional to 1/time.*

Results

Temperature /°C	***Temperature /K***	***1/T /K^{-1}***	***time /s***	***1/time /s^{-1}***	***ln 1/time***
24	297	3.37×10^{-3}	45	0.0222	–3.81
33	306	3.27×10^{-3}	25	0.0400	–3.22
45	318	3.14×10^{-3}	11	0.0909	-2.40
56	329	3.04×10^{-3}	6	0.1667	-1.79
10	283	3.53×10^{-3}	122	0.0082	-4.80

The Arrhenius equation is $\ln k = -E_a/R \times (1/T) + \text{constant}$

ln 1/time is proportional to ln k and so a graph of ln 1/time will have the same gradient as that of the Arrhenius plot of ln k against 1/Temperature

The student plotted the graph of ln 1/time against 1/Temperature and from this the activation energy, E_A, was calculated as + 51.3 kJ mol^{-1}.

(i) Suggest the reason for cleaning the magnesium ribbon with sand paper.

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(1)

(ii) Calculate the number of moles of hydrochloric acid used up when all the magnesium reacts in one experiment. Hence comment on whether the change in concentration during the reaction will have a significant effect on the validity of the assumption that the initial rate of reaction is proportional to 1/time. How would you overcome this potential error?

[Take the relative atomic mass of magnesium as 24 in this and subsequent calculations.]

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(5)

(iii) Use the value of ΔH and other information given in the question to calculate the temperature change in an experiment assuming no energy is lost to the surroundings. Hence comment on whether this change in temperature will have a significant effect. How would you overcome this potential error?

[$\Delta H = –467$ kJ mol^{-1}.

heat produced = mass × specific heat capacity × change in temperature.

Assume that the specific heat capacity of the solution is 4.18 J K^{-1} g^{-1}]

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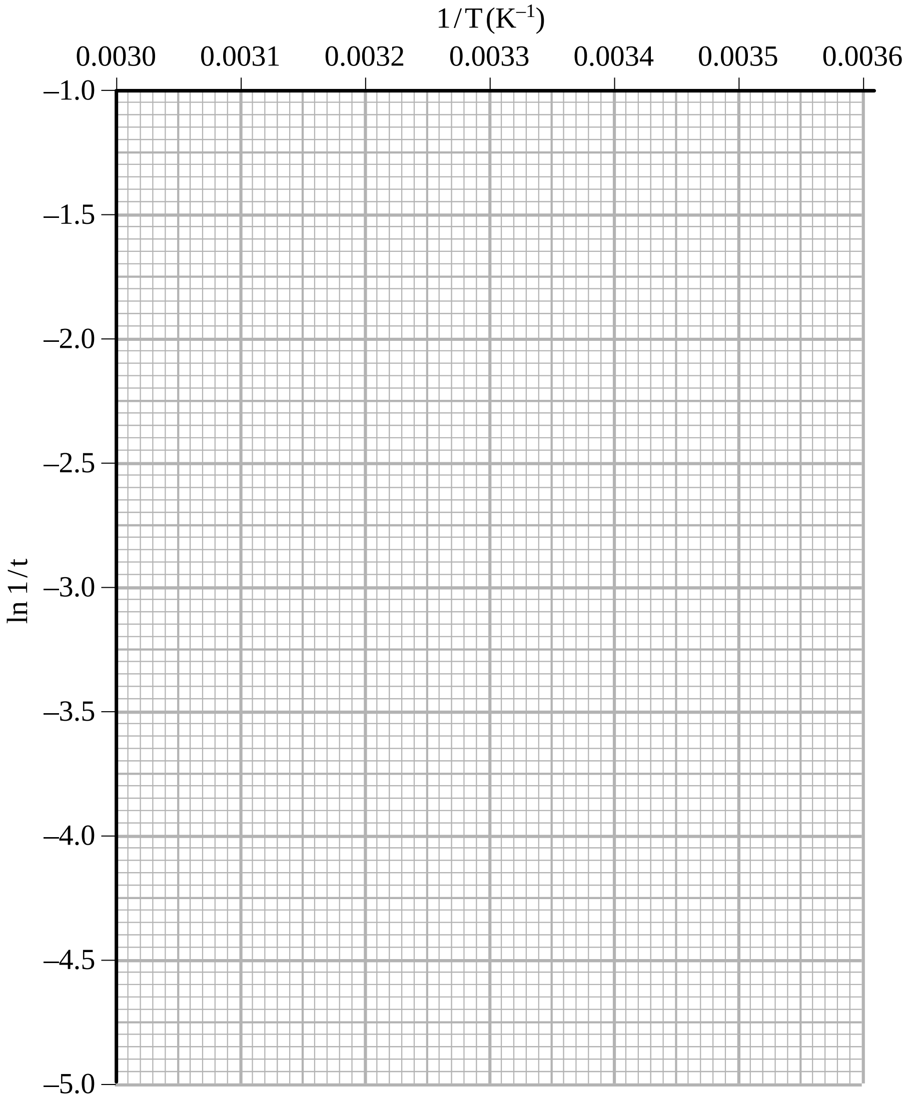
(4)

(iv) The most difficult thing to measure accurately is the time it takes for the magnesium to disappear and the time measured can be up to 2 seconds out. Assuming this error, calculate the shortest time at 56 °C **and** the longest time at 10 °C for this reaction.

Complete the table for these times. Plot the two points on the grid below and join them with a straight line. From the gradient, which equals $-E_A/R$, of this line calculate another value for the activation energy.

Temperature / °C	Temperature /K	1/T /K^{-1}	time /s	1/time /s^{-1}	ln 1/time
56	329	3.04×10^{-3}			
10	283	3.53×10^{-3}			



(v) If the reaction mixture is not stirred, the magnesium tends to float on the surface of the acid.

Suggest how this would affect the measurements of the rate of the reaction.

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(1)

(vi) Suggest **two** other improvements the student could do to this experiment to improve the accuracy or validity of the results.

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(2)

(vii) If ethanoic acid of the same concentration and at the same temperature is used instead of hydrochloric acid, explain how the rate would differ.

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(1)

(Total 24 marks)