4 The reaction of ammonia, NH_3, with oxygen to form nitrogen monoxide, NO, is an important industrial process.

The equation for this reaction is shown in **equilibrium 4.1** below.

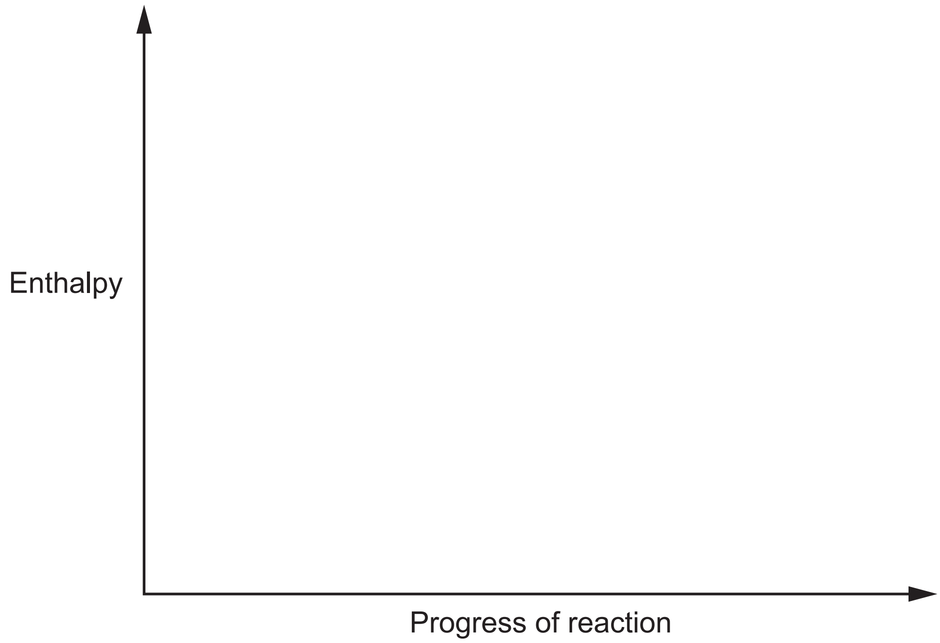
$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ $\Delta H = -905\ kJ\ mol^{-1}$ **Equilibrium 4.1**

(a) The forward reaction in **equilibrium 4.1** converts NH_3 into NO.

(i) Complete the enthalpy profile diagram for this reaction.

On your diagram:

- Label the activation energy, E_a
- Label the enthalpy change of reaction, ΔH
- Include the formulae of the reactants and products.



[2]

(ii) 5.10 tonnes of NH_3 are converted into NO.

Calculate the energy released, in kJ, for this conversion.

Give your answer in **standard form** and to an **appropriate** number of significant figures.

energy released = ... kJ **[4]**

(b) Write an expression for the equilibrium constant, K_c, in **equilibrium 4.1**.

[1]

(c) Predict the conditions of temperature and pressure for a maximum equilibrium yield of nitrogen monoxide in **equilibrium 4.1**.

- Explain your prediction in terms of le Chatelier's principle.
- State and explain how these conditions could be changed to achieve a compromise between equilibrium yield, rate and other operational factors.

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.... **[5]**

3 Nitrogen can be reacted with hydrogen in the presence of a catalyst to make ammonia in the Haber process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92 \text{ kJ mol}^{-1}$$

(a) Describe and explain the effect of increasing the pressure on the rate of this reaction.

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.... **[2]**

(b) A mixture of N_2 and H_2 was left to react until it reached equilibrium. The equilibrium mixture had the following composition:

N_2	1.20 mol dm^{-3}
H_2	2.00 mol dm^{-3}
NH_3	0.877 mol dm^{-3}

(i) Calculate a value for K_c for this equilibrium.

K_c = ... $dm^6 \text{ mol}^{-2}$ **[3]**

(ii) Explain how the following changes would affect the amount of NH_3 present in the equilibrium mixture.

Use of a catalyst:

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A higher temperature:

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[3]

(c) 1.00 tonne of ammonia from the Haber process is reacted with carbon dioxide to prepare the fertiliser urea, NH_2CONH_2.

$$2NH_3(g) + CO_2(g) \rightarrow NH_2CONH_2(s) + H_2O(l)$$

1.35 tonnes of urea are formed.

Calculate the percentage yield of urea.

Show **all** your working.

yield = ... % **[3]**

25 Sulfur trioxide, SO_3, is used for the industrial manufacture of sulfuric acid.

SO_3 is produced by reacting sulfur dioxide, SO_2, and oxygen, O_2, as shown in **equilibrium 25.1** below.

Equilibrium 25.1 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -197\,kJ\,mol^{-1}$

(a) Le Chatelier's principle can be used to predict how different conditions affect the equilibrium position.

- Using le Chatelier's principle, show that a low temperature and a high pressure should be used to obtain a maximum **equilibrium** yield of SO_3.
- Explain why the actual conditions used in industry may be different from the conditions needed for a maximum equilibrium yield.

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.... **[5]**

(b) Under certain conditions, K_c for **equilibrium 25.1** is 0.160 $dm^3 mol^{-1}$.

The equilibrium mixture under these conditions has the following concentrations of SO_2 and O_2.

Species	**Equilibrium concentration / $mol dm^{-3}$**
SO_2	2.00
O_2	1.20

- Using the value of K_c, explain whether the equilibrium position will be towards the right or towards the left under these conditions.
- Calculate the concentration of SO_3 in the equilibrium mixture.

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.... **[4]**

18 Nitrogen monoxide, NO, and oxygen, O_2, react to form nitrogen dioxide, NO_2, in the reversible reaction shown in **equilibrium 18.1**.

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ **Equilibrium 18.1**

(a) Write an expression for K_c for this equilibrium and state the units.

K_c =

Units = ... **[2]**

(b) A chemist mixes together nitrogen and oxygen and pressurises the gases so that their total gas volume is 4.0 dm^3.

- The mixture is allowed to reach equilibrium at constant temperature and volume.
- The equilibrium mixture contains 0.40 mol NO and 0.80 mol O_2.
- Under these conditions, the numerical value of K_c is 45.

Calculate the amount, in mol, of NO_2 in the equilibrium mixture.

amount of NO_2 = ... mol **[4]**

(c) The values of K_p for **equilibrium 18.1** at 298 K and 1000 K are shown below.

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ **Equilibrium 18.1**

Temperature / K	**K_p / atm^{-1}**
298	$K_p = 2.19 \times 10^{12}$
1000	$K_p = 2.03 \times 10^{-1}$

(i) Predict, with a reason, whether the forward reaction is exothermic or endothermic.

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.... **[1]**

(ii) The chemist increases the pressure of the equilibrium mixture at the same temperature.

State, and explain in terms of K_p, how you would expect the equilibrium position to change.

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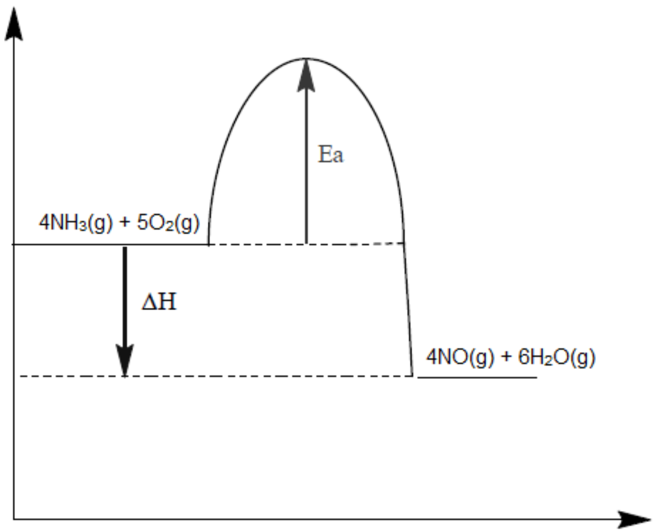
.... **[3]**

Question			Answer	Marks	Guidance
4	(a)	(i)	 **Reactants, products and E_a** Reactants on LHS **$4NH_{3(g)} + 5O_{2(g)}$** **AND** Products on RHS **$4NO_{(g)} + 6H_2O_{(g)}$** **AND** Activation energy correctly labelled / E_a ✓ **Δ*H*** Δ*H* labelled with product below reactant **AND** Arrow downwards ✓	2	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **IGNORE** state symbols ALLOW 1 mark for a correctly labelled endothermic diagram **E_a** **ALLOW** no arrowhead or arrowheads at both end of E_a line. E_a line must reach maximum (or near to maximum) on curve For E_a, **ALLOW** AE **OR** A_E **Δ*H*** **DO NOT ALLOW –Δ*H*** **DO NOT ALLOW** double headed arrow on Δ*H* **ALLOW** Δ*H* arrow even with small gap at the top and bottom, i.e. line does not quite reach reactant or product line. **ALLOW** –905 for Δ*H*

Question			Answer	Marks	Guidance
		(ii)	**FIRST CHECK ON ANSWER LINE** **If answer = 6.79 × 10^7 (kJ) award 4 marks** **If answer = 2.72 × 10^8 (kJ) award 3 marks** (no ÷ 4) -- ***n*(NH_3)** = $\frac{5.1 \times 10^6}{17}$ = 3.00 × 10^5 (mol) ✓ **Stoichiometry and Δ*H*** 1 mol NH_3 releases $\frac{905}{4}$ **OR** 226.25 (kJ) ✓ **Energy released** (3.00 × 10^5) × $\frac{905}{4}$ **OR** 67875000 (kJ) ✓ **Final answer to 3SF AND standard form** = 6.79 × 10^7 (kJ) ✓ *standard form* **AND** *3 SF required*	4	**IGNORE** (-) SIGN Throughout: **IGNORE** trailing zeroes in intermediate working, e.g. For *n*(NH_3) **ALLOW** 3 × 10^5 for 3.00 × 10^5 -- **ALLOW ECF** from incorrect *n*(NH_3) **OR** 905/4 **ALLOW 3 SF** up to calc value correctly rounded. Value will depend on intermediate rounding **Common Errors** 1.09 × 10^9 (x 4 instead of ÷ 4) 3 marks 2.72 × 10^8 (no ÷ 4) 3 marks 6.79 × 10^1 (no tonnes → g) 3 marks
	(b)		(K_c =) $\frac{[NO(g)]^4\,[H_2O(g)]^6}{[NH_3(g)]^4\,[O_2(g)]^5}$ ✓	1	Square brackets required **IGNORE** state symbols

Question			Answer	Marks	Guidance
4	(c)		***EQUILIBRIUM CONDITIONS*** **Temperature: 1 mark** (Forward) reaction is exothermic/Δ*H* is negative **OR** (Forward) reaction gives out heat ✓ **Pressure: 1 mark** Left-hand side has fewer (gaseous) moles **OR** 9 (gaseous) moles form 10 (gaseous) moles ✓ ***OPTIMUM EQUILIBRIUM CONDITIONS:* 1 mark** (for maximum yield of NO) Low temperature **AND** low pressure ✓ ***RATE:* 1 mark** Low temperature/pressure gives a slow rate/slower reaction so high temperatures / higher pressure needed to increase **rate OR frequency of collisions** ✓ ***INDUSTRIAL CONDITIONS* / OPERATIONAL FACTORS: 1 mark** High pressure provides a safety risk **OR** Higher temperatures increase energy costs / reduce yield / shift equilibrium to left **OR** (High) pressure is expensive (to generate) / uses a lot of energy ✓	5	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **ALLOW reverse arguments** Answer **MUST** relate temp/pressure to rate / frequency of collisions **ALLOW** Temperature / pressure not too high because yield reduced **IGNORE** stated temperatures and pressures **IGNORE** catalyst
			Total	**12**	

Question			Answer	Marks	Guidance
3	(a)		(Increase in pressure) increases the rate **AND** because molecules are closer together… ✓ … so there are more collisions per unit time ✓	2	**ALLOW** more particles per unit volume **NOT** molecules move faster or have more energy
	(b)	(i)	*Expression:* $K_c = [NH_3]^2 / [H_2]^3[N_2]$ ✓ *Calculation:* $= (0.877)^2/(2.00)^3(1.20)$ ✓ = 0.0801 ✓ ($dm^6\ mol^{-2}$)	3	Square brackets required **ALLOW** from 1 sig fig up to calculator display Correct answer alone scores all marks
		(ii)	*Catalyst:* No effect, it only changes the rate of reaction ✓ *Higher temperature:* Forward reaction is exothermic ✓ so position of equilibrium moves to the left and there will be less NH_3 ✓	3	

Question			Answer	Marks	Guidance
	(c)		**FIRST CHECK THE ANSWER ON THE ANSWER LINE** **IF** answer = 76.5 (%) award 3 marks $n(NH_3) = (1 \times 10^6) / 17 = 5.88 \times 10^4$ (58824) (mol) **AND** *Theoretical yield:* $n(NH_2CONH_2) = 5.88 \times 10^4 / 2 = 2.94 \times 10^4$ (29412) (mol) ✓ *Actual yield:* $n(NH_2CONH_2) = 1.35 \times 10^6 / 60 = 2.25 \times 10^4$ (22500) (mol) ✓ % yield = $(2.94 \times 10^4 / 2.25 \times 10^4) \times 100\%$ = 76.5(%) ✓	3	**If there is an alternative answer, check to see if there is any ECF credit possible using working below** **ALLOW** up to full calculator display For 2nd and 3rd marks, **ALLOW** calculation in mass. *Theoretical mass yield:* $m(NH_2CONH_2) = 60 \times 5.88 \times 10^4 / 2$ = 1.764 tonne ✓ % yield = (1.35 / 1.764) × 100 = 76.5% ✓ **ALLOW** 76% (2 sig figs) up to calculator answer correctly rounded from previous values **ALLOW ECF** from calculated actual and theoretical yields
			Total	**11**	

Question			Answer	Marks	AO element	Guidance
25	(a)		***EQUILIBRIUM CONDITIONS 3 MAX*** **4 marking points → 3 max** ✓✓✓ *Mark first three **CORRECT** responses seen* **Temperature**: (Forward) reaction is exothermic/Δ*H* is negative **OR** (Forward) reaction gives out heat ✓ **Pressure**: Right-hand side has fewer (gaseous) moles **OR** 3 (gaseous) moles form 2 (gaseous) moles ✓ **Equilibrium shift** Correct equilibrium shift in terms of **temperature** ✓ Correct equilibrium shift in terms of **pressure** ✓ -- ***INDUSTRIAL CONDITIONS*** Low temperature gives a slow rate/slower reaction **OR** high temperatures needed to increase rate ✓ (High) pressure provides a safety risk **OR** (High) pressure is expensive (to generate) /uses a lot of energy ✓	5	AO3.1 ×2 AO3.2 ×1 ----------- AO1.2 ×2	***FULL ANNOTATIONS MUST BE USED*** - **ALLOW** suitable alternatives for 'towards right', e.g.: towards SO_3/products **OR** in forward direction **OR** 'favours the right' **ALLOW reverse** reaction is endothermic /Δ*H* is positive/takes in heat For moles, **ALLOW** molecules/particles **ORA for** reverse reaction **IGNORE** responses in terms of activation energy **ALLOW** high pressure is dangerous/explosive **ALLOW** 'These conditions are expensive' *Statement subsumes **pressure** as 'these' will apply to **pressure** (required for this mark) and temperature* **ALLOW ORA** e.g. Lower pressure → less danger/uses less energy **IGNORE** 'It's expensive *Link with pressure required*

Question			Answer	Marks	AO element	Guidance
	(b)			4		***FULL ANNOTATIONS MUST BE USED***
			Value of K_c 1 mark K_c is small **OR** $K_c < 1$ **AND** equilibrium (position) is towards left ✓		AO3.2	**ALLOW** suitable alternatives for 'towards left, e.g.: towards SO_2/O_2 **OR** towards reactants **OR** in reverse direction **OR** 'favours the left
			Calculation: **FIRST CHECK ANSWER** **IF $[SO_3]$ = 0.876 *OR* 0.88 (mol dm^{-3})** **award all 3 marks available for calculation** ------------------------------------ **K_c expression 1 mark** $\frac{[SO_3]^2}{[SO_2]^2[O_2]}$ **OR** $\frac{[SO_3]^2}{2.00^2 \times 1.20}$ ✓ **Evaluation of K_c $[SO_2]^2[O_2]$ 1 mark** K_c $[SO_2]^2[O_2]$ = $0.160 \times 2.00^2 \times 1.20$ = 0.768 ✓ **Calculation of $[SO_3]$** ***ONLY*** *available from* ***correct*** *evaluation for 2nd mark* $[SO_3] = \sqrt{(0.160 \times 2.00^2 \times 1.20)}$ = 0.876 (mol dm^{-3}) ✓		AO1.2 AO2.6 AO2.6	Square brackets required in K_c expression **ALLOW ECF** from $\frac{[SO_3]}{[SO_2]^2[O_2]}$, i.e. no $[SO_3]^2$ **ALLOW 0.77 (2 SF)** **ALLOW 0.88** (**2 SF**) up to calculator value of 0.876356092 correctly rounded **IF** K_c expression is inverted 2nd and 3rd marks are available by **ECF**: $[SO_3]^2 = \frac{2.00^2 \times 1.20}{0.160}$ **OR** 30 ✓ $[SO_3] = \sqrt{30}$ = 5.48 **OR** 5.5 ✓ Any other K_c expression → **NO MARKS,** e.g. $\frac{[SO_3]^2}{[SO_2]^2 + [O_2]} \rightarrow \sqrt{0.832} \rightarrow 0.912$ **NO** marks
			Total	9		

Question			Answer	Marks	Guidance
18	(a)		$K_c = \frac{[NO_2]^2}{[NO]^2\,[O_2]}$ ✓ Units = $dm^3\ mol^{-1}$ ✓	2	Must be square brackets **IGNORE** state symbols **ALLOW** $mol^{-1}\ dm^3$ **ALLOW** $mol\ dm^{-3}$ as ECF from inverted K_c expression
	(b)		**FIRST CHECK THE ANSWER ON THE ANSWER LINE IF answer = 1.2 (mol) award 4 marks** **Unless otherwise stated, marks are for correctly calculated values. Working shows how values have been derived.** $[NO] = \frac{0.40}{4.0}$ = 0.1(0) ($mol\ dm^{-3}$) **AND** $[O_2] = \frac{0.80}{4.0}$ = 0.2(0) ($mol\ dm^{-3}$) ✓ $[NO_2]^2 = 45 \times 0.10^2 \times 0.20$ **OR** = 0.09(0) ✓ $[NO_2] = \sqrt{(45 \times 0.10^2 \times 0.20)}$ **OR** = 0.3(0) ($mol\ dm^{-3}$) ✓ amount NO_2 = 0.30 × 4 = 1.2 (mol) ✓	4	***ANNOTATIONS MUST BE USED*** For **all** parts, **ALLOW** numerical answers from 2 significant figures up to the calculator value Ignore rounding errors after second significant figure 1st mark is for realising that concentrations need to be calculated. **ALLOW ECF** **Correct numerical answer with no working would score all previous calculation marks** Making point 2 subsumes point 1 Making point 3 subsumes points 2 and 1 Common errors 9.6 = 3 marks mol of NO and O_2 used 0.36 = 3 marks mol of NO_2 calculated from $[NO_2]^2$ 2.4 = 2 marks mol of NO and O_2 used and no mol of NO_2 calculated

Question			Answer	Marks	Guidance
	(c)	(i)	Exothermic **AND** K_p decreases as temperature increases ✓	1	**ALLOW** K_c for K_p **ALLOW** Equilibrium shifts to left hand side as temperature increases
	(c)	(ii)	***Equilibrium shift*** (Equilibrium position) shifts to right / forward / towards products ✓ ***Effect of increased pressure on K_p expression*** Ratio (in K_p expression) decreases **OR** Denominator/bottom of K_p expression increases more (than numerator/top) ✓ ***Equilibrium shift (K_p expression)*** Ratio (in K_p expression) increases **to restore K_p** **OR** Numerator/top of K_p expression increases **to restore K_p** ✓	3	**FULL ANNOTATIONS NEEDED** **ALLOW** K_c for K_p throughout the response. **ALLOW** K_p (initially) decreases for second marking point **IF** K_p is seen to be restored later in the process. **ALLOW** more NO_2 / product formed to restore K_p **ALLOW** ratio adjusts to restore K_p
			Total	**10**	