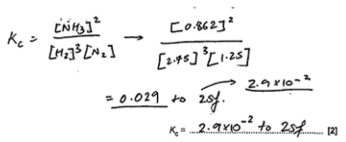
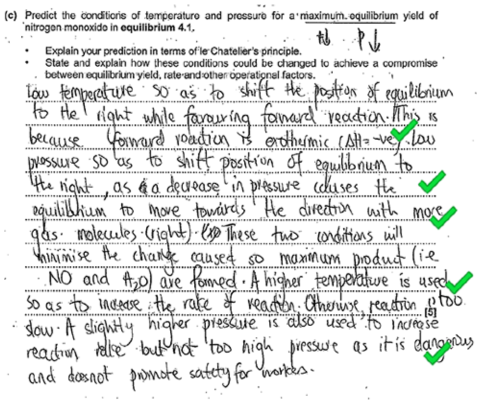
Mark scheme – Equilibrium

Question			Answer/Indicative content	Marks	Guidance
1		i	**Pressure:** Right-hand side has fewer (gaseous) moles **OR** 4 (gaseous) moles form 2 (gaseous) moles ✓ High pressure ✓ **Temperature:** (Forward) reaction is exothermic/ΔH is negative **OR** (Forward) reaction gives out heat ✓ Low temperature ✓	4 (AO1.2) (AO2.1) (AO1.2) (AO2.1)	FULL ANNOTATIONS MUST BE USED --- **ALLOW** suitable alternatives for right-hand side, e.g.: towards NH_3/products **OR** forward direction **OR** increases yield For moles, **ALLOW** molecules/particles **ALLOW reverse** reaction is endothermic /ΔH is positive/takes in heat **ORA** for reverse reaction **<u>Examiner's Comments</u>** This question was answered well with many candidates being given all 4 marks. Most candidates identified that there are fewer gaseous moles of products and that an increase the pressure will shift the equilibrium position to the right. Although the exothermic nature of the forward reaction was usually identified, candidates sometimes muddled the temperature conditions required, with 'higher temperature' being seen often instead of 'low temperature'. Lower attaining candidates often seemed to confuse equilibrium (in this question) with rates.
		ii	**FIRST CHECK THE ANSWER ON ANSWER LINE** **IF answer = 2.86 × 10^{-2} award 2 marks** ---– ***K_c* expression** $(K_c =)\ \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$ **OR** $\frac{0.862^2}{1.25 \times 2.75^3}$ **OR** 0.02858 ………… ✓ **Answer to 3 SF and in standard form** $Kc = 2.86 \times 10^{-2}$ ✓	2 (AO2.6×2)	**IF** there is an alternative answer, check for any **ECF** credit possible using working below. --- **ALLOW** calculated value 0.02858291 correctly rounded to 3 or more SF for 1st marking point **ALLOW ECF to 3 SF and standard form ONLY** from inverted K_c expression → 3.50×10^1 **DO NOT ALLOW** $\frac{[NH_3]^2}{[N_2] + [H_2]^3}$ = 0.0337 (no marks)

					IGNORE attempts at units **Examiner's Comments** **Exemplar 5**  This part discriminated well. Most candidates were able to write the correct expression for K_c as the starting point of the calculation. Candidates often got into a muddle in calculating K_c, perhaps due to issues inputting the calculation into their calculators. The question asked for 'an appropriate number of significant figures and in standard form'. As the provided data was all to 3 significant figures, this also indicates the required number of significant figures in the answer. A calculated value to 2 significant figures was often seen (see the response); also 0.0286 rather than the standard form: 2.86×10^{-2}. Some responses showed K_c inverted or added, rather than multiplying the two reactants in the denominator. Other candidates wrote the correct equilibrium expression but were then used 2.75^2, rather than 2.75^3, to obtain the standard form answer of 7.786×10^{-2} or 0.0786 with no standard form. Candidates are advised to check back through calculations to see if they have made any such errors.
			Total	**6**	
2	a		$(K_c =)\ \frac{[NO(g)]^4\,[H_2O(g)]^6}{[NH_3(g)]^4\,[O_2(g)]^5}$ ✓	1	Square brackets required **IGNORE** state symbols **Examiner's Comments** Generally, this question was well answered with only a small proportion of candidates adding the values together instead of multiplying.
	b		***EQUILIBRIUM CONDITIONS*** **Temperature: 1 mark** (Forward) reaction is exothermic/ΔH is negative **OR** (Forward) reaction gives out heat ✓	5	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC**

			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 ✓		**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 **<u>Examiner's Comments</u>** Most candidates answered this question very well, with the most common mark being 4/5. Many candidates put a lot of effort into explaining, in depth, Le Chatelier's principle, which was not required. The first three marking points were credited to most candidates. Responses were confident in their descriptions of equilibrium shifts and many candidates then went on to qualify their answers with operational factor considerations and/or rate. The explanation for pressure was described less commonly than temperature and many candidates did not appreciated that increased rate would lead to a decreased equilibrium yield. **Exemplar 3**  (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. T↓ P↓ low temperature so as to shift the position of equilibrium to the right while favouring forward reaction. This is because forward reaction is exothermic (ΔH = -ve). low pressure so as to shift position of equilibrium to the right, as a decrease in pressure causes the equilibrium to move towards the direction with more gas molecules (right). These two conditions will minimise the change caused so maximum product (i.e NO and H₂O) are formed. A higher temperature is used so as to increase the rate of reaction. Otherwise, reaction is too slow. A slightly higher pressure is also used to increase reaction rate but not too high pressure as it is dangerous and does not promote safety for workers. [5] This candidate scored all five marks for this well-reasoned approach to the question.
			Total	**6**	

3		i i	*Expression:* $K_c = [NH_3]^2 / [H_2]^3[N_2]$ (1) *Calculation:* $= (0.877)^2/(2.00)^3(1.20)$ (1) = 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 (1) *Higher temperature:* Forward reaction is exothermic (1) so position of equilibrium moves to the left and there will be less NH_3 (1)	3	
			Total	**6**	
4			**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = 14.6 ($dm^2\ mol^{-6}$) award 2 marks** --- **K_c expression** (K_c =) $\frac{[CH_3OH]}{[CO]\ [H_2]^2}$ **OR** 0.26 / 0.31□0.24^2 **OR** 14.56 …… ✓ **Answer to 3 SF** 14.6 ($dm^6\ mol^{-2}$) ✓	**2**	**FULL ANNOTATIONS MUST BE USED** --- **IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below. --- **ALLOW** calculated value 14.5609319 correctly rounded to 3 or more SF for 1st marking point **ALLOW ECF to 3 SF ONLY** from inverted K_c expression → 0.0687 **DO NOT ALLOW** $\frac{[CH_3OH]}{[CO] + [H_2]^2}$ = 0.707 (no marks) **Examiner's Comments** Most candidates were able to obtain a value of 14.56 using a correct K_c expression, but a significant number of candidates were unable to give their answer to an appropriate number of significant figures. Candidates should use the least accurate data provided, here three significant figures, and to indicate the appropriate number of significant figures in the final answer. Other common errors included the inverted K_c expressions and use of [CO] + [$2H_2$], rather than [CO] $[H_2]^2$, as the denominator. Answer = 14.6 $dm^6\ mol^{-2}$
			Total	**2**	

5	a		**Addition of acid** $[H^+]$ **OR** H^+ increases **AND** equilibrium (position) shifts to right ✓ **Addition of alkali** Alkali reacts with H^+ **OR** alkali removes H^+ **AND** equilibrium (position) shifts to left ✓	2	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **IGNORE** amount of acid increases *(in question)* **ALLOW** (added) acid reacts with CrO_4^{2-} **Note: ALLOW** suitable alternatives for 'to right', e.g.: towards products **OR** towards $Cr_2O_7^{2-}$ / H_2O **OR** in forward direction **OR** favours the right **ALLOW** $H^+ + OH^- \rightarrow H_2O$ **ALLOW** alkali reacts with (added) acid **Note: ALLOW** suitable alternatives for 'to left', e.g.: towards reactants **OR** towards CrO_4^{2-} / H^+ **OR** in reverse direction **OR** favours the left **IGNORE** just H^+ concentration decreases *(needs role of alkali)* **IGNORE** concentration of water increases *(needs role of alkali)* **Examiner's Comments** This question discriminated well and the strongest candidates provided succinct responses with the correct level of scientific content. The first mark was awarded for recognition that adding an acid would increase the concentration of H^+ ions, causing the equilibrium to shift to the right. Most candidates realised this was the case. However, it was not uncommon to see vague responses that simply re-stated the information in the question, rather than focussing on the effect it would have on the species in the equilibrium equation. The second mark proved more difficult. The strongest candidates identified that the added alkali would remove H^+ ions from the equilibrium mixture, and some supported this statement with an equation. Many however, simply stated that the equilibrium would shift left to reduce the concentration of the alkali without attempting to relate it to the equation provided. Candidates are advised to consider the chemical equations provided with a

					question as they will help form the basis from which to build a response.
	b	i	Equilibrium (position) shifts to right **AND** turns paler (brown) ✓ Right-hand side has fewer (gaseous) moles / molecules **OR** left-hand side has more (gaseous) moles / molecules ✓	2	**ALLOW** turns colourless **IGNORE** initially goes darker (brown) **Note: ALLOW** suitable alternatives for 'to right', e.g.: towards products **OR** towards N_2O_4 **OR** in forward direction **OR** favours the right **IGNORE** responses in terms of rate **Examiner's Comments** The effect of pressure on the position of an equilibrium is well known by candidates. Most were able to apply le Chatelier's principle accurately stating the equilibrium shifted to the right as that was the side with fewest moles of gas. However a significant proportion of the cohort did not comment on the effect on the appearance of the equilibrium mixture.
		ii	Equilibrium (position) shifts to left **AND** turns darker / deeper (brown) ✓ (Forward) reaction is exothermic **OR** (forward) reaction gives out heat **OR** reverse reaction is endothermic **OR** reverse reaction takes in heat ✓	2	**ALLOW** turns brown **Note: ALLOW** suitable alternatives for 'to left', e.g.: towards reactants **OR** towards NO_2 **OR** in reverse direction **OR** favours the left **IGNORE** comments about the 'exothermic side' or 'endothermic side' **ALLOW** 'equilibrium (position) shifts left **AND** in the endothermic direction' for second marking point **IGNORE** responses in terms of rate **Examiner's Comments** As with part (a)(i), candidates demonstrated an excellent grasp of le Chatelier's principle but it was only the most able candidates who referred to the appearance of the equilibrium mixture. Candidates should be encouraged to read questions carefully to ensure they include all the required information in their responses.
			Total	**6**	

6	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	***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* **<u>Examiner's Comments</u>** This longer answer was answered very well with the majority of candidates able to score 4 or 5 marks. Most candidates explained how the position of equilibrium shifts in response to low temperature and high pressure. The commonest omission was the link between low temperature and a slow reaction rate.
	b		***Value of K_c 1 mark*** K_c is small **OR** $K_c < 1$ **AND** equilibrium (position) is towards left ✓ ***Calculation:*** **FIRST CHECK ANSWER** **IF [SO_3] = 0.876 OR 0.88 (mol dm^{-3})** **award all 3 marks available for calculation** ___	4	***FULL ANNOTATIONS MUST BE USED*** ___ **ALLOW** suitable alternatives for 'towards left, e.g.: towards SO_2/O_2 **OR** towards reactants **OR** in reverse direction **OR** 'favours the left

			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** **Kc**$[SO_2]^2[O_2]$ = 0.160 × 2.00² × 1.20 = 0.768 ✓ **Calculation of $[SO_3]$** ***ONLY** available from **correct** evaluation for 2nd mark* $[SO_3]$ = √(0.160 × 2.00² × 1.20) = 0.876 (mol dm⁻³) ✓		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 ✓ $[SO_3]$ = √30 = 5.48 **OR** 5.5 ✓ Any other K_c expression → **NO MARKS,** e.g. $\frac{[SO_3]^2}{[SO_2]^2 + [O_2]}$ → √0.832 → 0.912 **NO** Marks **<u>Examiner's Comments</u>** Given that K_c is new to AS level in the reformed specification, this part was attempted well. However, writing a correct K_c did cause problems for weaker candidates, who sometimes inverted the expression, used the + sign from the equation, obtaining a denominator of $[SO_2]^2 + [O_2]$, or omitted the square from $[SO_2]^2$ and $[SO_3]^2$. Some excellent answers were seen and this part differentiated very well between candidates of different abilities. Answer: $[SO_3]$ = 0.876 mol dm⁻³
			Total	**9**	
7	a		The (position of a dynamic) equilibrium shifts to minimise (the effect of) any change ✓	1	**ALLOW** suitable alternatives for 'shifts' and 'minimises' **IGNORE** 'reaction shifts' **Examiner's Comments** Most candidates were able to describe le Chatelier's principle.
	b	i	**Pressure:** Right-hand side has fewer (gaseous) moles / molecules **OR** left-hand side has more (gaseous) moles / molecules ✓	3	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **DO NOT ALLOW** fewer atoms on right-hand side **OR** more atoms on left-hand side.

			Temperature: Statement that: (Forward) reaction is exothermic **OR** (forward) reaction gives out heat **OR** reverse reaction is endothermic **OR** reverse reaction takes in heat ✓ **Equilibrium** Lower temperature / cooling **AND** increasing pressure shifts (equilibrium position) to the right ✓		**IGNORE** comments about the 'exothermic side' or 'endothermic side' **Equilibrium mark** is for stating that **BOTH** low temperature and high pressure shift equilibrium to the right (Could be separate statements) **Note: ALLOW** suitable alternatives for 'to right' , e.g.: towards products **OR** towards CH_3OH / H_2O **OR** in forward direction **OR** favours the right **IGNORE** Increases yield of CH_3OH / products (*in question*) **IGNORE** responses in terms of rate **Examiner's Comments** A good discrimination was achieved by this question. The most able candidates gave succinct responses which related the low temperature and high pressure to the change in equilibrium position. Candidates are encouraged to write as accurately as possible in this type of question. For example, the effect of pressure is best explained by reference the relative number of moles on each side of the equation. A statement about the nature of the forward reaction, in this case exothermic, is appropriate to explain the effect of temperature.
		ii	Low temperature gives a slow rate **OR** high temperatures needed to increase rate ✓ High pressure is expensive (to generate) **OR** high pressure provides a safety risk ✓	2	**ALLOW** high pressure is dangerous **IGNORE** high pressure is explosive **Examiner's Comments** Most candidates identified high pressures as either dangerous or requiring expensive equipment. The strongest responses linked low temperature with a slow rate of reaction.
			Total	**6**	

8		i	Rate of the forward reaction is equal to the rate of the reverse reaction ✓ **OR** concentrations do not change✓	1	**ALLOW** both reaction**s** occur at same rate **IGNORE** conc. of reactants = conc. of products **Examiner's Comments** A good proportion of candidates recognised the need to provide one of the key features of a dynamic equilibrium as outlined in the specification.
		ii	More H_2 and I_2 OR less HI ✓ (equilibrium position shifts) to the left **AND** (Forward) reaction is exothermic **OR** reverse reaction is endothermic **OR** in the endothermic direction✓	2	**Mark each point independently** **ALLOW** more reactants **OR** less products **Note: ALLOW** suitable alternatives for to the left e.g. towards reactants **OR** towards H_2 / I_2 **OR** in reverse direction **OR** favours the left. **ALLOW** gives out heat for exothermic **ALLOW** takes in heat for endothermic **IGNORE** responses in terms of rate **Examiner's Comments** This question required candidates to apply le Chatelier's Principle to the equilibrium and in addition predict the effect it would have on the composition of the mixture. Most candidates were able to predict and explain the shift in the position of equilibrium and the most able stated the effect on the composition of the mixture. Candidates should be encouraged to read questions carefully to ensure they address all aspects in their response.
		iii	No effect **AND** Same number of (gaseous) moles on both sides ✓	1	**ALLOW** same number of molecules on each side **Examiner's Comments** This question was answered very well and most candidates picked up this mark.

			Total	**4**	
9			** Please refer to the marking instruction point 10 for guidance on how to mark this question.* **(Level 3)** All/most points covered and clearly linked. Must have points taken across all of the headings in the indicative points for Level 3. *The explanations show a well-developed line of reasoning linked to appropriate suggestions which is clear and logically structured. The compromises are relevant and well thought out and clearly linked to the explanations.* (5–6 marks) **(Level 2)** Suggests correct conditions with explanations **OR** comments on compromises with reference to yield **AND** rate effect. *The explanations are linked to appropriate suggestions and show a line of reasoning with some structure. The compromises are relevant but may not be clearly linked to the explanation.* (3–4 marks) **(Level 1)** Comments on conditions with some explanation **OR** comments on compromise with reference to yield **OR** rate. *The comments about yield / rate with explanation are basic and communicated in an unstructured way. The compromises may not be relevant with lack of reasoning.* (1–2 marks) No response or no response worthy of credit. (0 marks)	6	**Indicative scientific points may include** Yield • Increasing pressure increases yield of SO_3 • Decreasing temperature increases yield of SO_3 Explanation • (pressure) more moles / molecules on the reactant side **ORA** • (temp.) the forward reaction is exothermic **ORA** Rate • Increasing pressure increases rate • Increasing temperature increases rate Compromise • Choose a higher temperature which creates a reduced yield but in a shorter space of time **ignore** reference to increase pressure leading to safety / cost issues
			Total	**6**	
10	a	i	$K_c = \frac{[CH_3OH]}{[CO][H_2]^2}$	1	
		ii	$[CH_3OH] = 14.6 \times (3.10 \times 10^{-3}) \times (2.40 \times 10^{-3})^2$ (1) $= 2.61 \times 10^{-7}$ (mol dm^{-3}) (1)	2	
	b	i	Yield decreases **AND** Equilibrium (position) has moved to the left	1	**allow** moved towards reactants **OR** moved towards CO and H_2

		ii	Oxidised Nitrogen **AND** −3 **AND** +2 (1) Reduced Oxygen **AND** 0 **AND** −2 (1)	2	
			Total	**6**	