Mark scheme

<table>
<tr><th colspan="3">Question</th><th>Answer/Indicative content</th><th>Marks</th><th>Guidance</th></tr>
<tr>
<td>1</td><td></td><td>i</td>
<td>
FIRST CHECK THE ANSWER ON ANSWER LINE
IF answer = 0.455 award 4 marks
AND IF units = $\text{atm}^{1/2}$ award 5 marks

Equilibrium moles ✓
N SO_3 = 1.35 , *n* O_2 = 0.45(0) AND *n* total = 2.7(0)

Partial pressures ✓
<table>
<tr><td>$p(SO_3)$</td><td>$\frac{1.35}{2.7(0)} \times 2.80$ OR 1.4(0)</td></tr>
<tr><td>$p(SO_2)$</td><td>$\frac{0.900}{2.7(0)} \times 2.80$ OR 0.933</td></tr>
<tr><td>$p(O_2)$</td><td>$\frac{0.450}{2.7(0)} \times 2.80$ OR 0.467</td></tr>
</table>

$(K_p) = \frac{p(SO_2)\ p(O_2)^{1/2}}{p(SO_3)}$
OR $(K_p =)\ \frac{(0.933) \times (0.467)^{1/2}}{(1.40)}$ ✓ ✓

Answer to 3 SF
K_p= 0.455 ✓

Units
Substitution of units into correct K_p expression
$\frac{\text{atm}^1 \times \text{atm}^{1/2}}{\text{atm}^1} = \text{atm}^{\frac{1}{2}}$ ✓ ✓
</td>
<td>5</td>
<td>
IF there is an alternative answer, check for any
ECF credit possible using working below.

ALLOW 3SF or more unless there is a trailing zero
e.g. ALLOW $p(SO_3)$ = 1.4, n total =2.7

ALLOW all marks to be awarded if atmospheres are converted into other pressure units e.g. to kPa.

ALLOW use of fractions for intermediate working

ALLOW $(K_p) = \frac{p(SO_2)\ p^{1/2}(O_2)}{p(SO_3)}$
ALLOW
$K_p^2 = \frac{p(SO_2)^2 \times p(O_2)}{p(SO_3)^2}$

IGNORE [ ] (we are just looking for the calculation)

ALLOW ECF for units of an incorrect K_p expression

ALLOW $\text{atm}^{0.5}$

DO NOT ALLOW $\sqrt{\text{atm}}$

Common errors
4 marks
(3 marks for calculation + unit mark)

0.207 (from expression $\frac{p(SO_2)^2 \times p(O_2)}{p(SO_3)^2}$) Unit: atm
2.20 (from inverted expression) Unit: $\text{atm}^{-1/2}$

<u>Examiner’s Comments</u>

Candidates tend to find Kp calculations difficult and so a strategy to work their way through them could include:
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					• Write the Kp expression using the molar ratio given in the question. Care should be taken not to change the molar ratio to help an easier calculation. Square brackets should not be used as these represent concentration. • Calculation of initial moles present, with careful consideration of the use of appropriate significant figures • Calculation of the change in moles present • Deduction of the number of moles present at equilibrium • Determination of total moles present at equilibrium These steps are often best completed as RICE tables (Ratio, Initial, Change, Equilibrium) and should look to use the appropriate amount of significant figures to avoid having a rounding error in the final answer. ? **Misconception** K_p values are for the equation as stated. Candidates should recognise that changing the stoichiometry of the equation changes the K_p value.
		ii	ΔH is +ve / endothermic (in forward direction). **AND** (At higher temperature,) equilibrium shifts to right hand side ✓ (T_2) has greater K_p value **OR** $7.7 \times 10^{-2} > 3.3 \times 10^{-5}$ ✓	2	**ORA** throughout **ALLOW** towards the products for right hand side **ALLOW** increases yield of products **DO NOT ALLOW** T_1 has greater K_p value **Examiner's Comments** Candidates performed well with this question and many stated that K_p would increase. Some identified the forward reaction as endothermic but

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<tr><td></td><td></td><td></td><td></td><td></td><td>did not link this to equilibrium being shifted to the right, thus increasing the ratio within the K_p expression. A few candidates sought to incorrectly explain the effect by using Le Chatelier effect on pressure.</td></tr>
<tr><td></td><td></td><td>iii</td><td>One mark per correct row ✓ ✓
<table><tr><th>Change</th><th>Decrease</th><th>No change</th><th>Increase</th></tr><tr><td>No catalyst</td><td></td><td>✓</td><td></td></tr><tr><td>Increased pressure</td><td></td><td>✓</td><td></td></tr></table></td><td>2</td><td><u>Examiner's Comments</u>
This proved a challenging question where candidates did not stick to the principle that K_p (or K_a) values only change due to temperature changes. Only a few candidates scored both marks with many having the K_p value changing due to increased pressure.</td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>9</td><td></td></tr>
<tr><td>2</td><td></td><td>i</td><td>$(K_a) = \frac{[H^+]\,[ClCH_2COO^-]}{[ClCH_2COOH]}$</td><td>1</td><td>DO NOT ALLOW without square brackets
DO NOT ALLOW $\frac{[H^+]^2}{[ClCH_2COOH]}$
DO NOT ALLOW $\frac{[H^+][A^-]}{[HA]}$
<u>Examiner's Comments</u>
Most candidates scored the marking point. They realised that the full formulae were needed although some candidates left off the square brackets or used HA or $[H]^2$. Care should be taken in checking the correct amount and location of H in the formula. As an acid dissociates to form a H^+, it is important to acknowledge only one H^+ is dissociated from the correct part of the molecule.</td></tr>
<tr><td>2</td><td></td><td>ii</td><td>$[H^+] = [A^-]$
OR $[H^+]$ from water is negligible
OR dissociation of water is negligible
✓</td><td>1</td><td>Answer must be in terms of concentration
ALLOW $[H^+] \approx [A^-]$
IGNORE $HA \rightleftharpoons H^+ + A^-$ is a 1:1 mole ratio.
<u>Examiner's Comments</u>
This question required the candidate to understand that the dissociation of water to produce H^+ ions had no</td></tr>
</table>

					effect on the overall [H^+] of the solution, leading to [H^+] = [A^-]. This was mostly answered well but some candidates used the idea of [H^+] = [OH^-].
		iii	**FIRST CHECK ANSWER ON ANSWER LINE** **If answer = 2.85 OR 2.86 OR 2.87 award 3 marks** -- ([H^+] =) $10^{-1.95}$ **OR** = $1.1(22…) \times 10^{-2}$ ✓ $(K_a) = (\frac{[H^+]^2}{[ClCH_2COOH]})$ $= \frac{(1.122… \times 10^{-2})^2}{(0.090)}$ **OR** $\frac{(1.12 \times 10^{-2})^2}{(0.090)}$ **OR** $\frac{(1.1 \times 10^{-2})^2}{(0.090)}$ = $1.4(0) \times 10^{-3}$ **OR** = 1.39×10^{-3} **OR** = 1.34×10^{-3} ✓ ($pK_a = -\log_{10}(K_a)$ =) 2.85, 2.86 OR 2.87 (**2DP**) ✓	3	**ALLOW ECF** throughout **ALLOW** [H^+] =1.1×10^{-2} up to calculator value **ALLOW** 2 sig figs up to calculator value. **ALLOW** calculations based on finding the $[HA]_{equ}$ $\frac{(1.122… \times 10^{-2})^2}{(0.079)}$ **OR** $\frac{(1.12 \times 10^{-2})^2}{(0.079)}$ **OR** $\frac{(1.1 \times 10^{-2})^2}{(0.079)}$ = 1.59×10^{-3} **OR** = 1.59×10^{-3} **OR** = 1.53×10^{-3} ✓ ($pK_a = -\log_{10}(K_a)$ =) 2.80 **OR** 2.80 **OR** 2.81 (**2DP**) ✓ **Must be 2DP** **Common error:** **2 marks** 0.90 (not using [H^+]^2) **<u>Examiner's Comments</u>** Candidates made good progress with this calculation, many gaining 2 or 3 marks, including error carried forward. Common errors included, in various combinations: using -log[-1.95]; using an incorrect value for the concentration of $ClCH_2COOH$; and using 10^{-Ka}.
			Total	**5**	
3			**FIRST CHECK THE ANSWERS ON ANSWER LINE** **If K_c value = 2931 OR 2930 award 4 calc marks** **If units = $dm^3\ mol^{-1}$ OR $mol^{-1}\ dm^3$ award 1 unit mark** -- **SO_2 and O_2 equilibrium moles** ***n*(SO_2) = 6.20×10^{-3}** ($5.82 \times 10^{-2} - 5.20 \times 10^{-2}$) **AND *n*(O_2) = 4.80×10^{-2}** ✓ ($7.4 \times 10^{-2} - \frac{5.20 \times 10^{-2}}{2}$)	5 (AO 2.6 ×3) (AO 1.2 ×2)	**Use of fractions is fine but final answer MUST be shown using normal numbers** **COMMON ERRORS** **K_c = 1,465** (2,930/2) → ***3 calc marks*** Moles **not** converted to concentration (No ÷2) $\frac{(5.20 \times 10^{-2})^2}{(6.2 \times 10^{-3})^2\ (4.80 \times 10^{-2})}$

			Equilibrium concentrations (moles ÷ 2) $[SO_2]$ = **3.10 × 10^{-3}** $\frac{6.20 \times 10^{-3}}{2}$ (mol dm^{-3}) **AND** $[O_2]$ = **2.40 × 10^{-2}** $\frac{4.80 \times 10^{-2}}{2}$ (mol dm^{-3}) **AND** $[SO_3]$ = **2.60 × 10^{-2}** ✓ $\frac{5.20 \times 10^{-2}}{2}$ (mol dm^{-3}) ***K*$_c$ calculation** $K_c = \frac{(2.60 \times 10^{-2})^2}{(3.10 \times 10^{-3})^2 \, (2.40 \times 10^{-2})}$ ✓ = 2,930 **OR** 2,931 ✓ **At least 3 SF** required *Calc value from unrounded values: 2,930.974679* **Units** dm^3 mol^{-1} ✓ **DO NOT ALLOW** dm^3 mol$^-$ **For units, ALLOW ECF** using incorrect K_c expression Units must match K_c expression used		-- **K_c = 21.6** ***→ 3 calc marks*** Original values used, $\frac{(2.60 \times 10^{-2})^2}{(2.91 \times 10^{-2})^2 \, (3.70 \times 10^{-2})}$ -- **K_c = 10.8** ***→ 2 calc marks*** Original values used and no ÷2, $\frac{(5.20 \times 10^{-2})^2}{(5.82 \times 10^{-3})^2 \, (7.40 \times 10^{-2})}$ -- **K_c = 732.74** **→ 3 calc marks** × 2 instead of ÷ 2 for concentration $\frac{(0.104)^2}{(0.0124)^2 \, (0.096)}$ -- **K_c = 112729.8** **→ 3 calc marks** 2.60 × 10^{-2} not squared $\frac{(2.60 \times 10^{-2})}{(3.10 \times 10^{-3})^2 \, (2.40 \times 10^{-2})}$ -- **K_c = 3.41… × 10^{-4}** **→ 3 calc marks** Calculator 3.41183432 × 10^{-4} Inverted K_c $\frac{(3.10 \times 10^{-3})^2 \, (2.40 \times 10^{-2})}{(2.60 \times 10^{-2})^2}$ Units mol dm^{-3} **Examiner's Comments** As with the stock titration calculation in Question 5 (a), candidates were much more comfortable in tackling a stock K_c calculation. These have been assessed in several previous H432/01 exams and many excellent responses were seen, gaining all 5 marks. Error carried forwards allowed for an early slip in the calculation to be credited

					subsequently for a correct method. The hardest part of the calculation was the initial determination of the equilibrium moles and concentrations. The equilibrium moles of O_2 was the main error, presumably from the 2:1:2 stoichiometry. Some candidates multiplied by 2 instead of dividing by 2 for the concentration. A common error was for candidates to use a partial pressure approach. These errors lost intermediate marks by credit could then be awarded for using the correct K_c expression to generate a K_c value with correct units. Very few candidates did not gain any marks.
			Total	**5**	
4		i	$Mg + 2H^+ \rightarrow Mg^{2+} + H_2$ ✓	1 (AO 2.6)	**ALLOW** multiples **ALLOW** Mg^{+2} **IGNORE** state symbols **<u>Examiner's Comments</u>** Ionic equations still present candidates with a challenge. A few candidates scored the mark but many candidates gave a full equation or one that contained a mismatch of spectator ions as well as the correct ions.
		ii	HC*l* is a strong acid/completely dissociates **AND** CH_3COOH is a weak acid/partially dissociates ✓ Greater H^+ concentration in HC*l* **AND** More frequent collisions / faster rate of reaction ✓ More CH_3COOH dissociates until same number of moles of H^+ released **OR** same total moles H^+ produced (by the end) **OR**	3 (AO 1.1 × 1) (AO 3.1 × 2)	**IGNORE** HCl is a strong**<u>er</u>** acid than ethanoic acid. **ALLOW** ORA **DO NOT ALLOW** dibasic/tribasic **<u>Examiner's Comments</u>** This question proved challenging for the candidates to identify the three ideas: Those of comparing acids, comparing moles and comparing

			(Both acids are monobasic) and have the same number of moles of acid ✓		rates. Very few candidates were able to score the 3 marks. Most candidates recognised the different strength of the two acids, but some only used comparative language. Some linked the moles of acid used to the volume of gas produced but many simply restated the same volume and concentration which is given within the question. Only a few candidates linked the higher initial [H$^+$] in HCl to the increased rate through more frequent collisions. A common issue was describing the rate of dissociation rather than the [H$^+$] present in determining the rate of the reactions or mentioning that it dissociates more but not linking this to the H+ concentration.
			Total	**4**	
5	a		**Level 3 (5–6 marks)** Uses correct method to calculate K_c **AND** explains why most operational condition is different with few omissions in the explanation. *There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.* **Level 2 (3–4 marks)** Uses correct method to calculate K_c with few errors **OR** Derives a correct expression for K_c with an attempt at the K_c calculation **AND** explains why an operational condition is different with some omissions. *There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.* **Level 1 (1–2 marks)** Derives a correct expression for K_c **AND** explains why one operational condition is different with some omissions. **OR**	6(AO2.4×4 AO1.2×2)	**Indicative scientific points may include:** **IGNORE trailing zeroes** **Equilibrium amounts** $n(N_2)$: 1.20 − 0.08 = 1.12, $n(H_2)$: 3.60 − 0.24 = 3.36 **Equilibrium concentrations** $[N_2] = \frac{1.12}{8.00} = 0.140\ (\text{mol dm}^{-3})$ $[H_2] = \frac{3.36}{8.00} = 0.420\ (\text{mol dm}^{-3})$ $[NH_3] = \frac{0.160}{8.00} = 0.0200\ (\text{mol dm}^{-3})$ **Equilibrium expression and K_c value wih units** $K_c = \frac{[NH_3]^2}{[N_2] \times [H_2]^3}$ $K_c = \frac{0.0200^2}{0.140 \times 0.420^3} = 0.0386$ *Calculator: 0.03856417851* **Units:** dm^6 mol^{-2} **Explanation for operational differences.** **Temperature**

			explains why most operational conditions are different *There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.* **0 marks** *No response or no response worthy of credit.*		• Low temperature for maximum yield: (ΔH −ve \exothermic) • High temperature to increase rate **Pressure** • High pressure for maximum yield (fewer (gaseous) moles/molecules of products) • High pressure expensive to generate **OR** high pressure is a safety hazard **Catalyst** • Allows a lower temperature to be used for maximum yield. • Reducing fuel expense **OR** increasing rate **<u>Examiner's Comments</u>** This Level of Response question was generally well answered with many candidates achieving maximum marks by simply considering what was required in the question. Responses were often split between a calulation on the main paper and the conditions explanation on extra pages. The calculation errors included no shift or incorrect shift in the equilibrium values. Not calculating the concentration or incorrectly multiplying by 8 rather than dividing by 8. Some candidates attempted a 'hybrid' calculation of Kp by trying to calculate a mole fraction and partial pressures. There was a number of candidates who confidently worked out the value of K_c. There were also some very good analyses of the operational conditions. Many of those who had done well on the calculation treated the explanation as an afterthought, not giving it enough attention to give them an answer that would access Level 3. Exemplar 2

					 An example of a complete answer, showing a good level of communication in the description and the calculation layout, achieving Level 3 (6 marks) is shown above. This candidate gave a clear method using an "ICE" table to calculate the number of moles at equilibrium. The calculation of the new concentrations can be seen by the use of [ ] and division by 8. The candidate then shows the Kc expression and substitutes the numerical values before successfully calculating the value and includes the units. This is followed by a concise explanation of the conditions used by industry.
	b	i	Equilibrium (position) shifts to the left (as T is decreased) **AND** (forward) reaction is endothermic ✓	1(AO1.2)	**ALLOW** 'favours backward reaction' *Implies shift to left* **ALLOW** 'shifts in exothermic direction' BUT only if (forward) reaction stated as endothermic **<u>Examiner's Comments</u>** Candidates coped well with this question, but many candidates did not gain the mark due to ambiguous statements. Some identified the forward reaction as endothermic, but stated that Kp decreased which was given in the question. Others simply stated that the forward reaction was endothermic as the reverse reaction was exothermic.
		ii	Student 2 is correct **AND** same number of **gas** particles/	1(AO3.2)	**ALLOW AW** that suggests student 2 is correct **<u>Examiner's Comments</u>**

			gas(eous) molecules/moles of **gas** on each side (of equation) ✓		Many candidates gave the correct reason to agree with student 2. Those who agreed with student 1 did not see the equation as a heterogeneous equilibrium system. There were a small number of responses agreeing with student 2 but for the wrong reason – such as a confusion about how the position of equilibrium can change when the value of K_p stays constant. Candidates are advised to read through and address all parts of the question as a minority of students didn't identify which student was correct but gave a correct explanation.
			Total	**8**	
6			**At 90 °C**/higher temperature • Faster rate **AND** more frequent collisions ✓ • More particles have the activation energy/E_a or greater ✓ • $[Co(H_2O)_6]^{2+}$ is lower ✓ • (forward reaction) ΔH -ve **OR** exothermic ✓	4 (1 ×AO2.7) (1 ×AO1.2) (1 ×AO2.3) (1 ×AO1.2)	**ORA for 50 °C** **IGNORE** more successful collisions **ALLOW** more molecules have enough energy to react **ALLOW** atoms/molecules/ions **ALLOW** decreases **Examiner's Comments** This question asked candidates to explain the different rates from a novel experiment carried out at 50°C and 90°C, and to predict the ΔH sign for the forward reaction. Candidate explanations for the rates were often superficial, solely in terms of greater energy at 90°C. Many responses referred neither to the different frequency of collisions nor the greater number of particles exceeding the activation energy at 90°C. Most candidates predicted that ΔH would have a negative sign. Candidates were expected to link the evidence from the absorbance data in the graph to less $[Co(H_2O)_6]^{2+}$ being present at 90°C. When experimental information has been presented, candidates are advised to look for the evidence responsible in their explanations.
			Total	**4**	