Section A

Q1 The dissociation of dinitrogen tetraoxide into nitrogen dioxide is represented by the equation below.

\[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g); \quad \Delta H^\circ = +57 \text{ kJ mol}^{-1} \]

If the temperature of an equilibrium mixture of the gases is increased at constant pressure, will the volume of the mixture increase or decrease and why?

A The volume will increase, but only because of a shift of equilibrium towards the right.
B The volume will increase, both because of a shift of equilibrium towards the right and also because of thermal expansion.
C The volume will stay the same, because any thermal expansion could be exactly counteracted by a shift of equilibrium towards the left.
D The volume will decrease, because a shift of equilibrium towards the left would more than counteract any thermal expansion.

Q2 The reaction represented by the following equation was carried out.

\[ \text{HCO}_2\text{CH}_3\text{(aq)} + \text{NaOH(aq)} \rightarrow \text{HCO}_2\text{Na(aq)} + \text{CH}_3\text{OH(aq)} \]

Which graph best shows the relationship between [CH₃OH(aq)] and t, the time from mixing of the reactants?

![Graph Options]

Q3 At a total pressure of 1.0 atm, dinitrogen tetraoxide is 50 % dissociated at a temperature of 60°C, according to the following equation.

\[ \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \]

What is the value of the equilibrium constant, \( K_p \), for this reaction at 60°C?

A \( \frac{1}{2} \text{ atm} \)  \hspace{1cm} B \( \frac{2}{3} \text{ atm} \)  \hspace{1cm} C \( \frac{4}{5} \text{ atm} \)  \hspace{1cm} D \( 2 \text{ atm} \)

Q4 Swimming pool water can be kept free of harmful bacteria by adding aqueous sodium chlorate(I), NaOCl. This reacts with water to produce HOCl molecules which kill bacteria.

\[ \text{OCl}^-\text{(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{OH}^-\text{(aq)} + \text{HOCl}\text{(aq)} \]

In bright sunshine, the OCl⁻ ion is broken down by ultra-violet light.

\[ \text{OCl}^-\text{(aq)} + \text{uv light} \rightarrow \text{Cl}^-\text{(aq)} + \frac{1}{2}\text{O}_2\text{(g)} \]
Which method would maintain the highest concentration of HOCl (aq)?
A acidify the pool water  
B add a solution of chloride ions  
C add a solution of hydroxide ions  
D bubble air through the water

Q5 Two equilibria are shown below.

\[ \text{reaction I} \quad 2X_2(g) + Y_2(g) \rightleftharpoons 2X_2Y(g) \]
\[ \text{reaction II} \quad X_2Y(g) \rightleftharpoons X_2(g) + \frac{1}{2}Y_2(g) \]

The numerical value of \( K_c \) for reaction I is 2.
Under the same conditions, what is the numerical value of \( K_c \) for reaction II?

A \[ \frac{1}{\sqrt{2}} \]
B \[ \frac{1}{2} \]
C \[ \frac{1}{4} \]
D \[ -2 \]

Q6 For the reaction

\[ W(aq) + 2X(aq) \rightleftharpoons 2Y(aq) + 3Z(aq) \]

what are the correct units for the equilibrium constant \( K_c \)?
A \[ \text{mol dm}^{-3} \]
B \[ \text{mol}^2 \text{dm}^{-6} \]
C \[ \text{mol}^{-1} \text{dm}^3 \]
D \[ \text{mol}^{-2} \text{dm}^6 \]

Q7 The Haber process for the manufacture of ammonia is represented by the following equation.

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad \Delta H = -92 \text{kJ mol}^{-1} \]

Which statement is correct about this reaction when the temperature is increased?
A Both forward and backward rates increase.
B The backward rate only increases.
C The forward rate only increases.
D There is no effect on the backward or forward rate.

Q8 The percentage of ammonia obtainable, if equilibrium were established during the Haber process, is plotted against the operating pressure for two temperatures, 400 °C and 500 °C. Which diagram correctly represents the two graphs?
Q9 Ammonia is manufactured on a large scale by the Haber process. In a particular plant, conditions of 400 °C and 250 atm in the presence of an iron catalyst are used.

\[
\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad \Delta H^\circ = -92 \text{ kJ mol}^{-1}
\]

What could contribute most to increasing the equilibrium yield of ammonia?
A adding more catalyst
B increasing the pressure to 400 atm
C increasing the temperature to 1000 °C
D using air rather than nitrogen

Q10 Two moles of compound P were placed in a vessel. The vessel was heated and compound P was partly decomposed to produce Q and R. A dynamic equilibrium between chemicals P, Q and R was established. At equilibrium x moles of R were present and the total number of moles present was \(2 + \frac{x}{2}\).

What is the equation for this equilibrium reaction?
A \(P \rightleftharpoons 2Q + R\)
B \(2P \rightleftharpoons 2Q + R\)
C \(2P \rightleftharpoons Q + 2R\)
D \(2P \rightleftharpoons Q + 2R\)

Q11 An experiment is set up to measure the rate of hydrolysis of methyl ethanoate.

\[
\text{CH}_3\text{CO}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{OH}
\]

The hydrolysis is found to be slow in neutral aqueous solution but it proceeds at a measurable rate when the solution is acidified with hydrochloric acid.

What is the function of the hydrochloric acid?
A to dissolve the methyl ethanoate
B to ensure that the reaction reaches equilibrium
C to increase the reaction rate by catalytic action
D to suppress ionisation of the ethanoic acid formed

Q12 The equilibrium constant, \(K_c\), for the reaction to form ethyl ethanoate from ethanol and ethanoic acid, at 60 °C is 4.00.

\[
\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{CO}_2\text{H} \rightleftharpoons \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O}
\]

When 1.00 mol each of ethanol and ethanoic acid are allowed to reach equilibrium at 60 °C, what is the number of moles of ethyl ethanoate formed?
A \(\frac{1}{3}\)
B \(\frac{2}{3}\)
C \(\frac{1}{4}\)
D \(\frac{3}{4}\)

Q13 For the equilibrium given, what will change the value of \(K_p\)?

\[
2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)
\]

A adding a catalyst
B adding more \(\text{O}_2\)
C increasing the pressure
D increasing the temperature

Q14 Dinitrogen tetroxide dissociates into nitrogen dioxide on heating.

\[
\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)
\]

In an experiment the partial pressures of the gases at equilibrium were found to be \(\text{NO}_2, 0.33 \text{ atm}; \text{N}_2\text{O}_4, 0.67 \text{ atm}\). What is the numerical value of \(K_p\) at the temperature of the experiment?
A 0.16
B 0.49
C 0.65
D 2.03
Q15 The equilibrium

\[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \quad \Delta H = +180 \text{ kJ mol}^{-1} \]

contributes to a series of reactions producing photochemical smog. Which factors would affect the value of \( K_p \) of the above equilibrium?

<table>
<thead>
<tr>
<th></th>
<th>change in pressure</th>
<th>change in temperature</th>
<th>presence or absence of a catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>✓</td>
<td>✓</td>
<td>x</td>
</tr>
<tr>
<td>B</td>
<td>✓</td>
<td>x</td>
<td>✓</td>
</tr>
<tr>
<td>C</td>
<td>x</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>D</td>
<td>x</td>
<td>✓</td>
<td>x</td>
</tr>
</tbody>
</table>

Q16 Four reactions of the type shown are studied at the same temperature.

\[ X(g) + Y(g) \rightarrow Z(g) \]

Which is the correct reaction pathway diagram for the reaction that would proceed most rapidly and with the highest yield?

Q17 The following equilibrium is set up in a mixture of concentrated nitric and sulfuric acids.

\[ \text{HNO}_3 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{NO}_3^+ + \text{HSO}_4^- \]

Which row correctly describes the behaviour of each substance in the equilibrium mixture?

<table>
<thead>
<tr>
<th></th>
<th>( \text{HNO}_3 )</th>
<th>( \text{H}_2\text{SO}_4 )</th>
<th>( \text{H}_2\text{NO}_3^+ )</th>
<th>( \text{HSO}_4^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>acid</td>
<td>acid</td>
<td>base</td>
<td>base</td>
</tr>
<tr>
<td>B</td>
<td>acid</td>
<td>base</td>
<td>base</td>
<td>acid</td>
</tr>
<tr>
<td>C</td>
<td>base</td>
<td>acid</td>
<td>acid</td>
<td>base</td>
</tr>
<tr>
<td>D</td>
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<td>acid</td>
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<td>acid</td>
</tr>
</tbody>
</table>
Section B

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

Q18 The stoichiometry of a catalysed reaction is shown by the equation below.

\[ P(g) + Q(g) \rightleftharpoons R(g) + S(g) \]

Two experiments were carried out in which the production of R was measured against time. The results are shown in the diagram below.

Which changes in the conditions from experiment 1 to experiment 2 might explain the results shown?
1. Less of P was used.
2. A different catalyst was used.
3. Product S was continuously removed from the reaction vessel.

Q19 Two bulbs R and S, connected by a mercury manometer, are held in a thermostat, as shown. The volume of R is twice that of S. R contains gas, X, at the same pressure as the nitrogen in S.

When the temperature is increased, which gases in bulb R would cause the mercury level in the right-hand limb of the manometer to rise?
1. An equilibrium mixture \( N_2F_4(g) \rightleftharpoons 2NF_2(g); \Delta H \) positive
2. An equilibrium mixture \( CH_3NC(g) \rightleftharpoons CH_3CN(g); \Delta H \) negative
3. Nitrogen

Q20 Catalysts are used in many reversible reactions in the chemical industry. Vanadium(V) oxide is used in this way in the Contact process for the formation of SO₃.

\[ 2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \]

What effect does vanadium(V) oxide have on this equilibrium?
1. It speeds up the forward reaction.
2. It increases the value of \( K_p \).
3. It increases the value of \( E_a \) for the reverse reaction.
Q21 Concentrated sulfuric acid behaves as a strong acid when it reacts with water.

\[ \text{H}_2\text{SO}_4(l) + \text{aq} \rightarrow \text{H}^+(aq) + \text{HSO}_4^-(aq) \]

The HSO$_4^-$ ion formed behaves as a weak acid.

\[ \text{HSO}_4^-(aq) \rightleftharpoons \text{H}^+(aq) + \text{SO}_4^{2-}(aq) \]

Which statements are true for 1.0 mol dm$^{-3}$ sulfuric acid?

1. [H$^+(aq)$] is high
2. [SO$_4^{2-}(aq)$] is high
3. [HSO$_4^-(aq)$] = [SO$_4^{2-}(aq)$]

Q22 Silver chloride dissolves in aqueous ammonia. What happens in this process?

1. A co-ordinate bond is formed.
2. The oxidation number of nitrogen is unchanged.
3. Ammonia acts as a Brønsted-Lowry base.

Q23 Hydroxyapatite, Ca$_5$(PO$_4$)$_3$OH, is the main constituent of tooth enamel. In the presence of saliva, the following equilibria exist.

\[ \text{Ca}_5(\text{PO}_4)_3\text{OH}(s) \rightleftharpoons 5\text{Ca}^{2+}(aq) + 3\text{PO}_4^{3-}(aq) + \text{OH}^-(aq) \]

\[ \text{HPO}_4^{2-}(aq) \rightleftharpoons \text{H}^+(aq) + \text{PO}_4^{3-}(aq) \]

Which of the following statements help to explain why tooth enamel is dissolved more readily when saliva is acidic?

1. The hydroxide ions are neutralised by the acid.
2. The phosphate ion PO$_4^{3-}(aq)$ accepts H$^+(aq)$
3. Calcium ions react with acids.

Q24 Phosphorus pentachloride is introduced into an empty gas syringe which has a movable, tightly fitting plunger. The gas is allowed to expand until equilibrium is reached at a temperature at which the phosphorus pentachloride partially dissociates.

Which statements are correct?

1. The equilibrium pressure inside the syringe will be greater than atmospheric pressure.
2. When the plunger is pushed in the equilibrium adjusts to produce more PCl$_5$(g).
3. The volume of gas in the syringe at equilibrium will be greater than if no dissociation had occurred.

Q25 Under given conditions, what governs the rate of a forward reaction?

1. the activation energy of the reaction
2. the enthalpy change of the reaction
3. the equilibrium constant of the reaction

Q26 Which equilibria, in which all species are gaseous, would have equilibrium constants, K$_p$, with no units?

1. sulfur dioxide and oxygen in equilibrium with sulfur trioxide
2. hydrogen and iodine in equilibrium with hydrogen iodide
3. carbon monoxide and steam in equilibrium with carbon dioxide and hydrogen
1. B
2. A
3. C
4. A
5. A
6. B
7. A
8. A
9. B
10. D
11. C
12. B
13. D
14. A
15. D
16. C
17. C
18. B
19. D
20. D
21. D
22. B
23. B
24. C
25. D
26. C
Q1 Alcohols and esters are important organic compounds which are widely used as solvents. Esters such as ethyl ethanoate can be formed by reacting carboxylic acids with alcohols.

\[
\text{CH}_3\text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O}
\]

This reaction is an example of a dynamic equilibrium.

(a) Explain what is meant by the term *dynamic equilibrium*.

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

(c) For this equilibrium, the value of \(K_c\) is 4.0 at 298 K. A mixture containing 0.5 mol of ethanoic acid, 0.5 mol ethanol, 0.1 mol ethyl ethanoate and 0.1 mol water was set up and allowed to come to equilibrium at 298 K. The final volume of solution was \(V\) dm³. Calculate the amount, in moles, of each substance present at equilibrium.

(June 2007)

Q2 NO is also formed when nitrosyl chloride, \(\text{NOCl}\), dissociates according to the following equation.

\[
2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)
\]

Different amounts of the three gases were placed in a closed container and allowed to come to equilibrium at 230 °C. The experiment was repeated at 465 °C. The equilibrium concentrations of the three gases at each temperature are given in the table below.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>(\text{NOCl})</th>
<th>(\text{NO})</th>
<th>(\text{Cl}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>(2.33 \times 10^{-3})</td>
<td>(1.46 \times 10^{-3})</td>
<td>(1.15 \times 10^{-2})</td>
</tr>
<tr>
<td>465</td>
<td>(3.68 \times 10^{-4})</td>
<td>(7.63 \times 10^{-3})</td>
<td>(2.14 \times 10^{-4})</td>
</tr>
</tbody>
</table>

(a) (i) Write the expression for the equilibrium constant, \(K_c\), for this reaction. Give the units.

(ii) Calculate the value of \(K_c\) at each of the temperatures given.

230 °C
(iii) Is the forward reaction endothermic or exothermic? Explain your answer.

(b) The temperature of the equilibrium was then altered so that the equilibrium concentrations of NOCl and NO were the same as each other. What will be the effect on the equilibrium concentration of NOCl when the following changes are carried out on this new equilibrium? In each case, explain your answer.

(i) The pressure of the system is halved at constant temperature.

(ii) A mixture of NOCl(g) and NO(g) containing equal numbers of moles of each gas is introduced into the container at constant temperature.

Q3 Methanol may be manufactured catalytically from synthesis gas, a mixture of CO, CO2 and H2. The CO is reacted with H2 to form methanol, CH3OH.

(a) From your understanding of Le Chatelier’s principle, state two conditions that could be used in order to produce a high yield of methanol. In each case, explain why the yield would increase.

condition 1 .................................................................................................................................

explanation ................................................................................................................................

condition 2 ................................................................................................................................

explanation ...................................................................................................................................

Carbon monoxide, which can be used to make methanol, may be formed by reacting carbon dioxide with hydrogen.

(b) A mixture containing 0.50 mol of CO2, 0.50 mol of H2, 0.20 mol of CO and 0.20 mol of H2O was placed in a 1.0 dm3 flask and allowed to come to equilibrium at 1200 K. Calculate the amount, in moles, of each substance present in the equilibrium mixture at 1200 K.
Q4 Ethanoic acid can be reacted with alcohols to form esters, an equilibrium mixture being formed.

\[
\text{CH}_3\text{CO}_2\text{H} + \text{ROH} \rightleftharpoons \text{CH}_3\text{CO}_2\text{R} + \text{H}_2\text{O}
\]

The reaction is usually carried out in the presence of an acid catalyst.

(a) Write an expression for the equilibrium constant, \( K_c \), for this reaction, clearly stating the units.

\[
K_c = \text{units} \quad \text{................................................. [2]}
\]

In an experiment to determine \( K_c \) a student placed together in a conical flask 0.10 mol of ethanoic acid, 0.10 mol of an alcohol \( \text{ROH} \), and 0.005 mol of hydrogen chloride catalyst. The flask was sealed and kept at 25 °C for seven days. After this time, the student titrated all of the contents of the flask with 2.00 mol dm\(^{-3}\) NaOH using phenolphthalein indicator. At the end-point, 22.5 cm\(^3\) of NaOH had been used.

(b) (i) Calculate the amount, in moles, of NaOH used in the titration.

(ii) What amount, in moles, of this NaOH reacted with the hydrogen chloride?

(iii) Write a balanced equation for the reaction between ethanoic acid and NaOH.

(iv) Hence calculate the amount, in moles, of NaOH that reacted with the ethanoic acid.
(c) (i) Use your results from (b) to calculate the amount, in moles, of ethanoic acid present at equilibrium. Hence complete the table below.

<table>
<thead>
<tr>
<th></th>
<th>CH₃CO₂H</th>
<th>ROH</th>
<th>CH₃CO₂R</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.10</td>
<td>0.10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>amount/mol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>equilibrium</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>amount/mol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(ii) Use your results to calculate a value for $K_c$ for this reaction.

Q5 The synthesis of methanol is carried out at about 500 K with a pressure of between 40 and 100 atmospheres (between $4 \times 10^6$ Pa and $10 \times 10^7$ Pa) and using a catalyst. The use of such conditions will affect both the rate of reaction and the equilibrium yield. In the spaces below, explain the effects of higher temperature, higher pressure, and the use of a catalyst on the **equilibrium yield** of methanol.

$$\text{CO}_2(g) + 3\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g) + \text{H}_2\text{O}(g)$$

**higher temperature**

effect ........................................................................................................................................

explanation ................................................................................................................................

...................................................................................................................................................

**higher pressure**

effect ........................................................................................................................................

explanation ................................................................................................................................

...................................................................................................................................................

**use of catalyst**

effect ........................................................................................................................................

explanation ................................................................................................................................

...................................................................................................................................................

Q6 Atmospheric nitrogen is used in the Haber process for the manufacture of ammonia.

(a) Write an equation for the formation of ammonia in the Haber process.

..................................................................................................................................................
(b) The Haber process is usually carried out at a high pressure of between 60 and 200 atmospheres (between \(6 \times 10^5\) Pa and \(200 \times 10^5\) Pa). State two further important operating conditions that are used in the Haber process. For each of your conditions, explain why it is used.

condition 1 ...........................................................................
reason ..................................................................................................

condition 2 ...........................................................................
reason ...................................................................................................

(c) State one large-scale use for ammonia, other than in the production of nitrogenous fertilisers.

..........................................................................................................................

Q7 Hydrogen iodide can be made by heating together hydrogen gas and iodine vapour. The reaction is incomplete.

\[
\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)
\]

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

\[K_c = \text{........................................... units ...........................................} \]

(b) For this equilibrium, the numerical value of the equilibrium constant \(K_c\) is 140 at 500 K and 59 at 650 K. Use this information to state and explain the effect of the following changes on the equilibrium position.

(i) increasing the pressure applied to the equilibrium

..........................................................................................................................

...........................................................................................................................................

(ii) decreasing the temperature of the equilibrium

...........................................................................................................................................

..........................................................................................................................................

(c) A mixture of 0.02 mol of hydrogen and 0.02 mol of iodine was placed in a 1 dm\(^3\) flask and allowed to come to equilibrium at 650 K. Calculate the amount, in moles, of each substance present in the equilibrium mixture at 650 K.

\[
\begin{align*}
\text{H}_2(g) + \text{I}_2(g) &\rightleftharpoons 2\text{HI}(g) \\
\text{Initial moles} &\quad 0.02 \quad 0.02 \quad 0
\end{align*}
\]

Q8 Ammonia is an important industrial chemical which is manufactured on a large scale by using the Haber process.
(i) Write a balanced equation, with state symbols, for the reaction occurring in the Haber process.

(ii) Give three essential operating conditions that are used in the Haber process.

(iii) State one large scale use of ammonia.

Q9 One common way of producing hydrogen on a large scale for use in the chemical industry is by the steam ‘reforming’ of methane (natural gas), in which steam and methane are passed over a catalyst at 1000–1400 K to produce carbon monoxide and hydrogen.

\[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g) \quad \Delta H = +206 \text{ kJ mol}^{-1} \]

(a) Use the information above to state and explain the effect on the equilibrium position of the following changes.

(i) increasing the pressure applied to the equilibrium

(ii) decreasing the temperature of the equilibrium

(b) What will be the effect on the rate of the reaction of increasing the pressure at which it is carried out? Explain your answer.

(c) Further hydrogen can be obtained by the ‘water-gas shift’ reaction in which the carbon monoxide produced is reacted with steam.

\[ \text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \quad K_c = 6.40 \times 10^{-1} \text{ at } 1100 \text{ K} \]

A mixture containing 0.40 mol of CO, 0.40 mol of H\textsubscript{2}O, 0.20 mol of CO\textsubscript{2} and 0.20 mol of H\textsubscript{2} was placed in a 1 dm\textsuperscript{3} flask and allowed to come to equilibrium at 1100 K

(i) Give an expression for $K_c$ for this reaction.

(ii) Calculate the amount, in moles, of each substance present in the equilibrium mixture at 1100 K.