Equilibrium Review

Sulfuric acid, $\text{H}_2\text{SO}_4$, is made industrially by the Contact process. This reaction is an example of a dynamic equilibrium:

$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) \quad \Delta H = -98 \text{ KJmol}^{-1}$$

(a) State two features of a reaction with a dynamic equilibrium.

- The concentrations of the reactants and the products remain the same.
- The rate of the forward reaction is the same as the rate of the reverse reaction.

(b) State and explain what happens to the equilibrium position of this reaction as:

i) the temperature is raised

   moves to the left because the forward reaction is exothermic

ii) the pressure is increased

   moves to the right because there are fewer molecules of gas on the right

iii) Suggest the optimum conditions for the Contact process

Low temp and high pressure

(c) (i) The conditions used for the Contact process are a temperature of 450°C to 600°C and a pressure of around 10 atmospheres. Explain why the optimum conditions are not used.

Temp. A compromise is reached between rate and conversion.
At low temp the rate is too slow.

Pressure - a compromise is reached between cost and conversion.
Catalyst - a catalyst is used to speed up the rate of conversion so that it is cost effective to work at a low pressure.
(ii) Vanadium (V) oxide is used as a catalyst. What effect does this have on the conversion of SO$_2$(g) into SO$_3$(g).

The catalyst speeds up the reaction, but it doesn't change the equilibrium position because it speeds up the forward and reverse reactions equally.

(iii) At least three catalyst chambers are used to ensure maximum conversion of SO$_2$(g). The conversion yield can exceed 98%. State two advantages of this high conversion rate.

More cost efficient and reduces the amount of SO$_2$ pollution.
Le Chatelier's Principle

Hydrogen and Iodine react according to the equation:

\[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{H}_2\text{I}(g) \quad \Delta H = +530 \text{ KJmol}^{-1} \]

(a) State Le Chatelier's principle. When a system in dynamic equilibrium is subjected to a change, the position of equilibrium will shift to minimise the change.

(b) Use Le Chatelier's principle to predict what happens to the position of the equilibrium when:

(i) the temperature is increased
   
   moves to the right - forward reaction is endothermic

(ii) the pressure is increased
   
   No effect - equal number of moles of gas on both sides

(iii) a catalyst is used
   
   Does not alter the position of equilibrium speeds up the rate of the forward and reverse reactions equally

Justify each of your predictions.

(c) Write an expression for \( K_c \) for the equilibrium. State the units, if any.

\[ K_c = \frac{[\text{H}_2\text{I}]^2}{[\text{H}_2][\text{I}_2]} \]
Writing expressions for $K_c$

For each of the following reactions, write an expression for $K_c$. Assuming that the units of concentration are mol dm$^{-3}$, work out the units for $K_c$ in each case. If there are no units, state this.

1. $2$HBr(g) $\rightleftharpoons$ H$_2$(g) + Br$_2$(g)

2. $2$NH$_3$(g) $\rightleftharpoons$ 3H$_2$(g) + N$_2$(g)

3. $2$NO(g) + O$_2$(g) $\rightleftharpoons$ 2NO$_2$(g)

4. $4$PF$_3$(g) $\rightleftharpoons$ P$_4$(g) + 10F$_2$(g)

5. $2$NO(g) $\rightleftharpoons$ N$_2$(g) + O$_2$(g)

6. C$_2$H$_5$OH(l) + CH$_3$COOH(l) $\rightleftharpoons$ CH$_3$COOC$_2$H$_5$(l) + H$_2$O(l)

Look at all the examples in which $K_c$ has no units. What do all these reactions have in common?
Writing expressions for $K_c$

For each of the following reactions, write an expression for $K_c$. Assuming that the units of concentration are mol dm$^{-3}$, work out the units for $K_c$ in each case. If there are no units, state this.

1. \[ \text{2HBr(g)} \rightleftharpoons \text{H}_2(g) + \text{Br}_2(g) \]

   \[ K_c = \frac{[\text{H}_2(g)] [\text{Br}_2(g)]}{[\text{HBr(g)}]^2} \]

   no units

2. \[ \text{2NH}_3(g) \rightleftharpoons 3\text{H}_2(g) + \text{N}_2(g) \]

   \[ K_c = \frac{[\text{H}_2(g)]^3 [\text{N}_2(g)]}{[\text{NH}_3]_2} \]

   mol$^2$ dm$^{-6}$

3. \[ \text{NH}_3(g) \rightleftharpoons 1 \frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{N}_2(g) \]

   \[ K_c = \frac{[\text{H}_2(g)]^{1.5} [\text{N}_2(g)]^{0.5}}{[\text{NH}_3]} \]

   mol dm$^{-3}$

4. \[ \text{2NO(g)} + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g) \]

   \[ K_c = \frac{[\text{NO}_2(g)]^2}{[\text{NO}(g)]^2 [\text{O}_2(g)]} \]

   mol$^{-1}$ dm$^3$ $^+$

5. \[ 4\text{PF}_5(g) \rightleftharpoons \text{P}_4(g) + 10\text{F}_2(g) \]

   \[ K_c = \frac{[\text{P}_4(g)] [\text{F}_2(g)]^5}{[\text{PF}_5(g)]^4} \]

   mol$^7$ dm$^{-21}$

6. \[ \text{2NO(g)} \rightleftharpoons \text{N}_2(g) + \text{O}_2(g) \]

   \[ K_c = \frac{[\text{N}_2(g)] [\text{O}_2(g)]}{[\text{NO(g)}]^2} \]

   no units

7. \[ \text{C}_2\text{H}_5\text{OH(l)} + \text{CH}_3\text{COOH(l)} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5\text{(l)} + \text{H}_2\text{O(l)} \]

   \[ K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5\text{(l)}] [\text{H}_2\text{O}(l)]}{[\text{C}_2\text{H}_5\text{OH}(l)] [\text{CH}_3\text{COOH}(l)]} \]

   no units

Look at all the examples in which $K_c$ has no units. What do all these reactions have in common? **Same no. of moles at each side of equation**
Looking at $K_c$ Values

1. Consider the equilibrium:

$$\text{CH}_3\text{COOH(aq)} + \text{CH}_3\text{CH}_2\text{OH(aq)} \rightleftharpoons \text{CH}_3\text{COOCH}_2\text{CH}_3\text{(aq)} + \text{H}_2\text{O(l)}$$

a) Write an expression for $K_c$ for the esterification process.

$$K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$$

b) Write an expression for $K_c$ for the hydrolysis process.

$$K_c' = \frac{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}$$

c) The $K_c$ value for the esterification reaction is 4.0 at 298K. What is the $K_c$ for the hydrolysis reaction at 298K?

$$\sqrt{4}$$

d) Why is it important to quote the temperature?

$K_c$ alters with $T$

2. Use the data below to answer the questions which follow:

<table>
<thead>
<tr>
<th>example</th>
<th>$K_c$ at 298K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI(g)}$</td>
<td>794</td>
</tr>
<tr>
<td>$\text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{H}_2\text{O(g)} + \text{CO(g)}$</td>
<td>$1.00 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO(g)}$</td>
<td>$4 \times 10^{-31}$</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$</td>
<td>0.05 mol dm$^{-3}$</td>
</tr>
</tbody>
</table>

a) The equilibrium position depends on the value of $K_c$

i) For which of these reactions does the equilibrium lie furthest to the left?

$$\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$$

ii) Where does this reaction take place?

Atmosphere

b) What is the $K_c$ value, and units, for the reaction: $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$ at 298K

$$\sqrt{0.05} \text{ mol}^{-1} \text{ dm}^3$$
The effect of Temperature on $K_c$

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

The $K_c$ values for this reaction at four different temperatures are shown below:

<table>
<thead>
<tr>
<th>temperature/K</th>
<th>$K_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>794</td>
</tr>
<tr>
<td>500</td>
<td>160</td>
</tr>
<tr>
<td>700</td>
<td>54</td>
</tr>
<tr>
<td>1100</td>
<td>25</td>
</tr>
</tbody>
</table>

\[ \text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) + \text{CO}(g) \]

The $K_c$ values for this reaction at four different temperatures are shown below:

<table>
<thead>
<tr>
<th>temperature/K</th>
<th>$K_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$1.00 \times 10^{-5}$</td>
</tr>
<tr>
<td>500</td>
<td>$7.76 \times 10^{-3}$</td>
</tr>
<tr>
<td>800</td>
<td>$2.88 \times 10^{-1}$</td>
</tr>
<tr>
<td>900</td>
<td>$6.03 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

a) For which of these reactions is the forward reaction endothermic?

Explain your answer

\[ \text{H}_2(g) + \text{O}_2(g) \longrightarrow \text{H}_2\text{O}(g) + \text{O}(g) \]

b) Sketch graphs in the boxes below to show the change in $K_c$ with temperature for

i) an exothermic reaction

ii) an endothermic reaction.

Label the axes:

- i) exothermic
- ii) endothermic
**Kc Calculations**

Calculating $K_c$ values from equilibrium concentrations

1. Equilibrium was established at 308K for the system:

$$\text{CO(g)} + \text{Br}_2(g) \rightleftharpoons \text{COBr}_2(g)$$

Analysis of the mixture gave the following concentration values:

- $[\text{CO(g)}] = 8.78 \times 10^{-3} \text{ mol dm}^{-3}$
- $[\text{Br}_2(g)] = 4.90 \times 10^{-3} \text{ mol dm}^{-3}$
- $[\text{COBr}_2(g)] = 3.40 \times 10^{-3} \text{ mol dm}^{-3}$

Calculate the value of the equilibrium constant.

2. At 250°C, equilibrium for the following system was established:

$$\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$$

Analysis of the mixture showed that

- $[\text{PCl}_5(g)] = 1.50 \times 10^{-2} \text{ mol dm}^{-3}$
- $[\text{Cl}_2(g)] = 1.50 \times 10^{-2} \text{ mol dm}^{-3}$
- $[\text{PCl}_3(g)] = 1.18 \times 10^{-3} \text{ mol dm}^{-3}$

Calculate the value of the equilibrium constant.

**Calculating an equilibrium concentration from Kc**

3. For the equilibrium:

$$\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$$

$$K_c = \frac{[\text{PCl}_3(g)][\text{Cl}_2(g)]}{[\text{PCl}_5(g)]}$$

$K_c = 0.19 \text{ mol dm}^{-3}$ at 250°C.

One equilibrium mixture at this temperature contains PCl$_5$ at a concentration of 0.20 mol dm$^{-3}$ and PCl$_3$ at a concentration of 0.010 mol dm$^{-3}$.

Calculate the concentration of the chlorine in this mixture.

4. For the equilibrium:

$$2\text{H}_2\text{S}(g) \rightleftharpoons 2\text{H}_2(g) + \text{S}_2(g)$$

$$K_c = 2.25 \times 10^{-4} \text{ mol dm}^{-3} \text{ at } 1400K.$$  

In an equilibrium mixture,

- $[\text{H}_2\text{S}(g)] = 4.84 \times 10^{-3} \text{ mol dm}^{-3}$ and
- $[\text{S}_2(g)] = 2.33 \times 10^{-3} \text{ mol dm}^{-3}$.

Calculate the equilibrium concentration of hydrogen.
Calculating $K_c$ values from equilibrium numbers of moles

5. Some phosphorus (V) chloride was heated to 250°C in a sealed container until equilibrium was reached according to the following equation.

$$K_c = \frac{[0.044]^2 [0.044]}{[0.004]^2}$$

PCl$_3$(g) $\rightleftharpoons$ PCl$_5$(g) + Cl$_2$(g)

Analysis of the mixture showed that it contained 0.0042 mol of PCl$_3$(g), 0.040 mol of PCl$_5$(g) and 0.040 mol of Cl$_2$(g). The total volume was 2.0 dm$^3$.

Calculate the concentration of each component and hence determine $K_c$.

6. At 250°C, in another equilibrium mixture of the reaction

$$K_c = \frac{[0.15]^2 [0.090]}{[0.019]^2}$$

in a 2.0 dm$^3$ vessel, there is 0.15 mol of PCl$_3$(g) and 0.090 mol of Cl$_2$(g).

Calculate the number of moles of PCl$_5$(g) present at equilibrium.

$$0.0355 = 0.0178$$

The table below shows the composition of two equilibrium mixtures at 485°C.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>No. of moles of H$_2$(g)</th>
<th>No. of moles of I$_2$(g)</th>
<th>No. of moles of HI(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02265</td>
<td>0.02840</td>
<td>0.1715</td>
</tr>
<tr>
<td>2</td>
<td>0.01699</td>
<td>0.04057</td>
<td>0.1779</td>
</tr>
</tbody>
</table>

a) Write the equation for the formation of hydrogen iodide from hydrogen and iodine.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

b) Write an expression for the equilibrium constant, $K_c$.

c) For mixture 1, calculate a value for the equilibrium constant, assuming that the total volume is 2.0 dm$^3$.

d) For mixture 2, calculate a value for the equilibrium constant, assuming that the total volume is 2.0 dm$^3$.

8. This question concerns the equilibrium system

$$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

$$K_c = \frac{[0.66]^2 [0.66]}{[0.33]^2[alcohol]}$$

4.0 at 25°C

In a particular experiment, 0.33 mol of CH$_3$COOH(l), 0.66 mol of CH$_3$COOC$_2$H$_5$(l) and 0.66 mol of H$_2$O(l) are found to be present. Assuming that the total volume is 4.0 dm$^3$, calculate the number of moles of C$_2$H$_5$OH(l) present.

$$\frac{[alcohol]}{4.0} = 0.33$$

Are there any situations where numbers of moles can be used to calculate $K_c$ without having to be converted to concentrations first?

Equal moles on both sides of the balanced equation.
Calculating $K_c$ from Initial amounts

1. 1 mole of ethanoic acid was added to 0.5 moles of ethanol and left in a stoppered flask until equilibrium was reached. At equilibrium 0.58 moles of ethanoic acid were left. Calculate $K_c$ for the reaction:

$$\text{CH}_3\text{COOH(l)} + \text{CH}_3\text{CH}_2\text{OH(l)} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3(\text{l}) + \text{H}_2\text{O(l)}$$

(i) Initial moles

<table>
<thead>
<tr>
<th></th>
<th>CH₃COOH(l)</th>
<th>CH₃CH₂OH(l)</th>
<th>CH₃COOCH₂CH₃(l)</th>
<th>H₂O(l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Eqm</td>
<td>0.58</td>
<td>0.08</td>
<td>0.42</td>
<td>0.42</td>
</tr>
</tbody>
</table>

(ii) Eqm moles

(iii) Write down the concentrations at equilibrium in mol dm⁻³: assume the total volume is V dm³

$$\text{CH}_3\text{COOH(l)} \quad \frac{0.58}{V} \quad \text{CH}_3\text{CH}_2\text{OH(l)} \quad \frac{0.08}{V}$$

$$\text{CH}_3\text{COOCH}_2\text{CH}_3(\text{l}) \quad \frac{0.42}{V} \quad \text{H}_2\text{O(l)} \quad \frac{0.42}{V}$$

(iv) Write the expression for $K_c$

$$K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$$

(v) Use the values in (iii) to calculate $K_c$ and give its units

$$K_c = \frac{0.42 \times 0.42}{0.58 \times 0.08}$$

$$= 3.8 \text{ \ no units}$$
2. 24.0g of ethanoic acid was added to 13.8g of ethanol and left in a stoppered flask until equilibrium was reached. At equilibrium 20.0g of ethyl ethanoate were produced. Calculate K_c for the reaction:

\[ \text{CH}_3\text{COOH}(l) + \text{CH}_3\text{CH}_2\text{OH}(l) \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3(l) + \text{H}_2\text{O}(l) \]

\( i \) Calculate the moles of each substance using the mass provided and Mr:

\[
\begin{align*}
\text{CH}_3\text{COOH}(l) & \quad \frac{24.0}{60} = 0.4 \\
\text{CH}_3\text{CH}_2\text{OH}(l) & \quad \frac{13.8}{46} = 0.3 \\
\text{CH}_3\text{COOCH}_2\text{CH}_3(l) & \quad \frac{20.0}{88} = 0.227
\end{align*}
\]

\[ \text{CH}_3\text{COOH}(l) + \text{CH}_3\text{CH}_2\text{OH}(l) \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3(l) + \text{H}_2\text{O}(l) \]

\( i \) Initial moles

\[
\begin{align*}
0.4 & \quad 0.3 & \quad 0 & \quad 0 \\
0.227 & \quad 0.227 & \quad 0.227 & \quad 0.227
\end{align*}
\]

\( ii \) Eqm moles

\[
\begin{align*}
0.173 & \quad 0.073 & \quad 0.227 & \quad 0.227
\end{align*}
\]

\( iii \) Write down the concentrations at equilibrium in mol dm\(^{-3}\): assume the total volume is V dm\(^3\)

\[
\begin{align*}
\text{CH}_3\text{COOH}(l) & \quad \frac{0.173}{V} \\
\text{CH}_3\text{CH}_2\text{OH}(l) & \quad \frac{0.073}{V} \\
\text{CH}_3\text{COOCH}_2\text{CH}_3(l) & \quad \frac{0.227}{V} \\
\text{H}_2\text{O}(l) & \quad \frac{0.227}{V}
\end{align*}
\]

\( iv \) Write the expression for K_c

\[
K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3(l)][\text{H}_2\text{O}(l)]}{[\text{CH}_3\text{COOH}(l)][\text{CH}_3\text{CH}_2\text{OH}(l)]}
\]

\( v \) Use the values in (iii) to calculate K_c and give its units

\[
\begin{align*}
&= \frac{0.173 \times 0.227}{0.173 \times 0.073} \\
&= \frac{4.08}{\text{no units}}
\end{align*}
\]
3. 417g of PCl₅ vapour was heated in a vessel of volume 20dm³ at 500K. At equilibrium 85.2g of Cl₂ were present. Calculate Kc for the reaction:

\[ \text{PCl}_5(g) \rightarrow \text{PCl}_3(g) + \text{Cl}_2(g) \]

(i) Calculate the moles of each substance from the masses provided:

\[ \frac{417}{208.5} = 2 \quad \text{PCl}_5 \]
\[ \frac{85.2}{71} = 1.2 \quad \text{Cl}_2 \]

(ii) Initial moles

\[ \begin{align*}
\text{PCl}_5 & \quad 2 \quad \\
\text{Cl}_2 & \quad 0 \quad \\
\text{Total} & \quad 2 \quad 0
\end{align*} \]

(iii) Eqm moles

\[ \begin{align*}
\text{PCl}_5 & \quad 0.8 \quad \\
\text{Cl}_2 & \quad 1.2 \quad \\
\text{Total} & \quad 1.2 \quad 1.2
\end{align*} \]

(iv) Eqm concs

\[ \begin{align*}
\frac{0.8}{20} &= 0.04 \\
\frac{1.2}{20} &= 0.06 \\
\frac{1.2}{20} &= 0.06
\end{align*} \]

(iv) Write the expression for Kc

\[ K_c = \frac{[\text{PCl}_3(g)][\text{Cl}_2(g)]}{[\text{PCl}_5(g)]} \]

(v) Use the values in (iii) to calculate Kc and give its units

\[ K_c = \frac{0.06 \times 0.06}{0.04} \]
\[ = 0.09 \text{ mol dm}^{-3} \]
4.2 g of H₂ and 254 g of I₂ vapour were heated in a vessel of volume 5 dm³ at 600 K. At equilibrium 204.8 g of HI were present. Calculate Kc for the reaction:

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

(i) Calculate the moles of each substance using the masses provided and the M_r:

\[
\begin{align*}
\text{H}_2(\text{g}) & \quad \frac{2}{\text{g}} = 1 \\
\text{I}_2(\text{g}) & \quad \frac{254}{2\text{g}} = 1 \\
\text{HI}(\text{g}) & \quad \frac{204.8}{128} = 1.6
\end{align*}
\]

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

(ii) Initial moles

\[
\begin{pmatrix}
1 & 1.6 \\
-1 & -1.6
\end{pmatrix}
\]

(iii) Equilibrium mole:

\[
\begin{pmatrix}
0.2 & 0.2 & 1.6
\end{pmatrix}
\]

\[
\frac{0.2}{5} \quad \frac{0.2}{5} \quad \frac{1.6}{5}
\]

but v will cancel out so

(iv) Write the expression for Kc

\[
K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}
\]

(v) Use the values from (iii) to calculate Kc and give its units

\[
K_c = \frac{\left(\frac{1.6}{5}\right)^2}{\left(\frac{0.2}{5}\right)\left(\frac{0.2}{5}\right)} = 64 \text{ no units.}
\]
### Equilibrium Data for Kc

<table>
<thead>
<tr>
<th>Initial moles of acid (a)</th>
<th>Initial moles of alcohol (b)</th>
<th>Moles of acid at $=_{m}^{\text{a-x}}$</th>
<th>Moles of alcohol at $=_{m}^{\text{b-x}}$</th>
<th>Moles of ester at $=_{m}^{\text{x}}$</th>
<th>Moles of water at $=_{m}^{\text{x}}$</th>
<th>Kc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.18</td>
<td>0.829</td>
<td>0.009</td>
<td>0.171</td>
<td>0.171</td>
<td>3.92</td>
</tr>
<tr>
<td>1.00</td>
<td>0.33</td>
<td>0.707</td>
<td>0.037</td>
<td>0.293</td>
<td>0.293</td>
<td>3.28</td>
</tr>
<tr>
<td>1.00</td>
<td>0.50</td>
<td>0.586</td>
<td>0.086</td>
<td>0.414</td>
<td>0.414</td>
<td>3.40</td>
</tr>
<tr>
<td>1.00</td>
<td>1.00</td>
<td>0.333</td>
<td>0.333</td>
<td>0.667</td>
<td>0.667</td>
<td>4.01</td>
</tr>
<tr>
<td>1.00</td>
<td>2.00</td>
<td>0.142</td>
<td>1.142</td>
<td>0.858</td>
<td>0.858</td>
<td>4.54</td>
</tr>
<tr>
<td>1.00</td>
<td>8.00</td>
<td>0.034</td>
<td>7.034</td>
<td>0.966</td>
<td>0.966</td>
<td>3.90</td>
</tr>
</tbody>
</table>

NB. As the amount of alcohol added is increased the equilibrium shifts further to the right so the amount of products formed should also increase and the amount of acid left unreacted decreases.

On the addition of 8 moles of alcohol the reaction is virtually complete i.e. nearly 1 mole of ester and water are formed.
<table>
<thead>
<tr>
<th>Question</th>
<th>Expected Answers</th>
<th>Marks</th>
</tr>
</thead>
</table>
| 1 (a)    | $K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$ ✓ ✓  
award 1 mark if upside down | [2] |
| (b) (i)  | ![Table](CH_3COOH, C_2H_5OH, CH_3COOC_2H_5, H_2O) |
| (ii)     | $K_c = \frac{5 \times 5}{1 \times 7.5} = 3.3$ ✓ no units ✓  
(or ccf based on answers to (i) and/or (a)) | [2] |
| (c)      | leave experiment longer ✓  
monitor compositions and repeat until constant value ✓ | [2] |
| (d) (i)  | more CH_3COOC_2H_5 & H_2O / less CH_3COOH & C_2H_5OH ✓  
equilibrium $\rightarrow$ right ✓ AW | [2] |
| (ii)     | $K_c$ stays same ✓ | [1] |
| (e)      | stays the same/ catalyst does not shift equilibrium position ✓  
forward & reverse reactions altered by same amount/ equilibrium achieved in less time ✓ | [2] |
| (f) (i)  | equilibrium $\rightarrow$ left ✓  
more reactants / less products ✓ | [2] |
<p>| (ii)     | forward reaction is exothermic ✓ | [1] |
|          | <strong>Total: 16</strong> |       |</p>
<table>
<thead>
<tr>
<th>Question</th>
<th>Expected Answers</th>
<th>Marks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (a) (i)</td>
<td>( K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} ) ✓ ✓ award 1 mark if upside down ( K_p ) expression worth 1 mark</td>
<td>[2]</td>
</tr>
<tr>
<td>(ii)</td>
<td>Equilibrium shifts left because ( K_c ) is very small</td>
<td>[1]</td>
</tr>
<tr>
<td>(iii)</td>
<td>( [\text{O}_2(g)] = \frac{[\text{NO}]^2}{[\text{N}_2] \times K_c} = \frac{(4.0 \times 10^{-18})^2}{1.1 \times 4.8 \times 10^{-31}} ) ✓ ✓ = 0.30 mol dm(^{-3}) ✓ (calculator: 0.303030303) answer given to 2 sig figs ✓ 3.3 ✓ ✓ (upside down) calc: 3.3 7.6 \times 10^{14} ✓ ✓ (missing out (^2)) calc: 7.5757..... 0.37 ✓ ✓ (1.1 on top) calc: 0.366666.. 5.2 \times 10^{-46} ✓ ✓ ('4' values swapped) calc: 5.236363.x \times 10^{-46}</td>
<td></td>
</tr>
<tr>
<td>(b) (i)</td>
<td>( \Delta H ) is +ve ✓ equilibrium moves to the right to compensate for increase in temperature/to lower the temperature / to minimise the change ✓</td>
<td>[3]</td>
</tr>
<tr>
<td>(ii)</td>
<td>increase in proportion of NO ✓ because ( K_c ) increases Can be linked to either increased proportion of NO or enthalpy change ✓</td>
<td></td>
</tr>
<tr>
<td>(iii)</td>
<td>( 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 ) ✓ ✓ species correct for 1st mark 'simplest' balanced equation for 2nd mark NO + ( \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2 ) also gets both marks ( \text{N}_2\text{O}_4 ) is fine ( \text{NO}_2 ) for 1st mark</td>
<td>[2]</td>
</tr>
</tbody>
</table>
| (c) | Optimum Pressure  
      low pressure ✓  
      fewer gaseous moles on left ✓  

Optimum Temperature  
      optimum: low temperature ✓  
      forward reaction is exothermic ✓  

Reason mark can only be awarded if the condition mark is correct.

Condition mark is independent

1000°C used to increase rate with more energetic collisions  
OR so that a greater proportion of molecules exceed activation energy ✓

10 atm used to increase rate by increasing concentration OR increasing collisions ✓

Catalyst used to increase rate by lowering the activation energy/providing a lower energy route ✓  
      NOT increase equilibrium yield

Quality of written communication:
Recognition of a compromise between rate and equilibrium amount ✓

<table>
<thead>
<tr>
<th>[7]</th>
<th>[1]</th>
</tr>
</thead>
</table>

Total: 20
3 (a) Forward and reverse reactions at same rate ✓
Achievable from either direction ✓, requires closed system ✓
concentrations of reactants and products are constant ✓

(b) (i) 
\[ K_c = \frac{[\text{CH}_3\text{OH}(g)]}{[\text{CO}(g)][\text{H}_2(g)]} \]  ✓ ✓ 1 mark for top; 1 mark for bottom

(ii) 
\[ K_c = \frac{(2.6 \times 10^{-5})}{(3.1 \times 10^{-3}) (2.4 \times 10^{-2})^2} = 14.6 \text{ (dm}^3 \text{ mol}^{-2}) \]

(c) (i) Why did the equilibrium move to the right
fewer molecules on right ✓
reaction relieves increase in pressure ✓

(ii) What is the effect, if any, on \( K_c \)
\( K_c \) stays same ✓

(iii) Rate changes
Rate increases ✓
Increased collisions/more concentrated ✓
Rates initially forward faster than reverse ✓
At equil, rates same ✓

(d) (i) \( K_c \) decreases so products decrease/reactants increase ✓
Therefore equilibrium moves to the left/to endothermic side ✓
2nd mark dependent on first.

(ii) \( \Delta H \) is negative because of equilibrium change in (i) ✓
Mark consequential on (i)

| / | = alternative and acceptable answers for the same marking point |
| : | = separates marking points |
| NOT | = answers which are not worthy of credit |
| () | = words which are not essential to gain credit |
| _____ | = (underlining) key words which **must** be used to gain credit |
| ecf | = error carried forward |
| AW | = alternative wording |
| ora | = or reverse argument |

\[ a \]

(a) (i) \[ K_c = \frac{[\text{NO}_2(g)]^2}{[\text{N}_2\text{O}_4(g)]} \]  

(ii) \[ K_c = \frac{(0.0150)^2}{(0.0390)} = 5.77 \times 10^{-3} \]  

\[ \text{mol dm}^{-3} \]  

\[ \checkmark \]  

accept 5.76923 to 5.8 \times 10^{-3}  

If (i) is upside down: \[ \frac{[\text{N}_2\text{O}_4(g)]}{[\text{NO}_2(g)]} \]  

then ans = 173 \[ \checkmark \] \[ \text{dm}^3 \text{ mol}^{-1} \]  

\[ \checkmark \]  

accept 173.33333.....to 170  

If no square in (i): \[ \frac{[\text{NO}_2(g)]}{[\text{N}_2\text{O}_4(g)l} \]  

then ans = 0.384615..\[ \checkmark \] \[ \text{no units} \]  

\[ \checkmark \]  

(must be stated)  

If no square in (i) and inverse: \[ \frac{[\text{N}_2\text{O}_4(g)]}{[\text{NO}_2(g)l} \]  

2.6 \[ \checkmark \] \[ \text{no units} \]  

\[ \checkmark \]  

(must be stated)  

(b) \( \Delta H = (2 \times 33) -(9) \)  

= (+)57 \[ \text{kJ} \text{ mol}^{-1} \]  

\[ \checkmark \]  

common errors:  

\[ -57 \checkmark \times \]  

\[ +24 \checkmark \times \]  

\[ +75 \checkmark \times \]  

\[ -24 \times \]  

\[ \checkmark \]  

(c) **change**  

more \( \text{NO}_2 \) **/ less \( \text{N}_2\text{O}_4 \) \[ \checkmark \]  

**explanation**  

equilibrium position \[ \rightarrow \] right or forwards / \( K_c \) increases \[ \checkmark \]  

reaction is endothermic \[ \checkmark \]  

**THIS ANSWER IS CONSEQUENTIAL ON SIGN OF THE ANSWER TO (i)**  

**BUT**, a candidate interpreting a ‘+’ enthalpy change as ‘exothermic’ (or vice versa) will lose the 3rd mark but the 2 ‘logic marks’ before are still consequentially available.  

\[ d \]

1 mol \( \text{N}_2\text{O}_4 \) reacts with 2 mol \( \text{NaOH} \)  

\[ \checkmark \]  

amount of \( \text{NaOH} \) required = 0.00930 mol  

\[ \checkmark \]  

volume \( \text{NaOH} \) = 1000 \[ 0.0093/0.300 = 31.0 \text{ cm}^3 \]  

\[ / 0.0310 \text{ dm}^3 \]  

\[ \checkmark \]  

**Common errors**  

\[ 3.1 \times 10^x \text{ (where x is incorrect)} \]  

\[ \checkmark \times \]  

\[ 15.5 \text{ cm}^3 / 0.0155 \text{ dm}^3 \]  

\[ \checkmark \times \]  

\[ 1.55 \times 10^x \text{ (where x is incorrect)} \]  

\[ \checkmark \times \]  

\[ 62 \text{ cm}^3 / 0.062 \text{ dm}^3 \]  

\[ \checkmark \times \]  

\[ 6.2 \times 10^x \text{ (where x is incorrect)} \]  

\[ \checkmark \times [3] \]  

[Total: 11]