4.2 Equilibria

Many reactions are reversible

\[ \text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \]

All reversible reactions reach an **dynamic equilibrium** state.

Dynamic equilibrium occurs when **forward** and **backward** reactions are occurring at **equal rates**. The **concentrations** of reactants and products stays **constant** and the reaction is continuous.

We use the expression ‘**position of equilibrium**’ to describe the composition of the equilibrium mixture. If the position of equilibrium favours the reactants (also described as “towards the left”) then the equilibrium mixture will contain mostly reactants.

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**Le Chatelier’s Principle**

We use Le Chatelier’s principle to work out how changing external conditions such as temperature and pressure affect the position of equilibrium.

Le Chatelier’s principle states that if an external condition is changed the equilibrium will shift to oppose the change (and try to reverse it).

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**Effect of Changing Concentration**

\[ \text{A} + \text{B} \rightleftharpoons \text{C} + \text{D} \]

If extra A is added to the equilibrium mixture the forward reaction occurs more to oppose the change and remove some of the extra A and form extra C and D. The equilibrium has moved to the right.

If C is removed from the equilibrium mixture the forward reaction occurs more to oppose the change and replace some of the C removed; the amount of D therefore increases whilst A and B are used up. The equilibrium has moved to the right.
Effect of Concentration on equilibrium

Increasing the concentration OH\textsuperscript{-} ions causes the equilibrium to shift to oppose this and move in the forward direction to remove OH\textsuperscript{-} ions. The position of equilibrium will shift towards the right, giving a higher yield of I\textsuperscript{-} and IO\textsuperscript{-}. (The colour would change from brown to colourless)

Adding H\textsuperscript{+} ions reacts with the OH\textsuperscript{-} ions and reduces their concentration so the equilibrium shifts back to the left giving brown colour.

If the concentration of Cl\textsuperscript{-} ions is increased by adding extra HCl to an equilibrium mixture, the position of equilibrium will shift towards the products and thereby removing some of the extra Cl\textsuperscript{-} ions added. So the colour will change from pink to blue.

Effect of Temperature on equilibrium

If temperature is increased the equilibrium will shift to oppose this and move in the endothermic direction to try to reduce the temperature by absorbing heat.

Typical Exam question: What effect would increasing temperature have on the yield of ammonia?

\[ \text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \quad \Delta H = -\text{ve exo} \]

Exam level answer: must include bold points

If temperature is decreased the equilibrium will shift to oppose this and move in the exothermic, backwards direction to try to decrease temperature. The position of equilibrium will shift towards the left, giving a lower yield of ammonia.

Low temperatures may give a higher yield of product but will also result in slow rates of reaction. Often a compromise temperature is used that gives a reasonable yield and rate

Effect of Pressure on equilibrium

Increasing pressure will cause the equilibrium to shift towards the side with fewer moles of gas to oppose the change and thereby reduce the pressure.

Typical Exam question: What effect would increasing pressure have on the yield of methanol?

\[ \text{CO (g)} + 2\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH (g)} \]

Exam level answer: must include bold points

Decreasing pressure will cause the equilibrium to shift towards the side with more moles of gas to oppose the change and thereby increase the pressure.

If the number of moles of gas is the same on both sides of the equation then changing pressure will have no effect on the position of equilibrium

\[ \text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl} \]

Increasing pressure may give a higher yield of product and will produce a faster rate. Industrially high pressures are expensive to produce (high electrical energy costs for pumping the gases to make a high pressure) and the equipment is expensive (to contain the high pressures)
Effect of Catalysts on equilibrium

A catalyst has no effect on the position of equilibrium, but it will speed up the rate at which the equilibrium is achieved.

It does not effect the position of equilibrium because it speeds up the rates of the forward and backward reactions by the same amount.

Catalysts speeds up the rate allowing lower temperatures to be used (and hence lower energy costs) but have no effect on equilibrium.

Environmental benefits of Catalysts

Catalysed reactions can occur at lower temperature so less fuel needed and fewer emissions from fuels. Catalysed reaction enables use of an alternative process with higher atom economy so meaning fewer raw materials needed and less waste products are produced.

Importance of equilibrium to industrial processes

Both the rate of reaction and percentage yield must be considered. The key quantity to consider is mass of product produced per unit time.

Having a fast rate of reaction does not mean necessarily that a good yield will be achieved. Sometimes a compromise is needed.

Optimum conditions of temperature and pressure are used that give the lowest cost, rather than the fastest reaction or highest percentage yield.

Industrial processes cannot exist in true equilibrium since the products are removed as they are formed to improve conversion of reactants. They are not closed systems.

Haber process

\[ \text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \quad \Delta H = -\text{ve exo} \]

The Haber process is used to manufacture ammonia, which can be used to produce nitrogen-based fertilisers.

The raw materials for the Haber process are nitrogen and hydrogen. Nitrogen is obtained from the air and hydrogen may be obtained from natural gas or other sources.

Conditions used T= 450°C, P= 200 – 1000 atm, catalyst = iron

Low temperature gives good yield as equilibrium reaction will shift in the exothermic reaction to counteract the low temperature. A low temperature will produce a slow rate of reaction. Therefore a compromise temperature of 450°C is used that gives a fast reaction without giving a very small percentage yield.

A high pressure gives good yield because the reaction will shift to the products as there are fewer moles of gas on the products side. This opposes the low pressure.

In general increasing pressure will increase reaction rate. It is worth considering that increasing pressure has a limited effect on the rate of heterogeneous catalysed reactions because the reaction takes place on surface of the iron catalyst. The active sites on the iron catalyst surface are already saturated with reactant molecules so increasing pressure won’t make a significant increase in rate.

High pressures are expensive to generate. Too high a pressure would lead to too high electrical energy costs for pumps to produce the pressure. A moderately high pressure is used that balances the rate and yield with the cost of producing the pressure. In addition, the higher the pressure used, the higher the cost of the equipment needed to withstand the pressure.

The catalysts speeds up the rate of reaction which allows a lower temperature to be used to get the required rate of reaction. This significantly lowers the energy costs.

On leaving the reactor the gases enter a cooler. On cooling, the ammonia liquefies and is removed. Nitrogen and hydrogen stay as gases. The unreacted nitrogen and hydrogen are recycled back in to the reactor, so no raw materials are wasted and improve their atom economy.
**Uses of ammonia**

**Making fertilisers**
Reacting ammonia with acids can make fertilisers such as ammonium sulfate, ammonium nitrate or ammonium phosphate.

**Making nitric acid**
Ammonia is used to make nitric acid.

**Uses of nitric acid**
- make fertilisers such as ammonium nitrate.
- make explosives (e.g. TNT)
- making various dyes, drugs, polymers

\[
\begin{align*}
2\text{NH}_3 + \text{H}_2\text{SO}_4 &\rightarrow (\text{NH}_4)_2\text{SO}_4 \\
\text{Ammonia} + \text{sulfuric acid} &\rightarrow \text{ammonium sulfate} \\
\text{NH}_3 + \text{HNO}_3 &\rightarrow \text{NH}_4\text{NO}_3 \\
\text{Ammonia} + \text{nitric acid} &\rightarrow \text{ammonium nitrate}
\end{align*}
\]

---

**Contact process**
Sulfuric acid is produced by the contact process. There are several stages in the process.

**Stage 1** Sulfur is burnt in air to produce sulfur dioxide

\[
\text{S (s) + O}_2 (g) \rightarrow \text{SO}_2 (g)
\]

**Stage 2** Sulfur dioxide is reacted with oxygen to produce sulfur trioxide in a reversible reaction

\[
\text{SO}_2 (g) + \frac{1}{2} \text{O}_2 (g) \rightleftharpoons \text{SO}_3 (g) \quad \Delta H = -98 \text{ kJ mol}^{-1}
\]

Conditions used: \( T = 450^\circ \text{C}, P = 10 \text{ atm}, \text{catalyst} = \text{V}_2\text{O}_5 \)

Low temperatures give higher yields as the equilibrium reaction will shift in the exothermic reaction to oppose the low temperature. Low temperatures will produce a slow rate of reaction. Therefore a compromise temperature of 450°C is used that gives a fast reaction without giving a very small percentage yield.

The pressure used is just above atmospheric pressure. Higher pressure will not have much of an effect on the yield as there is only a slight increase in the moles of gaseous products compared to the moles of reactants. The vanadium (V) oxide catalyst used is a heterogeneous catalyst. Increasing pressure has a limited effect on the rate of heterogeneous catalysed reactions because the reaction takes place on the surface of the catalyst. The active sites on the \( \text{V}_2\text{O}_5 \) catalyst surface are already saturated with reactant molecules so increasing pressure will not make a significant increase in rate.

The vanadium (V) oxides catalyse the reaction in a two-step reaction. The \( \text{V}_2\text{O}_5 \) changes oxidation number in the first step but reforms in the second step.

**step 1** \( \text{SO}_2 + \text{V}_2\text{O}_5 \rightarrow \text{SO}_3 + \text{V}_2\text{O}_4 \)

**step 2** \( 2\text{V}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{V}_2\text{O}_5 \)

**Stage 3:** Sulphur trioxide is dissolved in 98% sulfuric acid to produce fuming sulfuric acid (called Oleum). The Oleum is the diluted to produce concentration sulfuric acid. The sulfur trioxide is not dissolved directly in water because the reaction is too exothermic. The heat produced causes the sulfuric acid to evaporate.

\[
\begin{align*}
\text{SO}_3 (g) + \text{H}_2\text{SO}_4 (l) &\rightleftharpoons \text{H}_2\text{SO}_7 (l) \\
\text{H}_2\text{SO}_7 (l) + \text{H}_2\text{O (l)} &\rightarrow \text{H}_2\text{SO}_4 (l)
\end{align*}
\]
The Equilibrium law:
Writing an expression for Equilibrium constant $K_c$

For a generalised reaction

$$mA + nB \rightarrow pC + qD$$

$m,n,p,q$ are the stoichiometric balancing numbers

A,B,C,D stand for the chemical formula

$K_c = \text{equilibrium constant}$

$$K_c = \frac{[C]^p[D]^q}{[A]^m[B]^n}$$

$[ \, ]$ means the equilibrium concentration

Example 1

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

**Example 2:** writing $K_c$ expression

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

$$K_c = \frac{[HCl(g)]^2}{[H_2(g)][Cl_2(g)]}$$

$K_c = \frac{[mol dm^{-3}]^2}{[mol dm^{-3}][mol dm^{-3}]} = \text{no unit}$

**Calculating $K_c$**

Most questions first involve having to work out the equilibrium moles and then concentrations of the reactants and products.

Usually the question will give the initial amounts (moles) of the reactants, and some data that will help you work out the equilibrium amounts.

**Calculating the moles at equilibrium**

moles of reactant at equilibrium = initial moles – moles reacted

moles of product at equilibrium = initial moles + moles formed
Example 3
For the following equilibrium

\[ \text{H}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{HCl}(g) \]

In a container of volume 600 cm\(^3\) there were initially 0.5 mol of \(\text{H}_2\) and 0.6 mol of \(\text{Cl}_2\). At equilibrium there were 0.2 mol of \(\text{HCl}\). Calculate \(K_c\).

<table>
<thead>
<tr>
<th>(\text{H}_2)</th>
<th>(\text{Cl}_2)</th>
<th>(\text{HCl})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial moles</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Equilibrium moles</td>
<td>0.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

It is often useful to put the mole data in a table.

It is often useful to put the mole data in a table.

Using the balanced equation if 0.2 mol of \(\text{HCl}\) has been formed it must have used up 0.1 mol of \(\text{Cl}_2\) and 0.1 mol of \(\text{H}_2\) (as 1:2 ratio).

Work out the moles at equilibrium for the reactants

- moles of hydrogen at equilibrium = 0.5 – 0.1 = 0.4
- moles of chlorine at equilibrium = 0.6 – 0.1 = 0.5

<table>
<thead>
<tr>
<th>(\text{H}_2)</th>
<th>(\text{Cl}_2)</th>
<th>(\text{HCl})</th>
</tr>
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<tbody>
<tr>
<td>Initial moles</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Equilibrium moles</td>
<td>0.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

| Equilibrium concentration (M) | 0.4/0.6 = 0.67 | 0.5/0.6 = 0.83 | 0.2/0.6 = 0.33 |

Finally put concentrations into \(K_c\) expression

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

\[ K_c = \frac{0.33^2}{0.67 \times 0.83} = 0.196 \text{ no unit} \]

Example 4
For the following equilibrium

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

Initially there were 1.5 moles of \(\text{N}_2\) and 4 mol of \(\text{H}_2\) in a 1.5 dm\(^3\) container. At equilibrium 30% of the Nitrogen had reacted. Calculate \(K_c\).

<table>
<thead>
<tr>
<th>(\text{N}_2)</th>
<th>(\text{H}_2)</th>
<th>(\text{NH}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial moles</td>
<td>1.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Equilibrium moles</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

30% of the nitrogen had reacted = 0.3 x 1.5 = 0.45 mol reacted. Using the balanced equation 3 x 0.45 mol of \(\text{H}_2\) must have reacted and 2 x 0.45 mol of \(\text{NH}_3\) must have formed.

Work out the moles at equilibrium for the reactants and products

- moles of hydrogen at equilibrium = 4.0 – 0.45 x 3 = 2.65
- moles of nitrogen at equilibrium = 1.5 – 0.45 = 1.05
- moles of ammonia at equilibrium = 0 + (0.45 x 2) = 0.9

<table>
<thead>
<tr>
<th>(\text{N}_2)</th>
<th>(\text{H}_2)</th>
<th>(\text{NH}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial moles</td>
<td>1.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Equilibrium moles</td>
<td>1.05</td>
<td>2.65</td>
</tr>
</tbody>
</table>

| Equilibrium concentration (M) | 1.05/1.5 = 0.7 | 2.65/1.5 = 1.77 | 0.9/1.5 = 0.6 |

Finally put concentrations into \(K_c\) expression

\[ K_c = \frac{[\text{NH}_3(g)]^2}{[\text{N}_2(g)][\text{H}_2(g)]^3} \]

\[ K_c = \frac{0.6^2}{0.7 \times 1.77^3} = 0.0927 \text{ mol}^{-2} \text{ dm}^6 \]
Calculating the amounts of the equilibrium mixture from Kc

Using algebra it is possible to work out the amounts of each component in an equilibrium mixture using the value of Kc.

Example 5

For the following equilibrium

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

If 0.200 mol of H\(_2\) and 0.200 mol of Br\(_2\) are mixed and allowed to reach equilibrium. If K\(_c\) = 0.210 what are the equilibrium amounts of each substance.

\[ K_c = \frac{[\text{HBr}]}{[\text{H}_2][\text{Br}_2]} \]

Make \(x\) = moles of H\(_2\) that have reacted at equilibrium

\[ \frac{V}{V} = \frac{(2x/V)^2}{(0.2-x)/V \cdot (0.2-x)/V} \]

\[ 0.21 = \frac{(2x)^2}{(0.2-x) \cdot (0.2-x)} \]

\[ 0.21 = \frac{(2x)^2}{(0.2-x)^2} \]

\[ \sqrt{0.21} = \frac{2x}{0.2-x} \]

\[ 0.458(0.2-x) = 2x \]

\[ 0.0917 - 0.458x = 2x \]

\[ 0.0917 = 2x + 0.458x \]

\[ x = \frac{0.0917}{2.458} \]

\[ x = 0.0373 \]

So at equilibrium

Moles of H\(_2\) = 0.2000 - 0.0373 = 0.163 mol

Moles of Br\(_2\) = 0.2000 - 0.0373 = 0.163 mol

Moles of HBr = 2x 0.0373 = 0.0746 mol
Practical: Working out equilibrium constant Kc

A common experiment is working out the equilibrium constant for an esterification reaction. Ethanol and ethanoic acid are mixed together with a sulfuric acid catalyst.

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

Ethanoic acid  Ethanol  Ethyl Ethanoate

Method

Part 1 Preparing the equilibrium mixture
1 Use burettes to prepare a mixture in boiling tube of carboxylic acid, alcohol, and dilute sulfuric acid.
2 Swirl and bung tube. Leave the mixture to reach equilibrium for one week

Part 2 Titrating the equilibrium mixture
1 Rinse a 250 cm\(^3\) volumetric flask with distilled water.
2 Use a funnel to transfer the contents of the boiling tube into the flask. Rinse the boiling tube with water and add the washings to the volumetric flask.
3 Use distilled water to make up the solution in the volumetric flask to exactly 250 cm\(^3\).
4 Stopper the flask, then invert and shake the contents thoroughly.
5 Use the pipette to transfer 25.0 cm\(^3\) of the diluted equilibrium mixture to a 250 cm\(^3\) conical flask.
6 Add 3 or 4 drops of phenolphthalein indicator to the conical flask.
7 Set up the burette with sodium hydroxide solution.
8 Add the sodium hydroxide solution from the burette until the mixture in the conical flask just turns pink. Record this burette reading in your table.
9 Repeat the titration until you obtain a minimum of two concordant titres.

The sodium hydroxide will react with the sulfuric acid catalyst and any unreacted carboxylic acid in the equilibrium mixture

There are many different calculations that can be based on this experiment. Let’s look at general stages. Not all calculations will use all the stages.

Working out initial amount of moles of reactants
The amount of moles of alcohol and carboxylic acid can be calculated from the densities and volumes of liquids added

\[\text{Moles} = \text{Mass} / \text{Mr}\]

The initial amount of moles of acid catalyst used is usually determined by titrating a separate sample of catalyst with sodium hydroxide

Working out equilibrium amount of moles of acid present from the titre results
39.0 cm\(^3\) of 0.400 mol dm\(^{-3}\) sodium hydroxide was used in the above titration. The initial moles of sulphuric acid was 5x10\(^{-4}\) mol. Calculate the moles of ethanoic acid present at equilibrium

\[\text{Amount of NaOH} = \text{vol} \times \text{conc}\]
\[= 0.039 \times 0.400\]
\[= 0.0156 \text{ mol}\]
So total amount of H\(^+\) present in 25cm\(^3\) = 0.0156 mol
So total amount of H\(^+\) present in 250cm\(^3\) = 0.156 mol

Total mol acid present = moles of carboxylic acid + moles of acid catalyst
So
\[\text{Amount of carboxylic acid at equilibrium} = 0.156 - (5 \times 10^{-4} \times 2)\]
\[= 0.155 \text{ mol}\]

The pink colour of the phenolphthalein in the titration can fade after the end-point of the titration has been reached because the addition of sodium hydroxide may make the equilibrium shift towards the reactants
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Calculating the equilibrium constant

Finally calculate the equilibrium constant. To work out equilibrium concentrations divide the equilibrium amounts by the total volume. Then put in Kc expression

\[ K_c = \frac{[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3] [\text{H}_2\text{O}]}{[\text{CH}_3\text{CO}_2\text{H}] [\text{CH}_3\text{CH}_2\text{OH}]} \]

In order to confirm that one week was sufficient time for equilibrium to be established in the mixture from Part 1, several mixtures could be made and left for different amount of time. If the resulting Kc is the same value then it can be concluded the time is sufficient.

Working out equilibrium amount of moles of other substances

Calculate the equilibrium amount of ethanol, ethyl ethanoate and water if there were initially 0.400 mol of ethanol and 0.500 mol of ethanoic acid and at equilibrium there were 0.155 mol of ethanoic acid.

Amount of ethanoic acid that reacted = initial amount – equilibrium amount

= 0.5 – 0.155

= 0.344 mol

Amount of ethanol at equilibrium = initial amount - amount that reacted

= 0.400 – 0.344

= 0.056 mol

Amount of ethyl ethanoate at equilibrium = initial amount + amount that formed

= 0 + 0.344

= 0.344 mol

Amount of water at equilibrium = initial amount + amount that formed

= 0 + 0.344

= 0.344 mol

The amount of water at equilibrium would not really be 0 as there would be water present in the acid catalyst.
Partial Pressures and Kp

If a reaction contains gases an alternative equilibrium expression can be set up using the partial pressures of the gases instead of concentrations.

Partial Pressure

The partial pressure of a gas in a mixture is the pressure that the gas would have if it alone occupied the volume occupied by the whole mixture.

If a mixture of gases contains 3 different gases then the total pressure will equal the 3 partial pressure added together

\[ P = p_1 + p_2 + p_3 \]

\[ p_1 = x_1 \cdot P \]

\[ \text{mole fraction} = \frac{\text{number of moles of a gas}}{\text{total number of moles of all gases}} \]

For a 3 part mixture

\[ x_1 = \frac{y_1}{y_1 + y_2 + y_3} \]

Example 6: A mixture contains 0.2 moles \( \text{N}_2 \), 0.5 moles \( \text{O}_2 \) and 1.2 moles of \( \text{CO}_2 \). If the total pressure is 3kPa. What are the partial pressures of the 3 gases?

Total moles of gas = 0.5 + 1.2 + 0.2
= 1.9

\begin{align*}
\text{mole fraction} \text{ of } \text{N}_2 &= \frac{0.2}{1.9} = 0.105 \\
\text{mole fraction} \text{ of } \text{O}_2 &= \frac{0.5}{1.9} = 0.263 \\
\text{mole fraction} \text{ of } \text{CO}_2 &= \frac{1.2}{1.9} = 0.632 \\
\text{Partial pressure} \text{ of } \text{N}_2 &= 0.105 \times 3 = 0.315 \\
\text{Partial pressure} \text{ of } \text{O}_2 &= 0.263 \times 3 = 0.789 \\
\text{Partial pressure} \text{ of } \text{CO}_2 &= 0.632 \times 3 = 1.896
\end{align*}

Writing an expression for \( K_p \)

\[ \text{Kp} = \frac{p^2 \text{NH}_3}{p \text{N}_2 \cdot \text{p}^3 \text{H}_2} \]

\( p \) means the partial pressure of that gas

\( K_p = \text{equilibrium constant} \)

Only include gases in the \( K_p \) expression. Ignore solids, liquids, and aqueous substances.
Working out the unit of Kp

Put the unit of pressure(kPa) into the Kp equation

\[
Kp = \frac{p^2 \text{NH}_3}{p\text{N}_2 \cdot p^3\text{H}_2}
\]

Unit = \frac{kPa^2}{kPa \cdot kPa^3} = \frac{1}{kPa^2}

Cancel out units

However, if the equation is written the other way round, the value of Kp will be the inverse of above and the units will be kPa^2. It is important therefore to write an equation when quoting values of Kp.

Heterogeneous equilibria for Kp

Kp expressions only contain gaseous substances. Any substance with another state is left out

\[
\text{CaCO}_3 (s) \rightleftharpoons \text{CaO} (s) + \text{CO}_2 (g)
\]

Kp = \text{p CO}_2

Unit kPa

Example 7

For the following equilibrium

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

1 mole of N₂ and 3 moles of H₂ are added together and the mixture is allowed to reach equilibrium. At equilibrium 20% of the N₂ has reacted. If the total pressure is 2kPa what is the value of Kp?

<table>
<thead>
<tr>
<th></th>
<th>N₂</th>
<th>H₂</th>
<th>NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial moles</td>
<td>1.0</td>
<td>3.0</td>
<td>0</td>
</tr>
<tr>
<td>Equilibrium moles</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

20% of the nitrogen had reacted = 0.2 x 1.0 = 0.2 moles reacted. Using the balanced equation 3 x 0.2 moles of H₂ must have reacted and 2x 0.2 moles of NH₃ must have formed

mole of nitrogen at equilibrium = 1.0 – 0.2 = 0.8

mole of hydrogen at equilibrium = 3.0 – 0.20 x3 = 2.40

mole of product at equilibrium = initial moles + moles formed

mole of ammonia at equilibrium = 0 + (0.2 x 2) = 0.4

<table>
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<tr>
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<th>N₂</th>
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<th>NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial moles</td>
<td>1.0</td>
<td>3.0</td>
<td>0</td>
</tr>
<tr>
<td>Equilibrium moles</td>
<td>0.80</td>
<td>2.40</td>
<td>0.40</td>
</tr>
<tr>
<td>Mole fractions</td>
<td>0.8/3.6 =0.222</td>
<td>2.40/3.6 =0.667</td>
<td>0.40/3.6 =0.111</td>
</tr>
<tr>
<td>Partial pressure</td>
<td>0.222 x2 = 0.444</td>
<td>0.667 x2 =1.33</td>
<td>0.111 x2 = 0.222</td>
</tr>
</tbody>
</table>

Finally put concentrations into Kp expression

\[
Kp = \frac{p^2 \text{NH}_3}{p\text{N}_2 \cdot p^3\text{H}_2}
\]

\[
Kp = \frac{0.222^2}{0.444 \times 1.33^3} = 0.0469 \text{kPa}^2
\]
Application of rates and equilibrium

Effect of changing conditions on value of $K_c$ or $K_p$

The larger the $K_c$ the greater the amount of products. If $K_c$ is small we say the equilibrium favours the reactants.

$K_c$ and $K_p$ only change with temperature. It does not change if pressure or concentration is altered. A catalyst also has no effect on $K_c$ or $K_p$.

Effect of Temperature on position of equilibrium and $K_c$

If $K_c$ is small we say the equilibrium favours the reactants.

In this equilibrium which is exothermic in the forward direction:

$$N_2(\text{g}) + 3H_2(\text{g}) \rightleftharpoons 2NH_3(\text{g})$$

If temperature is increased the reaction will shift to oppose the change and move in the backwards endothermic direction. The position of equilibrium shifts left. The value of $K_c$ gets smaller as there are fewer products.

Effect of Temperature on rate

As the temperature increases a significantly bigger proportion of particles have energy greater than the activation energy, so the frequency of successful collisions increases.

Effect of Concentration on position of equilibrium and $K_c$

Increasing concentration of $H_2$ would move equilibrium to the right lowering concentration of $H_2$ and $Cl_2$ and increasing concentration of HCl. The new concentrations would restore the equilibrium to the same value of $K_c$.

Effect of Concentration and pressure on rate

At higher concentrations(and pressures) there are more particles per unit volume and so the particles collide with a greater frequency and there will be a higher frequency of effective collisions.

Effect of Pressure on position of equilibrium and $K_p$

Increasing pressure does not change $K_p$. The increased pressure increases the pressure terms on bottom of $K_p$ expression more than the top. The system is no longer in equilibrium so the equilibrium shifts to the right increasing mole fractions of products and decreases the mole fractions of reactants. The top of $K_p$ expression therefore increases and the bottom decreases until the original value of $K_p$ is restored.

Increasing pressure does not change $K_p$. The increased pressure increases the pressure terms on bottom of $K_p$ expression more than the top. The system is no longer in equilibrium so the equilibrium shifts to the right increasing mole fractions of products and decreases the mole fractions of reactants. The top of $K_p$ expression therefore increases and the bottom decreases until the original value of $K_p$ is restored.

$$K_p = \frac{x^2NH_3 \cdot P^2}{xN_2 \cdot x^3H_2 \cdot P^4}$$

Where P is total pressure and $x$ mole fraction.

In this equilibrium which has fewer moles of gas on the product side:

$$N_2(\text{g}) + 3H_2(\text{g}) \rightleftharpoons 2NH_3(\text{g})$$

If pressure is increased the reaction will shift to oppose the change and move in the forward direction to the side with fewer moles of gas. The position of equilibrium shifts right. The value of $K_p$ stays the same though as only temperature changes the value of $K_p$.

The position of equilibrium will change if pressure is altered but the value of $K_p$ stays constant as $K_p$ only varies with temperature.

Changing concentration would shift the position of equilibrium but the value of $K_c$ would not change.
Equilibrium constants and feasibility

Values of equilibrium constants can all be used to predict the extent a reaction might occur.

<table>
<thead>
<tr>
<th>Reaction 'does not go'</th>
<th>Reactants predominate in an equilibrium</th>
<th>equal amounts of products and reactants</th>
<th>Products predominate in an equilibrium</th>
<th>Reaction goes to completion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_c &lt; 10^{-10}$</td>
<td>$K_c \approx 0.1$</td>
<td>$K_c \approx 1$</td>
<td>$K_c \approx 10$</td>
<td>$K_c &gt; 10^{10}$</td>
</tr>
</tbody>
</table>

$s_{total}$ increases the magnitude of the equilibrium constant increases since $S = R \ln K$

Where $K$ is equilibrium constant $K_c$ or $K_p$

This equation shows a reaction with a $K_c > 1$ will therefore have a positive $s_{total}$
Partition coefficients

Solvent extraction splits a solute between two immiscible liquid solvents. The solute will be split between the two solvents in an equilibrium.

Solute in aqueous solvent  \rightarrow  Solute in organic solvent

The partition coefficient $K_{pc}$ can be calculated from the equilibrium expression

$$K_{pc} = \frac{\text{[solute in organic]}}{\text{[solute in aqueous]}}$$

$K_{pc}$ is defined as equilibrium constant for the solution of a solute between two immiscible solvents.

Example 8

3.56g of phenylamine was produced in an experiment. It was present in 30cm$^3$ of an alkaline solution. The phenylamine was extracted by addition of 50cm$^3$ of an organic solvent dichloromethane. After the extraction, the dichloromethane layer contained 3.01g of phenylamine.

Calculate the partition coefficient, $K_{pc}$, of phenylamine between dichloromethane and water.

mass left in water layer = 3.56 – 3.01 = 0.55 g

$$K_{pc} = \frac{(3.01/50)}{(0.55/30)} = 3.28$$

Example 9

The partition coefficient of substance Y between ether and water is 35.0

A solution contains 3.50 g of Y dissolved in 0.500 dm$^3$ of water.

Calculate the mass of Y that can be extracted from this aqueous solution by mixing it with 0.050 dm$^3$ of ether.

mass left in water layer = 3.50 – $x$

$$K_{pc} = \frac{(x/0.05)}{((3.5-x)/0.50)} = 35$$

$$\frac{10x}{(3.5-x)} = 35$$

$x$=2.72g