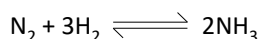


## 1.6 Equilibria

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

Many reactions are reversible



The term dynamic means both forward and backward reactions are occurring simultaneously

### Two features of Dynamic Equilibrium

1. **Forward** and **backward** reactions are occurring at **equal rates**.
2. The **concentrations** of reactants and products stays **constant**

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.

### 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).

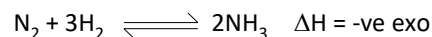
### Effect of Temperature on equilibrium

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.

And its reverse

If temperature is decreased the **equilibrium will shift to oppose** this and move in the **exothermic** direction to try to **increase the temperature** by giving out heat.

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



Exam level answer : must include bold points

If temperature is increased the **equilibrium will shift to oppose** this and move in the **endothermic, 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.

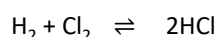
### Effect of Pressure on equilibrium

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**.

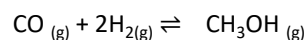
And its reverse

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



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

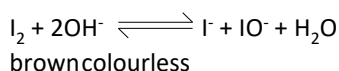


Exam level answer : must include bold points

If pressure is increased the **equilibrium will shift to oppose** this and move towards the side with **fewer moles of gas** to try to **reduce the pressure**. The position of equilibrium will **shift towards the right** because there are 3 moles of gas on the left but only 1 mole of gas on the right, giving a **higher yield of methanol**.

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 Concentration on Equilibrium



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

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

## 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.

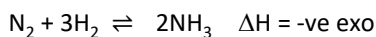
## Importance of equilibrium to industrial processes

You should be able to apply the above ideas to given reactions

Learn the equations for the production of methanol and ethanol below

Common examples

### Haber process

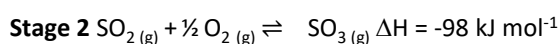
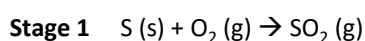


T= 450°C, P= 200 – 1000 atm, catalyst = iron

Low temp gives good yield but slow rate: compromise temp used

High pressure gives good yield and high rate: too high a pressure would lead to too high energy costs for pumps to produce the pressure

### Contact process

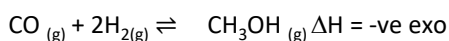


T= 450°C, P= 1 or 2 atm, catalyst =  $\text{V}_2\text{O}_5$

Low temp gives good yield but slow rate: compromise moderate temp used

High pressure only gives slightly better yield and high rate: too high a pressure would lead to too high energy costs for pumps to produce the pressure

### Production of methanol from CO

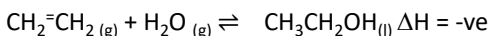


T= 400°C, P= 50 atm, catalyst = chromium and zinc oxides

Low temp gives good yield but slow rate: compromise temp used

High pressure gives good yield and high rate: too high a pressure would lead to too high energy costs for pumps to produce the pressure

### Hydration of ethene to produce ethanol



T= 300°C, P= 70 atm, catalyst = **conc  $\text{H}_3\text{PO}_4$**

Low temp gives good yield but slow rate: compromise temp used

High pressure gives good yield and high rate: too high a pressure would lead to too high energy costs for pumps to produce the pressure

High pressure also leads to unwanted polymerisation of ethene to poly(ethene)

In all cases catalysts speeds up the rate, allowing a lower temp to be used (and hence lower energy costs), but have no effect on position of equilibrium

In all cases high pressure leads to **too high energy costs for pumps** to produce the pressure and **too high equipment costs** to have equipment that can withstand high pressures.

**Recycling unreacted reactants** back into the reactor can improve the overall yields of all these processes.

Both methanol and ethanol can be used as fuels.

If the carbon monoxide used to make methanol in the above reaction was extracted from the atmosphere then it could be classed as carbon neutral.

It would only be carbon neutral, however, if the energy required to carry out the reaction was not made by combustion of fossil fuels.

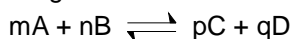
The term carbon neutral refers to “an activity that has **no net annual carbon** (greenhouse gas) emissions **to the atmosphere**”

## Equilibrium Equations

### Equilibrium constant $K_c$

$K_c$  = equilibrium constant

For a generalised reaction



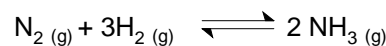
$m, n, p, q$  are the stoichiometric balancing numbers

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

[ ] means the equilibrium concentration

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

### Example 1



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

The unit of  $K_c$  changes and depends on the equation.

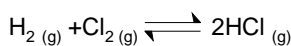
### Working out the unit of $K_c$

Put the unit of concentration ( $\text{mol dm}^{-3}$ ) into the  $K_c$  equation

$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} \rightarrow \text{Unit} = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}][\text{mol dm}^{-3}]^3} \xrightarrow{\text{Cancel out units}} \text{Unit} = \frac{1}{[\text{mol dm}^{-3}]^2} \rightarrow \text{Unit} = [\text{mol dm}^{-3}]^{-2} \downarrow$$

$$\text{Unit} = \text{mol}^{-2} \text{dm}^6$$

### Example 2: writing $K_c$ expression



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

Working out the unit

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

### 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



In a container of volume  $600\text{cm}^3$  there were initially  $0.500\text{mol}$  of  $H_2$  and  $0.600\text{mol}$  of  $Cl_2$ . At equilibrium there were  $0.200\text{mol}$  of  $HCl$ . Calculate  $K_c$

	$H_2$	$Cl_2$	$HCl$
Initial moles	0.5	0.6	0
Equilibrium moles			0.2

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

Using the balanced equation if  $0.2$  moles of  $HCl$  has been formed it must have used up  $0.1$  of  $Cl_2$  and  $0.1$  moles of  $H_2$  (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 reactant at equilibrium = initial moles – moles reacted

moles of chlorine at equilibrium =  $0.6 - 0.1 = 0.5$

	$H_2$	$Cl_2$	$HCl$
Initial moles	0.5	0.6	0
Equilibrium moles	0.4	0.5	0.2
Equilibrium concentration (M)	$0.4/0.6 = 0.67$	$0.5/0.6 = 0.83$	$0.2/0.6 = 0.33$

If the  $K_c$  has no unit then there are equal numbers of reactants and products. In this case you do not have to divide by volume to work out concentration. Equilibrium moles can be put straight into the  $K_c$  expression.

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

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

Work out the equilibrium concentrations

conc = moles / vol (in  $\text{dm}^3$ )

Finally put concentrations into  $K_c$  expression

**Example 4**

For the following equilibrium 
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$

Initially there were 1.50 moles of  $\text{N}_2$  and 4.00 mole of  $\text{H}_2$  in a  $1.50 \text{ dm}^3$  container. At equilibrium 30% of the Nitrogen had reacted. Calculate  $K_c$

	$\text{N}_2$	$\text{H}_2$	$\text{NH}_3$
Initial moles	1.50	4.0	0
Equilibrium moles			

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

Work out the moles at equilibrium for the reactants and products

moles of reactant at equilibrium = initial moles – moles reacted

moles of nitrogen at equilibrium =  $1.5 - 0.45 = 1.05$       moles of hydrogen at equilibrium =  $4.0 - 0.45 \times 3 = 2.65$

moles of product at equilibrium = initial moles + moles formed

moles of ammonia at equilibrium =  $0 + (0.45 \times 2) = 0.9$

	$\text{N}_2$	$\text{H}_2$	$\text{NH}_3$
Initial moles	1.5	4.0	0
Equilibrium moles	1.05	2.65	0.9
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

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

$$K_c = \frac{0.6^2}{0.7 \times 1.77^3} = 0.0927 \text{ mol}^{-2} \text{ dm}^6$$

Work out the equilibrium concentrations

conc = moles/ vol (in  $\text{dm}^3$ )

**Effect of changing conditions on value of  $K_c$** 

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

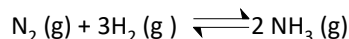
**$K_c$  only changes with temperature.**

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

**Effect of Temperature on position of equilibrium and  $K_c$** 

Both the **position of equilibrium** and the value of  **$K_c$  will change** if temperature is altered

In this equilibrium which is exothermic in the forward direction

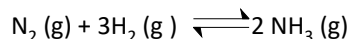


If temperature is increased the reaction will shift to oppose the change and move in the backwards endothermic direction. The position of equilibrium shifts left. The value of  $K_c$  gets smaller as there are fewer products.

**Effect of Pressure on position of equilibrium and  $K_c$** 

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

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



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  $K_c$  stays the same though as only temperature changes the value of  $K_c$ .

Catalysts have **no effect** on the value of  $K_c$  or the position of equilibrium as they speed up both forward and backward rates by the same amount.

## Calculating the amounts of the equilibrium mixture from K<sub>c</sub>

Using algebra it is possible to work out the amounts of each component in an equilibrium mixture using the value of K<sub>c</sub>

### Example 5

For the following equilibrium  $\text{H}_2(\text{g}) + \text{Br}_2(\text{l}) \rightleftharpoons 2\text{HBr}(\text{g})$

0.200 mol of H<sub>2</sub> and 0.200 mol of Br<sub>2</sub> are mixed and allowed to reach equilibrium. If K<sub>c</sub> = 0.210 calculate the equilibrium amounts, in mol, of each substance.

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

Make x = moles of H<sub>2</sub> that have reacted at equilibrium  
V = volume of container

$$0.21 = \frac{(2x/V)^2}{(0.2-x)/V \cdot (0.2-x)/V}$$

This reaction is equimolar (same number of moles of reactant as products) so it is possible to cancel out the volume V

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

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

Square root both sides

$$0.21 = \frac{2x}{0.2-x}$$

Rearrange to give x

$$0.458(0.2-x) = 2x$$

$$0.0917 - 0.458x = 2x$$

$$0.0917 = 2x + 0.458x$$

$$x = 0.0917/2.458$$

$$x = 0.0373$$

This example has been carefully set up to avoid the formation of a quadratic equation. It is not on the A-level syllabus to solve quadratic equations.

So at equilibrium

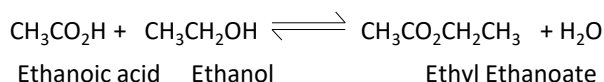
$$\begin{aligned} \text{Moles of H}_2 &= 0.2000 - 0.0373 \\ &= 0.163 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Moles of Br}_2 &= 0.2000 - 0.0373 \\ &= 0.163 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Moles of HBr} &= 2 \times 0.0373 \\ &= 0.0746 \text{ mol} \end{aligned}$$

## 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 sulphuric acid catalyst.



### 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<sup>3</sup> volumetric flask with distilled water. 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.
- 2 Use distilled water to make up the solution in the volumetric flask to exactly 250 cm<sup>3</sup>. Stopper the flask, then invert and shake the contents thoroughly.
- 3 Use the pipette to transfer 25.0 cm<sup>3</sup> of the diluted equilibrium mixture to a 250 cm<sup>3</sup> conical flask.
- 4 Add 3 or 4 drops of phenolphthalein indicator to the conical flask.
- 5 Set up the burette with sodium hydroxide solution..
- 6 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.
- 7 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.

Mass = density x volume

then

Moles = mass / 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<sup>3</sup> of 0.400 mol dm<sup>-3</sup> sodium hydroxide was used in the above titration. The initial moles of sulfuric acid was 5x10<sup>-4</sup> mol. Calculate the moles of ethanoic acid present at equilibrium.

Amount of NaOH = vol X conc  
= 0.039 x 0.400  
= 0.0156 mol

So total amount of H<sup>+</sup> present in 25cm<sup>3</sup> = 0.0156 mol

So total amount of H<sup>+</sup> present in 250cm<sup>3</sup> = 0.156 mol

Total mol acid present = moles of carboxylic acid + moles of acid catalyst

So

Amount of carboxylic acid at equilibrium = 0.156 - (5x10<sup>-4</sup> x 2)  
= 0.155 mol

X 2 because H<sub>2</sub>SO<sub>4</sub>  
has 2 H<sup>+</sup>

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.

### 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.

$$\begin{aligned}\text{Amount of ethanoic acid that reacted} &= \text{initial amount} - \text{equilibrium amount} \\ &= 0.5 - 0.155 \\ &= 0.344 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Amount of ethanol at equilibrium} &= \text{initial amount} - \text{amount that reacted} \\ &= 0.400 - 0.344 \\ &= 0.056 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Amount of ethyl ethanoate at equilibrium} &= \text{initial amount} + \text{amount that formed} \\ &= 0 + 0.344 \\ &= 0.344 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Amount of water at equilibrium} &= \text{initial amount} + \text{amount that formed} \\ &= 0 + 0.344 \\ &= 0.344 \text{ mol}\end{aligned}$$

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

### 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.