

## 11. Equilibrium II

Many reactions are reversible



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.

### Writing an expression for Equilibrium constant $K_c$

For a generalised reaction



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

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

$K_c$  = equilibrium constant

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

[ ] means the equilibrium concentration

Example 1



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

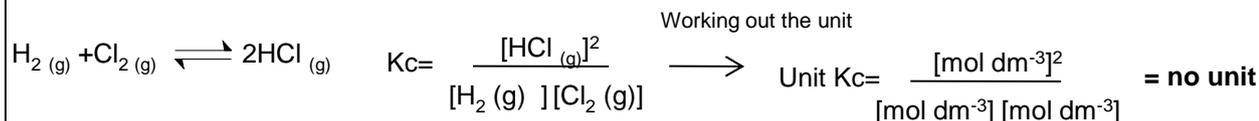
The unit of  $K_c$  changes and depends on the equation.

### Working out the unit of $K_c$

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

$$K_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})] [\text{H}_2(\text{g})]^3} \rightarrow \text{Unit} = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}] [\text{mol dm}^{-3}]^3} \xrightarrow{\text{Cancel out units}} \text{Unit} = \frac{1}{[\text{mol dm}^{-3}]^2} \rightarrow \text{Unit} = [\text{mol dm}^{-3}]^{-2} \downarrow \text{Unit} = \text{mol}^{-2} \text{dm}^6$$

Example 2: writing  $K_c$  expression



### 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  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$

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

	$\text{H}_2$	$\text{Cl}_2$	$\text{HCl}$
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  $0.2\text{moles}$  of  $\text{HCl}$  has been formed it must have used up  $0.1$  of  $\text{Cl}_2$  and  $0.1\text{moles}$  of  $\text{H}_2$  (as  $1:2$  ratio)

Work out the moles at equilibrium for the reactants

moles of reactant at equilibrium = initial moles – moles reacted

moles of hydrogen at equilibrium =  $0.5 - 0.1 = 0.4$

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

	$\text{H}_2$	$\text{Cl}_2$	$\text{HCl}$
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 and equilibrium moles could be put straight into the  $K_c$  expression

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

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

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  $1.5\text{moles}$  of  $\text{N}_2$  and  $4\text{mole}$  of  $\text{H}_2$  in a  $1.5\text{dm}^3$  container. At equilibrium  $30\%$  of the Nitrogen had reacted. Calculate  $K_c$

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

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

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

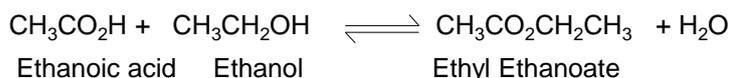
$$K_c = \frac{0.6^2}{0.7 \times 1.77^3} = 0.0927 \text{ mol}^{-2} \text{ dm}^6$$

Work out the equilibrium concentrations

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

## 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 sulphuric 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 X 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 sulphuric 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

## 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

$$P = p_1 + p_2 + p_3$$

partial pressure of gas 1 = mole fraction of gas 1 x total pressure of gas 1

$$p_1 = x_1 P$$

### mole fraction

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 :** A mixture contains 0.2 moles N<sub>2</sub>, 0.5 moles O<sub>2</sub> and 1.2 moles of CO<sub>2</sub>. If the total pressure is 3atm. What are the partial pressures of the 3 gases?

$$\begin{aligned} \text{Total moles of gas} &= 0.5 + 1.2 + 0.2 \\ &= 1.9 \end{aligned}$$

$$\begin{aligned} \text{mole fraction of N}_2 &= 0.2/1.9 \\ &= 0.105 \end{aligned}$$

$$\begin{aligned} \text{mole fraction of O}_2 &= 0.5/1.9 \\ &= 0.263 \end{aligned}$$

$$\begin{aligned} \text{mole fraction of CO}_2 &= 1.2/1.9 \\ &= 0.632 \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of N}_2 &= 0.105 \times 3 \\ &= 0.315 \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of O}_2 &= 0.263 \times 3 \\ &= 0.789 \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of CO}_2 &= 0.632 \times 3 \\ &= 1.896 \end{aligned}$$

### Writing an expression for K<sub>p</sub>



$$K_p = \frac{p^2 \text{NH}_3}{p \text{N}_2 p^3 \text{H}_2}$$

$p$  means the partial pressure of that gas

$K_p$  = equilibrium constant

Only include gases in the  $K_p$  expression. Ignore solids, liquids, and aqueous substances.

### Working out the unit of K<sub>p</sub>

Put the unit of pressure(atm) into the K<sub>p</sub> equation

$$\begin{aligned} K_p &= \frac{p^2 \text{NH}_3(\text{g})}{p \text{N}_2(\text{g}) p^3 \text{H}_2(\text{g})} & \text{Unit} &= \frac{\text{atm}^2}{\text{atm} \text{atm}^3} \\ & & \text{Unit} &= \frac{1}{\text{atm}^2} \\ & & \text{Unit} &= \text{atm}^{-2} \end{aligned}$$

Cancel out units

However, if the equation is written the other way round, the value of  $K_p$  will be the inverse of above and the units will be  $\text{atm}^2$ . It is important therefore to write an equation when quoting values of  $K_p$ .

#### Example 4

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

1 mole of  $\text{N}_2$  and 3 moles of  $\text{H}_2$  are added together and the mixture is allowed to reach equilibrium. At equilibrium 20% of the  $\text{N}_2$  has reacted. If the total pressure is 2atm what is the value of  $K_p$ ?

	$\text{N}_2$	$\text{H}_2$	$\text{NH}_3$
Initial moles	1.0	3.0	0
Equilibrium moles			

20% of the nitrogen had reacted =  $0.2 \times 1.0 = 0.2$  moles reacted.  
Using the balanced equation  $3 \times 0.2$  moles of  $\text{H}_2$  must have reacted and  $2 \times 0.2$  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 =  $1.0 - 0.2 = 0.8$       moles of hydrogen at equilibrium =  $3.0 - 0.20 \times 3 = 2.40$

moles of product at equilibrium = initial moles + moles formed

moles of ammonia at equilibrium =  $0 + (0.2 \times 2) = 0.4$

	$\text{N}_2$	$\text{H}_2$	$\text{NH}_3$
Initial moles	1.0	3.0	0
Equilibrium moles	0.80	2.40	0.40
Mole fractions	$0.8/3.6$ =0.222	$2.40/3.6$ =0.667	$0.40/3.6$ =0.111
Partial pressure	$0.222 \times 2$ =0.444	$0.667 \times 2$ =1.33	$0.111 \times 2$ =0.222

Finally put concentrations into  $K_p$  expression

$$K_p = \frac{p^2 \text{NH}_3(\text{g})}{p \text{N}_2(\text{g}) p^3 \text{H}_2(\text{g})}$$

$$K_c = \frac{0.222^2}{0.444 \times 1.33^3} = 0.0469 \text{ atm}^{-2}$$

#### Heterogeneous equilibria for $K_p$

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



$$K_p = p \text{CO}_2$$

Unit atm

#### Equilibrium constants and feasibility

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

Reaction 'does not go'	Reactants predominate in an equilibrium	equal amounts of products and reactants	Products predominate in an equilibrium	Reaction goes to completion
$K_c < 10^{-10}$	$K_c \approx 0.1$	$K_c = 1$	$K_c \approx 10$	$K_c > 10^{10}$

$S_{\text{total}}$  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  $S_{\text{total}}$

## 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

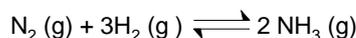
**$K_c$  and  $K_p$  only change with temperature.**

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 $K_c$

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

In this equilibrium which is exothermic in the forward direction



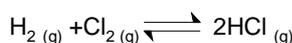
If temperature is increased the reaction will shift to oppose the change and move in the backwards endothermic direction. The position of equilibrium shifts left. The value of  $K_c$  gets smaller as there are fewer products.

### Effect of 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 $K_c$

Changing concentration would shift the **position of equilibrium** but the value of  **$K_c$  would not change.**



Increasing concentration of  $\text{H}_2$  would move equilibrium to the right lowering concentration of  $\text{H}_2$  and  $\text{Cl}_2$  and increasing concentration of  $\text{HCl}$ . The new concentrations would restore the equilibrium to the same value of  $K_c$

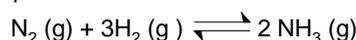
### Effect of Concentration and pressure on rate

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 $K_p$

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

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

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 now 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

$$K_p = \frac{p^2 \text{NH}_3}{p \text{N}_2 p^3 \text{H}_2}$$

$$K_p = \frac{x^2 \text{NH}_3 \cdot P^2}{x \text{N}_2 \cdot P \cdot x^3 \text{H}_2 \cdot P^3}$$

$$K_p = \frac{x^2 \text{NH}_3 \cdot P^2}{x \text{N}_2 \cdot x^3 \text{H}_2 \cdot P^4}$$

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

## Effect of catalysts on position of equilibrium and Kc

A catalyst has **no effect** on the position of equilibrium or values of Kc and Kp, 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.

## Importance of equilibrium to industrial processes

Common examples

### Haber process

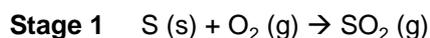


T= 450°C, P= 200 – 1000 atm, catalyst = iron

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 to 2 atm, catalyst = V<sub>2</sub>O<sub>5</sub>

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

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

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 and improve their atom economy

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