1B Equilibrium

The equilibrium constant, K_c

Characteristics of the equilibrium state

1) Equilibrium can only be established in a **closed system**. Matter cannot be exchanged with the surroundings (this will affect the position of the equilibrium), but energy can be exchanged.

2) Equilibrium can be approached from **either direction**. The products can be used as the reactants to set up the equilibrium – reversible reactions.

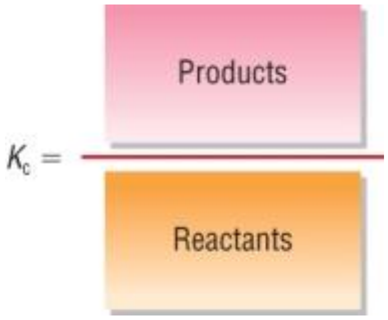
3) Equilibrium is a **dynamic state** – At equilibrium the rate in both directions **must** be the same.

4) Dynamic equilibrium is **stable under fixed conditions but is sensitive to changes** in **temperature, pH, pressure.**

- In AS we discovered that **Le Chatelier's Principle** was given as a way of determining how changes in the conditions can affect the extent to which a reaction will go.
- A more Quantitative approach is needed to understand more fully the ideas of equilibria

The equilibrium law:

- The equilibrium law is an expression of the amounts of **products : reactants** in an equilibrium.



$$K_c = \frac{[\text{PRODUCTS}]^p}{[\text{REACTANTS}]^r}$$

- Consider the reaction:

$$aA + bB \rightleftharpoons cC + dD$$

- Where **[A], [B], [C] and [D]** are the equilibrium concentrations of reactants and products
- The indices **a,b,c and d** are the stoichiometric numbers in the balanced chemical reaction

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

- This expression gives us a mathematical way of looking at the proportions of products and reactants in an equilibrium.
- At equilibrium these relative proportions will not change.
- This means a constant is produced, this is given by - K_c

Approaching equilibrium

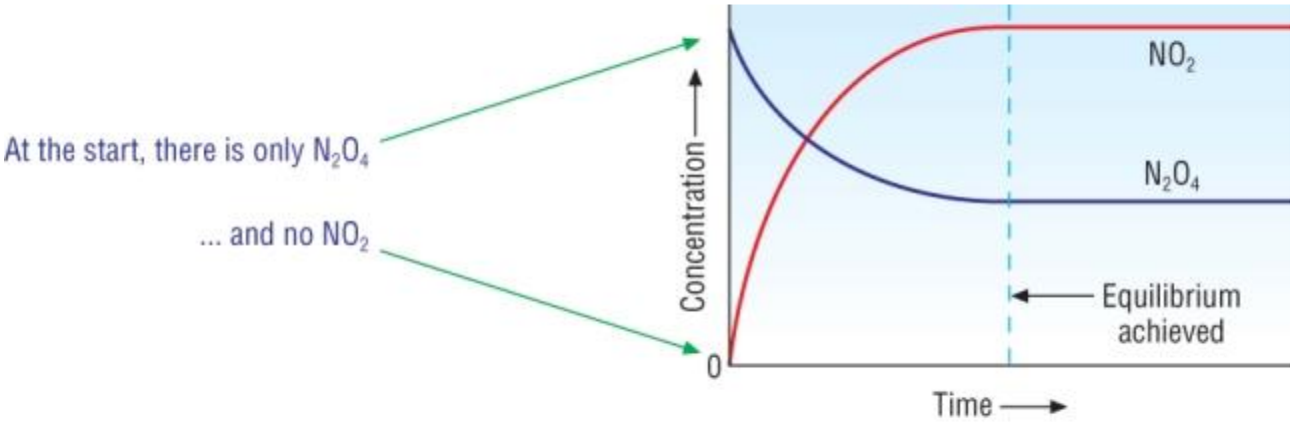
- Consider the reversible reaction:

$$N_2O_{4(g)} \quad \leftrightarrows \quad 2NO_{2(g)}$$

- N_2O_4 is a colourless gas, NO_2 is a brown gas.

Initially:	• N_2O_4 molecules decompose into 2 NO_2 molecules, the rate of the forward reaction is fast. • Because there are very few molecules of NO_2, the reverse reaction can only happen slowly.
As the reaction proceeds:	• There are now fewer N_2O_4 molecules available to decompose, the rate of the forward reaction decreases. • There are now more NO_2 molecules present so the rate of the reverse reaction increases.
At equilibrium:	• Eventually the forward reaction takes place at exactly the same rate as the reverse reaction. • **Dynamic equilibrium** is established and is denoted by $\leftrightarrows$ • The concentrations of reactants and products now remain constant.

- Graph shows how the concentrations of reactants and products change:



Writing expressions for K_c:

- At equilibrium the concentrations of NO_2 and N_2O_4 are constant:

$$N_2O_{4(g)} \quad \leftrightarrows \quad 2NO_{2(g)}$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

- A few other examples:

$$2SO_{2(g)} + O_{2(g)} \leftrightarrows 2SO_{3(g)}$$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

$$H_{2(g)} + I_{2(g)} \leftrightarrows 2HI_{(g)}$$

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

Units of K_c

- These have to be worked out for each **K_c**.
- Just like the rate constant, put the units into each expression:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]^1}$$

$$K_c = \frac{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}{\text{mol dm}^{-3}}$$

$$K_c = \frac{\text{mol dm}^{-3} \times \cancel{\text{mol dm}^{-3}}}{\cancel{\text{mol dm}^{-3}}}$$

$$K_c = \text{mol dm}^{-3}$$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

$$K_c = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^2 \quad \text{mol dm}^{-3}}$$

$$K_c = \frac{\cancel{(\text{mol dm}^{-3})^2}}{\cancel{(\text{mol dm}^{-3})^2} \quad \text{mol dm}^{-3}}$$

$$K_c = \frac{1}{\text{mol dm}^{-3}}$$

$$K_c = \text{dm}^3\ \text{mol}^{-1}$$

Calculations using K_c

- The equilibrium expression obviously allows you to calculate K_c if you know the concentrations at equilibrium.
- You can also calculate K_c and equilibrium concentrations knowing the starting concentrations and one of the equilibrium concentrations.

Determining K_c from equilibrium concentrations:

1) Hydrogen, Iodine, Hydrogen iodide equilibrium:

Reaction:	$H_{2(g)}$	+	$I_{2(g)}$	$\leftrightarrows$	$2HI_{(g)}$
Equilibrium concentrations:	**0.140**		**0.040**		**0.320**

- Write the **equilibrium expression**, put in the values, **calculate K_c** and work out the **units**:

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

$$K_c = \frac{(0.320)^2}{0.140 \times 0.040}$$

$$K_c = 18.3$$

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

$$K_c = \frac{\text{mol dm}^{-3}\ \text{mol dm}^{-3}}{\text{mol dm}^{-3}\quad \text{mol dm}^{-3}}$$

$$K_c = \frac{\cancel{\text{mol dm}^{-3}}\ \cancel{\text{mol dm}^{-3}}}{\cancel{\text{mol dm}^{-3}}\quad \cancel{\text{mol dm}^{-3}}}$$

K_c = **No units**

2) N_2O_4 / NO_2 equilibrium: Given the number of moles at equilibrium in a volume of $2dm^3$.

Reaction:	$N_2O_{4(g)}$	$\leftrightarrows$	$2NO_{2(g)}$
Mole quantities at equilibrium:	**0.400**		**3.20**
Equilibrium concentrations:	**0.400 / 2**		**3.20 / 2**
Equilibrium concentrations:	**0.20**		**1.60**

- As the quantities are given in moles, you have to calculate the equilibrium concentrations
- Write the **equilibrium expression**, put in the values, **calculate K_c** and work out the **units**:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{(1.60)^2}{0.20}$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{\text{mol dm}^{-3}\ \text{mol dm}^{-3}}{\text{mol dm}^{-3}}$$

$$K_c = 12.8 \text{ mol dm}^{-3}$$

$$K_c = \frac{\cancel{\text{mol dm}^{-3}} \text{ mol dm}^{-3}}{\cancel{\text{mol dm}^{-3}}}$$

$$K_c = \text{mol dm}^{-3}$$

Calculating the quantities and concentrations present at equilibrium:

3) Hydrogen, Iodine, Hydrogen iodide equilibrium:

- This time you are told the **mole quantities** at the start and **one equilibrium quantity**.
- From this you can work out all of the mole quantities at equilibrium.
- The final step is to convert to equilibrium concentrations, in this example the reaction is carried out in a **1 dm^3** vessel.

Reaction:	$H_{2(g)}$	+	$I_{2(g)}$	$\leftrightarrows$	$2HI_{(g)}$
At start:	**0.60**		**0.40**		**0.0**
At equilibrium:	**0.28**				
Reacted:					
Equilibrium concentrations:					

- Write the **equilibrium expression**, put in the values, **calculate K_c** and work out the **units**:

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

$$K_c = \frac{(0.64)^2}{0.28 \times 0.08}$$

$$K_c = 18.3$$

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

$$K_c = \frac{\text{mol dm}^{-3} \text{ mol dm}^{-3}}{\text{mol dm}^{-3} \quad \text{mol dm}^{-3}}$$

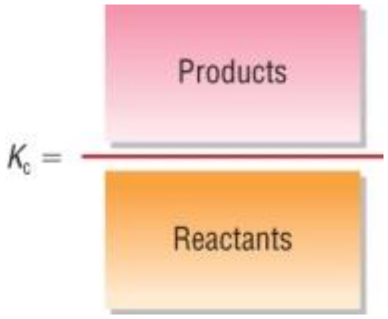
$$K_c = \frac{\cancel{\text{mol dm}^{-3}} \cancel{\text{mol dm}^{-3}}}{\cancel{\text{mol dm}^{-3}} \quad \cancel{\text{mol dm}^{-3}}}$$

$$K_c = \text{No units}$$

The equilibrium position and K_c

What is the significance of a K_c value?

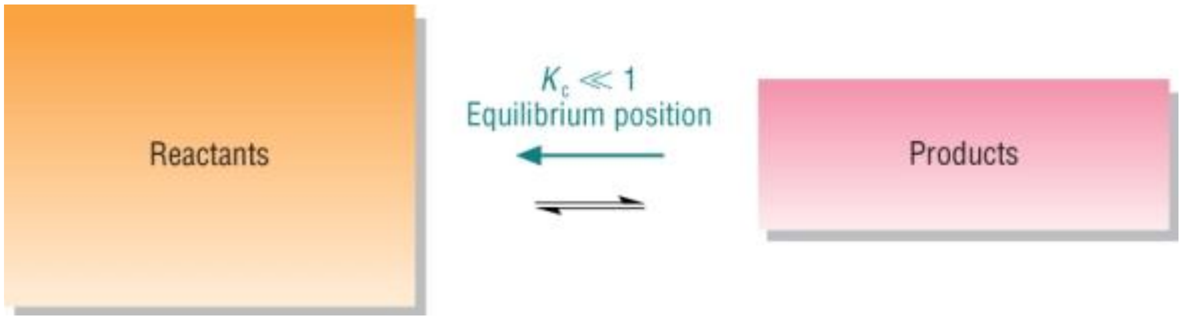
- **K_c** is a mathematical representation of the ratio of **products : reactants**.



- If the amount of products is equal to reactants then **$K_c = 1$**

Products favoured: $K_c > 1$

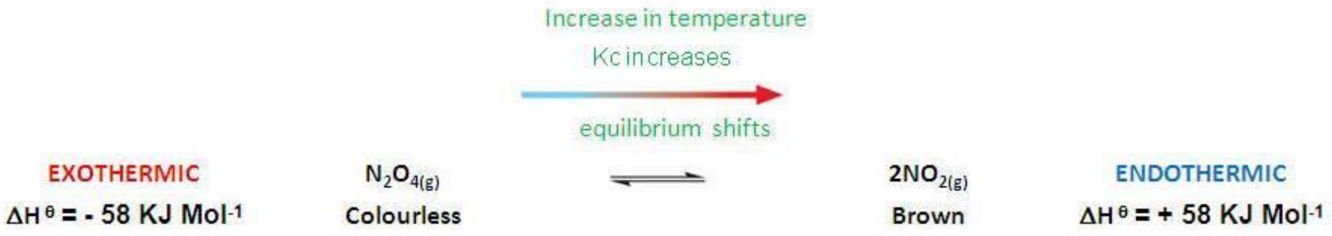
Reactants favoured: $K_c < 1$



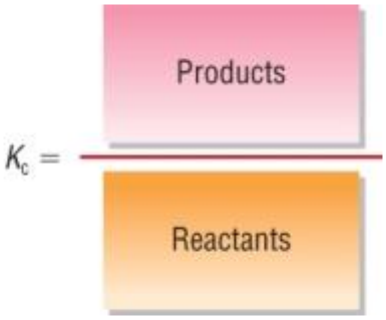
How do changes in temperature affect K_c?

- In AS we used **Le Chatelier's Principle** to predict the how temperature affects the position of equilibrium.
- We can use this to predict what happens to **K_c**.
- Apply the direction movement to the formula to work out whether **K_c** increases or decreases:

1) Endothermic reactions:



- Applying **LCP** means that an **increase in temperature** will shift the equilibrium to the **Products**.
- This means there will be **more Products** and **less Reactants**:

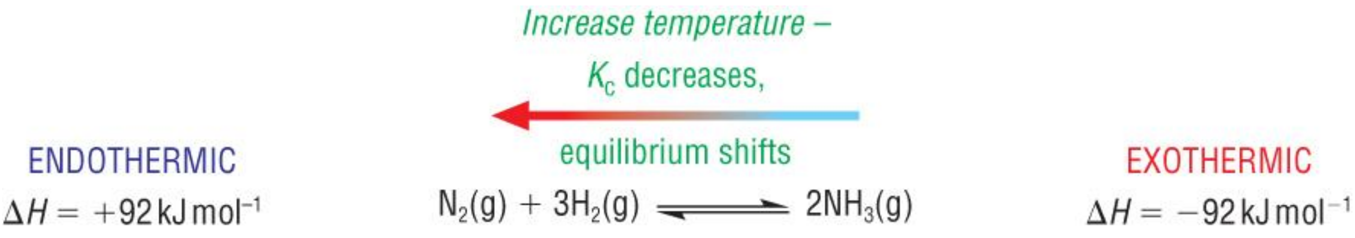


- The top number increases and the bottom number decreases.
- This makes K_c a larger value.

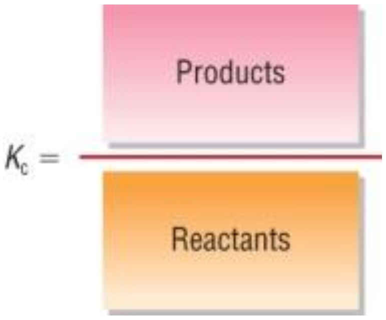
K_c increases

and vice versa

2) Exothermic reactions:



- Applying **LCP** means that an **increase in temperature** will shift the equilibrium to the **Reactants**.
- This means there will be **more Reactants** and **less Products**:



- The top number decreases and the bottom number increases.
- This makes K_c a lsmaller value.

K_c decreases

and vice versa

The equilibrium constant, K_c, and the rate constant, k

How does a change in concentration and pressure affect K_c?

- In AS we used **Le Chatelier's Principle** to predict the how **concentration** and **pressure** affects the position of equilibrium.
- The reasons for these changes in the position of the equilibrium lie with **K_c.**

K_c is unaltered by changes in concentration and pressure

1) Changes in concentration:

A change in Concentration has no effect on the equilibrium constant.

- Remember if a reactant / product is added the equilibrium shifts to the opposite direction to keep the 'proportions' the same - **K_c is unchanged**:

Reaction: $N_2O_{4(g)} \leftrightarrows 2NO_{2(g)}$

$[NO_2]$ = 1.60 Mol dm^{-3}		**$[NO_2]$ = 1.60 Mol dm^{-3}**
$[N_2O_4]$ = 0.20 Mol dm^{-3}	**Double [ ] :**	**$[N_2O_4]$ = 0.40 Mol dm^{-3}**
$K_c = \dfrac{[NO_2]^2}{[N_2O_4]}$		$K_c = \dfrac{[NO_2]^2}{[N_2O_4]}$
$K_c = \dfrac{(1.60)^2}{0.20}$		$K_c = \dfrac{(3.20)^2}{0.40}$
K_c = 12.8 Mol dm^{-3}		K_c = 6.4 Mol dm^{-3}

- If the concentrations are doubled, the system is no longer at equilibrium, **K_c = 12.8**
- To bring **K_c** back from 6.4 to 12.8**:**
- The system must **increase $[NO_2]$ and decrease $[N_2O_4]$**
- Remember if a reactant / product is added the equilibrium shifts to the opposite direction to keep the 'proportions' the same - **K_c is unchanged**:

2) Changes in Pressure:

A change in Pressure has no effect on the equilibrium constant.

- If **pressure** is **doubled -** the **volume** is **halved -** meaning that the **concentrations** will have **doubled**

Reaction: $N_2O_{4(g)} \leftrightarrows 2NO_{2(g)}$

$[NO_2]$ = 1.60 Mol dm^{-3}	**Double [ ] :**	$[NO_2]$ = 3.20 Mol dm^{-3}
$[N_2O_4]$ = 0.20 Mol dm^{-3}		$[N_2O_4]$ = 0.40 Mol dm^{-3}
$K_c = \frac{[NO_2]^2}{[N_2O_4]}$		$K_c = \frac{[NO_2]^2}{[N_2O_4]}$
$K_c = \frac{(1.60)^2}{0.20}$		$K_c = \frac{(3.20)^2}{0.40}$
K_c = 12.8 Mol dm^{-3}		K_c = 25.6 Mol dm^{-3}

- If the pressure is doubled, the system is no longer at equilibrium, **K_c = 12.8**
- To bring **K_c** back from 25.6 to 12.8**:**
- The system must **increase $[NO_2]$ and decrease $[N_2O_4]$**
- Remember if a reactant / product is added the equilibrium shifts to the opposite direction to keep the 'proportions' the same - **K_c is unchanged**:

How does the presence of a catalyst affect K_c?

A catalyst has no effect on the equilibrium constant.

- A catalyst speeds up both the forward and reverse reaction.
- Equilibrium is achieved more quickly.

The equilibrium constant K_c, and the rate constant, k

- These 2 constants tell us the most important things in the chemical industry:

a)	**Equilibrium**	**How far**
b)	**Rates**	**How fast**

a) The equilibrium constant, K_c

- K_c indicates the position of the equilibrium:

Large K_c	**Products predominate**
Small K_c	**Reactants predominate**

- Remember **LCP:**

Endothermic	**K_c increases with an increase in temperature (increases products)**
Exothermic	**K_c decreases with an increase in temperature (decreases products)**

Kc can be written from the balanced chemical equation

b) The rate constant, k

- **k** is a measure of the rate of a reaction:

Large k	**Fast rate**
Small k	**Slow rate**

- Remember:

k increases with an increase in temperature - Rate increases with an increase in temperature

k decreases with a decrease in temperature - Rate decreases with a decrease in temperature

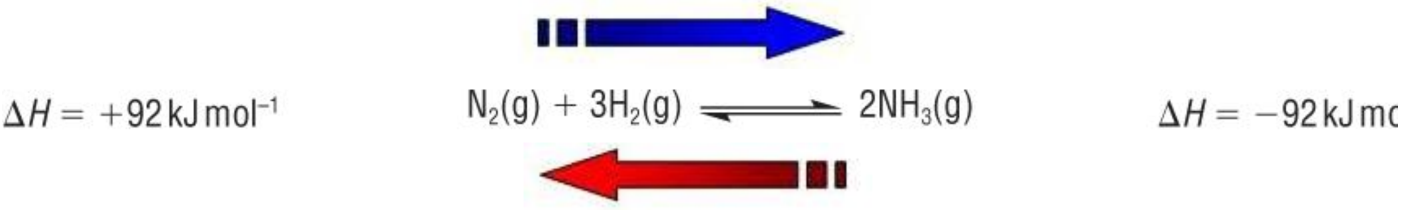
k can only be determined experimentally from the rate equation

The importance of compromise:

- The 2 desirable outcomes are a) increasing rate and b) increasing the amount:

a) Increasing the rate:

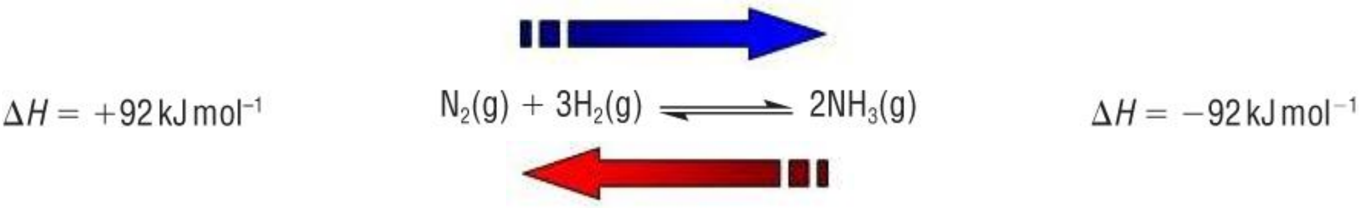
Increasing temperature: Increases the rate of production of product - desirable



Increasing temperature: Decreases the amount of product made - undesirable

b) Increasing the amount:

Decreasing the temperature: Increases the amount of product made - desirable



Decreasing temperature: Decreases the rate of production of product - undesirable

The compromise is:

Moderate temperature: k increases moderately - Rate increases by a moderate amount

Moderate temperature: K_c decreases by a moderate amount - allowing a moderate yield