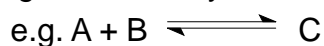


## Equilibrium, Kc

N Goalby  
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A reversible reaction goes both ways, as indicated by  $\rightleftharpoons$



When A and B are mixed they start to form C.

Initially the forward reaction is fast and the rate of the backward reaction is zero.

As more C is formed the backward reaction becomes faster and the forward reaction becomes slower as A and B are used up.

Eventually the reaction rates become equal.

At this point equilibrium has been reached and the physical properties (e.g. colour, pH, electrical conductivity) of the reaction mixture will not change unless the system is subjected to a change (e.g. temperature is changed, pressure is changed).

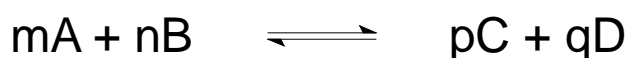
## Dynamic equilibrium

- An equilibrium mixture has constant amounts of products and reactants.
- Dynamic means the reactions are continuing.
- Equilibrium is reached when the forward rate of reaction = backwards rate of reaction.

The state of equilibrium can only be reached in a closed system (one in which no chemicals can enter or leave). In reality a state of equilibrium is often reached in an unsealed container – the reagents and products are dissolved in water. The container must, however, be sealed if gases or volatile liquids are involved.

## Equilibrium law

for a generalised reaction



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

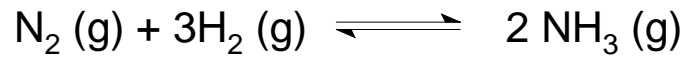
A,B,C,D stand for the chemical formula

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

[ ] means the equilibrium concentration

$K_c$  = equilibrium constant

## Example



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

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

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

Cancel out units

$$\text{Unit} = \frac{1}{[\text{mol dm}^{-3}]^2}$$

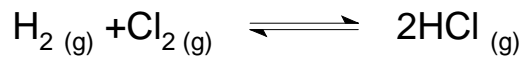
$$\text{Unit} = [\text{mol dm}^{-3}]^{-2}$$

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

However, if the equation is written the other way round, the value of  $K_c$  will be the inverse of above and the units will be  $\text{mol}^2 \text{dm}^{-6}$ .

It is important therefore to write an equation when quoting values of  $K_c$ .

### Example 2: writing Kc expression



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

#### Working out the unit

$$\text{Unit } K_c = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}][\text{mol dm}^{-3}]}$$

= no unit

### Calculating Kc

- Most questions first involve having to work out the equilibrium concentration.
- Usually the question will give the initial amounts (moles) of the reactants, and some data that will help you work out the equilibrium amounts.

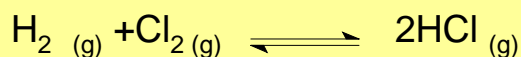
#### Calculating the moles at equilibrium

moles of reactant at equilibrium = initial moles – moles reacted

moles of product at equilibrium = initial moles + moles formed

### Example 1

For the following equilibrium



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  $0.2\text{mol}$  of  $\text{HCl}$ .

Calculate  $K_c$

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

	$\text{H}_2$	$\text{Cl}_2$	$\text{HCl}$
Initial moles	0.5	0.6	0
Equilibrium moles			0.2
Equilibrium concentration			

Work out the moles at equilibrium for the reactants

	$\text{H}_2$	$\text{Cl}_2$	$\text{HCl}$
Initial moles	0.5	0.6	0
Equilibrium moles	0.4		0.2
Equilibrium concentration			



moles of reactant at equilibrium = initial moles – moles reacted

$$\begin{aligned} \text{moles of hydrogen at equilibrium} &= 0.5 - 0.2/2 \\ &= 0.4 \text{ mol} \end{aligned}$$

Work out the moles at equilibrium for the reactants

	H <sub>2</sub>	Cl <sub>2</sub>	HCl
Initial moles	0.5	0.6	0
Equilibrium moles	0.4	0.5	0.2
Equilibrium concentration			



moles of reactant at equilibrium = initial moles – moles reacted

moles of chlorine at equilibrium = 0.6 – 0.2/2

= 0.5 mol

Work out the equilibrium concentrations

	H <sub>2</sub>	Cl <sub>2</sub>	HCl
Initial moles	0.5	0.6	0
Equilibrium moles	0.4	0.5	0.2
Equilibrium concentration (mol dm <sup>-3</sup> )	0.4/0.6 = 0.67	0.5/0.6 = 0.83	0.2/0.6 = 0.33

$$\text{Concentration} = \frac{\text{Moles}}{\text{Volume (in dm}^3\text{)}}$$

Finally put concentrations into Kc expression

	H <sub>2</sub>	Cl <sub>2</sub>	HCl
Initial moles	0.5	0.6	0
Equilibrium moles	0.4	0.5	0.2
Equilibrium concentration (mol dm <sup>-3</sup> )	0.4/0.6 = 0.67	0.5/0.6 = 0.83	0.2/0.6 = 0.33

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

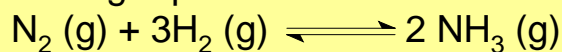
$$= \frac{0.33^2}{0.67 \times 0.83}$$

$$= 0.196 \text{ no unit}$$

(If the Kc has no unit then there are equal numbers of reactants and products. In this case you do not have to divide by volume)

### Example 2

For the following equilibrium



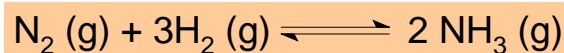
Initially there were 1.5 moles of N<sub>2</sub> and 4 mole of H<sub>2</sub>, in a 1.5 dm<sup>3</sup> container. At equilibrium 30% of the Nitrogen had reacted.

Calculate Kc

	N <sub>2</sub>	H <sub>2</sub>	NH <sub>3</sub>
Initial moles	1.5	4	0
Equilibrium moles			
Equilibrium concentration mol dm <sup>-3</sup>			

Work out the moles at equilibrium for the reactants

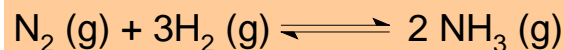
	N <sub>2</sub>	H <sub>2</sub>	NH <sub>3</sub>
Initial moles	1.5	4	0
Equilibrium moles	1.05		
Equilibrium concentration			



Moles of Nitrogen reacted = 30% of 1.5 = 0.45 moles  
 moles of reactant at equilibrium = initial moles – moles reacted  
 moles of nitrogen at equilibrium = 1.5 – 0.45  
 = 1.05 mol

Work out the moles at equilibrium for the reactants

	N <sub>2</sub>	H <sub>2</sub>	NH <sub>3</sub>
Initial moles	1.5	4	0
Equilibrium moles	1.05	2.65	
Equilibrium concentration			

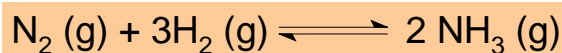


moles of reactant at equilibrium = initial moles – moles reacted  
 moles of hydrogen at equilibrium = 4 – (0.45 x 3)  
 = 2.65 mol



Work out the moles at equilibrium for the products

	N <sub>2</sub>	H <sub>2</sub>	NH <sub>3</sub>
Initial moles	1.5	4	0
Equilibrium moles	1.05	2.65	0.9
Equilibrium concentration			



moles of product at equilibrium = initial moles + moles formed

$$\begin{aligned} \text{moles of ammonia at equilibrium} &= 0 + (0.45 \times 2) \\ &= 0.9 \text{ mol} \end{aligned}$$

Work out the concentration at equilibrium

	N <sub>2</sub>	H <sub>2</sub>	NH <sub>3</sub>
Initial moles	1.5	4	0
Equilibrium moles	1.05	2.65	0.9
Equilibrium concentration mol dm <sup>-3</sup>	1.05/1.5 = 0.7	2.65/1.5 = 1.77	0.9/1.5 = 0.6

$$\begin{aligned} K_c &= \frac{[\text{NH}_3 (\text{g})]_{\text{eqm}}^2}{[\text{N}_2 (\text{g})]_{\text{eqm}} [\text{H}_2 (\text{g})]_{\text{eqm}}^3} \\ &= \frac{0.6^2}{0.7 \times 1.77^3} \\ &= 0.0927 \text{ mol}^{-2} \text{ dm}^+6 \end{aligned}$$

- $K_c$  is a numerical value for position of equilibrium.
- The larger the  $K_c$  the greater the amount of products.
- If  $K_c$  is small we say the equilibrium favours the reactants

roughly  $K_c = 1$  equal amounts of products and reactants

$K_c = 0.01$  means reactants predominate

$K_c = 100$  means products predominate

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

It does not change if pressure or concentration is altered.

A catalyst also has no effect on  $K_c$

### Determining $K_c$ experimentally

To work out  $K_c$  we must know the initial amount of reactants and products and we must be able to work out the concentration of one of the reactants or products at equilibrium

#### Method

-let reactants reach equilibrium (this can take a few hours for some reactants)

-remove a small sample of known volume with a volumetric pipette

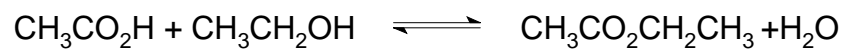
-quench sample by pouring sample on ice. (This freezes the equilibrium)

-titrate the sample with a suitable reagent of known concentration

• eg for an acid product  $H^+$ , titrate with NaOH

• eg  $I_2$  could be titrated with sodium thiosulphate with starch indicator

## Question



1 mole of ethanoic acid and 1 mole of ethanol are added together. A 10cm<sup>3</sup> sample was removed from the 100cm<sup>3</sup> mixture, and required 50 cm<sup>3</sup> of 1M NaOH reacted with the sample. What is K<sub>c</sub>?

Only CH<sub>3</sub>CO<sub>2</sub>H reacts with NaOH (1:1 ratio)