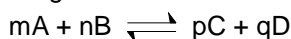


## 5.1.2 How Far? Equilibrium

### Equilibrium constant $K_c$

For a generalised reaction



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

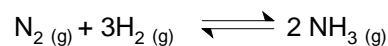
$A, B, C, D$  stand for the chemical formula

[ ] means the equilibrium concentration

$K_c$  = equilibrium constant

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

### 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.

liquid and solid concentrations are constant and are omitted in heterogeneous  $K_c$

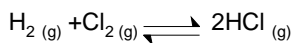
### Working out the unit of $K_c$

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

For the following equilibrium  $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

In a container of volume  $600\text{cm}^3$  there were initially  $0.5\text{mol}$  of  $H_2$  and  $0.6\text{mol}$  of  $Cl_2$ . At equilibrium there were  $0.2\text{moles}$  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  $0.2\text{moles}$  of  $HCl$  has been formed it must have used up  $0.1$  of  $Cl_2$  and  $0.1\text{moles}$  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 and equilibrium moles could be put straight into the  $K_c$  expression

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

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

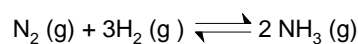
Work out the equilibrium concentrations

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

Finally put concentrations into  $K_c$  expression

#### Example 4

For the following equilibrium



Initially there were 1.5 moles of  $\text{N}_2$  and 4 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 =  $0.3 \times 1.5 = 0.45$  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

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

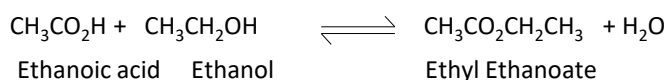
$$K_c = \frac{0.6^2}{0.7 \times 1.77^3} = 0.0927 \text{ mol}^{-2} \text{ dm}^6$$

Work out the equilibrium concentrations

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

#### Practical: Working out equilibrium constant $K_c$

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.



#### 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  $\text{cm}^3$  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  $\text{cm}^3$ .  
Stopper the flask, then invert and shake the contents thoroughly.
- 3 Use the pipette to transfer 25.0  $\text{cm}^3$  of the diluted equilibrium mixture to a 250  $\text{cm}^3$  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.

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

#### 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 = mole fraction x total pressure  
of gas 1 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 5** : 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  $K_p$  equation

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

Cancel out units

$$\text{Unit} = \frac{\text{atm}^2}{\text{atm} \text{atm}^3}$$

$$\text{Unit} = \frac{1}{\text{atm}^2}$$

$$\text{Unit} = \text{atm}^{-2}$$

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 6

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

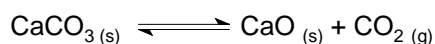
Finally put concentrations into  $K_p$  expression

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

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

### 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

### Effect of changing conditions on value of Kc or Kp

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

**Kc and Kp only change with temperature.**

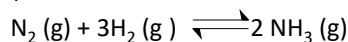
It does not change if pressure or concentration is altered.

A catalyst also has no effect on Kc or Kp

### Effect of Temperature on position of equilibrium and Kc

Both the **position of equilibrium** and the value of **Kc or Kp will change** if temperature is altered

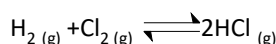
In this equilibrium which is exothermic in the forward direction



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 Kc gets smaller as there are fewer products.

### Effect of Concentration on position of equilibrium and Kc

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



Increasing concentration of H<sub>2</sub> would move equilibrium to the right lowering concentration of H<sub>2</sub> and Cl<sub>2</sub> and increasing concentration of HCl. The new concentrations would restore the equilibrium to the same value of Kc.

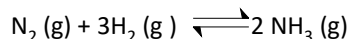
### Effect of catalysts on position of equilibrium and Kc and Kp

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

### Effect of Pressure on position of equilibrium and Kc

The position of equilibrium will change if pressure is altered but the value of **Kc stays constant** as Kc 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 Kc stays the same though as only temperature changes the value of Kc.

Increasing pressure does not change Kc.

The increased pressure increases concentration terms on bottom of Kc expression more than the top. The system is now no longer in equilibrium so the equilibrium shifts to the right increasing concentrations of products and decreases the concentrations of reactants. The top of Kc expression therefore increases and the bottom decreases until the original value of Kc is restored.

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

### Effect of Pressure on position of equilibrium and Kp

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

Increasing pressure does not change Kp.

The increased pressure increases the pressure terms on bottom of Kp 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 Kp expression therefore increases and the bottom decreases until the original value of Kp 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