

## 3.8 – Equilibrium constants

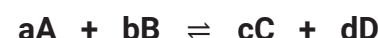
### 1. Dynamic equilibrium

If a **reversible reaction** is carried out in a closed container so that the reactants and products cannot escape, a **dynamic equilibrium** is established:

- the **rates** of the forward and backward reactions are **equal**
- the **concentrations** of the components of the reaction mixture remain **constant**.

### 2. Equilibrium constants

At equilibrium, the ratio of the concentrations of products to reactants is constant. The ratio value is called the **equilibrium constant**. It always has the same value for a particular reaction under fixed conditions.

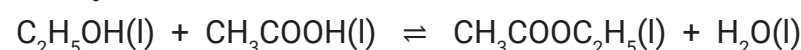


$K_c$  concentration terms – can be used for any reaction

$$K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \quad \text{concentration in mol dm}^{-3}$$

**Always** – products divided by reactants

**Example:** 0.10 mol of ethanol is mixed with 0.10 mol of ethanoic acid and allowed to reach equilibrium. The total volume of the system is made up to 50.0 cm<sup>3</sup> with water. We find by titration that 0.033 mol of ethanoic acid is present once equilibrium is reached. Calculate  $K_c$ .



<b>Initial moles:</b>	<b>0.10</b>	<b>0.10</b>	<b>0</b>	<b>0</b>
<b>At eqm:</b>	<b>0.033</b>	<b>0.033</b>	<b>0.067</b>	<b>0.067</b>

1 mol of CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> and 1 mol of H<sub>2</sub>O are produced for every 1 mol of CH<sub>3</sub>COOH that reacts.

Moles of CH<sub>3</sub>COOH that reacted = 0.10 – 0.033 = 0.067 mol

So, number of moles of CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> and H<sub>2</sub>O at equilibrium has increased by 0.067 mol.

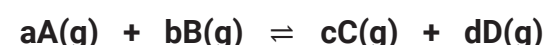
1 mol of CH<sub>3</sub>COOH reacts with 1 mol of C<sub>2</sub>H<sub>5</sub>OH, so 0.067 mol of C<sub>2</sub>H<sub>5</sub>OH also reacted and 0.033 mol left at equilibrium.

The  $K_c$  equation requires concentrations in mol dm<sup>-3</sup> but the number of moles can be used in this case, because all substances are in same the volume of solution.

$$K_c = \frac{0.067 \times 0.067}{0.033 \times 0.033} = 4.12 \text{ (no unit)}$$

There is no unit as there are equal numbers of moles of reactants and products on both sides.

$K_p$  uses **partial pressure** terms for gases only.



$$K_p = \frac{p(C)^c \times p(D)^d}{p(A)^a \times p(B)^b}$$

$p(C)^c$  is the partial pressure exerted by gas C.

It is acceptable to use no brackets but **do not** use square brackets – they represent concentration in mol dm<sup>-3</sup>.

Because partial pressures are directly proportional to the concentrations of each gas at equilibrium, they can be used in the  $K_p$  equation in a similar way to concentrations in  $K_c$ .

The sum of all the partial pressures exerted by each of the gases in a mixture is equal to the total pressure of the mixture.

**Example:** A sample of pure PCl<sub>5</sub> with a partial pressure of 1.01 × 10<sup>6</sup> Pa was introduced into a vessel. The equilibrium below was reached, where the partial pressure of PCl<sub>3</sub> was 4.02 × 10<sup>4</sup> Pa. Calculate  $K_p$ .



**Initial partial pressure:**

	<b>1.01 × 10<sup>6</sup></b>	<b>0</b>	<b>0</b>
<b>At eqm:</b>	<b>9.698 × 10<sup>5</sup></b>	<b>4.02 × 10<sup>4</sup></b>	<b>4.02 × 10<sup>4</sup></b>

*Partial pressure PCl<sub>5</sub>(g) at eqm*

$$= 1.01 \times 10^6 - 4.02 \times 10^4 = 9.698 \times 10^5$$

$$K_p = \frac{4.02 \times 10^4 \times 4.02 \times 10^4}{9.698 \times 10^5} = 1667 \text{ Pa}$$

$K_p$  has a unit this time, as the number of moles of reactants and products on both sides of the equation are not equal.

### 3. The effect of temperature on equilibrium constants

Temperature is the only factor that affects equilibrium constants  $K_c$  and  $K_p$ .

**Le Chatelier's principle:**

If a factor affecting the position of an equilibrium is changed, the position of the equilibrium shifts to oppose the effect of the change.

A change in temperature always changes the value of the equilibrium constant  $K_c$  or  $K_p$ . Le Chatelier's principle can be used to deduce whether this change involves an increase or a decrease in the value.

**Exothermic reactions:** An increase in temperature will cause the equilibrium to shift in the endothermic direction. This will decrease the number of products and increase the number of reactants.

**For an exothermic reaction, increasing the temperature decreases  $K_c$  and  $K_p$ .**

**Endothermic reactions:** An increase in temperature will cause the equilibrium to shift in the endothermic direction. This will increase the number of products and decrease the number of reactants.

**For an endothermic reaction, increasing the temperature increases  $K_c$  and  $K_p$ .**

*Note: If the temperature is increased, the rate of the forward and backward reactions are both increased.*

$K_c$  and  $K_p$  are not affected by a change in concentration of reactants or products, a change in pressure or by adding a catalyst.

### 4. The significance of the magnitude of $K_c$ and $K_p$

An equilibrium that has  $K_c = 1$  shows that there are equal amounts of reactants and products.

If  $K_c > 1$  then more of the reactants have been turned into products. This is typical for a reaction where  $\Delta G$  is negative, as the reaction will occur spontaneously.

If  $K_c < 1$  then the mixture contains more of the reactants, with fewer products formed. This is typical for a reaction where  $\Delta G$  is positive as the reaction will not occur spontaneously.

### 5. Industrial processes

For any industrial process, equilibrium and kinetic data are considered with the aim of producing the maximum amount of product using the least amount of energy and as quickly as possible. This usually involves a compromise.

**Equilibrium data:** The equilibrium yield can be changed by altering the temperature, pressure or concentration.  $K_c$  and  $K_p$  show which concentration or pressure values favour a high yield.

**Kinetic data:** Temperature/pressure can be increased as long as the yield is not significantly reduced. Catalysts are also used.