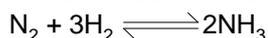


3. Equilibria

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



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

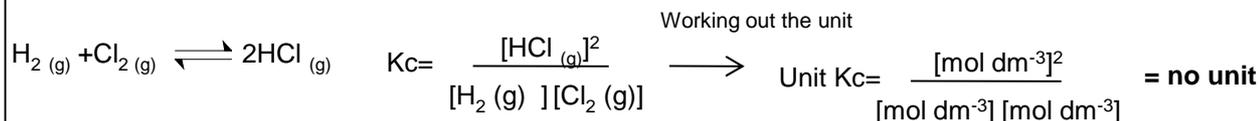
The unit of K_c changes and depends on the equation.

Working out the unit of K_c

Put the unit of concentration (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 600cm^3 there were initially 0.5mol of H_2 and 0.6mol of Cl_2 . At equilibrium there were 0.2moles 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 0.2moles of HCl has been formed it must have used up 0.1 of Cl_2 and 0.1moles of 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 = $0.6 - 0.1 = 0.5$

| | 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

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

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

Work out the equilibrium concentrations

conc = moles/vol (in 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 1.5moles of N_2 and 4moles of H_2 in a 1.5dm^3 container. At equilibrium 30% of the Nitrogen had reacted. Calculate K_c

| | N_2 | H_2 | 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 H_2 must have reacted and $2 \times 0.45\text{moles}$ of 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 = $0 + (0.45 \times 2) = 0.9$

| | N_2 | H_2 | 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 dm^3)

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 N₂, 0.5 moles O₂ and 1.2 moles of CO₂. 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_p



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

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_p

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 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 N_2 and 3 moles of H_2 are added together and the mixture is allowed to reach equilibrium. At equilibrium 20% of the N_2 has reacted. If the total pressure is 2atm what is the value of K_p ?

| | N_2 | H_2 | 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 3×0.2 moles of H_2 must have reacted and 2×0.2 moles of 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 = $0 + (0.2 \times 2) = 0.4$

| | N_2 | H_2 | 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 |
|------------------------|---|---|--|-----------------------------|
| $K_c < 10^{-10}$ | $K_c \approx 0.1$ | $K_c = 1$ | $K_c \approx 10$ | $K_c > 10^{10}$ |

ΔS_{total} increases the magnitude of the equilibrium constant increases since $\Delta S = R \ln K$

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 ΔS_{total}

Application of rates and equilibrium

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

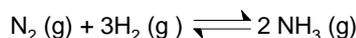
Kc and Kp only change with temperature.

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



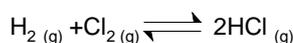
If temperature is increased the reaction will shift to oppose the change and move in the backwards endothermic direction. The position of equilibrium shifts left. The value of Kc gets smaller as there are fewer products.

Effect of 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 Kc

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



Increasing concentration of H₂ would move equilibrium to the right lowering concentration of H₂ and Cl₂ and increasing concentration of HCl. The new concentrations would restore the equilibrium to the same value of Kc

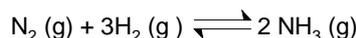
Effect of Concentration and pressure on rate

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 Kp

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

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

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.

Environmental benefits of Catalysts

Catalysed reactions can occur at lower temperature so less fuel needed and fewer emissions from fuels.

Catalysed reaction enables use of an alternative process with higher atom economy so meaning fewer raw materials needed and less waste products are produced

Heterogeneous catalysis

A **heterogeneous catalyst** is in a different phase from the reactants

Heterogeneous catalysts are usually solids whereas the reactants are gaseous or in solution. The reaction occurs at the surface of the catalyst.

Adsorption of reactants at active sites on the surface may lead to catalytic action. The **active site** is the place where the **reactants adsorb** on to the **surface of the catalyst**. This can result in the bonds within the reactant molecules becoming weaker, or the molecules being held in a more reactive configuration. There will also be a higher concentration of reactants at the solid surface so leading to a higher collision frequency

Effect of pressure on heterogenous Catalysis.

Increasing pressure has limited effect on the rate of heterogenous catalysed reactions because the reaction takes place on surface of the catalyst. The active sites on the catalyst surface are already saturated with reactant molecules so increasing pressure wont have an effect

Importance of equilibrium to industrial processes

Common examples

Haber process

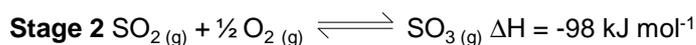
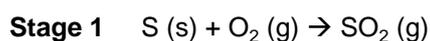


T= 450°C, P= 200 – 1000 atm, catalyst = iron

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= 10 atm, catalyst = V₂O₅

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