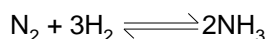


11. Equilibrium II

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 Kc

For a generalised reaction



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

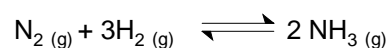
A, B, C, D stand for the chemical formula

Kc = equilibrium constant

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

[] means the equilibrium concentration

Example 1



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

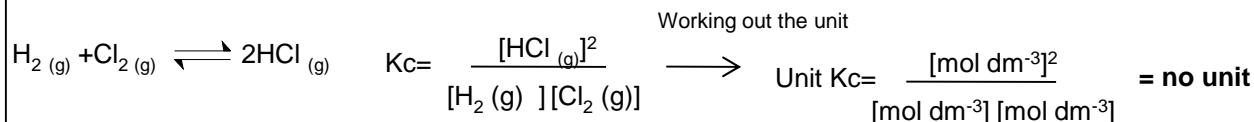
The unit of Kc changes and depends on the equation.

Working out the unit of Kc

Put the unit of concentration (mol dm^{-3}) into the Kc 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 Kc expression



Calculating Kc

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 0.2 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 moles of HCl has been formed it must have used up 0.1 of Cl_2 and 0.1 moles 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 1.5 moles of N_2 and 4 moles of H_2 in a 1.5 dm^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

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

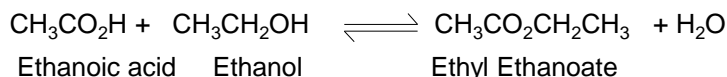
$$K_c = \frac{0.6^2}{0.7 \times 1.77^3} = 0.0927 \text{ mol}^{-2} \text{ dm}^6$$

Work out the equilibrium concentrations

conc = moles/vol (in dm^3)

Practical: Working out equilibrium constant Kc

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 cm³ 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 cm³.
Stopper the flask, then invert and shake the contents thoroughly.
- 3 Use the pipette to transfer 25.0 cm³ of the diluted equilibrium mixture to a 250 cm³ 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 cm³ of 0.400 mol dm⁻³ sodium hydroxide was used in the above titration. The initial moles of sulphuric acid was 5x10⁻⁴ 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⁺ present in 25cm³ = 0.0156 mol

So total amount of H⁺ present in 250cm³ = 0.156 mol

Total mol acid present = moles of carboxylic acid + moles of acid catalyst

So

Amount of carboxylic acid at equilibrium = 0.156 – (5x10⁻⁴ x 2)
= 0.155 mol

X 2 because H₂SO₄
has 2 H⁺

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.

$$\begin{aligned}\text{Amount of ethanoic acid that reacted} &= \text{initial amount} - \text{equilibrium amount} \\ &= 0.5 - 0.155 \\ &= 0.344 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Amount of ethanol at equilibrium} &= \text{initial amount} - \text{amount that reacted} \\ &= 0.400 - 0.344 \\ &= 0.056 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Amount of ethyl ethanoate at equilibrium} &= \text{initial amount} + \text{amount that formed} \\ &= 0 + 0.344 \\ &= 0.344 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Amount of water at equilibrium} &= \text{initial amount} + \text{amount that formed} \\ &= 0 + 0.344 \\ &= 0.344 \text{ mol}\end{aligned}$$

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 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

$$\begin{aligned} K_p &= \frac{p^2 \text{NH}_3(\text{g})}{p \text{N}_2(\text{g}) p^3 \text{H}_2(\text{g})} & \text{Unit} &= \frac{\text{atm}^2}{\text{atm} \text{atm}^3} \\ & & \text{Unit} &= \frac{1}{\text{atm}^2} \\ & & \text{Unit} &= \text{atm}^{-2} \end{aligned}$$

Cancel out units

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 atm². 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	0.222×2 =0.444	0.667×2 =1.33	0.111×2 =0.222

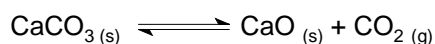
Finally put concentrations into K_p expression

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

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

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

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

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 S_{total}

Application of rates and equilibrium

Effect of changing conditions on value of K_c or K_p

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

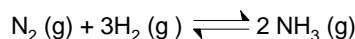
K_c and K_p only change with temperature.

It does not change if pressure or concentration is altered.
A catalyst also has no effect on K_c or K_p

Effect of Temperature on position of equilibrium and K_c

Both the **position of equilibrium** and the value of **K_c or K_p will change** if temperature is altered

In this equilibrium which is exothermic in the forward direction



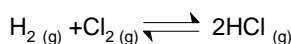
If temperature is increased the reaction will shift to oppose the change and move in the backwards endothermic direction. The position of equilibrium shifts left. The value of K_c gets smaller as there are fewer products.

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 K_c

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



Increasing concentration of H_2 would move equilibrium to the right lowering concentration of H_2 and Cl_2 and increasing concentration of HCl . The new concentrations would restore the equilibrium to the same value of K_c .

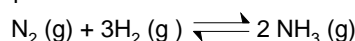
Effect of Concentration and pressure on rate

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 K_p

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

Increasing pressure does not change K_p .
The increased pressure increases the pressure terms on bottom of K_p 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 K_p expression therefore increases and the bottom decreases until the original value of K_p 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.

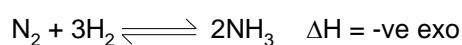
It does not effect the position of equilibrium because it speeds up the rates of the forward and backward reactions by the same amount.

Catalysts speeds up the rate allowing lower temperatures to be used (and hence lower energy costs) but have no effect on equilibrium.

Importance of equilibrium to industrial processes

Common examples

Haber process

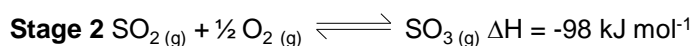
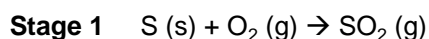


T= 450°C, P= 200 – 1000 atm, catalyst = iron

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= 1 to 2 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