4.2 Equilibria

Many reactions are reversible

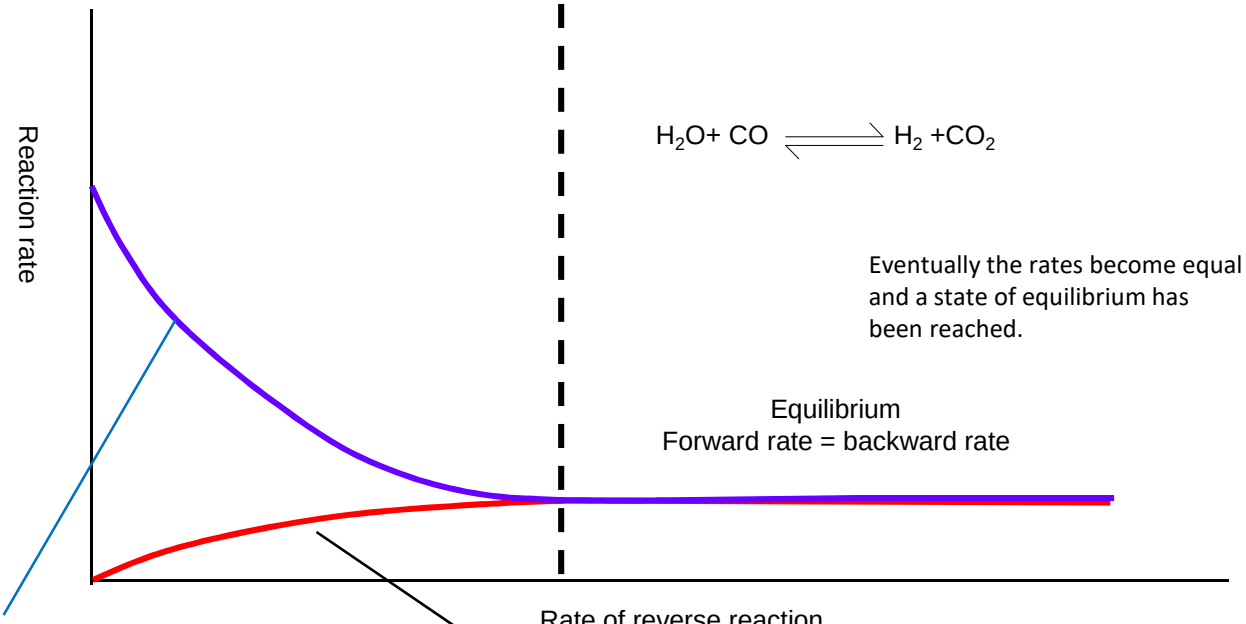
$N_2 + 3H_2 \rightleftharpoons 2NH_3$

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.

We use the expression '**position of equilibrium**' to describe the composition of the equilibrium mixture.

If the position of equilibrium favours the reactants (also described as "towards the left") then the equilibrium mixture will contain mostly reactants.



$H_2O + CO \rightleftharpoons H_2 + CO_2$

Eventually the rates become equal and a state of equilibrium has been reached.

Equilibrium
Forward rate = backward rate

Rate of forward reaction ($H_2O + CO \rightarrow$)

When H_2O and CO are initially mixed the forward reaction is relatively fast and the backward reaction cannot occur.

As the concentrations of H_2O and CO decrease the forward reaction will slow down.

Rate of reverse reaction ($H_2 + CO_2 \rightarrow$)

As the concentrations of H_2 and CO_2 increase the backward reaction will speed up.

Le Chatelier's Principle

We use Le Chatelier's principle to work out how changing external conditions such as temperature and pressure affect the position of equilibrium

Le Chatelier's principle states that if an external condition is changed the equilibrium will shift to oppose the change (and try to reverse it).

Effect of Changing Concentration

$A + B \rightleftharpoons C + D$

If extra A is added to the equilibrium mixture the forward reaction occurs more to oppose the change and remove some of the extra A and form extra C and D. The equilibrium has moved to the right.

If C is removed from the equilibrium mixture the forward reaction occurs more to oppose the change and replace some of the C removed; the amount of D therefore increases whilst A and B are used up. The equilibrium has moved to the right.

Effect of Concentration on equilibrium

$I_2 + 2OH^- \rightleftharpoons I^- + IO^- + H_2O$
brown colourless

Increasing the concentration OH^- ions causes the **equilibrium to shift to oppose** this and move in the **forward** direction **to remove OH^- ions**. The position of equilibrium will **shift towards the right,** giving a **higher yield of I^- and IO^-**. (The colour would change from brown to colourless)

Adding H^+ ions reacts with the OH^- ions and reduces their concentration so the equilibrium shifts back to the left giving brown colour.

$Co(H_2O)_6^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)} \rightleftharpoons CoCl_4^{2-}{}_{(aq)} + 6H_2O(l)$
pink blue

If the concentration of Cl^- ions is increased by adding extra HCl to an equilibrium mixture, the position of equilibrium will shift towards the products and thereby removing some the of the extra Cl^- ions added. So the colour will change from pink to blue.

Effect of Temperature on equilibrium

If temperature is increased the **equilibrium will shift to oppose** this and move in the **endothermic** direction to try and **reduce the temperature** by absorbing heat.

And its reverse

If temperature is decreased the **equilibrium will shift to oppose** this and move in the **exothermic** direction to try and **increase the temperature** by giving out heat.

Typical Exam question: What effect would increasing temperature have on the yield of ammonia?

$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -ve\ exo$

Exam level answer : must include bold points

If temperature is increased the **equilibrium will shift to oppose** this and move in the **endothermic, backwards** direction to try to **decrease temperature**. The position of equilibrium will **shift towards the left,** giving a **lower yield of ammonia**.

Low temperatures may give a higher yield of product but will also result in slow rates of reaction.
Often a compromise temperature is used that gives a reasonable yield and rate

Effect of Pressure on equilibrium

Increasing pressure will cause the equilibrium to shift towards the side with **fewer moles of gas** to **oppose the change** and thereby **reduce the pressure.**

And its reverse

Decreasing pressure will cause the equilibrium to shift towards the side with **more moles of gas** to **oppose the change** and thereby increase the pressure.

If the number of moles of gas is the same on both sides of the equation then changing pressure will have no effect on the position of equilibrium

$H_2 + Cl_2 \rightleftharpoons 2HCl$

Typical Exam question: What effect would increasing pressure have on the yield of methanol?

$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$

Exam level answer : must include bold points

If pressure is increased the **equilibrium will shift to oppose** this and move towards the side with **fewer moles of gas to try to reduce the pressure** . The position of equilibrium will **shift towards the right** because there are 3 moles of gas on the left but only 1 mole of gas on the right**,** giving a **higher yield of methanol**.

Increasing pressure may give a higher yield of product and will produce a faster rate. Industrially high pressures are expensive to produce (**high electrical energy costs for pumping** the gases to make a high pressure) and the **equipment is expensive** (to contain the high pressures)

Effect of Catalysts on equilibrium

A catalyst has **no effect** on the position of equilibrium, 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

Importance of equilibrium to industrial processes

Both the rate of reaction and percentage yield must be considered. The key quantity to consider is mass of product produced per unit time.

Having a fast rate of reaction does not mean necessarily that a good yield will be achieved. Sometimes a compromise is needed.

Optimum conditions of temperature and pressure are used that give the lowest cost, rather than the fastest reaction or highest percentage yield.

Industrial processes cannot exist in true equilibrium since the products are removed as they are formed to improve conversion of reactants. They are not closed systems

Haber process

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ ΔH = -ve exo

The Haber process is used to manufacture ammonia, which can be used to produce nitrogen-based fertilisers.

The raw materials for the Haber process are nitrogen and hydrogen. Nitrogen is obtained from the air and hydrogen may be obtained from natural gas or other sources.

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

Low temperature gives good yield as equilibrium reaction will shift in the exothermic reaction to counteract the low temperature. A low temperature will produce a slow rate of reaction. Therefore a compromise temperature of 450^{0}C is used that gives a fast reaction without giving a very small percentage yield

A high pressure gives good yield because the reaction will shift to the products as there are fewer moles of gas on the products side. This opposes the low pressure.
In general increasing pressure will increase reaction rate. It is worth considering that Increasing pressure has a limited effect on the rate of heterogeneous catalysed reactions because the reaction takes place on surface of the iron catalyst. The active sites on the iron catalyst surface are already saturated with reactant molecules so increasing pressure wont make a significant increase in rate.

High pressures are expensive to generate. Too high a pressure would lead to too high electrical energy costs for pumps to produce the pressure. A moderately high pressure is used that balances the rate and yield with the cost of producing the pressure. In addition, the higher the pressure used, the higher the cost of the equipment needed to withstand the pressure.

The catalysts speeds up the rate of reaction which allows a lower temperature to be used to get the required rate of reaction. This significantly lowers the energy costs.

On leaving the reactor the gases enter a cooler. On **cooling**, the ammonia liquefies and is removed.
Nitrogen and hydrogen stay as gases
The unreacted nitrogen and hydrogen are recycled back in to the reactor, so no raw materials are wasted and improve their atom economy

Uses of ammonia
Making fertilisers
Reacting ammonia with acids can make fetilisers such as ammonium sulfate, ammonium nitrate or ammonium phosphate.
Making nitric acid
Ammonia is used to make nitric acid.
Uses of nitric acid
• make fertilisers such as ammonium nitrate.
• make explosives (e.g. TNT)
• making various dyes, drugs, polymers

$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$
Ammonia + sulfuric acid → ammonium sulfate
$NH_3 + HNO_3 \rightarrow NH_4NO_3$
Ammonia + nitric acid → ammonium nitrate

Contact process

Sulfuric acid is produced by the contact process. There are several stages in the process.

Stage 1 Sulfur is burnt in air to produce sulfur dioxide

$S (s) + O_2 (g) \rightarrow SO_2 (g)$

Stage 2 Sulfur dioxide is reacted with oxygen to produce sulfur trioxide in a reversible reaction

$SO_{2\,(g)} + ½\,O_{2\,(g)} \rightleftharpoons SO_{3\,(g)}$ $\Delta H = -98$ kJ mol^{-1}

Conditions used T= 450°C, P= 10 atm, catalyst = V_2O_5

Low temperatures gives higher yields as the equilibrium reaction will shift in the exothermic reaction to oppose the low temperature. Low temperatures will produce a slow rate of reaction. Therefore a compromise temperature of 450^{0}C is used that gives a fast reaction without giving a very small percentage yield

The pressure used is just above atmospheric pressure. Higher pressure will not have much of an effect on the yield as there is only a slight increase in the moles of gaseous products compared to the moles of reactants. The vanadium (V) oxide catalyst used is a heterogeneous catalyst. Increasing pressure has a limited effect on the rate of heterogeneous catalysed reactions because the reaction takes place on surface of the catalyst. The active sites on the V_2O_5 catalyst surface are already saturated with reactant molecules so increasing pressure wont make a significant increase in rate.
The vanadium (V) oxides catalyses the reaction in a two step reaction. The V_2O_5 changes oxidation number in the first step but reforms in the second step

step 1 $SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$
step 2 $2V_2O_4 + O_2 \rightarrow 2V_2O_5$

Stage 3: Sulphur trioxide is dissolved in 98% sulfuric acid to produce fuming sulfuric acid (called Oleum). The Oleum is the diluted to produce concentration sulfuric acid. The sulfur trioxide is not dissolved directly in water because the reaction is too exothermic. The heat produced causes the sulfuric acid to evaporate

$SO_3 (g) + H_2SO_4 (l) \rightleftharpoons H_2S_2O_7 (l)$
$H_2S_2O_7 (l) + H_2O (l) \rightarrow H_2SO_4 (l)$

The Equilibrium law:
Writing an expression for Equilibrium constant Kc

For a generalised reaction

$mA + nB \rightleftharpoons pC + qD$

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

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

Kc = equilibrium constant

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

[ ] means the equilibrium concentration

Example 1

$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)}$

$$Kc = \frac{[NH_{3\,(g)}]^2}{[N_{2\,(g)}]\,[H_{2\,(g)}]^3}$$

Working out the unit of Kc

The unit of Kc changes and depends on the equation.

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

$$Kc = \frac{[NH_{3\,(g)}]^2}{[N_2\,(g)]\,[H_2\,(g)]^3} \rightarrow \text{Unit} = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}]\,[\text{mol dm}^{-3}]^3} \xrightarrow{\text{Cancel out units}} \text{Unit} = \frac{1}{[\text{mol dm}^{-3}]^2} \rightarrow \text{Unit} = [\text{mol dm}^{-3}]^{-2}$$

$\downarrow$

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

Example 2: writing Kc expression

$H_{2\,(g)} + Cl_{2\,(g)} \rightleftharpoons 2HCl_{(g)}$

$$Kc = \frac{[HCl_{(g)}]^2}{[H_2\,(g)]\,[Cl_2\,(g)]} \xrightarrow{\text{Working out the unit}} \text{Unit Kc} = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}]\,[\text{mol dm}^{-3}]}$$

= no unit

Calculating Kc

Most questions first involve having to work out the equilibrium 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 600cm^3 there were initially 0.5mol of H_2 and 0.6 mol of Cl_2. At equilibrium there were 0.2 moles of HCl. Calculate Kc

	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 Kc 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 kc expression

$$Kc = \frac{[HCl_{(g)}]^2}{[H_2\,(g)]\,[Cl_2\,(g)]}$$

Work out the equilibrium concentrations

conc = moles/ vol (in dm^3)

Finally put concentrations into Kc expression

$$Kc = \frac{0.33^2}{0.67 \times 0.83} = \mathbf{0.196\ no\ unit}$$

Example 4

For the following equilibrium $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$

Initially there were 1.5 moles of N_2 and 4 mole of H_2, in a 1.5 dm^3 container. At equilibrium 30% of the Nitrogen had reacted. Calculate Kc

	N_2	H_2	NH_3
Initial moles	1.5	4.0	0
Equilibrium moles			

30% of the nitrogen had reacted = 0.3 x1.5 = 0.45 moles reacted. Using the balanced equation 3 x 0.45 moles of H_2 must have reacted and 2x 0.45 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 x3 = **2.65**

moles of product at equilibrium = initial moles + moles formed

moles of ammonia at equilibrium = 0 + (0.45 x 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 Kc expression

$$Kc = \frac{[NH_{3\,(g)}]^2}{[N_2\,(g)]\,[H_2\,(g)]^3}$$

$$Kc = \frac{0.6^2}{0.7 \times 1.77^3} = \mathbf{0.0927\ mol^{-2}\ dm^{+6}}$$

Work out the equilibrium concentrations

conc = moles/ vol (in dm^3)

Calculating the amounts of the equilibrium mixture from Kc

Using algebra it is possible to work out the amounts of each component in an equilibrium mixture using the value of Kc

Example 5

For the following equilibrium $H_{2\,(g)} + Br_{2\,(l)} \rightleftharpoons 2HBr_{(g)}$

If 0.200 mol of H_2 and 0.200 mol of Br_2 are mixed and allowed to reach equilibrium. If Kc = 0.210 what are the equilibrium amounts of each substance.

$$Kc = \frac{[HBr_{(g)}]^2}{[H_2\,(g)]\,[Br_2\,(g)]}$$

Make x = moles of H_2 that have reacted at equilibrium
V = volume of container

$$0.21 = \frac{(2x/V)^2}{(0.2-x)/V\ .\ (0.2-x)/V}$$

This reaction is equimolar (same number of moles of reactant as products) so it is possible to cancel out the volume V

$$0.21 = \frac{(2x)^2}{(0.2-x)\ .\ (0.2-x)}$$

$$0.21 = \frac{(2x)^2}{(0.2-x)^2}$$

Square root both sides

$$\sqrt{0.21} = \frac{2x}{0.2-x}$$

Rearrange to give x

$0.458(0.2-x) = 2x$

$0.0917 - 0.458x = 2x$

$0.0917 = 2x + 0.458x$

$x = 0.0917/2.458$
$x = 0.0373$

This example has been carefully set up to avoid the formation of a quadratic equation. It is not on the A-level syllabus to solve quadratic equations.

So at equilibrium
Moles of H_2 = 0.2000- 0.0373
= 0.163 mol

Moles of Br_2 = 0.2000- 0.0373
= 0.163mol

Moles of HBr = 2x 0.0373
= 0.0746mol

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 sulphuric acid catalyst.

$$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$

Ethanoic acid Ethanol Ethyl Ethanoate

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 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 cm^3.
Stopper the flask, then invert and shake the contents thoroughly.
3 Use the pipette to transfer 25.0 cm^3 of the diluted equilibrium mixture to a 250 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 sulphuric 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 x 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^3 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 25cm^3 = 0.0156 mol
So total amount of H^+ present in 250cm^3 = 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 H_2SO_4 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.

Amount of ethanoic acid that reacted = initial amount – equilibrium amount
= 0.5 – 0.155
= 0.344mol

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

$$Kc = \frac{[CH_3CO_2CH_2CH_3]\ [H_2O]}{[CH_3CO_2H]\ [CH_3CH_2OH]}$$

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 x total pressure of gas 1

$$p_1 = x_1 P$$

mole fraction

$$\text{mole fraction} = \frac{\text{number of moles of a gas}}{\text{total number of moles of all gases}}$$

For a 3 part mixture

$$x_1 = \frac{y1}{y_1 + y_2 + y_3}$$

Example 6 : A mixture contains 0.2 moles N_2, 0.5 moles O_2 and 1.2 moles of CO_2. If the total pressure is 3kPa. What are the partial pressures of the 3 gases?

Total moles of gas = 0.5 + 1.2+ 0.2
= 1.9

mole fraction of N_2	= 0.2/1.9 =0.105	mole fraction of O_2	= 0.5/1.9 =0.263	mole fraction of CO_2	= 1.2/1.9 =0.632
Partial pressure of N_2	=0.105x 3 =0.315	Partial pressure of O_2	= 0.263 x 3 =0.789	Partial pressure of CO_2	= 0.632 x 3 =1.896

Writing an expression for K_p

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2\ NH_3 (g)$$

$$Kp = \frac{p^2 NH_3}{p\ N_2\ p^3 H_2}$$

p means the partial pressure of that gas

Kp = equilibrium constant

Only include gases in the K_p expression. Ignore solids, liquids, and aqueous substances.

Working out the unit of Kp

Put the unit of pressure(kPa) into the Kp equation

$$Kp = \frac{p^2 NH_{3\,(g)}}{pN_{2\,(g)}\, p^3 H_{2\,(g)}}$$

Cancel out units

$$\text{Unit} = \frac{kPa^2}{kPa \quad kPa^3}$$

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

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

However, if the equation is written the other way round, the value of Kp will be the inverse of above and the units will be kPa^2.
It is important therefore to write an equation when quoting values of Kp.

Heterogeneous equilibria for Kp

Kp expressions only contain gaseous substances. Any substance with another state is left out

$$CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)}$$

$Kp = p\,CO_2$

Unit kPa

Example 7

For the following equilibrium $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$

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 2kPa what is the value of Kp?

	N_2	H_2	NH_3
Initial moles	1.0	3.0	0
Equilibrium moles			

20% of the nitrogen had reacted = 0.2 x1.0 = 0.2 moles reacted.
Using the balanced equation 3 x 0.2 moles of H_2 must have reacted and 2x 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 x3 = **2.40**

moles of product at equilibrium = initial moles + moles formed

moles of ammonia at equilibrium = 0 + (0.2 x 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 x2 = 0.444	0.667 x2 =1.33	0.111 x2 = 0.222

Finally put concentrations into Kp expression

$$Kp = \frac{p^2 NH_{3\,(g)}}{pN_{2\,(g)}\, p^3 H_{2\,(g)}}$$

$$Kp = \frac{0.222^2}{0.444 \times 1.33^3} = 0.0469\ kPa^{-2}$$

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** it temperature is altered

In this equilibrium which is exothermic in the forward direction

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$$

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.**

$$H_{2\,(g)} + Cl_{2\,(g)} \rightleftharpoons 2HCl_{(g)}$$

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 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 it 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

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$$

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 *K*p.
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 *K*p is restored

$$Kp = \frac{p^2 NH_3}{p\,N_2\,p^3 H_2}$$

$$Kp = \frac{x^2 NH_3 \,.\, P^2}{x\,N_2.P\;\; x^3 H_2.P^3}$$

$$Kp = \frac{x^2 NH_3 \,.\, P^2}{x\,N_2\;\; x^3 H_2.\;\; P^4}$$

Where P is total pressure and x mole fraction

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 Kc or Kp

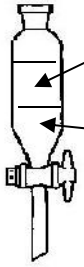
This equation shows a reaction with a Kc >1 will therefore have a positive ΔS_{total}

Partition coefficients

Solvent extraction splits a solute between two immiscible liquid solvents. The solute will be split between the two solvents in an equilibrium.

Solute in aqueous solvent $\rightleftharpoons$ Solute in organic solvent

Separating funnel



The partition coefficient K_{pc} can be calculated from the equilibrium expression

$$K_{pc} = \frac{[\text{ solute in organic}]}{[\text{ solute in aqueous}]}$$

The concentration term is usually mol dm^{-3}. As the expression has the same substance in both terms it is also possible to use g dm^{-3} or gcm^{-3}

K_{pc} is defined as equilibrium constant for the solution of a solute between two immiscible solvents

Example 8

3.56g of phenylamine was produced in an experiment. It was present in 30cm^3 of an alkaline solution. The phenylamine was extracted by addition of 50cm^3 of an organic solvent dichloromethane. After the extraction, the dichloromethane layer contained 3.01g of phenylamine.

Calculate the partition coefficient, K_{pc}, of phenylamine between dichloromethane and water.

mass left in water layer = 3.56 – 3.01 = 0.55 g

$$K_{pc} = \frac{(3.01/50)}{(0.55/30)} = 3.28$$

Example 9

The partition coefficient of substance Y between ether and water is 35.0

A solution contains 3.50 g of Y dissolved in 0.500 dm^3 of water.

Calculate the mass of Y that can be extracted from this aqueous solution by mixing it with 0.050 dm^3 of ether.

mass left in water layer = 3.50 – x

$$K_{pc} = \frac{(x/0.05)}{((3.5-x)/0.50)} = 35$$

$$\frac{10x}{(3.5-x)} = 35$$

x=2.72g