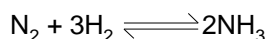


10. Equilibrium I

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.

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.

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).

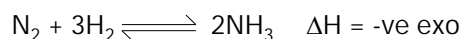
Effect of temperature on equilibrium

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

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



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

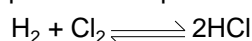
Effect of pressure on equilibrium

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**.

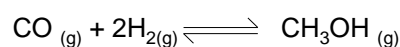
And its reverse

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



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

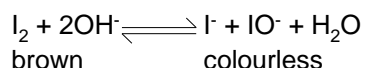


Exam level answer : must include bold points

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 Concentration on equilibrium



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.

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.

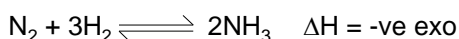
It does not effect the position of equilibrium because it speeds up the rates of the forward and backward reactions by the same amount.

Importance of equilibrium to industrial processes

You should be able to apply the above ideas to given reactions

Common examples

Haber process

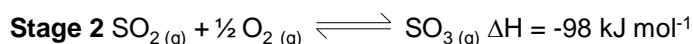
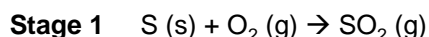


T= 450°C, P= 200 – 1000 atm, catalyst = iron

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

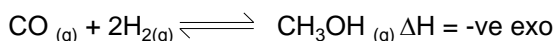


T= 450°C, P= 1 to 2 atm, catalyst = V_2O_5

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

Production of methanol from CO

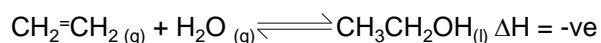


T= 400°C, P= 50 atm, catalyst = chromium and
zinc oxides

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

Hydration of ethene to produce ethanol



T= 300°C, P= 70 atm, catalyst = **conc H_3PO_4**

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

High pressure also leads to unwanted polymerisation of
ethene to poly(ethene)

In all cases catalysts speeds up the rate allowing lower temp to be used (and hence lower energy costs)
but have no effect on equilibrium

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

Equilibrium constant K_c

K_c = equilibrium constant

For a generalised reaction



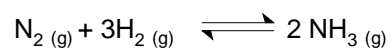
m, n, p, q are the stoichiometric balancing numbers

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

[] means the equilibrium concentration

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

Example 1



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

Liquid and solid concentrations are constant, and are not included in heterogeneous K_c expressions.

Calculating K_c

Example

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 600 cm^3 at equilibrium the concentrations of the substances were 0.67 mol dm^{-3} of H_2 and 0.83 mol dm^{-3} of Cl_2 and 0.33 mol dm^{-3} HCl . Calculate K_c

$$K_c = \frac{[\text{HCl}(\text{g})]^2}{[\text{H}_2(\text{g})] [\text{Cl}_2(\text{g})]}$$
$$K_c = \frac{0.33^2}{0.67 \times 0.83} = 0.196 \text{ no unit}$$

Effect of changing conditions on value of K_c

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 only changes with temperature.

It does not change if pressure or concentration is altered.

A catalyst also has no effect on K_c