

## 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 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?



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

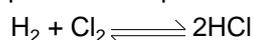
### Effect of Pressure on equilibrium

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?

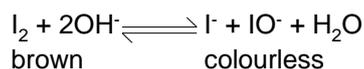


Exam level answer : must include bold points

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

Adding  $\text{H}^+$  ions reacts with the  $\text{OH}^-$  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

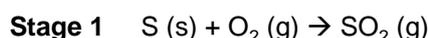


T= 450°C, P= 200 – 1000 atm, catalyst = iron

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 =  $\text{V}_2\text{O}_5$

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  $\text{H}_3\text{PO}_4$**

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

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

## Example 1



$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)] [H_2(g)]^3}$$

## Calculating $K_c$

### Example

For the following equilibrium  $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

In a container of volume  $600\text{cm}^3$  at equilibrium the concentrations of the substances were  $0.67\text{ mol dm}^{-3}$  of  $H_2$  and  $0.83\text{ mol dm}^{-3}$  of  $Cl_2$  and  $0.33\text{ mol dm}^{-3}$   $HCl$ . Calculate  $K_c$

$$K_c = \frac{[HCl(g)]^2}{[H_2(g)] [Cl_2(g)]}$$

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

## 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  $K_c$