

# Chapter 7a (AS-Level)

## Equilibria

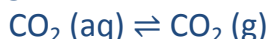
### Reversible Changes:

#### 1. Physical changes, examples:

- Melting of ice, freezing of  $\text{H}_2\text{O}$



- Dissolving  $\text{CO}_2$  in  $\text{H}_2\text{O}$  like in fizzing drinks



#### 2. Chemical changes, examples:

- Formation of ozone and its decomposition to oxygen



- Thermal decomposition of  $\text{CaCO}_3$  to  $\text{CaO}$  and  $\text{CO}_2$ , and the formation of  $\text{CaCO}_3$  from  $\text{CaO}$  left in an atmosphere of  $\text{CO}_2$



### Equilibrium, a state of balanced change:

#### Examples:

- Dissolve salt in  $\text{H}_2\text{O}$  until no more dissolves (saturated solution + non-dissolved salt) = equilibrium between solution and solid, which is concentration of saturated solution stays constant (at a constant temperature).

Although the ions are in constant motion, moving from solid to solution and to solution to solid.



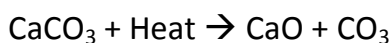
- Similar equilibrium in butane cylinder.

Molecules in liquid are in equilibrium with those in the gas phase

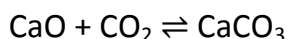


### Equilibrium and chemical changes

For example:



There is no equilibrium in an open container.



In an atmosphere of carbon dioxide in a closed container.

- Both reactions occur when put in a closed container at a high temperature. Balance is reached between reactants and products
- All chemical reactions can reach equilibrium where reactants are in equilibrium with the products (Dynamic equilibrium)
- In some reactions, the degree of conversion of reactants into products is so large, e.g. burning Magnesium in air. In others, e.g. nitrogen and oxygen, seem not to react at all
- Equilibrium is highly in favor of products or reactants. So some are almost irreversible

### Characteristic features of equilibrium

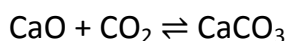
- It is dynamic at molecular and ionic levels
- Both forward and backward reactions take place at equal rate
- A closed system is required
- Macroscopic properties remain constant

### Le Chatelier's principle

- When any condition affecting equilibrium is changed, the position of the equilibrium will shift in the direction to minimize that change

#### Effect of temperature on the position of the equilibrium

For example:



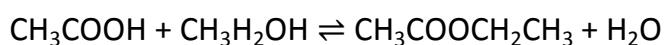
The higher the temperature, the more decomposition happens, so the equilibrium position shifts to the left.

*If the forward reaction is exothermic, raising the temperature moves the equilibrium to the right and vice versa.*

#### Effect of changing the concentration on equilibrium position

For example:

We will consider the formation of the ester, ethyl ethanoate. When Ethanoic acid is warmed with ethanol, in the presence of a few drops of concentrated sulphuric acid, ethyl ethanoate is formed.



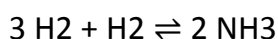
The sulphuric acid is a catalyst for this reaction. Equilibrium is formed as soon as the reactants are mixed. If we increase the concentration of one of the reactants, the equilibrium moves to the right to increase the concentration of the products, to decrease the concentration of the reactants.

*Increasing the concentration of a reactant makes the equilibrium move in the direction that decreases the concentration of the reactant.*

#### Effect of pressure on equilibrium position

If we increase the pressure of a gas, its concentration would also increase.

For example:



Increasing the pressure moves the equilibrium to the right, producing fewer molecules.

*In general, increasing the pressure shifts the equilibrium to the side of fewer gaseous molecules and vice versa.*

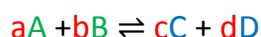
### Effect of catalyst on equilibrium

*Catalysts have no effect on equilibrium, but allow the equilibrium to be achieved faster.*

They do this by decreasing the activation energy, and hence speed it up. More catalyst could mean a faster reaction rate, but doesn't change the equilibrium concentration of reactants or products.

### Law of chemical equilibrium

For the general equation:



The following is always true:

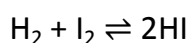
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad K_c = \frac{[\text{Products}]^{\text{Moles}}}{[\text{Reactants}]^{\text{Moles}}}$$

$K_c$  is the equilibrium constant;

**A**, **B**, **C** and **D** are the concentration of the corresponding substances in the general equation;

The superscript, **a**, **b**, **c** and **d** are moles of the corresponding substances in the general equation.

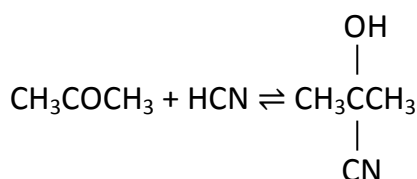
For example:



$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

### Calculating $K_c$

For example:



Initial concentration	0.05 mol/dm <sup>3</sup>	0.05 mol/dm <sup>3</sup>	0.00 mol/dm <sup>3</sup>
Change	-0.0233 mol/dm <sup>3</sup>	-0.0233 mol/dm <sup>3</sup>	+0.0233 mol/dm <sub>3</sub>

$$K_c = \frac{[0.0233]}{[0.0267][0.0267]} = 32.68 \approx 32.7 \text{ dm}^3\text{mol}^{-1}$$

**K<sub>c</sub> and Le Chatelier's principle**

For example:



When the temperature is raised:

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

The concentration of products increase, while the concentration of reactants decrease, so K<sub>c</sub> has to increase.

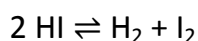
Example 2:



The concentration of the product decrease as the temperature is increased, while the concentration of the reactants increases, so K<sub>c</sub> has to decrease.

**K<sub>c</sub> and concentration changes**

For example:



At 500°K,

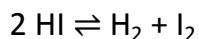
$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 6.25 \times 10^{-3}$$

If the concentration of HI is increased, K<sub>c</sub> decreases. So to maintain equilibrium, the concentration of H<sub>2</sub> and I<sub>2</sub> has to increase so the value of K<sub>c</sub> reaches 6.25x10<sup>-3</sup>.

**Equilibrium constants and pressure changes**

In reactions involving gases, K<sub>p</sub> (of pressures) is used.

E.g.



$$K_p = \frac{p(\text{H}_2) \cdot p(\text{I}_2)}{p(\text{HI})^2}$$

p(H<sub>2</sub>) indicates the equilibrium partial pressures of H<sub>2</sub> in a closed system containing the equilibrium mixture at constant temperature.

The partial pressure of a gas in a mix of gases is the pressure exerted by that gas alone, if it occupies the container alone.

**Calculating partial pressures**

For example, air at 500kPa has 1 mole oxygen and 4 moles nitrogen.

$$(1) \text{ Mole fraction} = \frac{\text{Number of moles}}{\text{Total number of moles}}$$

Of oxygen = 1/5, and of nitrogen = 4/5

$$(2) \text{ Partial pressure} = \text{mole fraction} \times \text{total pressure}$$

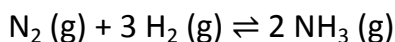
$$p(\text{O}_2) = \frac{1}{5} \times 500 = 100\text{kPa}$$

$$p(\text{N}_2) = \frac{4}{5} \times 500 = 400\text{kPa}$$

### Haber process and $K_p$

The Haber process is a process in which ammonia is produced from reacting hydrogen and nitrogen together.

The reaction is:



The conditions are:

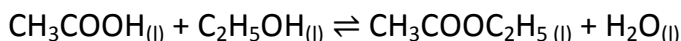
- A pressure between 2.5 and 15 MPa
- A temperature between 670°K to 770°K

In terms of partial pressures of nitrogen, hydrogen and ammonia, the equilibrium constant expression is:

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

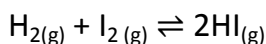
### Using $K_c$ and $K_p$

Example 1:



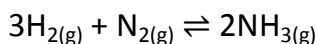
$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

Example 2:



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

Example 3:

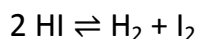


$$K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}$$

Example 4:

Mixture of 0.500 mol/dm<sup>3</sup> H<sub>2</sub> and 0.500 mol/dm<sup>3</sup> I<sub>2</sub> was placed in a 1.00 dm<sup>3</sup> stainless-steel flask at 430 degree Celsius. Calculate the equilibrium concentration of H<sub>2</sub>, I<sub>2</sub> and HI.

$K_c$  of the reaction is 54.3 at this temperature.



Initial	0.500 mol/dm <sup>3</sup>	0.500 mol/dm <sup>3</sup>	0.00 mol/dm <sup>3</sup>
Change	-X mol/dm <sup>3</sup>	-X mol/dm <sup>3</sup>	2x mol/dm <sup>3</sup>
Equilibrium	(0.500 - x) mol/dm <sup>3</sup>	(0.500 - x) mol/dm <sup>3</sup>	2x mol/dm <sup>3</sup>

$$K_c = \frac{(HI)^2}{(H_2)(HI_2)}$$

$$54.3 = \frac{(2x)^2}{(0.500 - x)^2}, \quad \sqrt{54.3} = \frac{(2x)}{(0.500 - x)}$$

$$\sqrt{54.3} = \frac{(2x)}{(0.500 - x)}, \quad (\sqrt{54.3})(0.500 - x) = 2x$$

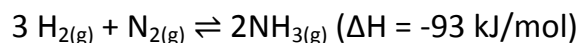
$$4x^2 + (\sqrt{54.3})x - (\sqrt{54.3})(0.5) = 0$$

$$x = 0.409, \text{ or } x = -2.25 \text{ (rejected)}$$

So the equilibrium concentrations are:

Equilibrium	0.091 mol/dm <sup>3</sup>	0.091 mol/dm <sup>3</sup>	0.818 mol/dm <sup>3</sup>
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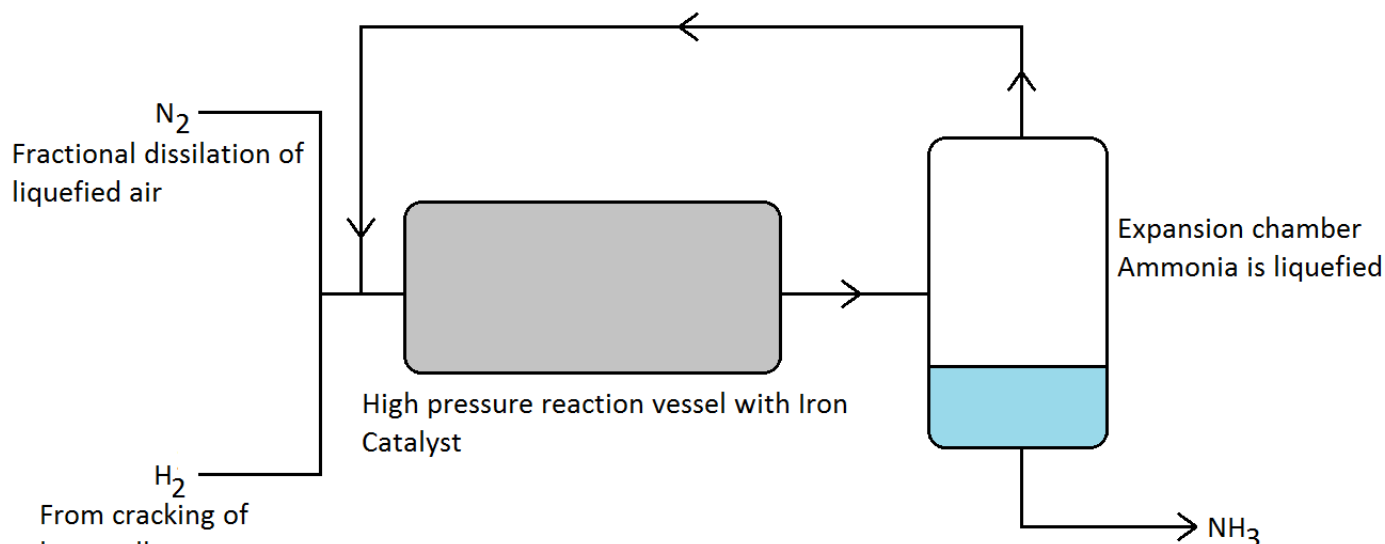
## The Haber process



- Due to the unreactive nature of nitrogen, a high amount of energy is needed. Increasing the temperature would drive the equilibrium to the left as the forward reaction is exothermic.
- Pressure is also used to increase the reaction rate, which would drive the equilibrium to the right. Very high pressures increase the cost of the plant, and low pressures make the reaction very slow.
- A catalyst can be used to overcome the problem of the low rate of reaction. An iron catalyst is used, with small amounts of K, Mg, Al, and Si oxides that improve the efficiency of the catalyst.
- The rate of the reaction can be increased by increasing the temperature and by accepting a lower equilibrium percentage of ammonia in the mixture.
- Ammonia is removed as it is formed, so the reaction mixture is not left to reach equilibrium.
- Rapid expansion is used to cool the mixture. Ammonia liquefies, while unreacted nitrogen and hydrogen are recycled into the reaction vessel.

Conditions are:

- Between 2.5 and 15MPa pressure
- 670 to 770°K temperature
- Finely divided or porous iron catalyst with metal oxide promoters



## The contact process

In this process, sulphuric acid is manufactured from sulphur.

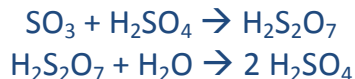
(1) Sulphur is burned in air at 1000°C to make SO<sub>2</sub>



(2) Sulphur dioxide is converted into Sulphur trioxide by using vanadium (v) oxide catalyst.



(3) Sulphur trioxide is dissolved in sulphuric acid to make oleum (H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>) which is then diluted into sulphuric acid.



Conditions are:

- V<sub>2</sub>O<sub>5</sub> catalyst
- Temperature of 400 to 600°C
- Pressure just above atmospheric pressure

These conditions used to convert sulphur dioxide into sulphur trioxide are a compromise. Higher yields of SO<sub>3</sub> are produced when using air in excess, forcing equilibrium to the right.

A temperature of 400°C is used because the catalyst is inactivated below it.

Uses of sulphuric acid include:

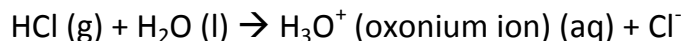
- The manufacture of paints
- The manufacture of detergents and soaps
- The manufacture of phosphate fertilizers
- The manufacture of dyestuff

## Acids and their reactions

General properties of acids:

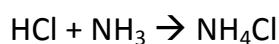
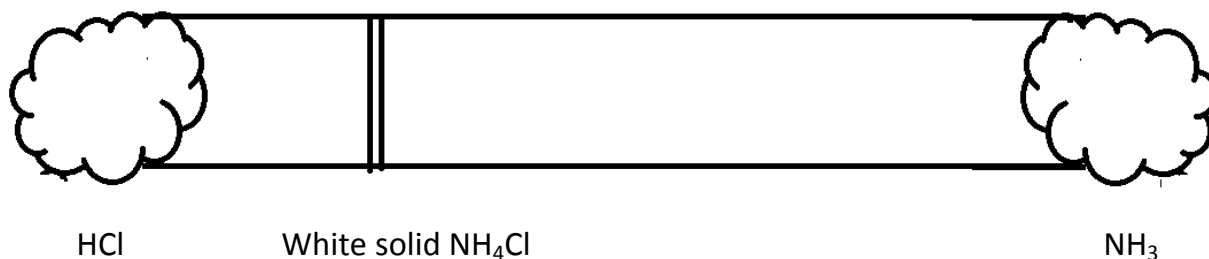
- Turn blue litmus red
- Have a pH below 7
- Produce  $\text{CO}_2$  when they react with carbonates
- Neutralized by alkalis and bases

E.g.:

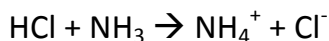


### Salt formation by acids

Reaction of hydrogen chloride and ammonia:



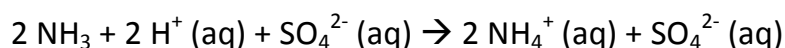
Or



### Production of fertilizers



$\text{H}_2\text{SO}_4$  donated a proton to ammonia to make the  $\text{NH}_4^+$  ions.

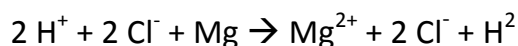


Simplified into:

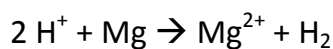


### Formation of salts with metals, metal oxides and metal carbonates

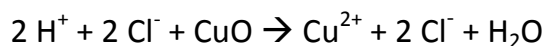
**With metals**



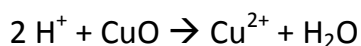
Cancelling out spectator ions:

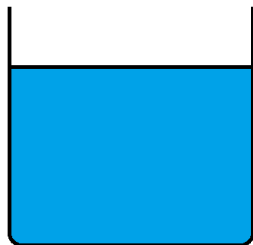


**With metal oxides**

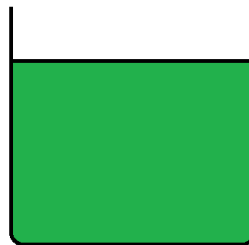


Cancelling out spectator ions:



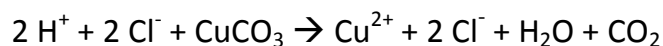


Blue solution  
 $\text{CuO} + \text{H}_2\text{SO}_4$

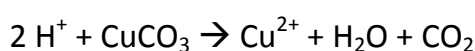


Green solution  
 $\text{CuO} + \text{HCl}$

#### With metal carbonates



Net ionic equation:



### Definition of acids and bases

#### Arrhenius (1884):

An acid is a substance that produces an excess of  $\text{H}^+$  in aqueous solutions

A base is a substance that produces excess of  $\text{OH}^-$  in aqueous solutions.

#### Brønsted & Lowry

An acid is proton donor.

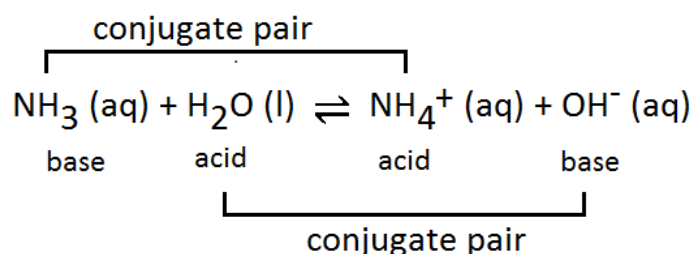
A base is a proton acceptor.

Examples:

- When hydrochloric acid dissolves in water:

HCl	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	+	$\text{Cl}^-$
Proton Donor		Proton Acceptor		Conjugate acid of $\text{H}_2\text{O}$		Conjugate base of HCl

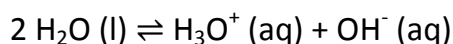
- When ammonia dissolves in water:



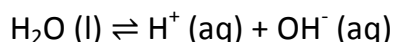
Ammonia accepts a proton from the water and so it's a base. The ammonium ion is its conjugate acid. Water donates a proton, so it's an acid. The hydroxide ion is its conjugate base.

## The role of water

Pure water conducts electricity. This is a fact. This means that pure water contains ions of itself. Pure water can also be electrolyzed by a direct current. Every now and then, one water molecule reacts with another water molecule to form ions. A proton leaves one water molecule and is accepted by the other. These ions transfer electrons during electrolysis.

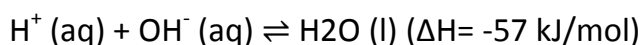


Or more simply as:



## Base behavior and neutralization

When acid and bases react, they are said to neutralize each other. For example, in the acid HCl, there are 2 ions,  $\text{H}^+$  and  $\text{Cl}^-$  and a water molecule. In the base NaOH, there are  $\text{Na}^+$  and  $\text{OH}^-$  ions and a water molecule. When these are mixed, the protons and hydroxide ions react to form water.

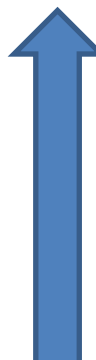



This is what neutralization is – the formation of water by the exothermic forward reaction. The ions remaining stay dissolved in water.

## Acids and bases of varying strength

Strong acid and bases are those which are totally ionized when dissolved in water. The strong acids include hydrogen halides and strong bases include the group I hydroxides.

Weak acids and bases don't ionize totally when they dissolve in water. They even might not ionize at all. Examples for weak acids include Ethanoic acid. They hardly donate protons at all. Organic acids like Ethanoic acid and citric acids are typical weak acids. Weak acids are similarly weak in accepting protons. These include the conjugate bases of strong acids, such as sulphate and chloride ions.

	Acid		Base	
 <p>Strongest acid</p>      <p>Weakest acid</p>	Hydrochloric	$\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$	Chloride	 <p>Weakest base</p>      <p>Strongest base</p>
	Benzoic	$\text{C}_6\text{H}_5\text{COOH} \rightleftharpoons \text{H}^+ + \text{C}_6\text{H}_5\text{COO}^-$	Benzoate	
	Ethanoic	$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$	Ethanoate	
	Ammonium	$\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3$	Ammonia	
	Phenol	$\text{C}_6\text{H}_5\text{OH} \rightleftharpoons \text{H}^+ + \text{C}_6\text{H}_5\text{O}^-$	Phenoxide	
	Hydrogen carbonate	$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	Carbonate	
	Water	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	hydroxide	

**END OF LESSON**