EQUILIBRIUM

A system that is at equilibrium has the following properties.

1. The rates of the forward and reverse reactions are equal.
2. The concentrations of all species in the system are constant.

Nb: For equilibrium to occur it must be a closed system and the temperature must remain constant.

At equilibrium both the forward and reverse reaction occur at a molecular level but they are occurring at the same rate but in opposite directions. This is why it is called **DYNAMIC EQUILIBRIUM**.

**PHASE EQUILIBRIA:**

# Water vapour

# Liquid water

H2O (l) ↔ H2O (g)

If some water is placed in a closed container at a constant temperature, some of the liquid will evaporate and become a gas. As soon as some gas is formed there is the possibility that it will condense back into a liquid.

After a period of time the rates of evaporation and condensation will become equal and the system has reached equilibrium.

If the temperature is increased, the extra energy will increase the rate of evaporation. After time a new equilibrium position will be reached.

**SOLUTION EQUILIBRIA:**

# Dissolved sugar

C12H22O11 (s) ↔ C12H22O11 (aq)

# Undissolved sugar

sugar

When a solid solute is placed in water it will start to dissolve. If there is excess solute, a saturated solution is formed, then the macroscopic properties will become constant. Some of the dissolved solid can also crystallises out of solution.

When the rate of dissolving and crystallising become constant the solution is at equilibrium.

For a **solution** to reach equilibrium it must be a saturated solution and the temperature must be kept constant.

CHEMICAL EQUILIBRIUM:

N2O4 (g) ↔ 2NO2 (g)

# Colourless Brown

# Reaction rate

# Time

The system has reached equilibrium

# Reverse reaction

# Forward reaction

**EQUILIBRIUM CONSATANT:**

**aA + bB** ↔ **cC + dD**

# K = [C]c[D]d Solids and liquids are not included as they do

[A]a[B]b  not have a concentration (molL-1).

Example:

N2O4 (g) ↔ 2NO2 (g)

# K = [NO2]2 = 0.213 at 100**°**C

[N2O4]

The value of the equilibrium constant stays the same as long as the temperature remains constant.

This means if you know the concentration of one substance (at equilibrium) you can calculate the other.

Also if the concentration of a reactant changes the new concentration of other substances can be calculated.

H2 (g) + I2 (g) ↔ 2HI(g)

# 3K = [HI]2 = 57 at 425**°**C

[H2][I2]

# What does the equilibrium constant say about the system?

If K is large –

If K is small –

If K is close to 1 –

*If a chemical system at equilibrium is subjected to a change in conditions, the system will adjust to establish equilibrium in such a way to partially counteract the imposed change.*

***There are three main ways to change the conditions of an equilibrium system.***

***Concentration, Pressure, Temperature.***

**An *increase* in the *temperature* of the system will *favour* the *endothermic* reaction.**

**A *decrease* in the *temperature* of the system will *favour* the *exothermic* reaction.**

In your own words explain why.

**An *increase* in the *concentration* of a reactant or product of the system will *favour* the direction, which will *decrease* the *concentration* of that substance.**

**A *decrease* in the *concentration* of a reactant or product of the system will *favour* the direction, which will *increase* the *concentration* of that substance.**

**If an equilibrium system involves one or more gaseous reactants or products the partial pressure of these substances is a measure of their concentration.**

**An *increase* in the *partial pressure* of a gaseous reactant or product of the system will *favour* the direction, which will *decrease* the *partial pressure* of that gaseous substance.**

**If the external pressure of a system at equilibrium is changed the volume will be altered.**

**If *decreasing* the *volume* of the system *increases* the *pressure* it will *favour* the direction, which will *reduce* the *pressure*. This can be achieved by favouring the production of *fewer moles* of** *gaseous* **substances.**

**If *increasing* the *volume* of the system *decreases* the *pressure* it will *favour* the direction, which will *increase* the *pressure*. This can be achieved by favouring the production of *more moles* of** *gaseous* **substances.**

**If there are the same number of moles of gaseous substances in the reactants and products a change in the external pressure will favour** *neither* **direction.**

|  |  |  |
| --- | --- | --- |
| **Change made to the system** | **Effect on the Yield (amount of product)** | **Effect on the rate of reaction** |
| Temperature **Exothermic reaction** |  |  |
| **Endothermic reaction** |  |  |
| **Concentration of reactants** |  |  |
| **Pressure of the system** |  |  |
| **Partial pressure of a reactant or product** |  |  |
| **Catalyst** |  |  |
| **Sub-division of reactants.** |  |  |

|  |  |  |
| --- | --- | --- |
| **Change made to the system** | **Effect on the Yield (amount of product)** | **Effect on the rate of reaction** |
| Temperature **Exothermic reaction** | **Increases temp decreases yield** | **Increased temp increases** |
| **Endothermic reaction** | **Increases temp increases yield** | **the rate of all reactions** |
| **Concentration of reactants** | **Increase in conc favours the direction which consumes extra** | **Increase in conc increases reaction rate.** |
| **Pressure of the system** | **Increase in pressure favours less moles of gas** | **Increase in pressure increases rate** |
| **Partial pressure of a reactant or product** | **Increase in partial pressure favours direction which consumes** | **Increase in partial pressure increases rate** |
| **Catalyst** | **No effect just gets to equilibrium quicker** | **Increase rate of forward & reverse** |
| **Sub-division of reactants.** | **No effect** | **Increase in SA increases rate** |

In Industry chemist must find a compromise between the factors that favour a fast reaction and the factors that favour a high yield of the product.

## THE HABER PROCESS (Ammonia production)

The main use of ammonia in WA is to make fertilisers and explosives in the form of ammonium nitrate and ammonium sulfate.

**N2 + 3H2 ⬄ 2NH3 + 92kJmol-1**

The factors that favour a **high reaction rate** are:

* **High temperature**
* **High Pressure**
* **Addition of a catalyst** (**Fe/Fe2O3** ie rusty iron)

The factors that favour a **high yield** are:

* **Low temperature** (favours the forward reaction that is exothermic)
* **High pressure** (favours the forward reaction due to the 4:2 mole ratio of gases)

The actual conditions used are:

* **500°C, 350atm, Fe/Fe2O3 catalyst.**

The ammonia is liquefied under pressure and the unused N2 and H2 gas are recycled.

**NH3 + HNO3 🡪 NH4NO3**

**2NH3 + H2SO4 🡪 (NH4)2SO4**

**THE CONTACT PROCESS (Sulfuric acid production)**

The main uses of H2SO4 are in the production of fertilisers and explosives, batteries and many industrial processes.

To start the process sulfur can be burnt or the roasting of zinc blend (ZnS ore).

**2ZnS + 3O2 🡪 2ZnO + 2SO2**

The second step involves the oxidation of SO2

# **2SO2 + O2 ⬄ 2SO3 + heat**

The factors that favour a **high reaction rate** are:

* **High temperature**
* **High Pressure**
* **Addition of a catalyst (V2O5 Vanadium oxide)**

The factors that favour a **high yield** are:

* **Low temperature** (favours the forward reaction that is exothermic)
* **High pressure** (favours the forward reaction due to the 3:2 mole ratio of gases)

The actual conditions used are:

* **600°C, 1atm, V2O5 catalyst.**

This is quick but gives a low yield, the gas is removed and cooled to 400°C, which gives a high yield.

The SO3 cannot be dissolved in water because it forms a mist when it comes near water that cannot be condensed.

The SO3 is then dissolved in concentrated (18M) H2SO4 to produce oleum, and the oleum is diluted and some is removed and the rest recycled.

**SO3 + H2SO4 🡪 H2S2O7**

**H2S2O7 + H2O 🡪 2H2SO4 (98% or 18M)**

**2NH3 + H2SO4 🡪 (NH4)2SO4**

**Ca3(PO4)2 + 2H2SO4 + 5H2O 🡪 Ca(H2PO4)2.H2O + CaSO4.2H2O**

**superphosphate**