How Far, How Fast?

Chemical Equilibrium

Introduction

Many physical and chemical processes exist in a state of balance.

In these reactions, the reactants are not always completely converted into products.

Many reactions including most organic reactions, all acid-base and redox reactions involve a competition between present species for different reactions.

The *general* meaning of the term **'equilibrium'** is a state of balance in which nothing appears to change. For example, a see-saw is in a state of balance if the moment is the same on each side.

Equilibria in Physical Processes

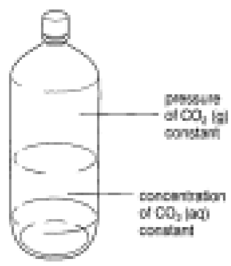
Physical processes do not involve a chemical change, where new substances are produced. We will have a quick look at two such processes.

Solution – Vapour Equilibrium

Syllabus Statements:

- *explain the features of a dynamic equilibrium.*

Consider a **sealed** bottle of soda water. The bottle and its contents make a **closed system**.



The carbon dioxide equilibrium on a macroscopic scale

The carbon dioxide is present in solution and as a gas above the liquid. If the system remains at constant temperature, then the **pressure of the CO_2 gas and the concentration of the dissolved CO_2 remains constant.**

The carbon dioxide equilibrium on a microscopic scale

$$CO_{2\,(aq)} \rightleftharpoons CO_{2\,(g)}$$

macroscopic properties → which are 'bulk' properties that we can observe

→ concentrations and pressures do not change

microscopic properties → changes are taking place

→ we see the molecules moving quickly

→ some are dissolving and some are escaping from the solution

→ but the molecules are **dissolving and escaping at the same speed**

→ the concentration and pressure stay the same

When a forward process and a backward process occur at the same speed, the system is said to be in *dynamic equilibrium*

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1. What happens to the equilibrium if the bottle cap is removed (system is 'opened')?

2. Write down one other physical equilibrium present in a soda bottle. This is a liquid-vapour equilibrium (vapour pressure).

Solubility: Solute – Solution Equilibrium

When a teaspoon of sugar is added to a cup of tea, all the sugar dissolves. If you keep adding sugar, then eventually the solution is saturated and solid sugar sits in the tea.

On a macroscopic level, nothing appears to be happening, but on a microscopic level, the particles of sugar are dissolving and crystallising at the same rate. Evidence from radioisotope labelling provides evidence for this dynamic equilibrium.

$$\textbf{Sugar(s)} \rightleftharpoons \textbf{Sugar(aq)}$$

1. For this equilibrium to be established, the system must be closed. Why can the solute – solution equilibrium not establish in an open system?

2. Produce a summary of the key features of a dynamic equilibrium.

Equilibria in Chemical Processes

Syllabus Statements:

- *state le Chatelier's principle and apply it to deduce qualitatively (from appropriate information) the effect of a change in temperature, concentration or pressure, on a homogeneous system in equilibrium.*

Many chemical reactions can reach a state of dynamic equilibrium also. For example, when calcium carbonate is heated it decomposes to form calcium oxide and carbon dioxide.

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

This reaction can reach a state of equilibrium, but only if you close the system.

If the system is open, then the CO_2 escapes, but if you heat $CaCO_3$ in a container then the amounts of each substance reach a constant level.

1. What would you expect to happen if you heated a mixture of CaO and CO_2 at the same temperature in the container?

2. What is happening at equilibrium at the molecular level?

3. Back in the soda bottle there is a chemical equilibrium involving the reaction of carbon dioxide and water to form a hydrogencarbonate ion and a hydrogen ion. Construct an equation to show this.

Le Chatelier's Principle

We use the term **'position of equilibrium'** to describe the equilibrium concentrations or pressures.

1. What happens to the concentrations of reactants and products if the position of euilibrium moves to the left or right?

It stands to reason that the position of equilibrium will alter if you change the conditions of a system. You could do this by changing:

- the **concentration** of a reactant or product
- by changing the **temperature**
- by changing the **pressure** (only important for reactions with gases)

The effect of changing the conditions on the position of equilibrium, is governed by **Le Chatelier's principle**:

Write down Le Chatelier's Principle and commit it to memory.

Effect of Concentration Changes

Consider the general equilibrium system:

$$A + B \rightleftharpoons C + D$$

1. What happens to the position of equilibrium if the concentration of A is increased? Relate this effect to Le Chatelier's principle.

2. Explain this by describing what happens on the molecular level and discussing reaction rates.

3. Describe and explain what happens to the position of equilibrium if the concentration of C is decreased.

Effect of Pressure Changes

For a reaction involving gases, altering the pressure may cause a change in the position of equilibrium.

For the reaction:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

Comment on the number of moles of reactants and products. Use this to deduce the effect on the position of equilibrium of increasing or decreasing pressure <u>in this reaction.</u>

In the following reaction, there are more moles of gas on the left:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

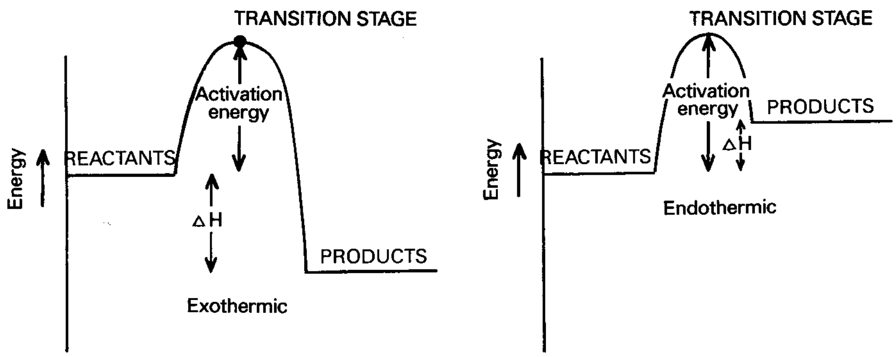
In the final reaction, there are more moles of gas on the right:

$$N_2O_{4(g)} \rightleftharpoons 2NO_2$$

Write some notes on separate paper to explain the effect of increasing and decreasing gas pressure on each of these reactions. Explain this by reference to Le Chatelier's principle. A diagram may help.

Effect of Temperature Changes

The change that takes place in an equilibrium when temperature is altered depends upon whether the forward reaction is exothermic or endothermic.



Energy changes in exothermic and endothermic reactions

If the forward reaction is exothermic, then the reverse reaction will be endothermic:

$A + B \rightleftharpoons C + D$ ΔH is __________ (exothermic)

$C + D \rightleftharpoons A + B$ ΔH is __________ (endothermic)

Describe and explain what happens to the position of equilibrium if temperature is increased or decreased. Refer to Le Chatelier's principle. Insert into your notes.

Effect of Adding a Catalyst

This often causes some confusion.

Catalysts lower the activation energy for a reaction, and so they increase the rate of a reaction.

However, they do so with no more product being produced – they make the *same* amount of product in *less* time.

Comment on the effect of a catalyst on the position of equilibrium.

The Haber Process

Syllabus Statements:

- *describe and explain the conditions used in the Haber process for the formation of ammonia, as an example of the importance of a compromise between chemical equilibrium and reaction rate in the chemical industry.*
- *outline the importance of ammonia and nitrogen compounds derived from ammonia, for example, fertilisers, polyamides and explosives.*
- *describe ammonia as a base, in terms of its reaction with an acid (e.g. sulphuric acid) to form ammonium salts, used in fertilisers.*

We are going to apply Le Chatelier's principle to the important industrial process, the **Haber Process**.

We need large amounts of nitrogen compounds, particularly for making **nitrogenous fertilisers**, **polyamide polymers** and **explosives**. The Haber process 'fixes' nitrogen into the compound ammonia (NH_3), which is a plentiful raw material, being 78% of the air. Ammonia can be converted into nitric acid using the Ostwald process.

By the end of the 19th century, there was a shortage of nitrogen compounds. Industry wanted them to make dyes and explosives. Agriculture wanted them to grow more food for an increasing population. Ready supplies were dwindling, notably sodium nitrate from Chile.

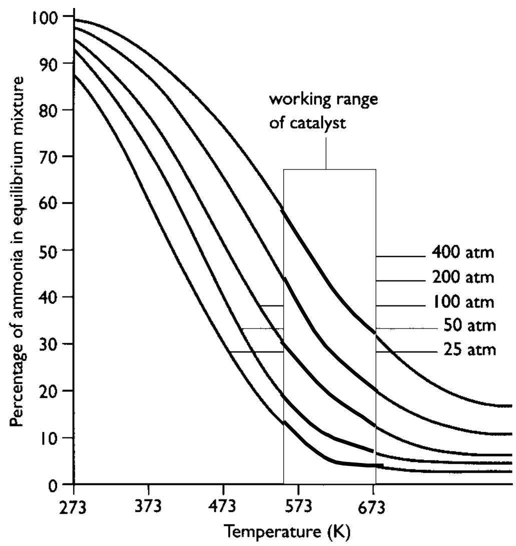
The war preparations of Germany between 1909 and 1914 solved the problem. Germany realised that in a war, imports would be blockaded and would need more food and a lot of explosive.

The German chemical company (BASF) developed an industrial plant to manufacture ammonia under the leadership of their chemical engineer, Carl Bosch. He used the discovery of Fritz Haber (a research chemist) that a temperature of 600°C and a pressure of 200atm would produce ammonia.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H^{\theta} = -92\ kJ$$

This process is sometimes called the Haber-Bosch process, but is more commonly referred to as the Haber process. Note that the above reaction is the key element of the process, but does not represent the whole system.

The following graph shows the effect of changing temperature and pressure on the Haber process.



You will be given a separate sheet with details of the Haber process. This sheet, together with the answers to the questions, form the important notes for this section.

Making Fertilisers

Ammonia is a base. It can **neutralise** acids, forming a salt and water. These salts can be used as fertilisers.

The reaction of ammonia with an acid forms the ammonium ion. The general reaction is:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Write balanced equations to represent the reactions of ammonia with sulphuric acid and phosphoric acid (H_3PO_4). Name the products formed.

Acids, Bases and Equilibria

Brønsted-Lowry Theory

Syllabus Statement:

- *describe an acid as a species that can donate a proton.*

Johannes Brønsted (Danish) and Thomas Lowry (British) were independently responsible for The Brønsted-Lowry theory of acids and bases. This is basically an alternative definition for acids and bases, and can be compared to Lewis acids/bases or the Arrhenius definition. It defines:

an acid $\rightarrow$ proton (H^+) donor

This is the definition which is most often used in chemistry, and certainly in the study of acid-base equilibria processes.

e.g. HCl donates a proton and NaOH accepts a proton:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

Written as an ionic equation ignoring spectator ions:

$$H^+ + OH^- \rightarrow H_2O$$

Reactions of Acids

Syllabus Statements:

- *describe the reactions of an acid, typified by hydrochloric acid with metals, carbonates, bases and alkalis.*
- *interpret the reactions above using ionic equations to emphasise the role of H^+(aq).*

Write your own notes on the reactions listed above, including at least one example of each reaction. Use one example of an insoluble base and one example of a soluble base. You should employ full balanced equations, then write down the simplest ionic equation for each process, which emphasises the role of H^+.

Strong and Weak Acids

Syllabus Statement:

- *explain qualitatively, in terms of dissociation, the differences between strong and weak acids.*

It is important not to confuse the idea of **strong** and **weak** acids with the idea of **concentrated** and **dilute** acids.

All acids can be expressed as equilibria. For example, hydrochloric acid:

$$HCl_{(aq)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

However, hydrochloric acid is considered to be a **strong acid**, because it has a very high tendency to donate protons. We can approximate it to be **completely dissociated**, so we normally write:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

A **weak acid is only partly dissociated** and we must write it as an equilibrium expression. For example, ethanoic acid is weak:

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

Write equations to represent the dissociation of some strong acids and weak acids. Strong acids: sulphuric acid and nitric acid. Weak acids: nitrous acid (HNO_2) and hydrocyanic acid (HCN).