FACTFILE:
GCE CHEMISTRY
2.10 EQUILIBRIUM

Rewarding Learning

Learning Outcomes

Students should be able to:

2.10.1 demonstrate understanding that many chemical reactions are reversible and define the terms dynamic equilibrium, homogeneous and heterogeneous;

2.10.2 deduce the qualitative effects of changes of temperature, pressure, concentration and catalysts on the position of equilibrium for a closed homogeneous system;

2.10.3 deduce an expression for the equilibrium constant, Kc, and its units for a given homogeneous equilibrium system;

2.10.4 relate the magnitude of Kc to the position of equilibrium and extent of reaction;

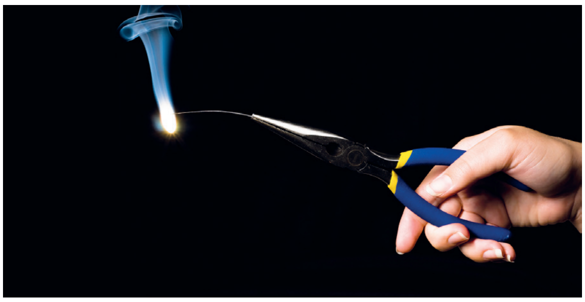
2.10.5 describe and explain the conditions used in industrial processes, for example the Haber process for the formation of ammonia and the Contact process for sulfuric acid; and

2.10.6 demonstrate understanding of the importance of a compromise between equilibrium and reaction rate in the chemical industry.

Chemical Equilibrium

Many chemical reactions take place and reach completion, that is, they keep going until all the starting materials have been converted to products. For example, when magnesium is burned in oxygen, all of the magnesium is used up and all that is left is the product, magnesium oxide:

$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$



Many reactions are reversible. A reversible reaction is one which goes in both the forward and backwards direction. For example, the formation of ammonia in the Haber process, is a reversible reaction:

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

The nitrogen and hydrogen begin to react, making ammonia. As ammonia is made, it breakdown into nitrogen and hydrogen. Eventually, the rates of the two reactions will become equal and there won't be any further change in the amounts of the reactants or product. A dynamic equilibrium has been established.

Equilibrium is a reversible reaction in which the amount of each reactant/product remains the same.

In a dynamic equilibrium the rate of the forward reaction is equal to the rate of the reverse reaction.

A homogeneous reaction is one in which all the reactants and products are in the same physical state.

A heterogeneous reaction is one in which all the reactants and products are not in the same physical state.

A dynamic equilibrium can only be achieved in closed systems, that is, a system in which none of the components can escape. By opening up a closed system conditions can be changed after which the system can be allowed to reach equilibrium again. The equilibrium position and product yield of a system may be altered by the following changes:

- Changing the concentration of a reactant or product;
- Changing the pressure of a gaseous equilibrium;
- Changing the temperature.

Changing concentration

Increasing the concentration of a reactant, or decreasing the concentration of a product moves the equilibrium to the right in order to oppose the change made to the system. This increases the yield of product. Conversely, if the concentration of a reactant is decreased, or product concentration increased, the equilibrium will move to the left. This leads to a decreased yield of product.

Changing pressure

For an equilibrium system involving gases, changing pressure will affect the position of the equilibrium. An increase in pressure will cause the equilibrium to move to the side with fewer gas molecules in order to undo the external change. A decrease in pressure will have the opposite effect.

Changing temperature

The effect of temperature depends on the enthalpy change for the forward and reverse reactions. Increasing temperature causes the equilibrium to move in the endothermic direction to use up the extra heat applied. Decreasing temperature cause the equilibrium to move in the exothermic direction to generate more heat.

Equilibrium constant

Every reversible reaction has a characteristic constant called the equilibrium constant which is expressed in terms of concentrations, K_c. It is a ratio of product concentrations to reactant concentrations and expresses the position of the equilibrium mathematically.

For a reaction in the format
$aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

[A] means the concentration of substance A measured in mol dm^{-3}.

The units of K_c depend on the values of a, b, c and d in the expression. If a + b = c + d then K_c will have no units.

For example, one of the key reactions in the **Contact process** is the reversible homogeneous reaction between sulphur dioxide and oxygen to form sulfur trioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The equilibrium constant, K_c, is given by:

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

$$\text{Unit of } K_c = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^2(\text{mol dm}^{-3})} = \frac{1}{(\text{mol dm}^{-3})} = \text{mol}^{-1}\text{ dm}^3$$

The value of the equilibrium constant gives an estimate of how complete a reaction is at a particular temperature.

- Very large values of ($>10^{10}$) indicate the reaction is almost complete.
- Large values of K_c (between 10^4 and 10^{10}) indicates the equilibrium position is far to the right, product side of the system.
- Intermediate values of K_c (between 10^{-4} and 10^4) indicates reactants and products are present in similar amounts.
- Small values of K_c (between 10^{-10} and 10^{-4}) indicates the equilibrium position is far to the left, reactant side of the system.
- Very small values of K_c ($<10^{-10}$) indicates the forward reaction is not noticeable.

Industrial Chemistry

When devising multi-tonne processes, industrial chemists must consider a number of factors, such as reaction kinetics and equilibrium, when deciding on optimum reaction conditions.

For example, consider the Haber process:

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\Delta H = -92$ kJ

From a kinetics perspective, high temperature and pressure leads to a faster reaction. However, from an equilibrium perspective, whilst a high pressure favours the forward reaction it is costly to maintain and the pipes and equipment are expensive. The forward reaction is exothermic, so a high temperature would reduce the yield of product but a lower temperature would make the rate very slow. Reaction conditions are chosen which are a **compromise** between cost, kinetics and equilibrium considerations: 400-450 °C, 200-250 atmospheres and an iron catalyst.

For the Contact process

$2SO_2 + O_2 \rightleftharpoons 2SO_3$ $\Delta H = -196$ kJ

The reaction is exothermic so a low temperature favours the forward reaction, however this would give a slow rate of reaction. A high pressure favours the forward reaction as there are fewer gas moles on the right hand side. High pressure is expensive to maintain. The compromise conditions are: temperature of 450 °C and 1-2 atm pressure. A vanadium(V) oxide catalyst is used. Vanadium(V) oxide is a solid. It is a heterogeneous catalyst as it is in a different phase from the reactants. A catalyst does not have any effect on the position of equilibrium.

Revision Questions

1 The reaction of bromine with water can be represented by the following equation:

$$Br_2 + H_2O \rightleftharpoons Br^- + OBr^- + 2H^+$$

Which one of the following reagents would move the equilibrium position to the right?

A. nitric acid

B. sodium carbonate

C. sodium bromide

D. sulfuric acid [1]

2 The second stage in the production of nitric acid involves the reaction of nitrogen monoxide with oxygen to form nitrogen dioxide. When nitrogen monoxide and oxygen are mixed under suitable conditions a dynamic equilibrium is established.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = -116\ kJ\ mol^{-1}$$

(a) Explain what is meant by the term **dynamic equilibrium**.

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(b) State and explain how increasing the pressure will affect the equilibrium yield of nitrogen dioxide.

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(c) State and explain how increasing the temperature will affect the equilibrium yield of nitrogen dioxide.

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(d) State and explain the effect a catalyst has on the equilibrium yield of nitrogen dioxide.

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(e) The first stage in the production of nitric acid involves ammonia.

(i) State the temperature and pressure used in the production of ammonia by the Haber process.

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(ii) Why is the temperature used in the Haber process described as a compromise temperature?

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Credits

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