SUBJECT: Chemistry

TOPIC: Chemical Equilibrium

LEARNING OBJECTIVES: At the end of the lesson, students should be able to:

i. Describe reversible reactions and conditions under which they take place.
ii. Write Equilibrium constants for chemical reactions.
iii. State Le Chatelier's principle
iv. Describe the factors that affect equilibrium position

CHEMICAL EQUILIBRIUM

A chemical reaction is said to be in equilibrium when the rate of forward reaction is equal to the rate of backward reaction. Equilibrium may be static or dynamic.

An example of a static equilibrium is a balanced see-saw because it is stationary, while a saturated solution is an example of dynamic equilibrium.

$$NaCl_{(s)} \longleftrightarrow NaCl_{(aq)}$$

Dissolution Deposition

Equilibrium in reversible reaction

A reversible reaction is a reaction that can be made to proceed in either direction under suitable conditions. A reversible reaction is in dynamic equilibrium when both the forward and backward reactions are occurring at the same rate.

A reversible reaction can only reach dynamic equilibrium in a closed system i.e. closed container or vessel. In an open system, one or more of the substances are being removed; the reaction cannot attain equilibrium even if it is reversible. The concentration of all the chemical species present must remain constant for a system to be in dynamic equilibrium.

Equilibrium constant (K_c)

Law of mass action

The law of mass action states that, at constant temperature the rate of reaction is proportional to the active masses of each of the reactants.

Calculating K_c for a reaction of the form $aA + bB \rightleftharpoons cC + dD$

then (at constant temperature) $\frac{[C]^c . [D]^d}{[A]^a . [B]^b}$ = a constant, (K_c)

[ ] denotes the equilibrium concentration in mol dm^{-3}

K_c is known as the Equilibrium Constant

Value of K_c

- AFFECTED by: a change of temperature
- NOT AFFECTED by:
  - a change in concentration of reactants
  - a change in concentration of products
  - a change of pressure
  - adding a catalyst

Classwork

Write expressions for the equilibrium constant, K_c of the following reactions. Remember, equilibrium constants can have units.

$$Fe^{3+}_{(aq)} + NCS^{-}_{(aq)} \rightleftharpoons FeNCS^{2+}_{(aq)}$$

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^{+}{}_{(aq)} + OH^{-}_{(aq)}$$

$$2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \rightleftharpoons 2Fe^{2+}_{(aq)} + I_{2(aq)}$$

LE CHATELIER'S PRINCIPLE

Le Chatelier's principle states that in a reversible reaction at equilibrium, if any of the factors affecting equilibrium is altered, the equilibrium position will shift so as to annul the effect of the change

Factors affecting equilibrium position

(I) Change in temperature

(II) Change in concentration

(III) Change in pressure (gaseous system)

Effect of change in temperature on a system in equilibrium

In a thermochemical equation, if H is positive, the forward reaction is endothermic and the backward reaction is exothermic and vice versa.

An increase in temperature will favour an endothermic reaction, while a decrease in temperature will favour an exothermic process. For example, in the reaction below

$$N_{2\,(g)} + O_{2\,(g)} \longleftrightarrow 2NO_{(g)};\ H = +90.4KJ$$

Increasing the temperature of the reaction overleaf/ below

$$N_{2\,(g)} + O_{2\,(g)} \longleftrightarrow 2NO_{(g)};\ H = +90.4KJ$$

Will shift the equilibrium position to the right, favouring the forward reaction i.e. product formation. Hence, the value of K_c increases. A higher value of K_c would mean a greater yield of the product(s).

Decreasing or lowering the temperature of the reaction above will shift the equilibrium position to the left favouring the backward reaction i.e. reactant formation. This results in the lowering of the value of K_c. A lower value of K_c would mean a greater yield of reactant(s)

Classwork

$$2SO_{2\,(g)} + O_{2\,(g)} \longleftrightarrow 2SO_3;\quad H= 395KJmol^{-1}$$

Effect of change in pressure on a system in equilibrium

For a change in pressure to affect a chemical system in equilibrium.

(I) it must be a reaction involving gases

(II) The total number of moles of gaseous molecules on the left-hand side of the equation must be different from the total number of moles of gaseous molecules on the right hand side. Consider the equation below:

$N_{2\,(g)}$	$+$ $3H_{2\,(g)}$	$\longleftrightarrow$	$2NH_{3\,(g)}$
1 mole/volume	3 moles/volume		2moles/volume
	4 moles/volume		2 moles/volume

According to Le Chatelier's principle, in the formation of ammonia, a high pressure will favour the forward reaction where there is reduction in volume, causing the equilibrium position to shift to the right (product). Thus lowering the pressure and keeping the equilibrium constant K, unchanged. In the process, a high yield of the product is obtained.

On the other hand, a low pressure will cause the equilibrium position of this system to shift to the left favouring the backward reaction. It will result in high yield of the reactant(s). However, in a system where there is no net change in the total number of molecules of gases, imposing a change in pressure will produce no effect on the equilibrium.

For example:

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

$$3Fe_{\,(s)} + 4H_2O_{\,(g)} \longleftrightarrow Fe_3O_{4\,(s)} + 4H_{2\,(g)}$$

Any change in pressure will not affect the equilibrium position of the equations/reactants above.

Effect of a change in concentration on equilibrium

In an equilibrium mixture, there is a balance between the concentrations of the reactants and the products. If more reactant(s) is added into the system, the balance will be upset. In order to relieve this constraint (i.e. increase the concentration of the reactants) the equilibrium position will shift to the right favouring the forward reaction i.e. the product and so the equilibrium constant K remains unchanged.

In general, an increase in concentration of a reactant in equilibrium favours the formation of more of the products, while an increase in the concentration of products at equilibrium favours the formation of more of the reactants.

NOTE: If the product formed is continually removed from the system, the equilibrium will shift to the right to produce more of the product. For example, $3Fe_{(s)} + 4H_2O \longleftrightarrow Fe_3O_4 + 4H_2$
If hydrogen is constantly removed, the equilibrium position will shift to the right.

EFFECT OF A CATALYST

Catalyst does not change the position of equilibrium. For a reversible reaction, catalyst speeds up both the forward and backward reactions at the same time.

APPLICATIONS OF CHEMICAL EQUILIBRIUM

The concept of chemical equilibrium and Le Chatelier's principle are applied to optimize production. It also helps to:

- Minimize cost of production
- Maximize yield of product(s)
- Ensuring that the shortest possible time is taken to reach equilibrium

1. The Haber Process (Industrial method of preparing ammonia):

   $3H_{2\,(g)} + N_{2\,(g)} \longleftrightarrow 2NH_{3\,(g)}$: H= 46.1KJmol^{-1}

   Optimum conditions for the reaction are:

- Low temperature of about 450ºC – 500ºC
- High pressure of about 200atmosphere
- Iron catalyst

2. <u>The Contact Process (Industrial method of preparing H_2SO_4)</u>

$$2SO_{2\,(g)} + O_{2\,(g)} \longleftrightarrow 2SO_{3\,(g)} : H = -395.7 KJmol^{-1}$$

Optimum/operating conditions:

- Low temperature about 450°C
- Low pressure of about 1atmosphere
- Vanadium (V) oxide catalyst

Overall Assessment

Predict the effect on the equilibrium position of an increase in pressure.

a) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

b) $H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

c) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

Predict the effect of a temperature increase on the equilibrium position of,

a) $H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)} \qquad \Delta H = +40\ kJ\ mol^{-1}$

b) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -\ ive$

In the reaction $A + 2B \rightleftharpoons C + D$ predict where the equilibrium will move when ... a) more B is added b) some A is removed c) some D is removed.