ST. LAWRENCE HIGH SCHOOL

A JESUIT CHRISTIAN MINORITY INSTITUTION

STUDY MATERIAL FOR CHEMISTRY (CLASS-11)

TOPIC- CHEMICAL EQUILIBRIUM

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Physical and Chemical Processes

Physical processes involve such changes, which only affects the physical properties of the substance undergoing changes but have no effect on the chemical composition and properties.

Chemical processes involve changes in chemical composition and properties. Whenever a chemical change occurs, we can say that a chemical reaction has taken place.

Types of Chemical Reactions

1. **Combination Reactions**

In such reactions two or more substances combine to form a single compound.

e.g.,

$2Mg + O_2 \rightarrow 2MgO$

2. **Decomposition Reactions**

In these reactions. a compound decomposes to produce two or more different substances.

e.g., $PCl_5 \Leftrightarrow PCl_3 + Cl_2$

Digestion of food is also a decomposition reaction.

[Decomposition by heat IS called thermal decomposition and decomposition by sunlight is called photo decomposition.]

3. **Displacement Reactions**

These reactions involve displacement of one element or group by another. These are infact, redox reactions, e.g.,

$Zn(s) + H_2SO_4$

4. **Double Displacement or Metathesis Reactions**

In these. reactions two compounds react to form two new compounds and no change in oxidation state take place, e.g., precipitation reactions, neutralisation, reactions.

$AgNO_3(aq) + NaCl(aq) \rightarrow \rightarrow AgCl(s) + NaNO_3(aq)$

5. Reversible and Irreversible Reactions

	Irreversible reactions	Reversible reactions
1.	Chemical reactions which always proceed to completion in only forward direction, e.g., $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$.	Reactions which do not proceed to completion in forward direction and also proceed in the backward direction under suitable conditions, e.g., $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$
2.	These reactions never attain equilibrium.	These reactions attain equilibrium.

Equilibrium State

Under given set of conditions if a reversible process or chemical reaction is carried out in a closed container, a constancy in some observable properties like colour intensity, pressure, density, is observed. Such a state is referred to as an equilibrium state.

Equilibrium may be classified as :

Physical Equilibrium

Equilibrium set up in physical processes like evaporation of water, melting of solids, dissolution of solutes, etc., is called physical equilibrium, e.g., Ice ⇔ Water

At equilibrium,

Rate of melting of ice = Rate of freezing of water

Chemical Equilibrium

If a reversible reaction is carried out in a closed vessel, a stage is attained where the speed of the forward reaction equals the speed of the backward reaction. It corresponds to chemical equilibrium. At equilibrium,

Rate of forward reaction = Rate of backward reaction

Law of Chemical Equilibrium or Mass Action

At equilibrium,

$r_f = r_b$

$$K_{eq} \text{ or } K_c = \frac{[C]^x[D]^y}{[A]^m[B]^m}$$

Where $K_c = k_f / k_b$

Where [ ] is used to indicate “molar concentration”.

Equilibrium Constant in terms of Partial Pressure

In a gaseous system, we can use partial pressure terms in places of active masses. Thus, for the above gaseous equilibrium,

$$K_p = \frac{p_C^{m_1} \, p_D^{m_2}}{p_A^{n_1} \, p_B^{n_2}}$$

Where Kp is an equilibrium constant in terms of partial pressure.

Equilibrium Constant in terms of Mole Fraction

$$K_x = \frac{x_C^c \, x_D^d}{x_A^a \, x_B^b}$$

Where Kx is the equilibrium constant in terms of mole fraction.

Relation between Kp and Kc

$K_p = K_c (RT)^{\Delta n}$

where R is gas constant 0.0821 liter.atm/degree/mole and Δn is the total number of molecules of the product – total number of molecules of the reactants.

Relation between Equilibrium Constant and Standard Free Energy

$\Delta G^o = - RT \ln K_{eq}$

(or)

$\Delta G^o = - 2.303 RT \log K_{eq}$

Reaction Quotient (Q)

The reaction quotient has the same algebraic form as K_{eq} but the current concentrations nor specifically the equilibrium concentrations are used in calculations.

The expression for Q is

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

Degree of Dissociation

Degree of dissociation (α) = No. of molecules dissociated/Total no.of molecules taken.

Dissociation constant, K_{diss}

$$K_{diss} = \frac{\alpha^2 \cdot C}{(1-\alpha)} \text{ mol dm}^{-3}$$

Factors affecting Equilibrium

Types of Equilibrium

Homogeneous Equilibrium

In homogeneous equilibrium, the reactants and products arc present in the same phase or physical suite (gaseous or liquid).

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

Heterogeneous Equilibrium

In heterogeneous equilibrium the reactants and products are present in two or more physical states or phases.

$3Fe(s) + 4H_2O(g) \Leftrightarrow Fe_3O_4(s) + 4H_2(g)$

Reaction Quotient

For any reversible reaction at any stage other than equilibrium, the ratio of the molar concentrations of the products to that of the reactants. where each concentration term is raised to the power equal to the stoichiometric coefficient to the substance concerned, is called the reaction quotient, Q_c.

For a general reaction

$aA + bB \Leftrightarrow cC + dD$

which is not at equilibrium,

$Q_c = [C]^c + [D]^d / [A]^a [B]^b$

If

(i) $Q_c > K_c$, the value of Q_c will tend to decrease to reach the value of K_c (towards equilibrium) and the reaction will proceed in the reverse direction.

(ii) $Q_c < K_c$ it will lend to increase and the reaction will proceed in the forward direction.

(ii) $Q_c = K_c$, the reaction is at equilibrium.

Le – Chatelier’s Principle

There are three main factors which affect the state of equilibrium.

They are

1. **concentration**
2. **temperature**
3. **pressure.**

Le – Chatelier’s principle states that if a system at equilibrium is subjected to a change in concentration. pressure or temperature. the equilibrium equilibrium change.

Effect of Change of Concentration
If at equilibrium the concentration of one of the reactants is increased. the equilibrium will shift in the forward direction and vice-versa.

Effect of Change in Pressure
No effect of pressure on equilibria having same moles of reactants and products. e.g., $N_2 + O_2 \Leftrightarrow 2NO$.
When there is change in the number of moles, the equilibrium will shift in the direction having smaller number of moles when the pressure is increased and vice-versa, e.g.,

$N_2 + 3H_2 \Leftrightarrow 2NH_3$ [High p. high yield of NH_3]
Effect of Temperature
When process is exothermic, low temperature favours the forward reaction. When process is endothermic. high temperature favours the formation of products.

Effect of Addition of Inert Gas
(i) **Addition of inert gas at constant pressure** At constant pressure. if an inert gas is added. it will increase the volume of the system. Therefore. the equilibrium will shift in a direction in which there is an increase in the number of moles of gases.
(ii) **Addition of inert gas at constant volume** If keeping volume of the system constant, an inert gas is added. the relative molar concentration of the substance will not change. Hence. the equilibrium position of the reaction remains unaffected.
Effect of Catalyst
The presence of catalyst does not change the position of equilibrium. It simply fastens the attainment of equilibrium.

Le-Chatelier's Principle Applicable to Physical Equilibrium
(i) **Effect of pressure on solubility** The increased pressure, will increase the solubility of gas and vice-versa.
(ii) **Effect of temperature on solubility** Some substances dissolve with the absorption of heat. Solubility of such substances will increase with increase of temperature and vice-versa, e.g., dissolution of NH_4Cl, KCl, KNO_3, etc. The dissolution of calcium acetate and calcium hydroxide is exothermic, so their solubility is lowered at higher temperature.
(iii) **Effect of pressure on the melting point of ice**
Ice $\Leftrightarrow$ liquid water

The ice occupy the more volume than liquid water, so increased pressure will result in melting of ice according to Le-Chatelier principle.

Favourable conditions for some chemical equilibria to get higher yield of product.

Chemical equilibria	Favourable condition for forward direction
$N_2 + 3H_2 \rightleftharpoons 2NH_3$	High pressure, low temperature and isolation of NH_3 by liquefaction.
$N_2 + O_2 \rightleftharpoons 2NO$	High temperature and isolation of NO.
$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	Low pressure, high temperature and isolation of PCl_3 and Cl_2.

Calculation of the Degree of Dissociation (α) from Density Measurement

α = D – d / d

where, D = theoretical vapour density

d = observed vapour density

Now, molecular mass = 2 * VD

∴ α = M_c – M_o / M_o

where, M_c = calculated molecular weight

M_o = observed molecular weight

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