

SYNOPSIS

(PHYSICAL CHEMISTRY)

Introduction

Physical chemistry deals with the principles, laws, concepts and various practices of physics used in chemical interactions to examine how matter behaves on a atomic and molecular level and how does the chemical reaction occurs.

Physical chemistry also deals with the importance of mathematics in solving numerical in chemistry. Physical chemistry provides number of tools and mathematical models to elucidate the structure and dynamics of molecules.

Physical chemistry deals with the calculation of bond parameters in molecules, calculation of energy changes in chemical reaction, prediction of direction and extent of reaction and also deals with solubility criteria and acidic and basic nature of the solutions.

There are four main chapters of physical chemistry in class 11; these are

1. **States of Matter**
2. **Thermodynamics**
3. **Chemical Equilibrium**
4. **Ionic equilibrium**

1. States of Matter

Matter exist in three states: solid, liquid and gas. Solids have definite size, shape, volume, density and are non-compressible. Liquids do not have definite shape and assume shape of the container but have definite volume. Gases do not have definite shape or volume. Gases are highly compressible, exert pressure. Intermolecular interactions in the form of intermolecular forces of attractions are responsible for three states of matter. There are three main types of intermolecular interaction.

- (i) **Dipole-dipole**
- (ii) **Dipole-induced dipole**
- (iii) **Dispersion forces or London forces.**

These forces are collectively called van der Waal's forces. Hydrogen bonding is an additional type of intermolecular interactions in which the H-atom is connected to highly electronegative atom F, O and N by covalent bond and form an additional bond with electronegative atom of other molecule. The molecules of gases are in continuous motion and exert pressure. Pressure, volume, temperature and number of moles are related with one another by different gas laws.

Boyle's law relates P and V $(PV = K)$

Charles's law relates V and T $\left(\frac{V}{T} = K\right)$

Gay Lussac's law deals with relationship between P and T $\left(\frac{P}{T} = K\right)$

Avagadro's law gives relation between volume and number of moles of gas.

All these gas laws are combined together to give ideal gas equation, $PV = nRT$ where R is a universal gas constant. Ideal gas show deviations at higher pressure and at lower temperature. The gases which deviates from ideal gas equation are called real or non-ideal gases. The ideal gas equation $PV = nRT$ is corrected to $PV = ZnRT$ where Z is called compressibility factor.

For ideal gases, $Z = 1$,

Van der Waal equation $\left(P + \frac{an^2}{V}\right)(V - nb) = nRT$ is used for real gases where a and b are constant.

Liquefaction of gases can be explained by using Andrews isotherms, variation of P with V at different temperatures.

The highest temperature at which liquefaction of gas takes place is called **Critical temperature**. The minimum pressure at critical temperature is called critical pressure and molar volume at critical pressure and temperature is called critical volume.

Liquids undergo evaporation, vapours formed undergo condensation. Liquid state shows different phenomenon:

- (i) Vapour pressure \rightarrow the pressure exerted by vapours over a liquid when both are in the state of equilibrium.
- (ii) Surface tension \rightarrow surface of liquid act as stretched membrane due to surface tension.
- (iii) Viscosity \rightarrow force of friction between successive layers of liquid, depends on intermolecular forces of attraction and temperature.

2. Thermodynamics

Thermodynamics plays a central role in chemistry because changes are very important in chemical reactions. Chemical processes lead to evolution of heat (q), part of which gets converted into work (w).

Q and w are related by the equation

$$\Delta U = q + w \text{ (first law of thermodynamics)}$$

ΔU = internal energy change.

q and w are path dependent function and thus are not state functions.

Work results when a force generates a displacement. Work of expansion against a constant external pressure is given by $w = -P_{\text{ext}} \Delta V$

$w = 0$ when volume of system remains fixed no expansion work occur. Hence $q_v = \Delta U$.

Internal energy (U) and enthalpy (H) both are state functions enthalpy is defined as $H = U + PV$.

At constant pressure, enthalpy change is given by

$$\Delta H = \Delta U + P\Delta V = q_p$$

All the physical transformation such as fusion, vapourisation, sublimation, dissolution of solute in a solvent, dilution of a solution, are associated with enthalpy changes. Enthalpy of a chemical reaction (ΔH) is the difference between the sum of the enthalpies of products and of the reactants.

According to Hess's law, the sum of the enthalpy changes for individual steps is equal to the overall enthalpy change for the entire system.

$$\Delta_r H^\circ = \sum \nu_p \Delta_f H^\circ_{(\text{prod})} - \sum \nu_R \Delta_f H^\circ_{(\text{react})}$$

Where $\Delta_f H^\circ$ is the standard enthalpy of formation.

Enthalpy changes of a chemical reaction in gaseous state can also be estimated using bond enthalpy data.

$$\Delta_r H^\circ = \sum \text{bond enthalpies of reactants} - \sum \text{bond enthalpies of products.}$$

Spontaneous process is process that occurs on its own without the external help. The sign of enthalpy change cannot be used as a criteria for a spontaneous process.

The entropy (S) is a thermodynamic state function which measure the degree of randomness.

It is defined as $\Delta S = \frac{q}{T}$

According to **second law of thermodynamics**, the total entropy of the universe (system plus surrounding increases) is a spontaneous process.

$\Delta S_{\text{total}} > 0$ (for spontaneous process)

The criteria of spontaneity is expressed in terms of Gibbs energy of system, given by

$$\Delta G = \Delta H - T\Delta S$$

ΔH , ΔS together along with T decides the spontaneity of the reaction.

$\Delta G < 0$ spontaneous

$\Delta G > 0$ non-spontaneous

$\Delta G = 0$ equilibrium.

According to the **third law of thermodynamics** the entropy of a pure perfectly ordered crystalline substance is zero at 0 K. The third law of thermodynamics is useful to determine the absolute entropies of substance. The standard molar entropy of a substance is the absolute entropy of 1 mol of the pure substance at 1 atm pressure and 298 K. The standard entropy of a reaction is given by

$$\Delta_r S^\circ = \sum S^\circ (\text{products}) - \sum S^\circ (\text{reactants})$$

3. Chemical equilibrium

Reversible reaction do not go to completion and occur in either direction whereas in irreversible reactions, the reactants are almost completely converted into the products.

An equilibrium between two phases of the same substance is called **physical equilibrium**.

A chemical equilibrium is a state of reacting system at which the concentrations of reactants and products remain constant because the rates of forwards and backward reactions are equal. The equilibrium is dynamic because the individual molecules are continuously reacting although composition of reaction mixture does not change. The equilibrium constant, K_C is the product of equilibrium concentrations of the products divided by the product of equilibrium concentrations of reactants with each concentration term raised to a stoichiometric coefficient.

For gas phase reaction, the equilibrium constant K_p is used.



$$K_C = \frac{[M]^m [N]^n}{[A]^a [B]^b} \quad K_P = \frac{P_M^m P_N^n}{P_A^a P_B^b}$$

K_C and K_P are related by an equation $K_p = K_C (RT)^{\Delta n_g}$

The K_C and K_P are used to calculate the equilibrium concentrations and equilibrium pressure respectively of various species.

The Le-Chatelier's principle states that if a stress is applied on the reacting system at equilibrium, the system responds so as to reduce the effect of the applied stress.

The changes in concentration, temperature or pressure and volume change the composition of equilibrium mixture until new equilibrium is established.

The change in concentration of a substance on one side of a balanced equation shifts the equilibrium to the opposite side.

The increase in temperature favours the endothermic reaction and decrease in temperature favours the exothermic reaction.

If the pressure of equilibrium mixture is increased by decreasing its volume at constant temperature, the net reaction occurs in the direction of decreasing number of moles of gases. Conversely, decreasing pressure favours the reaction that occurs in the direction of increasing number of moles of gases. A catalyst increases the speed at which the system approaches equilibrium but it does not shift the direction of equilibrium and there is no change in the value of equilibrium constant.

The value of equilibrium constant changes with change in temperature.

$$\log \frac{K_2}{K_1} = \frac{\Delta_r H}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

4. Ionic Equilibrium

All the electrolytes are acids, bases and salts and the conduction of electricity by their aqueous solutions is due to the ions produced by dissociation of electrolytes.

The strong electrolytes are completely dissociated whereas in weak electrolytes, there is an equilibrium between the ions and the unionized electrolyte.

According to Arrhenius, acid gives hydrogen ion while base gives hydroxyl ion in aqueous solution.

In Bronsted-lowry theory, acid is proton donor and base is a proton acceptor.

A conjugate acid base pair differ by only proton, HCl/Cl^- , $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ or $\text{H}_2\text{O}/\text{OH}^-$.

Lewis define acid as an electron pair acceptor and base as an electron pair donor.

The K_a (ionization constant) for weak acid HA is given by

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+][\text{conjugate base}]}{[\text{acid}]}$$

and K_b for weak base BOH is given by

$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]}$$

The degree of dissociation (α), concentration are related by

$$K_b \text{ or } K_a = \frac{C\alpha^2}{1-\alpha}$$

The pH of a solution can be defined as $\text{pH} = -\log [\text{H}^+]$ and this can be extended to other quantities such as

$$\text{p(OH)} = -\log [\text{OH}^-], \quad \text{pKa} = -\log K_a$$

The ionic product of water, K_w is defined as

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ for pure H}_2\text{O at } 25^\circ\text{C and } \text{p}K_w = \text{pH} + \text{p(OH)}.$$

Hydrolysis is an interaction between ions of salt and ions of water to produce acidic, alkaline or neutral solution.

The salts of strong acids and strong bases do not undergo hydrolysis, only undergo hydration to give neutral solution.

The solution of a salt of strong acids and weak bases will be acidic and the solution of a salt of weak acids and strong bases will be alkaline.

The solutions of the salts of weak acids and weak bases may be acidic, alkaline or neutral depending upon the values of K_a and K_b .

Buffer solutions resist the change in pH on addition of small amount of either an acid or a base. Acidic buffer is a mixture of weak acid and salt of its conjugate base. The pH of acidic buffer is given by

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Basic buffer is a mixture of weak base and salt of its conjugate acid. The pH of basic buffer is given by

$$\text{pH} = 14 - \text{p}(\text{OH}) = 14 - \left[\text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]} \right]$$

The pH of a buffer solution does not change on dilution.

The buffer solution possesses reserve acidity and reserve alkalinity.

The **solubility product** is an equilibrium constant for the solubility equilibrium of sparingly soluble salt in aqueous solutions. It is the product of equilibrium molar concentration of the constituent ions of a sparingly soluble salt in its saturated solution at a given temperature.



$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

$$K_{sp} = x^x y^y (S)^{x+y} \quad \text{where } S \text{ is the molar solubility.}$$

Common ion effect describes the behavior of a solution in which the same ion (cation or anion) is produced by two different solutes. It states that the degree of dissociation of a weak electrolyte decreases by the addition of a strong electrolyte containing one of the ions identical to that of the weak electrolyte.

The solubility of a sparingly soluble salt decreases in the presence of strong electrolyte that contains an ion common to the sparingly soluble salt. Also, the precipitation of a salt from the solution takes place when the ionic product exceeds the solubility product.

