Question Set 6

LAWS AND THEORIES

Q. Answer the following : ***(1 to 3 marks each)***

[**Note :** Statement of a law carries one mark and remaining marks are for explanation or applications of it.]

Chapter 2. Solutions

(1) State Henry's law.

Ans. Statement of Henry's law : It states that the solubility of a gas in water at constant temperature is proportional to the pressure of the gas above the solution.

(2) State Raoult's law.

Ans. Statement of Raoult's law : The law states that, at constant temperature, the partial vapour pressure of any volatile component of a solution is equal to the product of vapour pressure of the pure component and the mole fraction of that component in the solution.

Chapter 3. Ionic Equilibria

(3) Give mathematical expression for Ostwald's dilution law.

Ans. Ostwald's dilution law is expressed as

$$K = \frac{C\alpha^2}{(1-\alpha)} \quad OR \quad K = \frac{\alpha^2}{V(1-\alpha)}$$

where K is a dissociation constant of a weak electrolyte,

α is degree of dissociation,

C is concentration in mol dm^{-3}

V is dilution in dm^3 mol^{-1}.

Chapter 4. Chemical Thermodynamics

(4) State the first law of thermodynamics in different ways.

Ans. The first law of thermodynamics is based on the principle of conservation of energy and can be stated in different ways as follows :

(1) Energy can neither be created nor destroyed, however, it may be converted from one form into another.

(2) Whenever, a quantity of one kind of energy is consumed or disappears, an equivalent amount of another kind of energy appears.

(3) The total mass and energy of an isolated system remain constant, although there may be interconservation of energy from one form to another.

(4) The total energy of the universe remains constant.

(5) Give the mathematical statement of first law of thermodynamics.

Ans. From the conservation of energy we can write first law of thermodynamics as,

Increase in internal energy of the system = Quantity of heat absorbed by the system + Work done on the system

$\therefore \ \Delta U = Q + W$

(6) State Hess's law of constant heat summation. Illustrate with an example. State its applications.

Ans. Statement of Hess's law of constant heat summation : It states that, the heat of a reaction or the enthalpy change in a chemical reaction depends upon initial state of reactants and final state of products and independent of the path by which the reaction is brought about (i.e. in a single step or in a series of steps). *OR*

Heat of reaction is same whether it is carried out in one step or in several steps.

Explanation :

Consider the formation of $CO_{2(g)}$.

In one step : $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H = -394$ kJ

In two steps : $C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \quad \Delta H_1 = -83$ kJ

$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H_2 = -311$ kJ

$\therefore \ \Delta H = \Delta H_1 + \Delta H_2$

$-394 \text{ kJ} = -83 \text{ kJ} + (-311) \text{ kJ}$

Hess's law treats thermochemical equations mathematically, i.e. they can be added, subtracted or multiplied by numerical factors like algebraic equations.

Applications : Hess's law is used for :

(1) To calculate heat of formation, combustion, neutralisation, ionization, etc.

(2) To calculate the heat of reactions which may not take place normally or directly.

(3) To calculate heats of extremely slow or fast reactions.

(4) To calculate enthalpies of reactants and products.

Chapter 5. Electrochemistry

(7) State and explain Kohlrausch's law of independent migration of ions. ***(Sept. '21)***

Ans. (A) Statement of Kohlrausch's law : This states that at infinite dilution of the solution, each ion of an electrolyte migrates independently of its co-ions and contributes independently to the total molar conductivity of the electrolyte, irrespective of the nature of other ions present in the solution.

(B) Explanation : Both the ions, cation and anion of the electrolyte make a definite contribution to the molar conductivity of the electrolyte at infinite dilution or zero concentration ($\wedge_0$).

If λ_+^0 and λ_-^0 are the molar ionic conductivities of cation and anion respectively at infinite dilution, then $\wedge_0 = \lambda_+^0 + \lambda_-^0$.

This is known as Kohlrausch's law of independent migration of ions.

For an electrolyte, B_xA_y giving x number of cations and y number of anions, $\wedge_0 = x\lambda_+^0 + y\lambda_-^0$.

(C) Applications of Kohlrausch's law :

(1) With this law, the molar conductivity of a strong electrolyte at zero concentration can be determined. For example,

$$\wedge_{0(KCl)} = \lambda_{K^+}^0 + \lambda_{Cl^-}^0$$

(2) $\wedge_0$ values of weak electrolyte with those of strong electrolytes can be obtained. For example,

$$\wedge_{0(CH_3COOH)} = \wedge_{0(HCl)} + \wedge_{0(CH_3COONa)} - \wedge_{0(NaCl)}$$
$$= (\lambda_{H^+}^0 + \lambda_{Cl^-}^0) + (\lambda_{CH_3COO^-}^0 + \lambda_{Na^+}^0) - (\lambda_{Na^+}^0 + \lambda_{Cl^-}^0).$$

Chapter 6. Chemical Kinetics

(8) Explain the rate law with example. Give illustrations.

Ans. Explanation : Consider the following reaction,

$a\mathrm{A} + \mathrm{bB} \longrightarrow$ products

If the rate of the reaction depends on the concentrations of the reactants A and B, then, by rate law,

$R \propto [A]^a [B]^b$

$\therefore R = k [A]^a [B]^b$

where $[A]$ = concentration of A and $[B]$ = concentration of B

The proportionality constant k is called the velocity constant, rate constant or specific rate of the reaction.

a and b are the exponents or the powers of the concentrations of the reactants A and B respectively when observed experimentally.

Example :

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

$R = k[H_2] [I_2]$