Topic on Chemistry

CHEMICAL EQUILIBRIUM

(Point wise Synopsis Based on Teach Yourself Style)

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1. Introduction :

Common understanding about chemical reactions is that they complete when reactants in exact amount as required by balanced chemical equations are mixed together.

2. Types of Reactions :

(A) **Irreversible Reactions**—An irreversible reaction takes place in a direction from reactants to products and products are not able to combine with themselves to give back reactants.

Represented by (→) sign.

Examples—

(a) **Decomposition of $KClO_3$**—

$$2KClO_3 \rightarrow 2KCl + 3O_2.$$

(b) **Decomposition of N_2O_5**—

$$2N_2O_5 \rightarrow 4NO_2 + O_2.$$

(c) **Reactive (metal-acid) reactions**—

$$Mg + 2HCl \rightarrow MgCl_2 + H_2.$$

(d) **Precipitation reaction**—

$$BaCl_2 + K_2SO_4 \rightarrow BaSO_{4(s)} + 2KCl$$

(e) **Combustion reaction**—

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O.$$

(B) **Reversible Reactions**—Chemical reactions in which the products formed react themselves to give back the original reactants. Such reactions are called **Reversible Reactions**.

Represented by ($\rightleftharpoons$) sign

Examples—

(a) **Dissociation of HI**—

$$2HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$$

(b) **Formation of PCl_5**—

$$PCl_3\ (g) + Cl_2\ (g) \rightleftharpoons PCl_5\ (g)$$

(c) **Synthesis of NH_3**—

$$N_2\ (g + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$$

(d) **Dissociation of SO_3**—

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

(e) **Dissociation of N_2O_4**—

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

(f) **Esterification reaction**—

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5\ (\text{Ester}) + H_2O$$

3. Law of Mass Action :

First stated by Norwegian chemists Cato Guldberg and Peter Waage in 1863.

Statement—"At constant temperature, the rate of a homogeneous reaction at a given instant is usually proportional to some power of the concentration of each reactant at that instant."

Note—The concentration is expressed in moles of reactants per litre solution.

Equilibrium Constant Expression—Let us consider a homogeneous reversible reaction

$$A + B \rightleftharpoons C + D$$

By applying law of mass action in this reversible reaction, we get

$$r_f \ \alpha\ [A]^1\ [B]^1$$

$$\Rightarrow \quad r_f = K_1\ [A]^1\ [B]^1 \quad \ldots(i)$$

Similarly, $r_b \ \alpha\ [C]^1\ [D]^1$

$$\Rightarrow \quad r_b = K_2\ [C]^1\ [D]^1 \quad \ldots(ii)$$

where K_1 & K_2 are called velocity constants for forward & backward reactions.

Now, at equilibrium

$$r_f = r_b$$

From (i) & (ii)

$$K_1\ [A]^1\ [B]^1 = K_2\ [C]^1\ [D]^1$$

$$\Rightarrow \quad \frac{K_1}{K_2} = \frac{[C]^1\ [D]^1}{[A]^1\ [B]^1}$$

$$\Rightarrow \quad \boxed{K_C = \frac{[C]\ [D]}{[A]\ [B]} = \frac{K_1}{K_2}}$$

where, K_C is called equilibrium constant.

Illustrations—Reactions—

(a) $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$—

$$K_c = \frac{[NH_3]^2}{[N_2]^1\ [H_2]^3}$$

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

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\ [O_2]^1}$$

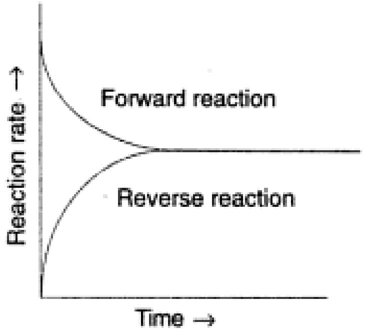
(c) $PCl_3\ (g) + Cl_2\ (g) \rightleftharpoons PCl_5\ (g)$—

$$K_c = \frac{[PCl_5]^1}{[PCl_3]^1\ [Cl_2]^1}$$

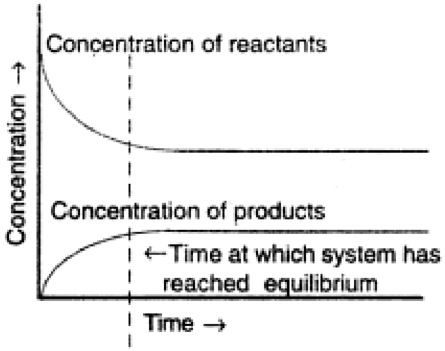
(d) $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

$$K_c = \frac{[CH_3COOC_2H_5]^1\ [H_2O]^1}{[CH_3COOH]^1\ [C_2H_5OH]^1}$$

Graphs—(a) Reaction rate *vs* Time



(b) Concentration *vs* Time of reactants & products



4. Characteristics of Reversible Reactions :

(a) A reversible reaction never goes to completion unless it is acted upon by some external factors *e.g.*, the removal of the product from the reaction system, the effect of pressure etc.

(b) The equilibrium is **dynamic** and **permanent**.

(c) The reaction can be approached from both sides of the equation.

(d) After a lapse of certain time the reversible reaction attains a state of chemical equilibrium. At this state the rates of forward reaction and backward reaction are equal.

(e) The concentrations at equilibrium do not change with time unless there is a change in conditions.

Remember—Products over reactants—Each concentration is raised to a power equal to the corresponding coefficient in the chemical equation

Concentrations are multiplied never added. Since, Concentration in terms of pressure is usually used for substances in the gas phase. One would like to define another equilibrium constant K_p in terms of the partial pressures of the gaseous reactants and products.

For the general reaction where all the substances are gases.

$$K_p = \frac{P_X{}^g \cdot P_Y{}^h}{P_A{}^l \cdot P_B{}^m}$$

where, P terms denote partial pressures of the substances, for the reaction,

$$lA + mB = gX + hY$$

5. Characteristics of Equilibrium Constant :

The numerical value of the equilibrium constant does not depend on—

(a) Concentration

(b) Pressure

(c) Catalyst

(d) The value of K for a particular reaction is always the same, and is different for different reactions.

(e) The value of K does depend on temperature.

(f) The numerical value of K also indicates the **extent** of chemical reaction. A very large numerical value of K signifies that the forward reaction, as written, **goes to completion** or very nearly so, and the equilibrium mixture is mostly products and vice versa.

When K is around 1, the equilibrium mixture contains appreciable amounts of reactants and products.

(g) The magnitude of K also depends on how the balanced chemical equation of a given reaction is written.

For as an example,

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

$$K_1 = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

and, $SO_2\,(g) + \frac{1}{2}O_2\,(g) \rightleftharpoons SO_3\,(g),$

$$K_2 = \frac{[SO_3]}{[SO_2]\,[O_2]^{1/2}}$$

Evidently, $K_1 = K_2{}^2$

So, we can then state that the equilibrium constant is raised to a factor by which the balanced equation is multiplied.

(h) The equilibrium constant of a net reaction is the product of the values of equilibrium constants of individual reactions (equations), if they give the net reaction on addition.

Example—

(i) $CO\,(g) + 3H_2\,(g) \rightleftharpoons CH_4\,(g) + H_2O\,(g)$

$$K_1 = \frac{[CH_4]\,[H_2O]}{[CO]\,[H_2]^3}$$

(ii) $CH_4\,(g) + 2H_2S\,(g) \rightleftharpoons CS_2\,(g) + 4H_2\,(g)$

$$K_2 = \frac{[CS_2]\,[H_2]^4}{[CH_4]\,[H_2S]^2}$$

The sum of equations (i) & (ii), gives

$$CO\,(g) + 2H_2S\,(g) \rightleftharpoons CS_2\,(g) + H_2O\,(g) + H_2\,(g)$$

$$K_3 = \frac{[CS_2]\,[H_2O]\,[H_2]}{[CO]\,[H_2S]^2}$$

Now, $$K_1 \times K_2 = \frac{[CH_4]\,[H_2O]}{[CO]\,[H_2]^3} \times \frac{[CS_2]\,[H_2]^4}{[CH_4]\,[H_2S]^2} = \frac{[CS_2]\,[H_2O]\,[H_2]}{[CO]\,[H_2S]^2} = K_3$$

Hence, $K_1 \times K_2 = K_3$

(i) **Equilibrium involving pure Solids and Liquids (Heterogeneous reactions)**—A homogeneous system involves substances in a single phase.

A heterogeneous system consists of substances in more than one phase and the decomposition of $CaCO_3$ (Calcium carbonate) to solid CaO and CO_2 (g) is an example of heterogeneous system.

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

In writing equilibrium constant expression the concentration terms for pure solids and pure liquids are omitted,

Thus, $K_c = [CO_2]$

The value of K_c is a constant, and is independent of the quantities of $CaCO_3$ and CaO as long as both solids are present.

(j) The equilibrium constant expression is independent of the mechanism of reversible reactions.

6. Relationship Between K_p & K_c :

Let us assume a homogeneous reversible gaseous reaction

$$lA + mB \rightleftharpoons gX + hY$$

$$K_c = \frac{[X]^g\,[Y]^h}{[A]^l\,[B]^m} \qquad \ldots(A)$$

$$K_p = \frac{P_X{}^g \cdot P_Y{}^h}{P_A{}^l \cdot P_B{}^m} \qquad \ldots(B)$$

For gases the partial pressure is related to the molar concentration in a simple way.

$$P_A = \frac{n_A\,RT}{V} = [A]\,RT$$

where, [A] = concentration of A, no. of moles/litre or molar concentration

Similarly, $P_B = [B]\,RT$

$P_X = [X]\,RT$

and, $P_Y = [Y]\,RT$

By putting these values in equation (B) for K_p, we get

$$K_p = \frac{\{[X]\,RT\}^g\,\{[Y]\,RT\}^h}{\{[A]\,RT\}^l\,\{[B]\,RT\}^m}$$

$$= \frac{[X]^g\,[Y]^h}{[A]^l\,[B]^m} \times \frac{(RT)^{g+h}}{(RT)^{l+m}}$$

$$K_p = K_c \cdot (RT)^{(g+h)-(l+m)}$$

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

Since, $K_c = \dfrac{[X]^g\,[Y]^h}{[A]^l\,[B]^m}$

Δn = (number of moles of gaseous products) − (number of moles of gaseous reactants)

$$\therefore \quad \boxed{K_p = K_c\,(RT)^{\Delta n\,\text{(change in no. of moles)}}}$$

Illustrations—

Case I

For the following gaseous reactions,

$$K_p = K_c \text{ (when } \Delta n = 0)$$

(a) **Formation of HI—**

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

(b) **Dissociation of HI—**

$$2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$$

(c) **Formation of NO—**

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$$

(d) **Reaction between H_2O & CO—**

$$H_2O\,(g) + CO\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)$$

Case II

For the following gaseous reactions,

$$K_p > K_c \text{ (when } \Delta n > 1)$$

(a) **Dissociation of PCl_5—**

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

(b) **Dissociation of NOCl—**

$$2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$$

(c) **Dissociation of $COCl_2$—**

$$COCl_2\,(g) \rightleftharpoons CO\,(g) + Cl_2\,(g)$$

Case III

For the following gaseous reactions

$$K_p < K_c \text{ (when } \Delta n < 1)$$

(a) **Formation of NH_3—**

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

(b) **Formation of SO_3—**

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

7. Variation of K with the Different forms of Balanced Equations :

K_c for the reaction, $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

and that for the reaction,

$$2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$$

$$K'_c = \frac{[H_2]\,[I_2]}{[HI]^2}$$

$$\therefore \quad K'_c = \frac{1}{K_c}$$

Similarly, the value of equilibrium constant (K_c'') for the reaction

$$\frac{1}{2}H_2\,(g) + \frac{1}{2}I_2\,(g) \rightleftharpoons HI\,(g)$$

$$K''_c = \frac{[HI]}{[H_2]^{1/2}\,[I_2]^{1/2}}$$

Hence, $K_c = (K_c'')^2$

Summary If the coefficients in the chemical equation are	**Value of K**
Doubled ⟶	Squared
Halved ⟶	Replaced by its square root
Multiplied by *n* ⟶	Raised to the *n*th power

Note—When a number of reactions are added the equilibrium constant for the overall reaction is the product of the equilibrium constants of respective reactions.

Example—$N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$

$$K_1 = \frac{[NO]^2}{[N_2]\,[O_2]} \qquad \ldots(i)$$

$$N_2O\,(g) \rightleftharpoons N_2\,(g) + \frac{1}{2}O_2\,(g)$$

$$K_2 = \frac{[N_2]\,[O_2]^{1/2}}{[N_2O]} \qquad \ldots(ii)$$

By adding these equations (i) & (ii), we get

$$N_2O\,(g) + \frac{1}{2}O_2\,(g) \rightleftharpoons 2NO\,(g)$$

$$K_3 = \frac{[NO]^2}{[N_2O]\,[O_2]^{1/2}}$$

We find that, $K_1 \times K_2 = K_3$

8. The Reaction Quotient :

The ratio of concentration terms having the same form as the equilibrium constant expression at each point in a reaction and when the system is not at equilibrium is called the reaction quotient designated by Q. It has a different numerical value which changes as the reaction progresses and becomes equal to equilibrium constant K for a reaction at equilibrium, that is $Q = K$

We can thus predict the direction of spontaneous change for a reaction, which is not at equilibrium

For the reaction

$$aA + bB \rightleftharpoons cC + dD$$

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

when the system is not at equilibrium

When $Q < K$	When $Q > K$
Numerator is too small	Numerator is too large
Denominator is too large	Denominator is too small
Reaction can proceed.	Reaction can proceed.

9. Le-Chatelier's Principle :

First of all stated in 1884.

The effect of pressures, temperature and concentration on the equilibrium condition of system may be predicted by the application of a general rule known as **Le-Chatelier's Principle**.

Statement—According to this principle "If a system at equilibrium is subjected to a stress by changing pressure, temperature or concentration, the reaction proceeds in such a way as to tend to minimise the effect of that change. The presence of catalyst has no effect on the position of equilibrium."

(A) **Effect of Pressure**—Change in pressure or volume affect the equilibrium system in which at least one of the components is gas and also in which the no. of moles of gaseous reactants and gaseous products are different

$$(i.e.\ \Delta n \neq 0)$$

Readymade-Techniques—

(a) If $\Delta n = 0$, no. effect of pressure

For example— $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(b) If $\Delta n > 0$, *i.e.*, + ve, low pressure will be favourable

For example—

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(c) If $\Delta n < 0$, *i.e.*, −ve, high pressure will be favourable.

For example—

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(B) **Effect of concentration of one of the Components**—

General Rules—The increase in the concentration of one substance in the equilibrium mixture displaces the equilibrium in that direction which uses up some of the materials added. Conversely, by decreasing the concentration of a substance causes the production of more of that substance.

Example—For the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

At equilibrium if more N_2 is added without changing the volume, the reaction quotient Q is smaller than K, because, $Q = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$.

The numerator must increase to maintain constancy of K, hence $[NH_3]$ must increase.

(C) **Effect of Temperature**—

General Rule—Increase in the temperature causes reaction to occur in that direction which results in the absorption of heat, that is, endothermic reactions are favoured at high temperature.

Obviously, exothermic reactions give high yield at low temperature.

Remember—

(a) K increases with increase in temperature for an endothermic reaction (ΔH = positive)

(b) K decreases with increase in temperature for an exothermic reaction (ΔH = negative)

(c) When $\Delta H = 0$, the temperature change has no effect on the equilibrium composition, because, K is independent of temperature for which $\Delta H = 0$.

Cause—The equilibrium constant K, is constant only as long as the temperature does not change, since $K = \frac{K_1}{K_2}$ and rate constant

$$K = Ae^{-Ea/RT}$$

At a particular temperature the activation energies for the forward and reverse reactions are different.

The values of K_1 and K_2 change disproportionately, hence, the change in value of K.

The variation of K with temperature is expressed quantitatively as,

$$\boxed{\log\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2{\cdot}303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

where $T_2 > T_1$ and ΔH° = enthalpy of reaction assumed to be constant for the given temperature range.

(D) **Effect of Catalyst**—The addition of a catalyst has no effect on the position of equilibrium in a reversible reaction, since it accelerates the forward and reverse reactions to the same extent and equilibrium is achieved more rapidly. Consequently the composition of the equilibrium mixture is unchanged by the presence of a catalyst.

(E) **Effect of an Inert Gas**—Inert gases do not participate in the reaction. By the addition of an inert gas—

(i) **When the Volume is Constant**—The total gas pressure will increase but the concentrations (or partial pressures) of all the components will remain constant.

Hence an inert gas has no effect on an equilibrium condition.

(ii) **When the pressure is constant**—The reaction volume will increase and the equilibrium condition will shift to the side of the reaction where there is greater number of moles of gas.

10. Guidelines for Solving Problems :

The following steps are useful while solving numerical problems on chemical-equilibrium.

(a) Write down the balanced chemical equation indicating physical states of the substances.

(b) Ensure volume of reaction mixture must be in litre.

(c) If $\Delta n = 0$, volume does not affect the value of equilibrium constant.

(d) Be certain to know the no. of moles of reactants taken initially when there is no product.

(e) On the basis of balanced chemical equation determine the no. of moles of the reactants and the corresponding number of moles of product formed.

(f) Finally, find out the number of moles of reactants and products at equilibrium.

(g) Calculate the molar concentration or partial pressure of each substance.

(h) Write down the mathematical expression of equilibrium constant for the given reaction.

(i) At last by putting the values of molarity or partial pressures in the equlibrium (mol/litre) expression, calculate the value of K_p and K_c.

Important Numerical Examples with Complete Solution

Type I

For a hypothetical gaseous reaction.

$2AB_3\,(g) \rightleftharpoons A_2\,(g) + 3B_2\,(g)$, 2 moles of AB_3 are introduced into an evacuated 1 litre flask. At equilibrium 1 mole of AB_3 remains the equilibrium constant K_c for the reaction will be—

(A) 1·69 (B) 16·9 (C) 27 (D) 2·7

Solution— $2AB_3\,(g) \rightleftharpoons A_2\,(g) + 3B_2\,(g)$

Initially, 2 moles 0 0

At equilibrium, 1 mole $\frac{1}{2}$ mole $\frac{3}{2}$ mole

$\because$ volume = 1 litre, mole = concentration

$$\because \quad K_c = \frac{[A_2]\,[B_2]^3}{[AB_3]^2} = \frac{\frac{1}{2} \times \left(\frac{3}{2}\right)^3}{1}$$

$$= \frac{27}{16} = 1{\cdot}69$$

Hence (A) is correct.

Type II

Equilibrium constant for the reaction

$H_2 + I_2 \rightleftharpoons 2HI$ is 50 at 700 K, the value of equilibrium constant for the reaction

$HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$ will be—

(A) 5 (B) 1 (C) 0·25 (D) 0·141

Solution—For the reaction, $H_2 + I_2 \rightleftharpoons 2HI$

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = 50 \qquad \text{(given)}$$

Now, equilibrium constant (K'_c) for the reaction

$HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$ will be

$$K'_c = \frac{[H_2]^{1/2}\,[I_2]^{1/2}}{[HI]} = \frac{1}{\sqrt{K_c}}$$

$$= \frac{1}{\sqrt{50}} = 0{\cdot}141$$

Hence (D) is correct.

Type III

2 moles of PCl_5 were introduced in a 2 litre flask and heated at 250°C to establish equilibrium, when 60% of PCl_5 dissociated into PCl_3 and Cl_2. The value of equilibrium constant, K_c, for the reaction

$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$ will be—

(A) 0·6 (B) 0·9 (C) 1·8 (D) 0·45

Solution—Since only 60% PCl_5 dissociated

$\therefore$ PCl_5 actually reacted

$$= 2 \times \frac{60}{100} = 1{\cdot}2 \text{ moles}$$

Reaction—$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Initially, 2 moles 0 0

Since, 1·2 moles of PCl_5 reacted, so, moles of PCl_5, PCl_3 and Cl_2 at equilibrium will be—

$$[PCl_5] = (2 - 1{\cdot}2) = 0{\cdot}8 \text{ moles}$$

$$[PCl_3] = (0 - 1{\cdot}2) = 1{\cdot}2 \text{ moles}$$

$$[Cl_2] = (0 - 1{\cdot}2) = 1{\cdot}2 \text{ moles}$$

Since, volume is 2 litres

$\therefore$ At equilibrium,

$$[PCl_5] = \frac{0{\cdot}8}{2} = 0{\cdot}4 \text{ mole/litre}$$

$$[PCl_3] = \frac{1{\cdot}2}{2} = 0{\cdot}6 \text{ mole/litre}$$

$$[Cl_2] = \frac{1{\cdot}2}{2} = 0{\cdot}6 \text{ mole/litre}$$

$$\therefore \qquad K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \frac{0.6 \times 0.6}{0.8} = 0.9$$

Hence, (B) is correct.

Type IV

The value of equilibrium constant for $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is K, the equilibrium constant for $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$ will be—

(A) $\sqrt{K}$ (B) $\frac{K}{2}$ (C) 2K (D) K^2

Solution—For the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$K_c = K = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

Similarly, for the reaction

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$$

$$K'_c = \frac{[NH_3]^1}{[N_2]^{1/2}\,[H_2]^{3/2}}$$

Obviously, $K'_c{}^2 = K_c = K$

$\therefore \qquad K'_c = \sqrt{K}$

Hence, (A) is correct.

Type V

Consider the gaseous equilibria below and their equilibrium constants at 298 K

$SO_2\,(g) + \frac{1}{2}O_2\,(g) \rightleftharpoons SO_3\,(g),\ K_1$

and, $2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g),\ K_2$

the values of equilibrium constants are related as—

(A) $K_2 = K_1$ (B) $K_2 = K_1^2$

(C) $K_2 = \frac{1}{K_1^2}$ (D) $K_2 = \frac{1}{K_1}$

Solution—K_c for the reaction

$$SO_2\,(g) + \frac{1}{2}O_2\,(g) \rightleftharpoons SO_3\,(g)$$

$$K_c = K_1 = \frac{[SO_3]}{[SO_2]\,[O_2]^{1/2}} \qquad \text{...(i)}$$

Similarly, K_c' for the reaction

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

$$K'_c = K_2 = \frac{[SO_2]^2\,[O_2]}{[SO_3]^2} \qquad \text{...(ii)}$$

It is clear from the equation (i) & (ii), that

$$K_2 = \frac{1}{K_1^2}$$

Hence (C) is correct.

Type VI

In the equilibrium

$$A\,(g) + B\,(g) \rightleftharpoons C\,(g) + D\,(g)$$

When one mole each of the two reactants is mixed, 0.6 mole each of the products is formed the value of equilibrium constant will be—

(A) 1 (B) 0.36 (C) $\frac{4}{9}$ (D) 2.25

Solution—For the reaction,

$$A\,(g) + B\,(g) \rightleftharpoons C\,(g) + D\,(g)$$

It is given that,

Initially,	1 mole	1 mole	0	0
(moles at equilibrium)	(1–0.6)	1–0.6)	(0.6)	(0.6)
	0.4 mole	0.4 mole	0.6 mole	0.6 mole

$$\therefore \qquad \text{Value of } K_c = \frac{[C]\,[D]}{[A]\,[B]} = \frac{0.6 \times 0.6}{0.4 \times 0.4} = \frac{36}{16} = \frac{9}{4} = 2.25$$

Hence (D) is correct.

Type VII

The dissociation of H_2S gas in water may be written as—

(i) $H_2S\,(aq) \rightleftharpoons H^+\,(aq) + HS^-\,(aq)$

(ii) $HS^-\,(aq) \rightleftharpoons H^+\,(aq) + S^{2-}\,(aq)$ and

(iii) $H_2S\,(aq) \rightleftharpoons 2H^+\,(aq)\ S^{2-}\,(aq)$

The dissociation constants of these ionizations are K_1, K_2 and K_3 respectively. These constants may be related as—

(A) $K_3 = K_2 + K_2$ (B) $K_3 = K_1 \times K_2$

(C) $K_3 = \sqrt{K_1 \times K_2}$ (D) $K_3 = (K_1 \times K_2)^2$

Solution—K_c for the reaction

$$H_2S\,(aq) \rightleftharpoons H^+\,(aq) + HS^-\,(aq)$$

$$K_c = K_1 = \frac{[H^+]\,[S^-]}{[H_2S]} \qquad \text{...(i)}$$

Similarly, $$K_2 = \frac{[H^+]\,[S^{2-}]}{[HS^-]} \qquad \text{...(ii)}$$

and, $$K_3 = \frac{[H^+]^2\,[S^{2-}]}{[H_2S]} \qquad \text{...(iii)}$$

It is obvious that,

$$K_1 \times K_2 = \frac{[H^+]\,[HS^-]}{[H_2S]} \times \frac{[H^+]\,[S^{2-}]}{[HS^-]} = \frac{[H^+]^2\,[S^{2-}]}{[H_2S]} = K_3$$

$\therefore \qquad K_3 = K_1 \times K_2$

Hence (B) is correct.

Type VIII

The equilibrium constant K_p, for the reaction

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)$$

is 4.0 at a certain temperature. If we start with equimolar amounts of CO and H_2O and their amounts at equilibrium are 1 mole each the amount of each of CO_2 and H_2 will be—

(A) 4 moles (B) 3 moles
(C) 2 moles (D) 1 mole

Solution—For the reaction

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)$$

1 mole 1 mole x mole x mole

At equilibrium, according to the question

From the reaction it is clear that the number of moles of reactants and products are equal.

Hence, $K_p = K_c$ and the volume terms cancel out in equilibrium constant expression.

Again, we have supposed, that x moles each of CO_2 and H_2 are present in equilibrium.

$$\text{Now,} \quad K_p = K_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]}$$

$$\Rightarrow \quad 4 = \frac{x \times x}{1 \times 1}$$

$$\Rightarrow \quad x = 2 \text{ moles}$$

Hence (C) is correct.

Type IX

At 600 K PCl_5 dissociated to the extent of 40%. The total pressure exerted by the equilibrium mixture, when $K_p = 2{\cdot}4$ is—

(A) 1·2 atm (B) 12·6 atm
(C) 1·5 atm (D) 0·2 atm

Solution—For the reaction,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initially, x atm 0 0
Finally $(x - 0{\cdot}4x)$ $(0 - 0{\cdot}4x)$ $(0 - 0{\cdot}4x)$
(Since, PCl_5 is only 40 % dissociated)

At equilibrium,
$0{\cdot}6x$ $0{\cdot}4x$ $0{\cdot}4x$

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{0{\cdot}4x \times 0{\cdot}4x}{0{\cdot}6x}$$

$$\Rightarrow \quad 2{\cdot}4 = \frac{0{\cdot}8x}{3}$$

$$\Rightarrow \quad 0{\cdot}8x = 7{\cdot}2$$

$$\Rightarrow \quad x = 9$$

Total pressure at equilibrium

$$= P_{PCl_5} + P_{PCl_3} + P_{Cl_2}$$
$$= (0{\cdot}6x + 0{\cdot}4x + 0{\cdot}4x) \text{ atm}$$
$$= 1{\cdot}4x \text{ atm} = 1{\cdot}4 \times 9 \text{ atm}$$
$$= 12{\cdot}6 \text{ atm}$$

Hence (B) is correct.

Type X

In which of the following cases does the reaction go farthest to completion ?

(A) $K = 10^2$ (B) $K = 10^{-2}$ (C) $K = 10$ (D) $K = 1$

Solution—The correct answer is (A)

As, K will be very large, the forward reaction goes nearly to completion.

Type XI

In the reaction

$$A_2\,(g) + 4B_2\,(g) \rightleftharpoons 2AB_4\,(g);\ \Delta H < 0$$

the formation of AB_4 (g) will be favoured at—

(A) low temperature and high pressure
(B) high temperature and low pressure
(C) low temperature and low pressure
(D) high temperature and high pressure

Solution—The correct answer is (A)

As we know

If, $\Delta H < 0$ *i.e.*, –ve, reaction will be exothermic and low temperature will be favourable.

Similarly, if $\Delta n = -$ve
high pressure will be favoured
Hence (A) is correct answer.

Type XII

The equilibrium constants of a homogeneous reaction determined at different temperatures 60°C, 80°C, 100°C and 140°C are 4, 0·4, 0·01 and 0·004 respectively.

The data indicate that the reaction is—

(A) an exothermic reaction
(B) an endothermic reaction
(C) a reversible reaction
(D) a complex reaction

Solution—The correct answer is (A)

As with increase of temperature, the value of K_c decreases, reaction is exothermic.

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