
***COURSE* : B.Sc I**

***PAPER* : I**

TOPIC : EQUILIBRIUM

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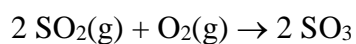
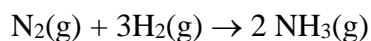
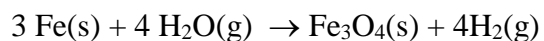
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CHEMICAL EQUILIBRIUM

Chemical reactions can be divided into two categories

Reversible reaction

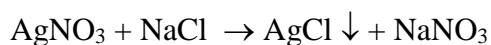
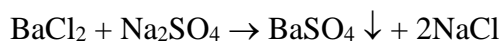
Those reactions in which products can react to form reactants back are called reversible reactions. They proceed in both the directions and do not reach completion e.g.



Irreversible reactions

Those reactions which proceed only in one direction and it is not easily possible to convert the products into reactants are known as Irreversible reactions

They reach completion e.g.

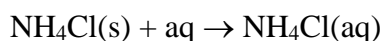
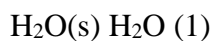


Equilibrium

The stage at which the rate of forward reaction becomes equal to the rate of backward reaction is called equilibrium. It is the condition in which the properties of system do not change with time.

Physical Equilibrium

When there is equilibrium between two physical states of same substances it is called physical equilibrium e.g.

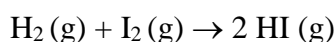


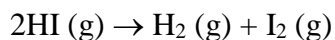
Chemical Equilibrium

When there is equilibrium between two processes involving change of chemical species, it is called chemical equilibrium.

Characteristics of Chemical Equilibrium

1. When chemical equilibrium is attained, there is no further change in pressure, concentration, density or colour at a fixed temperature.
2. It is dynamic in nature i.e. reaction does not stop after the equilibrium is reached rather it appears to stop because there is no further change in concentration, pressure or density because rate of forward reaction is equal to rate of backward reaction.
3. It can be approached from either direction e.g.





4. A catalyst can hasten the approach of equilibrium but does not alter the equilibrium.

Forward reaction

The reaction which proceeds from reactants to products is called forward reaction. The rate of forward reaction is denoted by r_f .

Backward reaction

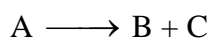
The reaction which proceeds from products to reactants is called backward reaction. The rate of backward reaction is denoted by r_b .

Active Mass

The concentration of a reactant in moles per litre or partial pressure of a reacting gas in atmosphere is known as its active mass. It is expressed by enclosing the symbol or formula of the substance in square brackets e.g. [A]. These days active mass is replaced by molar concentration.

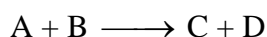
Law of mass action

The rate at which a substance reacts at any instant is proportional to its active mass (molar concentration) and the rate of chemical reaction is proportional to product of active mass (molar concentration) of reactants e.g.



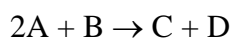
$$\text{Rate} \propto [\text{A}]$$

or, $\text{Rate} = k [\text{A}]$ where 'k' is rate constant or velocity constant



$$\text{Rate} \propto [\text{A}] [\text{B}]$$

$$\text{Rate} = k[\text{A}] [\text{B}]$$



$$\text{Rate} \propto [\text{A}]^2 [\text{B}]$$

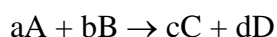
$$\text{Rate} = k [\text{A}]^2 [\text{B}]$$

Thus, the concentration term is raised to the power equal to Stoichiometric coefficient in the chemical equation.

Equilibrium Constant

It is defined as ratio of product of molar concentration of products to the product of molar concentration of reactants raised to the power equal to their Stoichiometric coefficient in a chemical reaction at particular temperature. The *equilibrium constant* measures the *extent to which a reaction takes place before equilibrium is reached*.

If equilibrium constant (K) is large, the equilibrium mixture will have high proportion of products. If it is small, the equilibrium mixture will contain high proportion of reactants.



$$k_f \alpha [\text{A}]^a [\text{B}]^b \longrightarrow r_b \alpha [\text{C}]^c [\text{D}]^d$$

$$r_f = k_f [\text{A}]^a [\text{B}]^b \longrightarrow r_b = k_b [\text{C}]^c [\text{D}]^d$$

Where k_f and k_b are rate constants for forward and backward reactions respectively.

At equilibrium $r_f = r_b$

$$k_f [\text{A}]^a [\text{B}]^b = k_b [\text{C}]^c [\text{D}]^d$$

$$K_C = \frac{k_f}{k_b} = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

Where K_C is equilibrium constant in terms of molar concentration of reactants and products.

In case of gaseous reactions, it is more convenient to use partial pressures instead of molar concentrations. The equilibrium constant in terms of partial pressures of reactants and products is called K_p .



$$K_p = \frac{(pC)^c (pD)^d}{(pA)^a (pB)^b} \quad \text{Reaction coefficient} \quad Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Note 1 : If $Q < K$ it means equilibrium has not reached the and system is moving towards right.

$$\text{At equilibrium} \quad Q_c = \frac{(pC)^c (pD)^d}{(pA)^a (pB)^b}$$

Note 2 : $Q > K$ equilibrium has not reached. The reaction must proceed backwards.

$$\therefore pv = nRT$$

$$p = \frac{n}{v} RT = CRT \quad \text{where 'c' is molar concentration in mol L}^{-1}$$

$$K_p = \frac{\{[C]RT\}^c \{[D]RT\}^d}{\{[A]RT\}^a \{[B]RT\}^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \times \frac{(RT)^{c+d}}{(RT)^{a+b}} = K_c (RT)^{(c+d)-(a+b)}$$

$$K_p = K_c (RT)^{\Delta n} \quad \text{where } \Delta n = (c + d) - (a + b)$$

Where Δn is no. of moles of gaseous products – no. of moles of gaseous reactants.

Δn may be zero, positive or negative e.g.

If $\Delta n = 0$, K_p and K_c are equal and have no units. In other case i.e. for $\Delta n = +ve$ or $-ve$, K_p is expressed as (Unit of pressure Δn) e.g. $(\text{atm})^{\Delta n}$, K_c is expressed as (Unit of concentration) $^{\Delta n}$ e.g. $(\text{mol L}^{-1})^{\Delta n}$

Relationship between degree of dissociation and Vapour density

In all cases, where number of moles are being changed from reactants to products, so Vapour density will also change. If we consider, say dissociation of PCl_5 , the initial and equilibrium states are represented as follows



Initial	1	0	0
Moles at Equilibrium	$1 - x$	x	x

$$\text{Total number of moles} = 1 - x + x + x = 1 + x$$

Here we start with 1 mole of PCl_5 and 'x' is degree of dissociation. If 1 mole at temperature T and pressure P occupies a volume 'v' litres, the volume of resulting mixture will be $(1 + x)$ litres, where $(1 + x)$ represents the number of moles at equilibrium.

$$D = \frac{M}{V}$$

$$D \propto \frac{1}{\text{volume}} \quad (\text{since mass is constant})$$

If 'D' is density of gas before dissociation and 'd' is density of equilibrium mixture then in case of dissociation of PCl_5

$$D \propto \frac{1}{V} \rightarrow \dots(\text{i})$$

$$d \propto \frac{1}{(1+x)V} \rightarrow \dots(\text{ii})$$

$$\text{From (i) and (ii)} \quad \frac{D}{d} = \frac{(1+x)V}{V}$$

$$\frac{D}{d} = 1 + x$$

$$x = \frac{D}{d} - 1 = \frac{D-d}{d}$$

$$x = \frac{D-d}{d}$$

For a molecule of gas which on dissociation gives 'n' molecules of products:

$$x = \frac{D-d}{d(n-1)}$$

This relationship can be used for calculation of degree of dissociation from “Vapor Density Measurement”

Illustration 1

K_p for the reaction $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ at 250°C is 0.82. Calculate the degree of dissociation at given temperature under a total pressure of 5 atm. What will be the degree of dissociation if the equilibrium pressure is 10 atm. at same temperature.

Solution

Let 1 mole of PCl_5 be taken initially. If 'x' moles of PCl_5 dissociate at equilibrium, its degree of dissociation = x.

Moles	PCl_5	PCl_3	Cl_2
Initially	1	0	0
At equilibrium	$1 - x$	x	X
Total moles	$1 - x + x + x = 1 + x$		

$$P = 5 \text{ atm. } K_p = 0.82$$

$$P_{\text{PCl}_5} = \left(\frac{1-x}{1+x} \right) P, P_{\text{PCl}_3} = \frac{xP}{1+x}, P_{\text{Cl}_2} = \frac{xP}{1+x}$$

$$K_p = \frac{(P_{\text{PCl}_3})(P_{\text{Cl}_2})}{(P_{\text{PCl}_5})}$$

$$K_p = \frac{x^2}{1-x^2} P = 0.82$$

$$\frac{x^2(5)}{1-x^2} = 0.82 \Rightarrow x^2 = \sqrt{\frac{0.82}{5.82}}$$

$$x = 0.375 \text{ (or 37.5\%)}$$

Now the new pressure $P = 10 \text{ atm}$.

Let y be the new degree of dissociation. As the temperature is same (250°C), the value of K_p will remain same.

$$K_p = \frac{(y)^2 P}{1-(y)^2} \Rightarrow 0.82 = \frac{(y)^2 10}{1-(y)^2}$$

$$\Rightarrow y = \sqrt{\frac{0.82}{10.82}} \text{ or } y = 0.275 \text{ (or 27.5\%)}$$

Note : By increasing pressure, degree of dissociation has decreased, as depicted in illustration $\left(x \propto \frac{1}{\sqrt{P}}\right)$ i.e., the system shifts to reverse direction. We can also compare the result by applying Le Chatelier's principle.

Illustration 2

Vapour density of the equilibrium mixture of NO_2 and N_2O_4 is found to be 40 for the equilibrium



Calculate (i) abnormal molecular weight

ii) degree of dissociation

iii) percentage of NO_2 in the mixture

Solution



Observed value of vapour density (d) = 40

Hence, abnormal molecular weight = $40 \times 2 = 80$

ii) $D \times 2 = \text{theoretical molecular weight} = 92$

$$\therefore D = \frac{92}{2} = 46$$

$$\therefore x = \frac{D-d}{d} = \frac{46-40}{40} = 0.15$$



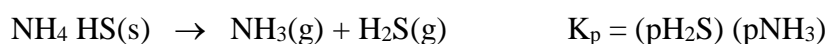
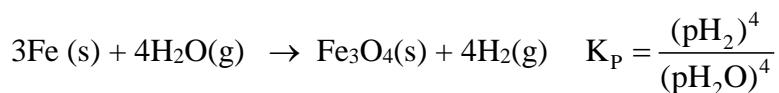
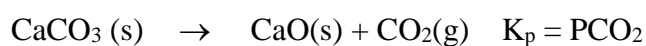
Initial mol	1	0
At equilibrium	(1 - x)	2x
	0.85	0.30

Total moles at equilibrium = $(1 + x) = 1 + 0.15 = 1.15$

$$\therefore \text{Percentage of NO}_2 = \frac{2x}{1+x} \times 100 = \frac{0.30}{1.15} \times 100 = 26.08\%$$

Heterogeneous equilibrium

When reactants and products are in different physical states, it is called heterogeneous equilibrium e.g.



The molar conc. of solid and liquid reactant or product in equilibrium involving gases is taken as unity. K_p is written for heterogeneous reactions and analysis is done in terms of partial pressure.

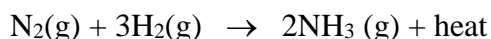
Le-Chatelier's Principle

When a system in equilibrium is subjected to change in temperature, pressure or concentration, the equilibrium shifts in that direction so as to counterbalance the effect of the change.

This principle is extremely useful in predicting the effect of changes in temperature, pressure or concentration upon a system at equilibrium.

Effect of temperature

In case of exothermic reaction, increase in temperature favours backward reaction where as decrease in temperature favours forward reaction e.g.



Increase in temperature, generally favours an increase in rate but extent of increase will be different for backward and forward reactions owing to the differences in their energies of activation. So the numerical value of 'k' (equilibrium constant) will change with change in temperature.

The variation is expressed by the relation:

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

Where K_1 and K_2 are equilibrium constant at temperature T_1 and T_2 respectively

ΔH = Standard enthalpy of reaction

Note 1 : For endothermic reaction

$$\Delta H = +ve \text{ and if } T_2 > T_1 \text{ then } \log \frac{K_2}{K_1} = +ve$$

$$\log K_2 > \log K_1 \quad K_2 > K_1$$

i.e. K increases with increase in temperature for endothermic reactions.

Note 2 : For exothermic reactions

$$\Delta H = -ve \text{ and } T_2 > T_1 \quad \therefore \log \frac{K_2}{K_1} = -ve$$

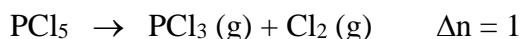
$$\log K_2 < \log K_1 \quad K_2 < K_1$$

i.e. K decreases with increase in temperature for exothermic reactions.

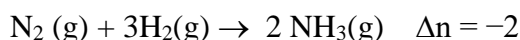
Note 3 : The new equilibrium state has a new value of equilibrium constant 'k' on changing the temperature

Effect of pressure

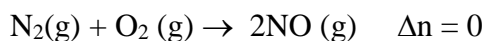
If there is an overall increase in number of moles of products from reactants, low pressure is favourable for forward reactions e.g. in dissociation of $\text{PCl}_5(\text{g})$ low pressure is favourable



If there is decrease in number of moles from reactants to products, high pressure is favourable for forward reaction e.g. high pressure is favourable for manufacture of NH_3 .



If the number of moles of reactants and products are equal is no effect of pressure e.g.



Effect of Concentration

If at equilibrium some quantity of reactant or product is added, the equilibrium will shift in the direction in which added substance is consumed e.g. in $\text{N}_2(\text{g}) + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3(\text{g})$.

If at equilibrium, we increase the concentration of reactant (N_2 or H_2 or both), the rate of forward reaction will increase. But if we increase the concentration of NH_3 , the reaction proceeds towards backward direction. If we increase the conc. of NH_3 , the reaction proceeds towards backward direction. If we decrease the conc. of NH_3 , rate of forward reaction will increase. Therefore, product should be removed as soon as it is formed.

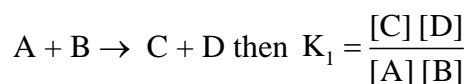
Effect of Catalyst

Catalyst increases the rate of forward as well as backward reaction equally but equilibrium is reached faster in presence of catalyst. It does not effect value of 'k'.

Effect of addition of inert gas

At constant volume, the various concentration terms are not changed. Hence the equilibrium will not be affected. However at constant pressure, the addition of inert gas will increase the volume of the system and thus decrease the concentration and partial pressures of the species involved. Hence the equilibrium will shift in the direction in which concentration of species increase i.e. degree of dissociation should increase i.e. formation of products should be favoured if $\Delta n = +ve$. If $\Delta n = -ve$, addition of inert gas will favour backward reaction.

Note 1 : If K_1 is equilibrium constant for



K_2 for $C + D \rightarrow A + B$ is equal to $\frac{1}{K_1}$

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

K_3 for $nA + nB \rightarrow nC + nD$ is , $(K_1)^n$, 'n' can be in fraction also.

$$K_3 = \frac{[C]^n [D]^n}{[A]^n [B]^n} = (K_1)^n$$

K_4 for $nC + nD \rightarrow nA + nB$ is $\frac{1}{(K_1)^n}$

$$K_4 = \frac{[A]^n [B]^n}{[C]^n [D]^n} = \frac{1}{(K_1)^n}$$

Note 2 : If K_1 be equilibrium constant for $P \rightarrow Q$ and $K_1 = \frac{[Q]}{[P]}$

If K_2 be equilibrium constant for $R \rightarrow S$ then $K_2 = \frac{[S]}{[R]}$

K for $P + R \rightarrow Q + S$ in equal $K_1 \times K_2$

$$K = \frac{[Q][S]}{[P][R]} = K_1 \times K_2$$

Note 3 : If K_1 , be equilibrium constant or $A \rightarrow B$ $K_1 = \frac{[B]}{[A]}$

K_2 be equilibrium constant for $C \rightarrow D$ $K_2 = \frac{[D]}{[C]}$

' K ' for $A + D \rightarrow B + C$

$$K = \frac{[B][C]}{[A][D]} = \frac{K_1}{K_2}$$

Illustration 3

Consider the reaction $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$; at 37°C the value of equilibrium constant for the reaction is 0.0032. It was observed that concentration of the three species is 0.050 mol/lit. each at a certain instant. Discuss what will happen in the reaction vessel ?

Solution

In this question, concentration of three species i.e. SO_2Cl_2 , SO_2 and $\text{Cl}_2(\text{g})$ each is given, but is is not mentioned that whether the system is at equilibrium or not. So first check it. Find reaction coefficient for given equation.

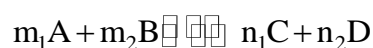
$$Q = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]} = \frac{(0.05)(0.05)}{(0.05)} = 0.05$$

$\Rightarrow Q \neq K$, so system is not at equilibrium state.

As $Q > K$, the concentrations must adjust till $Q = K$ for equilibrium. This can happen only if reaction shifts backwards, and products recombine to give back reactants. Hence in the reaction vessel, the system will move backward so that it can achieve equilibrium state.

Relationship between K_p and K_c

Consider a gaseous reaction



$$K_p = \frac{(P_c)^{n_1} \times (P_D)^{n_2}}{(P_A)^{m_1} \times (P_B)^{m_2}} \quad \dots(i)$$

$$K_c = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}} \quad \dots(ii)$$

Applying ideal gas equation

$$PV = nRT$$

$$P = \frac{n}{V} RT$$

or $P = CRT$

Where C is molarity

$$P_A = C_A RT ; P_B = C_B RT$$

$$P_C = C_C RT ; P_D = C_D RT$$

Substituting this in equation (i)

$$\frac{(C_C RT)^{n_1} \times (C_D RT)^{n_2}}{(C_A RT)^{m_1} \times (C_B RT)^{m_2}} = \frac{C_C^{n_1} \times C_D^{n_2}}{C_A^{m_1} \times C_B^{m_2}} \times \frac{(RT)^{n_1+n_2}}{(RT)^{m_1+m_2}}$$

$$= K_c \times (RT)^{(n_1+n_2)-(m_1+m_2)}$$

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

Δn = number of moles of products in gaseous state – number of moles of reactants in gaseous state.

If $\Delta n = 0$

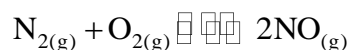
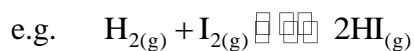
$$K_p = K_c$$

Gaseous equilibria are of two types

Type I :

In which $\Delta n = 0$

$$K_p = K_c$$



Type II :

In which $\Delta n \neq 0$

So $K_p \neq K_c$



Illustration 4

For a homogenous gaseous reaction $X + 2Y \rightleftharpoons Z$, at 473 K, the value of $K_c = 0.35$ concentration units. When 2 moles of Y are mixed with 1 mole of X, at what pressure 60% of X is converted to Z?

Solution

Since pressure is to be calculated, so first find K_p using the relation between K_c and K_p ,

$$K_c = 0.35, R = 0.0821, T = 473, \Delta n = 1 - 3 = -2$$

$$K_p = K_c (RT)^{\Delta n} = 0.35 \times (0.0821 \times 473)^2 = 2.32 \times 10^{-4}$$

The expression for K_p is : $K_p = \frac{P_Z}{P_X (P_Y)^2}$

Moles	X	Y	Z
Initially	1	2	0
At equilibrium	$1 - x$	$2 - 2x$	x

$$\Rightarrow \text{total moles } n_T = 3 - 2x$$

Let P = equilibrium pressure

$$\Rightarrow P_X = \frac{1-x}{3-2x} P, P_Y = \frac{2-2x}{3-2x} P, P_Z = \frac{x}{3-2x} P$$

$$K_p = \frac{\frac{x}{3-2x} P}{\frac{1-x}{3-2x} P \left(\frac{2-2x}{3-2x} P \right)^2} = \frac{x(3-2x)^2}{P^2(1-x)(2-2x)^2}$$

$$x = 0.6 \text{ (given)}$$

$$K_p = \frac{0.6(3-1.2)^2}{P^2(1-0.6)^2 - 1.2)^2} = 2.32 \times 10^{-4} \Rightarrow P^2 = (1.8 \times 10^2)^2$$

$$\Rightarrow P = 180 \text{ atm}$$

HOMOGENOUS GASEOUS REACTIONS

Here, we will discuss some important reversible reactions and the calculations for K_c and K_p .

Illustration 5

The value of K_c for the reaction : $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ is 45.9 at 773 K. If one mole of H_2 , two mole of I_2 and three moles of HI are taken in a 1.0 L flask, find the concentrations of I_2 and HI at equilibrium at 773 K.

Solution

$$\text{Reaction quotient} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{3^2}{1 \times 2} = \frac{9}{2}$$

Note : When $\Delta n = 0$, not only $K_p = K_c$, but volume terms always cancels in the expression of K .

$\Rightarrow Q < K (=45.9)$. Hence the reaction proceeds to forward direction to achieve equilibrium. Let x mole of H_2 and I_2 combine to produce $2x$ mole of HI.

Moles	H_2	I_2	2HI
Initially	1	2	3
At equilibrium	$1 - x$	$2 - x$	$3 + 2x$

$$K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 45.9$$

concentration of species at equilibrium are :

$$[\text{H}_2] = (1-x)/1, [\text{I}_2] = (2-x)/1, [\text{AB}] = (3+2x)/1$$

$$K_C = \frac{\left(\frac{3+2x}{1}\right)^2}{\left(\frac{1-x}{1}\right)\left(\frac{2-x}{1}\right)} = \frac{(3+2x)^2}{(1-x)(2-x)} = 45.9$$

$$\Rightarrow x = 0.68$$

$$[\text{I}_2] = 2 - x = 2 - 0.68 = 1.32\text{M}$$

(Note that volume = 1.0 L)

$$[\text{HI}] = 3 + 2x = 3 + 1.36 = 4.36\text{ M}$$

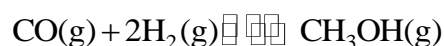
Illustration 6

0.15 mol of CO taken in a 2.5 L flask is maintained at 750 K along with a catalyst so that the following reaction can take place; $\text{CO}(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$. Hydrogen is introduced until the total pressure of the system is 8.5 atm. At equilibrium 0.08 mol of methanol is formed. calculate:

i) K_p and K_c

ii) The final pressure if the same amount of CO and H_2 as before are used but no catalyst so that the reaction does not take place.

Solution



$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$$

Let y moles of H_2 were initially.

Moles	$\text{CO}(\text{g})$	$2\text{H}_2(\text{g})$	CH_3OH
Initially	0.15	y	0
At equilibrium	$0.15 - x$	$y - 2x$	x

$$x = 0.08 \text{ (given)}$$

$$\Rightarrow \text{moles of CO} = 0.15 - 0.08 = 0.07,$$

$$\text{moles of H}_2 = y - 0.16, \text{ moles of CH}_3\text{OH} = 0.08$$

$$\Rightarrow \text{total moles} = n_T = 0.07 + (y - 0.16) + 0.08$$

$$\text{Equilibrium pressure (P)} = 8.5 \text{ atm}$$

$$\text{Volume of vessel (V)} = 2.5 \text{ L, T} = 750 \text{ K}$$

Using the Gas equation, $PV = nRT$, we have :

$$n_T = \frac{PV}{RT} = \frac{8.5 \times 2.5}{0.0821 \times 750} = 0.345$$

$$\Rightarrow 0.345 = 0.07 + (y - 0.16) + 0.08$$

$$\Rightarrow y = 0.355 \text{ moles}$$

$$\Rightarrow \text{moles of H}_2 \text{ at equilibrium} = y - 0.16 = 0.355 - 0.16 = 0.195$$

Now find K_c as follows :

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{\frac{0.08}{2.5}}{\frac{0.07}{2.5} \left(\frac{0.195}{2.5} \right)^2} = 187.84 \text{ concentration units .}$$

Now find K_p using the relation : $K_p = K_c (RT)^{\Delta n}$

$$\Delta n = 1 - 3 = -2$$

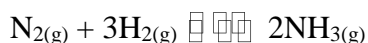
$$\Rightarrow K_p = 187.84 (0.0821 \times 750)^{-2} = 0.0495 \text{ atm units.}$$

ii) when no reaction takes place, then the total pressure is simply due to H_2 and CO present initially.

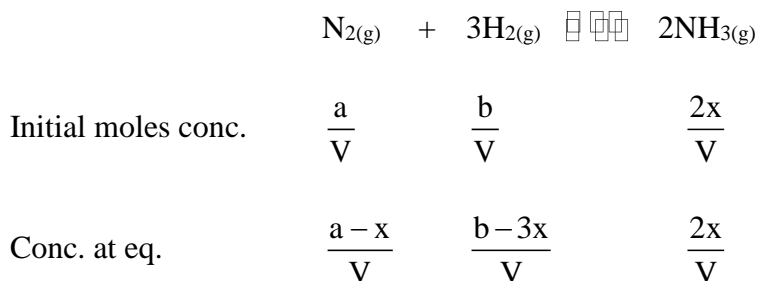
$$n_T = n(\text{CO}) + n(\text{H}_2) = 0.15 + 0.355 = 0.505$$

$$\Rightarrow P = \frac{nRT}{V} = \frac{0.505 \times 0.0821 \times 750}{2.5} = 12.438 \text{ atm}$$

FORMATION OF NH_3



Suppose a moles of N_2 are heated with b moles of H_2 in a V litre container. Let x moles of N_2 be reacted at equilibrium.



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\frac{4x^2}{V^2}}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3}$$

If $a = 1$ and $b = 3$ then

$$K_c = \frac{4x^2V^2}{(1-x)(3-3x)^3} = \frac{4x^2V^2}{27(1-x)^4}$$

If $x \ll 1$

$$K_c = \frac{4x^2V^2}{27} = \text{constant}$$

$$x^2 \propto \frac{1}{V^2} \text{ or } x \propto \frac{1}{V} \text{ but } P \propto \frac{1}{V} \text{ So, } x \propto P$$

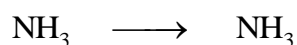
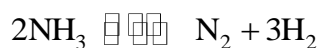
Thus fraction of N_2 converted into NH_3 is proportional to total pressure.

Illustration 7

Ammonia under a pressure of 15 atm. At 27°C is heated to 347°C in a closed vessel in the presence of catalyst. Under these conditions, NH_3 partially decomposes to H_2 and N_2 . The vessel is such that the volume remains effectively constant, whereas the pressure increases to 50 atm. Calculate the % age of NH_3 actually decomposed.

Solution

Ammonia decomposes to N_2 and H_2 as follows :



at 27°C at 347°C

(15 atm.) (P = ?) V remains constant

First, let us find initial pressure of NH_3 at 347°C .

$$\Rightarrow P \propto T \text{ (V is constant)}$$

$$\Rightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2} = p_2 = \frac{P_1 T_2}{T_1} = \frac{15 \times 620}{300} = 31 \text{ atm.}$$

Partial pressure	2NH_3	3H_2	N_2
Initial	31	0	0
At equilibrium	$31 - x$	$\frac{3}{2}x$	$x/2$

Now final equilibrium pressure = 50 atm.

$$\Rightarrow 50 = 31 - x + \frac{3}{2}x + \frac{x}{2} \Rightarrow x = 19 \text{ atm.}$$

$$\Rightarrow \% \text{ NH}_3 \text{ decomposed} = \frac{19}{31} \times 100 = 61.2\%$$

Alternative method:



Let x be the degree of dissociation

Moles	2NH_3	3H_2	N_2
At equilibrium	$1 - x$	$3/2x$	$x/2$

$$\Rightarrow \text{total moles} = 1 + x$$

$$\frac{\text{initial moles}}{\text{final moles}} = \frac{\text{initial pressure}}{\text{final pressure}}$$

$$\frac{1}{1+x} = \frac{31}{50} \Rightarrow x = \frac{19}{31} \Rightarrow \% \text{ dissociation} = \frac{19}{31} \times 100 = 61.2\%$$

Illustration 8

Solid $\text{NH}_4\text{HS}_{(s)}$ (Ammonium hydrogen sulphide) dissociates to give $\text{NH}_{3(g)}$ and $\text{H}_2\text{S}_{(g)}$ and is allowed to attain equilibrium at 100°C . If the value of K_p for its dissociation is found to be 0.34. find the total pressure at equilibrium and partial pressure of each component.

Solution

$\text{NH}_4\text{HS}_{(s)} \rightleftharpoons \text{NH}_{3(g)} + \text{H}_2\text{S}_{(g)}$; since NH_4HS is a solid, hence, $a_{\text{NH}_4\text{HS}} = 1$ and its undissociated amount will not effect the total pressure (due to gaseous NH_3 and H_2S only). Let 'x' be its moles decomposed at equilibrium and P be the equilibrium pressure.

Moles	NH_4HS	NH_3	H_2S
Initial	1	0	0
at equilibrium	$1 - x$	x	X

Total moles at equilibrium = moles of NH_3 and $\text{H}_2\text{S} = 2x$

$$P = ? \quad K_p = 0.34$$

$$P_{\text{H}_2\text{S}} = \frac{x}{2x} P = \frac{P}{2} \quad \& \quad P_{\text{NH}_3} = \frac{x}{2x} P = \frac{P}{2}$$

(for equimolar proportions, partial pressures are equal)

$$K_P = P_{\text{H}_2\text{S}} \cdot P_{\text{NH}_3} \quad (a_{\text{NH}_4\text{HS}} = 1)$$

$$\Rightarrow 0.34 = \frac{P}{2} \times \frac{P}{2}$$

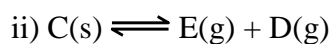
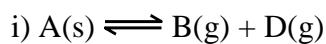
$$\Rightarrow \frac{P^2}{4} = 0.34 \Rightarrow P = \sqrt{4 \times 0.34} = 1.17$$

$$P_{\text{NH}_3} = \frac{P}{2} = \frac{1.17}{2} = 0.585 \text{ atm} \quad P_{\text{H}_2\text{S}} = \frac{P}{2} = \frac{1.17}{2} = 0.585 \text{ atm}$$

HETROGENEOUS SIMULTANEOUS EQUILIBRIUM

Illustration 9

Two solid compounds A and C dissociates into gaseous product at temperature T as follows:



At 20°C pressure over excess solid A is 50 atm and that over excess solid C is 68 atm. Find the total pressure of the gases over the solid mixture.

Solution

When A(s) dissociates alone in a vessel, the pressure over excess solid A is 50 atm. The product gases B and D are present in the molar ratio of 1:1, this means that the pressure of each gas will be half of total pressure.

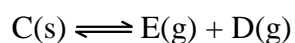
$$\therefore K_{P_1} = 25 \times 25 = 625 \text{ atm}^2$$

$$\therefore K_{P_2} = 34 \times 34 = 1156 \text{ atm}^2$$

But when A(s) and C(s) are placed together in the container, the degree of dissociation of each will be suppressed by the presence of other. (Le-Chatelier Principle)



$$x \quad x \quad (x < 25)$$

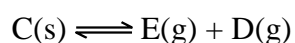


$$y \quad y \quad (y < 34)$$

we have to deal with two equilibriums simultaneously. Write separate dissociation for each equilibrium and then make the concentration or pressure of common species as same.



$$X \quad (x + y)$$



$$Y \quad (x + y)$$

$$625 = x(x + y) \quad \dots(1)$$

$$1156 = y(x + y) \quad \dots(2)$$

From eq. (1) and eq. (2) we get

$$x = 14.8 \text{ atm}, y = 27.37 \text{ atm.}$$

$$\therefore \text{Total pressure of the gases over the solid mixture} = 2(x + y) = 84.34 \text{ atm.}$$

EFFLORESCENT AND DELIQUESCENT

The moisture content of a gas is often expressed in terms of the dew point which is the temperature to which a gas must be cooled before it becomes saturated with water vapours. At this temperature, water or ice (depending on the temperature) will be deposited on a solid surface. Dew point of H₂O is 43°C at which vapour pressure of ice formed is 0.07 Torr.



CaCl₂ (s) has its desiccating properties due to the formation of CaCl₂·2H₂O(s)

$$K_p = p_{\text{H}_2\text{O}}^2 = \left(\frac{0.07}{760} \text{ atm} \right)^2$$

A substance is the most effective drying agent, if it has the lowest vapour pressure of water in equilibrium with it.

A hydrated salt will lose water (a property called efflorescent) below the vapor pressure of water at that temperature.



$$\text{At } 0^\circ\text{C}, \quad K_p = 4.08 \times 10^{-25}, \quad K_p = p_{\text{H}_2\text{O}}^{10}$$

$$\begin{aligned} \square \quad p_{\text{H}_2\text{O}} &= (4.08 \times 10^{-25})^{1/10} \\ &= 3.64 \times 10^{-3} \end{aligned}$$

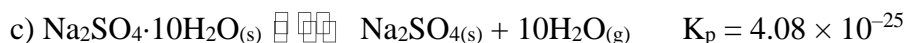
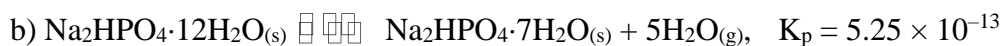
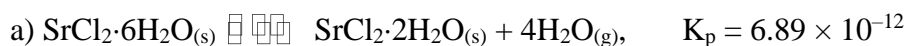
Hence, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ will effloresce at a vapour pressure below 3.64×10^{-3} atm at 0°C , or above relative humidity.

$$\text{Relative humidity} = \frac{\text{partial pressure of H}_2\text{O}}{\text{vapour pressure of H}_2\text{O}} \times 100$$

An anhydrous salt will absorb water below relative humidity.

Illustration 10

Equilibrium constants are given (in atm) for the following reactions at 0°C



The vapour pressure of water at 0°C is 4.58 torr.

i) Calculate the pressure of water vapour in equilibrium at 0°C with each of (a), (b) and (c).

ii) Which is the most effective drying agent at 0°C?

iii) At what relative humidities with Na₂SO₄·10H₂O be efflorescent when exposed to air at 0°C?

iv) At what relative humidities will Na₂SO₄ be deliquescent (i.e., absorb moisture) when exposed to air at 0°C?

Solution

From the values of K_p, partial pressure of H₂O in each case is calculated. Smaller the vapour pressure, better the drying the agent.

i) For a) $K_p = (P_{\text{H}_2\text{O}})^4 = 6.89 \times 10^{-12}$, $P_{\text{H}_2\text{O}} = 1.62 \times 10^{-3}$ atm

b) $K_p = (P_{\text{H}_2\text{O}})^5 = 5.25 \times 10^{-13}$, $P_{\text{H}_2\text{O}} = 3.53 \times 10^{-3}$ atm

c) $K_p = (P_{\text{H}_2\text{O}})^{10} = 4.08 \times 10^{-25}$, $P_{\text{H}_2\text{O}} = 3.64 \times 10^{-3}$ atm

ii) SrCl₂·2H₂O is the most effective drying agent since it has the lowest vapour pressure of water in equilibrium with it.

iii) The hydrate, Na₂SO₄·10H₂O will lose water (efflorescence) below 3.64×10^{-3} atm (2.77 torr) and relative humidity (R.H.) at 0°C will be

$$(\text{R.H.}) = \frac{2.77}{4.58} \times 100 = 60.5\%$$

iv) The dehydrated salt will absorb water above 60.5% R.H.

Illustration 11

For the reaction : CO₂(g) + H₂(g) ⇌ CO(g) + H₂O(g), K is 0.63 at 700°C and 1.66 at 1000°C.

-
- a) What is the average ΔH for the temperature range considered ?
- b) What is the value of K at 800°C ?

Solution

a) $T_1 = 700 + 273 = 973 \text{ K}$

$T_2 = 1000 + 273 = 1273 \text{ K}$

$K_1 = 0.63, K_2 = 1.66$

using the Vant' Hoff equation :

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

$$\Rightarrow \log \left(\frac{1.66}{0.63} \right) = \frac{\Delta H}{2.303 \times 2} \left(\frac{1273 - 973}{1273 \times 973} \right)$$

$$\Rightarrow \Delta H = 8.0 \times 10^3 \text{ cal} = 8.0 \text{ kcal}$$

Note : The units of R and ΔH must be same.

b) Let K_2 be the equilibrium constant at $T_2 = 1073 \text{ K}$

$T_1 = 973 \text{ K}$ and then $K_1 = 0.63$

$$\Rightarrow \log \left(\frac{K_2}{0.63} \right) = \frac{8.0 \times 10^3}{2.303(1.99)} \left(\frac{1073 - 973}{1073 \times 973} \right) \Rightarrow K_2 = 0.93$$

Le Chatelier's Principle and Physical Equilibrium

Le Chatelier's principle, as already stated, is applicable to all types of equilibria involving not only chemical but physical changes as well. A few examples of its application to physical equilibria are discussed below.

1. **Vapour pressure of a liquid:** Consider the equilibrium

Liquid \rightleftharpoons Vapour

It is well known that the change of a liquid into its vapour is accompanied by absorption of heat whereas the conversion of vapour into liquid state is accompanied by evolution of heat. According to Le Chatelier's principle, therefore, addition of heat to such a system will shift the equilibrium towards the right. On raising the temperature of the system, liquid will evaporate. This will raise the vapour pressure of the system. Thus, the vapour pressure of a liquid increases with rise in temperature.

2. Effect of pressure on the boiling point of a liquid: The conversion of liquid into vapour, as represented by the above equilibrium, is accompanied by increase of pressure (vapour pressure). Therefore, if pressure on the system is increased, some of the vapours will change into liquid so as to lower the pressure. Thus, the application of pressure on the system tends to condense the vapour into liquid state at a given temperature. In order to counteract it, a higher temperature is needed. This explains the rise of boiling point of a liquid on the application of pressure.

3. Effect of pressure on the freezing point of a liquid (or melting point of a solid): At the melting point, solid and liquid are in equilibrium:

Solid \rightleftharpoons Liquid

Now, when a solid melts, there is usually a change, either increase or decrease, of volume. For example, when ice melts, there is decrease in volume, or at constant volume, there is decrease in pressure. Thus, increase of pressure on ice \rightleftharpoons water system at a constant temperature will cause the equilibrium to shift towards the right, i.e., it will cause the ice to melt. Hence, in order to retain ice in equilibrium with water at the higher pressure it will be necessary to lower the temperature. Thus, the application of pressure will lower the melting point of ice.

When sulphur melts, there is increase in volume or at constant volume, there is increase in pressure. From similar considerations, it follows that if the pressure on the system, sulphur (solid) \rightleftharpoons sulphur (liquid) is increased, the melting point is raised.

4. Effect of temperature on solubility: In most cases, when a solute passes into solution, heat is absorbed, i.e., cooling results. Therefore according to Le Chatelier's principle, when heat is applied to a saturated solution in contact with solute, the change will take place in that direction which absorbed heat (i.e., which tends to produce cooling). Therefore, some more of the solute will dissolve. In other words, the solubility of the substance increases with rise in temperature.

Dissociation of a few salts (e.g., calcium salts of organic acids) is accompanied by evolution of heat. In such cases, evidently, the solubility decreases with rise in temperature.

Illustration 12

H_2 and I_2 are mixed at 400°C in a 1.0 L container and when equilibrium is established, the following concentration are present : $[\text{HI}] = 0.49 \text{ M}$, $[\text{H}_2] = 0.08 \text{ M}$ and $[\text{I}_2] = 0.06 \text{ M}$. If now an additional 0.3 mol of HI are added, what are the new equilibrium concentrations, when the new equilibrium $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ is re-established ?

Solution

First determine the equilibrium constant K_C for $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$.

$$K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.49)^2}{(0.08)(0.06)} = 50$$

When 0.3 mole of HI are added, equilibrium is disturbed. At instant,

$$[\text{HI}] = 0.49 + 0.3 = 0.79 \text{ M}$$

$$\Rightarrow Q > K_C \text{ since } \left(K_C = \frac{(0.79)^2}{(0.08)(0.06)} = 130 \right)$$

\Rightarrow backward reaction dominate and the equilibrium shifts to the left.

Let $2x =$ concentration of HI consumed (while going left) then concentration of each of H_2 & I_2 formed = x

$$\Rightarrow [\text{HI}] = 0.79 - 2x, [\text{H}_2] = 0.08 + x, [\text{I}_2] = 0.06 + x \text{ and } K_C = 50$$

$$\Rightarrow K_C = \frac{(0.79 - 2x)^2}{(0.08 + x)(0.06 + x)} = 50$$

$$\Rightarrow 46x^2 + 10.2x - 0.35 = 0$$

$\Rightarrow x = 0.033$ or -0.25 (neglecting the $-ve$ value)

Finally, the equilibrium concentrations are :

$$[\text{HI}] = 0.79 - 2x = 0.79 - 0.033 \times 2 = 0.724 \text{ M}$$

$$[\text{H}_2] = 0.08 + x = 0.08 + 0.033 = 0.113 \text{ M}$$

$$[\text{I}_2] = 0.06 + x = 0.06 + 0.033 = 0.093$$

RELATION BETWEEN STANDARD FREE ENERGY CHANGE (ΔG^0) AND EQUILIBRIUM CONSTANT

The Gibbs free energy function is a true measure of chemical affinity under conditions of constant temperature and pressure. The free energy change in a chemical reaction can be defined as

$$\Delta G = G_{(\text{products})} - G_{(\text{reactants})}$$

When $\Delta G = 0$, there is no net work obtainable. The system is in a state of equilibrium. When ΔG is positive, net work must be put into the system to effect the reaction, otherwise it cannot take place. When ΔG is negative, the reaction can proceed spontaneously with accomplishment of the net work. The larger the amount of this work that can be accomplished, the farther away is the reaction from equilibrium. For this reason $-\Delta G$ has often been called the driving force of the reaction. From the statement of the equilibrium law, it is evident that the driving force depends on the concentration of the reactants and products. It also depends upon the temperature and pressure which determine the molar free energies of the reactants and products.

The reaction conducted at constant temperature (i.e., in a thermostat)

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

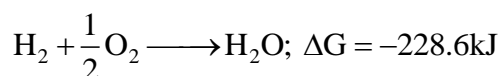
The driving force is made up of two parts, $-\Delta H$ term and $T\Delta S$ term. The $-\Delta H$ term is the heat of reaction at constant pressure and $T\Delta S$ is heat involved when the process is carried out reversibly. The difference is the amount of heat of reaction which can be converted into net work ($-\Delta G$), i.e., total heat minus unavailable heat.

If the reaction is carried out at constant volume, the decrease in Helmholtz function $-\Delta G = -\Delta E + T\Delta S$ would be the proper measure of affinity of the reactant or the driving force of the reaction.

Now we can see why Berthelot and Thompson were wrong in assuming that driving force of the reaction was the heat of reaction. They neglected the $T\Delta S$ term. The reasons for the apparent validity of their principle was that for many reactions, ΔH term far outweighs the $T\Delta S$ term. This is especially true at low temperature, since at higher temperature, $T\Delta S$ term increases.

The fact that driving force for a reaction is large (ΔG is large negative quantity) does not mean that the reaction will necessarily occur under any given conditions.

For example, the reaction

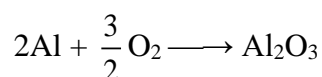


does not occur at the laboratory temperature. The reaction mixture may be kept for years without any detectable formation of water. Here ΔH factor favours, but ΔS factor disfavors the reaction.

Similarly, the reaction



is not favoured. However, the thermite reaction



with large value of $-\Delta G$ proceeds favourably.

Standard Free Energy and Equilibrium Constant

The change in free energy for a reaction taking place between gaseous reactants and products represented by the general equation.



According to Van't Hoff reaction isotherm

$$\Delta G = \Delta G^0 + RT \ln \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} = \Delta G^0 + RT \ln Q_p$$

the condition for a system to be at equilibrium is that

$$\Delta G = 0$$

Thus at equilibrium

$$0 = \Delta G^0 + RT \ln \left[\frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} \right] = \Delta G^0 + RT \ln K_p^0$$

Whence $\Delta G^0 = -RT \ln K_p^0$

$$\text{Hence } \ln K_p^0 = \frac{-\Delta G^0}{RT}$$

Note

1. In the reaction, where all gaseous reactants and products; K represents K_p
2. In the reaction, where all solution reactants and products; K represents K_c
3. A mixture of solution and gaseous reactants; K_x represents the thermodynamic equilibrium constant and we do not make the distinction between K_p and K_c .

we may conclude that for standard reactions, i.e., at 1 M or 1 atm.

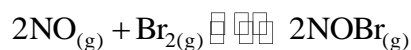
When $\Delta G^0 = -ve$ or $K > 1$: forward reaction is feasible

$\Delta G^0 = +ve$ or $K < 1$: reverse reaction is feasible

$\Delta G^0 = 0$ or $K = 1$: reaction is at equilibrium (very rare)

Illustration 13

NO and Br₂ at initial pressures of 98.4 and 41.3 torr respectively were allowed to react at 300K. At equilibrium the total pressure was 110.5 torr. Calculate the value of equilibrium constant, K_p and the standard free energy change at 300K for the reaction



Solution

From the initial and final pressures of the reaction species, partial pressures of each are determined, hence K_p and ΔG⁰ are calculated

	2NO _(g)	+	Br _{2(g)}	⇌	2NOBr _(g)
Initial	98.4		41.3		0
Used up	2x		x		—
Produced	—		—		2x
Equilibrium	(98.4 – 2x)		(41.3 – x)		2x

$$\begin{aligned} \text{Total pressures at equilibrium} &= P_{\text{NO}} + P_{\text{Br}_2} + P_{\text{NOBr}} \\ &= (98.4 - 2x) + (41.3 - x) + 2x = 139.7 - x = 110.5 \end{aligned}$$

This gives, x = 29.2

$$\text{Hence, } P_{\text{NO}} = (98.4 - 2 \times 29.2) = 40 \text{ Torr}$$

$$P_{\text{Br}_2} = (41.3 - 29.2) = 12.1 \text{ Torr}$$

$$P_{\text{NOBr}} = 2 \times 29.2 = 58.4 \text{ Torr}$$

$$\therefore K_p = \frac{P_{\text{NOBr}}^2}{P_{\text{NO}}^2 P_{\text{Br}_2}} = \frac{(58.4)^2}{(40)^2 (12.1)} = 0.1762 \text{ Torr}^{-1} = 133.88 \text{ atm}^{-1}$$

$$\Delta G^0 = -2.303RT \log K = -2.303 \times 8.314 \times 300 \times \log 133.88$$

$$= 12216.26\text{J} = 12.22\text{ kJ mol}^{-1}$$

SOLVED EXAMPLES

Example 1

The equilibrium constant for the reaction $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ at 1000K is 3.5. What would partial pressure of oxygen gas have to be, to give equal moles of SO_2 and SO_3 ?

- (a) 0.29 atm (b) 3.5 atm
(c) 0.53 atm (d) 1.87 atm.

Solution

$$K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2 p_{\text{O}_2}} = \frac{1}{p_{\text{O}_2}}$$

Here, partial pressure of SO_3 and SO_2 same because moles of SO_2 and SO_3 are equal at equilibrium.

$$p_{\text{O}_2} = \frac{1}{K_p} = 0.285$$

Ans. (a)

Example 2

PCl₅ is 50% dissociated into PCl₃ and Cl₂ at 1 atmosphere. It will be 40% dissociated at :

- (a) 1.75 atm (b) 1.84 atm
(c) 2.00 atm (d) 1.25 atm.

Solution



Let x = degree of dissociation of PCl₅ at pressure P

y = degree of dissociation of PCl₅ at pressure p'

$$K_p = \frac{px^2}{(1-x^2)} = \frac{p'y^2}{(1-y^2)}$$

given, $x = 0.50$, $p = 1$ atm

$y = 0.40$, $p' = ?$

$$\frac{1 \times 0.25}{0.75} = \frac{p' \times 0.16}{0.84}$$

$p' = 1.75$ atm

Ans. (a)

Example 3

For the reaction



The equilibrium constant $K_p = 2.9 \times 10^{-5}$ atm³. The total pressure of gases at equilibrium when 1.0 mole of reactant was heated will be :

- (a) 0.0194 atm (b) 0.0388 atm
 (c) 0.0580 atm (d) 0.0667 atm.

Solution



Initially	1	0	0
At equi.	(1-x)	2x	x

Total moles of gaseous substances at equilibrium = 3x

Equilibrium pressure = P

$$p_{\text{NH}_3} = \frac{2}{3}P, \quad p_{\text{CO}_2} = \frac{P}{3}$$

$$K_p = (p_{\text{NH}_3})^2 p_{\text{CO}_2}$$

$$2.9 \times 10^{-5} = \frac{4}{27}P^3$$

$$P = 0.0580 \text{ atm}$$

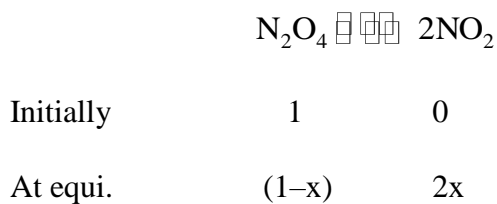
Ans. (c)

Example 4

One mole of $\text{N}_2\text{O}_4(\text{g})$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% of $\text{N}_2\text{O}_4(\text{g})$ decomposes to $\text{NO}_2(\text{g})$. The resultant pressure is

- (a) 1.2 atm(b) 2.4 atm
 (c) 2.0 atm(d) 1.0 atm.

Solution



Total mole at equilibrium = $1 + x = 1.2 \quad \therefore x = 0.2$

$$\therefore \frac{P_1}{n_1 T_1} = \frac{P_2}{n_2 T_2} \text{ or } \frac{1}{1 \times 300} = \frac{P_2}{1.2 \times 600} \text{ or } P_2 = 2.4 \text{ atm}$$

Ans. (b)

Example 5

For the reversible reaction, $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightleftharpoons 2\text{NH}_{3(\text{g})}$ at 500°C , the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c with concentration in mole litre⁻¹, is

(a) $1.44 \times 10^{-5} / (0.082 \times 500)^{-2}$ (b) $1.44 \times 10^{-5} / (8.314 \times 773)^{-2}$

(c) $1.44 \times 10^{-5} / (0.082 \times 773)^2$ (d) $1.44 \times 10^{-5} / (0.082 \times 773)^{-2}$.

Solution

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

Since $\Delta n_g = -2$

$$\therefore K_c = 1.44 \times 10^{-5} \times (0.082 \times 773)^2$$

Ans. (d)

Example 6

One mole of $\text{N}_2\text{O}_{(g)}$ is kept in a closed container along with gold catalyst at 450 K under one atmosphere. It is heated to 900 K when it dissociates to $\text{N}_{2(g)}$ and $\text{O}_{2(g)}$ giving an equilibrium pressure of 2.4 atm. The degree of dissociation of $\text{N}_2\text{O}_{(g)}$ is

- (a) 20% (b) 40%
 (c) 50% (d) 60%.

Solution



$$P_0(1 - \alpha) \quad P_0\alpha \quad P_0\frac{\alpha}{2}$$

When temperature of N_2O is doubled, its pressure also doubles.

$$\therefore \text{Pressure of } \text{N}_2\text{O at 900K, } P_0 = 2\text{atm}$$

Total pressure at equilibrium = 2.4 atm

$$P_0\left(1 + \frac{\alpha}{2}\right) = 2.4$$

$$\alpha = 0.4$$

$$\therefore \text{Degree of dissociation of } \text{N}_2\text{O}_{(g)} = 40\%$$

Ans. (b)

Example 7

For the reaction : $2\text{HI}_{(g)} \rightleftharpoons \text{H}_{2(g)} + \text{I}_{2(g)}$; the degree of dissociation (α) of $\text{HI}_{(g)}$ is related to equilibrium constant K_p by the expression

(a) $\frac{1 + 2\sqrt{K_p}}{2}$ (b) $\sqrt{\frac{1 + 2K_p}{2}}$

$$(c) \sqrt{\frac{2K_p}{1+2K_p}} \quad (d) \frac{\sqrt{2K_p}}{1+2\sqrt{K_p}}$$

Solution



$$1-\alpha \quad \frac{\alpha}{2} \quad \frac{\alpha}{2}$$

$$K_p = \frac{\left(\frac{\alpha}{2}P\right)^2}{(1-\alpha)^2P^2}$$

$$\frac{\alpha}{1-\alpha} = 2\sqrt{K_p}$$

$$\alpha = \frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$$

Ans. (d)

Example 8

For which of the following reactions, the degree of dissociation cannot be calculated from the vapour density data



(a) I and III (b) II and IV

(c) I and II(d) III and IV.

Solution

The degree of dissociation cannot be calculated from the vapour density data if the number of moles remains unchanged before and after reaching equilibrium.

Ans. (a)

Example 9

At a certain temperature the following equilibrium is established.



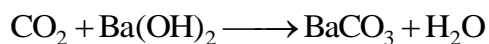
One mole of each of the four gases is mixed in one litre container and the reaction is allowed to reach equilibrium state. When excess of baryta water is added to the equilibrium mixture, the weight of white precipitate obtained is 236.4 g. The equilibrium constant K_c of the reaction is

- (a) 1.2 (b) 2.25
(c) 2.1 (d) 3.6.

Solution



Initially	1	1	1	1
At equi.	1-x	1-x	1+x	1+x



$$\text{Moles of BaCO}_3 = \frac{236.4}{197} = 1.2$$

∴ Moles of CO_2 at equilibrium = 1.2

or, $1 + x = 1.2$; $x = 0.2$

$$\therefore K_c = \left(\frac{1+x}{1-x} \right)^2 = \left(\frac{1.2}{0.8} \right)^2 = 2.25$$

Ans. (b)

Example 10

In a reversible reaction, study of its mechanism says that both the forward and backward reactions follow first order kinetics. If the half life of forward reaction $(t_{1/2})_f$ is 400 sec. and that of backward reaction $(t_{1/2})_b$ is 250 sec. The equilibrium constant of the reaction is



- (a) 1.6 (b) 0.433
 (c) 0.625 (d) 1.109.

Solution

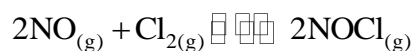
$$k_f = \frac{0.693}{400} \text{sec}^{-1}; \quad k_b = \frac{0.693}{250} \text{sec}^{-1}$$

$$K = \frac{k_f}{k_b} = \frac{250}{400} = 0.625$$

Ans. (c)

Example 11

At 27°C NO and Cl₂ gases are introduced in a 10 litre flask such that their initial partial pressures are 20 and 16 atm respectively. The flask already contains 24 g of magnesium. After some time, the amount of magnesium left was 0.2 moles due to the establishment of following two equilibrium



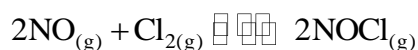


The final pressure of NOCl would be

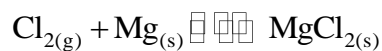
- (a) 7.84 atm (b) 18.06 atm
 (c) 129.6 atm (d) 64.8 atm.

Solution

$$K_p = 0.2 = \frac{1}{P_{\text{Cl}_2}} \Rightarrow P_{\text{Cl}_2} \text{ at equilibrium} = 5 \text{ atm}$$



Initially	20	16	0
At equi.	20-2x	16-x-y	2x



Initially	16	1	0
At equi.	16-x-y	1-y'	y'

$$= 0.2$$

$$y' = 0.8$$

(since y' is the moles while y is pressure in atm)

$$y = \frac{0.8 \times 0.082 \times 300}{10} = 1.97$$

We know that,

$$16 - x - y = 5$$

or, $x = 9.03$; $P_{\text{NOCl}} = 18.06 \text{ atm}$

Ans. (b)

Example 12

The CaCO_3 is heated in a closed vessel of volume 1 litre at 600 K to form CaO and CO_2 . The minimum weight of CaCO_3 required to establish the equilibrium $\text{CaCO}_{3(s)} \rightleftharpoons \text{CaO}_{(s)} + \text{CO}_{2(g)}$ is ($K_p = 2.25 \text{ atm}$)

- (a) 2g (b) 4.57 g
(c) 10g (d) 100 g.

Solution

$$K_p = P_{\text{CO}_2} = 2.25 \text{ atm}$$

$$\text{Number of moles of } \text{CO}_2 = \frac{2.25 \times 1}{0.0821 \times 600}$$

The minimum moles of CaCO_3 required = 0.0457

The minimum weight CaCO_3 required = $0.0457 \times 100 = 4.57 \text{ g}$

Ans. (b)

Example 13

An acid reacts with glycerine to form complex and equilibrium is established. If the heat of reaction at constant volume for above reaction is 1200 cal more than at constant pressure and the temperature is 300 K, then which of the following expression is true ?

- (a) $K_p < K_c$ (b) $K_c < K_p$
(c) $K_p = K_c$ (d) none of these.

Solution

Given : $\Delta E - \Delta H = 1200 \text{ cal}$

$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta n = -2$$

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

$$\frac{K_p}{K_c} = 1.648 \times 10^{-3}$$

$$K_p < K_c$$

Ans. (a)

Example 14

When pure NH_3 is maintained at 480°C and a pressure of 1 atm, it dissociates to give a gaseous mixture containing 20% NH_3 by volume. The degree of dissociation of NH_3 is

- (a) $2/3$ (b) $3/2$
(c) $5/2$ (d) $2/5$.

Solution



Initial a 0 0

At equi. $a(1-\alpha)$ $a\alpha/2$ $3a\alpha/2$

$$\therefore \% \text{ of } \text{NH}_3 \text{ by volume} = \frac{a(1-\alpha)}{a(1-\alpha) + \frac{a\alpha}{2} + \frac{3a\alpha}{2}} \times 100 = \frac{1-\alpha}{1+\alpha} \times 100$$

By condition,

$$\frac{1-\alpha}{1+\alpha} \times 10 = 20$$

$$\therefore \alpha = \frac{2}{3}$$

Ans. (a)

Example 15

Steam at pressure of 1 atm is passed through a furnace at 2000 K wherein the reaction $\text{H}_2\text{O}_{(g)} \rightleftharpoons \text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)}$; $K_p = 6.4 \times 10^{-5}$ occurs. The percentage of oxygen in the exit steam would be

- (a) 0.32 (b) 0.08
(c) 0.04 (d) 0.16

Solution



Initially 2 atm 0 0

At equi. 2 - x x x/2

$$\frac{x(x/2)^{1/2}}{2-x} = 6.4 \times 10^{-5}$$

$$\frac{x^{3/2}}{\sqrt{2}(2-x)} = 6.4 \times 10^{-5}$$

Dissociation of H_2O is so small that we can assume $P_{\text{H}_2\text{O}} \approx 2$ atm

i.e. $2 - x \approx 2$

$$x^{3/2} = 2\sqrt{2} \times 6.4 \times 10^{-5} x \text{ or } x^{3/2} = (2 \times 16)^{3/2} \times 10^{-6}$$

$$x = 2 \times 16 \times 10^{-4} = 0.0032$$

$$\therefore \quad \% \text{ of } O_2 \text{ in the exit steam} = \frac{0.0032/2}{2} \times 100 = 0.08\%$$

Ans. (b)

Example 16

Two moles of an equimolar mixture of two alcohols, R_1-OH and R_2-OH are esterified with one mole of acetic acid. If 80% of the acid is consumed and the quantities of ester formed under equilibrium are in the ratio of 3 : 2, the value of the equilibrium constant for the esterification of R_1-OH with acetic acid is

- (a) 3.3 (b) 3.7
 (c) 3.5 (d) 3.9.

Solution



$$(1-x) \quad (1-x-y) \quad \quad \quad x \quad (x+y)$$



$$(1-y) \quad (1-x-y) \quad \quad \quad y \quad (x+y)$$

Since, the amount of acid consumed is 80% in complete esterification process, therefore

$$x + y = 0.8$$

$$\text{Also, } \frac{x}{y} = \frac{3}{2}$$

$$\therefore \quad x = 0.48 \text{ and } y = 0.32$$

Thus, equilibrium constant for first esterification process = $\frac{x(x+y)}{(1-x)(1-x-y)}$

$$K_{C_1} = \frac{0.48 \times 0.8}{0.52 \times 0.2}$$

$$K_{C_1} \approx 3.7$$

Ans. (b)

Example 17

Solubility of a substance which dissolves with a decrease in volume and absorption of heat will be favoured by

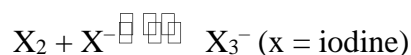
- (a) high P and high T (b) low P and low T
(c) high P and low T (d) low P and high T.

Solution

The substance dissolves with a decrease in volume and absorption of heat. Therefore according to Le Chalelier's principle the process of dissolution will be favoured by high pressure and high temperature.

Ans. (a)

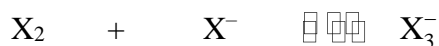
Example 18



This reaction is set up in aqueous medium. We start with 1 mol of X_2 and 0.5 mol of X^{-} in 1L flask. After equilibrium is reached, excess of $AgNO_3$ gave 0.25 mol of yellow ppt. equilibrium constant is

- (a) 1.33 (b) 2.66
(c) 2.00 (d) 3.00

Solution



$$1 \qquad 0.5 \qquad 0$$

$$(1 - x) \qquad (0.5 - x) \qquad x$$

$$(0.5 - x) = \text{unreacted } X^-$$

$$X^- \equiv Ag + 0.25$$

$$x = 0.25$$

$$K_c = \frac{[X_3^-]}{[X_2][X^-]} = \frac{0.25}{0.75 \times 0.25} = 1.33$$

Ans. (a)

Example 19

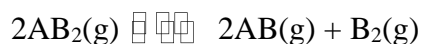
At temperature T, a compound $AB_2(g)$ dissociates according to the reaction $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$ with degree of dissociation α , which is small compared with unity. The expression for K_p , in terms of α and the total pressure, P_T is

$$(a) \quad \frac{P_T \alpha^3}{2} \quad (b) \quad \frac{P_T \alpha^2}{3}$$

$$(c) \quad \frac{P_T \alpha^3}{3} \quad (d) \quad \frac{P_T \alpha^2}{2}$$

Solution

For the given equilibrium, the equilibrium concentrations are



$$\text{Equilib. conc. } c(1 - \alpha) \qquad c\alpha \qquad \frac{c\alpha}{2}$$

$$\therefore K_P = \frac{(P_{B_2})(P_{AB})^2}{(P_{AB_2})^2} = \frac{\frac{c\alpha}{2} \times (c\alpha)^2 \times P_T}{[c(1-\alpha)]^2 [c(1+\frac{\alpha}{2})]} ; K_P = \frac{\alpha^3 \times P_T}{2(1-\alpha)^2 \left(1 + \frac{\alpha}{2}\right)}$$

Since, α is small compared to unity, so $1 - \alpha \approx 1$ and $1 + \frac{\alpha}{2} \approx 1$.

$$\therefore K_P = \frac{\alpha^3 \times P_T}{2}$$

Ans. (a)

Example 20

2.0 mol of PCl_5 were introduced in a vessel of 5.0 L capacity at a particular temperature. At equilibrium, PCl_5 was found to be 35% dissociated into PCl_3 and Cl_2 . The value of K_c for the reaction is

- (a) 1.89 (b) 0.377
(c) 0.75 (d) 0.075.

Solution

$$\text{Moles of } \text{PCl}_5 \text{ dissociated} = \frac{2 \times 35}{100} = 0.7$$

$$\text{Moles of } \text{PCl}_5 \text{ left undissociated} = 2 - 0.7 = 1.3 \text{ mol}$$

$$[\text{PCl}_5] = \frac{1.3}{5} \text{ M}, [\text{PCl}_3] = \frac{0.7}{5} \text{ M}, [\text{Cl}_2] = \frac{0.7}{5} \text{ M}$$

$$K = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\left(\frac{0.7}{5}\right)\left(\frac{0.7}{5}\right)}{\left(\frac{1.3}{5}\right)} = 0.75$$

Ans. (c)

SOLVED SUBJECTIVE EXAMPLES

Example 1

The equilibrium constant for the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$; is found to be 64 at 450°C . If 6 mole of hydrogen are mixed with 3 mole of iodine in a litre vessel at this temperature; what will be the concentration of each of the three components, when equilibrium is attained ?

If the volume of reaction vessel is reduced to half; then what will be the effect on equilibrium ?

Solution

The given equilibrium reaction is :

	H_2	+	I_2	\rightleftharpoons	2HI
At $t = 0$	6		3		0
At equilibrium	$6 - x$		$3 - x$		$2x$
concentration at equilibrium	$\frac{6 - x}{1}$		$\frac{3 - x}{1}$		$\frac{2x}{1}$

$$K_C = \frac{(2x)^2}{(6-x)(3-x)}$$

$$64 = \frac{4x^2}{x^2 + 18 - 9x}$$

$$16(x^2 - 9x + 18) = x^2$$

On solving $x = 2.84$

$$[\text{HI}] = \frac{2x}{1} = \frac{2 \times 2.84}{1} = 5.68$$

$$[\text{H}_2] = \frac{6-x}{1} = \frac{6-2.84}{1} = 3.16$$

$$[\text{I}_2] = \frac{3-x}{1} = \frac{3-2.84}{1} = 0.16$$

In the present reaction $\Delta n = 0$ hence, volume change will not affect the equilibrium.

Example 2

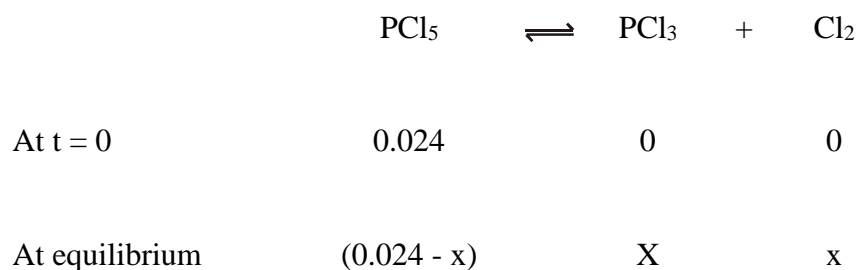
5 gm of PCl_5 were completely vaporized at 250°C in a vessel of 1.9 litre capacity. The mixture at equilibrium exerted a pressure of one atmosphere. Calculate the degree of dissociation, K_C and K_p for this reaction.

Solution

No. of moles of PCl_5

$$= \frac{\text{Weight}}{\text{Molecularweight}} = \frac{5}{208.5} = 0.024$$

The equilibrium for dissociation of PCl_5 maybe represented as



Total moles of gas components

$$= 0.024 - x + x + x = (0.024 + x)$$

We know, $PV = nRT$

$$1 \times 1.9 = (0.024 + x) 0.0821 \times 523$$

$$(0.024 + x) = \frac{1.9}{0.0821 \times 523}$$

$$x = 0.0202$$

$$\text{Degree of dissociation} = \frac{0.0202}{0.024} = 0.843$$

$$[\text{PCl}_5] = \frac{0.024 - x}{1.9} = \frac{0.024 - 0.0202}{1.9} = \frac{0.0038}{1.9}$$

$$[\text{PCl}_3] = [\text{Cl}_2] = \frac{x}{V} = \frac{0.0202}{1.9}$$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\left[\frac{0.0202}{1.9}\right]^2}{\frac{0.0038}{1.9}} = \frac{4.08 \times 10^{-4}}{1.9 \times 0.0038} = 0.0565 \text{ mole/litre}$$

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

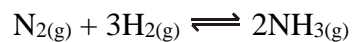
Where $K_c = 0.0565$

$$\Delta n = 2 - 1 = 1$$

$$K_p = 0.0565 \times 0.0821 \times 523 = 2.43 \text{ atm}$$

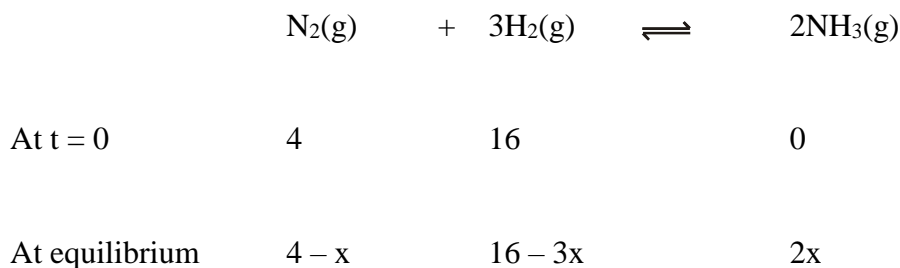
Example 3

16 moles of H_2 and 4 moles of N_2 are sealed in a one litre vessel. The vessel is heated at a constant temperature until the equilibrium is established, when it is found that the pressure in the vessel has fallen to 9/10 of its original value. Calculate K_c for the reaction



Solution

The given equilibrium is



Total gaseous moles at equilibrium

$$= 4 - x + 16 - 3x + 2x = (20 - 2x)$$

Since, pressure has fallen to 9/10 of its original value, hence no. of mole will also fall up to the same extent.

$$\therefore (20 - 2x) = \frac{9}{10} \times 20 = 18$$

$$x = 1$$

$$\therefore [\text{N}_2] = \frac{4-x}{1} = \frac{4-1}{1} = 3 \text{ mole/litre}$$

$$[\text{H}_2] = \frac{16-3x}{1} = 13 \text{ mole/litre}$$

$$[\text{NH}_3] = \frac{2x}{1} = 2 \text{ mole/litre}$$

$$K_C = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{2^2}{(3)(13)^3} = 6.07 \times 10^{-4}$$

Example 5

The value of K for the reaction



Changed from 0.096 at 298K to 1.4 at 373K. Above what temperature will the reaction become thermodynamically spontaneous in the forward direction assuming that ΔH^0 and ΔS^0 values for the reaction do not change with change in temperature? Given that, $\Delta S_{298}^0 = 10.296 \text{JK}^{-1}$.

Solution

We have,

$$\log \frac{K_2}{K_1} = \frac{\Delta H^0}{2.303R} \frac{(T_2 - T_1)}{T_1 T_2}$$

$$\log \frac{1.4}{0.096} = \frac{\Delta H^0}{2.303 \times 8.314} \left(\frac{373 - 298}{373 \times 298} \right)$$

$$\Delta H^0 = 33025 \text{J}$$

Now the temperature above which the forward reaction will be spontaneous is actually the temperature at which the reaction attains equilibrium, that is, when $K = 1$ or $\log K = 0$

$$\therefore \Delta G^0 = -2.303 RT \log K = -2.303 RT \log 1.0 = 0$$

From thermodynamics, we get

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$0 = 33025 - T \times 10.296$$

$$\text{or } T = 320.75 \text{ K}$$

Example 6

A mixture of SO₃, SO₂ and O₂ gases is maintained in a 10.0 litre flask at a temperature at which equilibrium constant K_c for the reaction

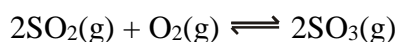


i) If the number of mole of SO₂ and SO₃ in the flask are equal; how many mole of O₂ are present ?

ii) If the number of mole of SO₃ in the flask is twice the number of mole of SO₂, how many mole of O₂ are present ?

Solution

The given equilibrium is



$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \quad \dots \text{ (i)}$$

i) If [SO₃] = [SO₂]

$$\text{Then } K_c = \frac{1}{[\text{O}_2]}$$

$$[\text{O}_2] = \frac{1}{K_c} = \frac{1}{100} = 0.01 \text{ mole/litre}$$

Total moles of O₂ present = 0.01 × 10 = 0.1 mole

∴ Volume of vessel is 10 litre

ii) When [SO₃] = 2[SO₂]

$$\text{Then } K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \quad \text{from Eq. (i)}$$

$$100 = \frac{4}{[\text{O}_2]}$$

$$[\text{O}_2] = 4/100 = 0.04 \text{ mole/litre}$$

$$\text{Total moles of O}_2 \text{ in vessel at equilibrium} = 0.04 \times 10 = 0.4 \text{ mole}$$

Example 7

A saturated solution of iodine in water contains 0.33g of I_2 per litre of solution. More than this can dissolve in KI solution because of the following equilibrium.



A 0.1 M KI solution actually dissolves 12.5g of I_2 /litre, most of which is converted to I_3^- . Assuming that the concentration of I_2 in all saturated solutions is the same, calculate the equilibrium constant for the above reaction.

Solution

	I_2	+	I^-	\rightleftharpoons	I_3^-
Initially	$\frac{12.5}{254} \text{M}$		0.1M		0
At equb.	$\frac{0.33}{254} \text{M}$		$\left(0.1 - \frac{12.17}{254}\right) \text{M}$		$\frac{12.17}{254} \text{M}$

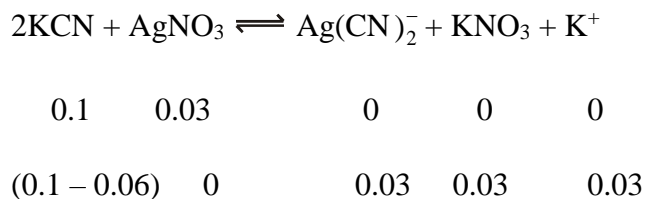
Thus,

$$K = \frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]} = \frac{\frac{12.17}{254}}{\frac{0.33}{254} \times \frac{13.23}{254}} = 708$$

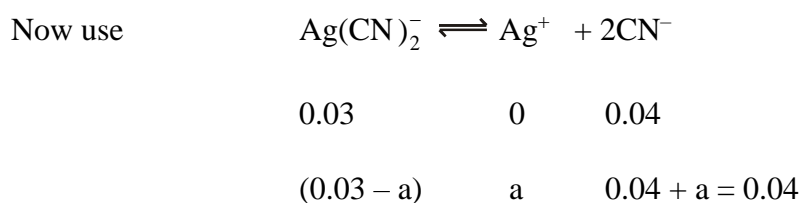
Example 8

For the reaction $\text{Ag}(\text{CN})_2^- \rightleftharpoons \text{Ag}^+ + 2\text{CN}^-$, the K_C at 25°C is 4×10^{-19} . Calculate $[\text{Ag}^+]$ in solution which was originally 0.1 M in KCN and 0.03 M in AgNO_3 .

Solution



$$\therefore [\text{Ag}(\text{CN})_2^-] = 0.03 \text{ M}$$



Since K_C is too small and dissociation of $\text{Ag}(\text{CN})_2^-$ is very less and thus,

$$\therefore 0.04 + a \approx 0.04 \text{ and } 0.03 - a \approx 0.03$$

$$\therefore [\text{Ag}(\text{CN})_2^-] = 0.03; [\text{Ag}^+] = a; [\text{CN}^-] = 0.04$$

$$\text{Now } K_C = \frac{[\text{Ag}^+][\text{CN}^-]^2}{[\text{Ag}(\text{CN})_2^-]} = \frac{a \times (0.04)^2}{0.03}$$

$$\therefore a = 7.5 \times 10^{-18}$$

Example 9

When baking soda is heated in a sealed tube, following equilibrium exists:



If the equilibrium pressure is 1.04 atm at 398 K, calculate the equilibrium constant for the reaction at 398 K.

Solution

Since, there are only two gaseous species in the above equilibrium

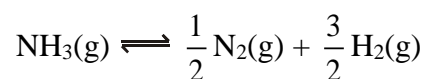
$$\therefore p_{\text{CO}_2} = p_{\text{H}_2\text{O}} = \frac{1}{2} \text{ total pressure}$$

$$= \frac{1}{2} \times 1.04 = 0.52 \text{ atm}$$

$$K_p = p_{\text{CO}_2} \times p_{\text{H}_2\text{O}} = [0.52]^2$$

Example 10

For the reaction



Show that degree of dissociation of NH_3 is given as :

$$\alpha = \left[1 + \frac{3\sqrt{3}}{4} \frac{P}{K_p} \right]^{-1/2}$$

where 'P' is equilibrium pressure. If K_p of the above reaction is 78.1 atm at 400°C , calculate K_c .

Solution

	$\text{NH}_3(\text{g})$	\rightleftharpoons	$\frac{1}{2} \text{N}_2(\text{g})$	+	$\frac{3}{2} \text{H}_2(\text{g})$	Total moles
Initial moles t = 0	1		0		0	1
Moles equilibrium	$1 - \alpha$		$\alpha/2$		$3\alpha/2$	$1 + \alpha$
Partial pressure	$\left\{ \frac{1-\alpha}{1+\alpha} \right\} p$		$\left\{ \frac{\alpha}{2(1+\alpha)} \right\} p$		$\left\{ \frac{3\alpha}{2(1+\alpha)} \right\} p$	

$$K_p = \frac{[\text{N}_2]^{1/2} [\text{H}_2]^{3/2}}{[\text{NH}_3]}$$

$$\frac{\left[\frac{\alpha}{2(1+\alpha)}p\right]^{1/2} \left[\frac{3\alpha}{2(1+\alpha)}p\right]^{3/2}}{\left[\frac{1-\alpha}{1+\alpha}p\right]} = \frac{p\alpha^2\sqrt{27}}{4(1-\alpha^2)}$$

Solving for ' α ' we get :

$$\alpha = \left[1 + \frac{3\sqrt{3}}{4} \frac{p}{K_p}\right]^{-1/2}$$

We know,

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

$$78.1 = K_C (0.0821 \times 673)^1$$

$$K_C = 1.413 \text{ moles litre}^{-1}$$

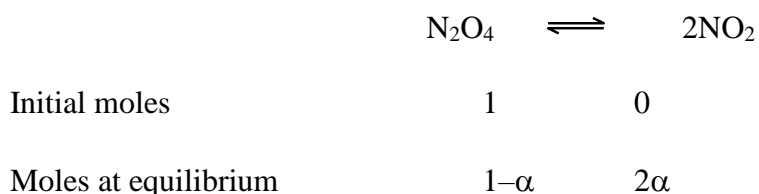
Example 11

K_p for the reaction $N_2O_4 (g) \rightleftharpoons 2NO_2 (g)$ is 0.66 at 46°C . Calculate the percent dissociation of N_2O_4 at 46°C and a total pressure of 0.5 atm. Also calculate the partial pressure of N_2O_4 and NO_2 at equilibrium.

Solution

This Example can be solved by two methods.

Method 1: Let the number of moles of N_2O_4 initially be 1 and α is the degree of dissociation of N_2O_4 .



$$\text{Total moles at equilibrium} = 1-\alpha + 2\alpha = 1+\alpha$$

$$p_{\text{N}_2\text{O}_4} = \frac{1-\alpha}{1+\alpha} \times P_T$$

$$p_{\text{NO}_2} = \frac{2\alpha}{1+\alpha} \times P_T$$

$$\therefore K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}} = \frac{4\alpha^2 P_T}{(1-\alpha)(1+\alpha)} = \frac{4\alpha^2 \times 0.5}{1-\alpha^2}$$

$\alpha = 0.5$ i.e., 50% dissociation

Hence, partial pressure of $\text{N}_2\text{O}_4 = 0.167$ atm.

and partial pressure of $\text{NO}_2 = 0.333$ atm.

Method 2 : Let the partial pressure of NO_2 at equilibrium be p atm, then the partial pressure of N_2O_4 at equilibrium will be $(0.5-p)$ atm.

$$\therefore K_p = \frac{p^2}{(0.5-p)} = 0.66$$

$$p^2 + 0.66p - 0.33 = 0$$

On solving $p = 0.333$ atm.

$$\therefore p_{\text{NO}_2} = 0.333 \text{ atm and } p_{\text{N}_2\text{O}_4} = 0.167 \text{ atm.}$$

Example 12

At 1000 K, the pressure of iodine gas is found to be 0.112 atm due to partial dissociation of $\text{I}_2(\text{g})$ into I. Had there been no dissociation, the pressure would have been 0.074 atm. Calculate the value of K_p for the reaction: $\text{I}_2(\text{g}) \rightleftharpoons 2\text{I}(\text{g})$.

Solution

Analysing in terms of pressure directly

Partial pressure	I ₂	2I
Initial	0.074	0
At equilibrium	0.074 - p	2p

⇒ total pressure at equilibrium

$$= (0.074 - p) + 2p = 0.112 \text{ (given)} \Rightarrow p = 0.038 \text{ atm}$$

$$K_p = \frac{(P_I)^2}{P_{I_2}} = \frac{(2p)^2}{(0.074 - p)}$$

Substituting value of p ⇒ K_p = 0.16 atm

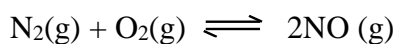
Example 13

Determine K_c for the reaction $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$ from the following information (at 298°K)

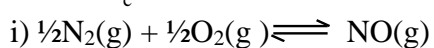
$$K_c = 2.4 \times 10^{30} \text{ for } 2NO(g) \rightleftharpoons N_2(g) + O_2(g) ;$$

$$K_c''' = 1.4 \text{ for } NO(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$$

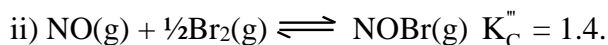
Solution



$$K_c' = \frac{1}{K_c} = \frac{1}{2.4 \times 10^{30}}$$



$$K_c'' = \sqrt{K_c'} = \sqrt{\frac{1}{2.4} \times 10^{-30}} = 0.6455 \times 10^{-15}$$

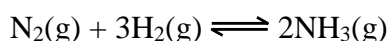


(i) + (ii) gives the net reaction:

$$\begin{aligned} \frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) + \frac{1}{2}\text{Br}_2(\text{g}) &\rightleftharpoons \text{NOBr}(\text{g}) \\ K &= \frac{[\text{NO}]}{[\text{N}_2]^{\frac{1}{2}}[\text{O}_2]^{\frac{1}{2}}} \times \frac{[\text{NOBr}]}{[\text{NO}][\text{Br}_2]^{\frac{1}{2}}} = \frac{[\text{NOBr}]}{[\text{N}_2]^{\frac{1}{2}}[\text{O}_2]^{\frac{1}{2}}[\text{Br}_2]^{\frac{1}{2}}} \\ &= K_C'' \times K_C''' = 0.6455 \times 10^{-15} \times 1.4 = 9.037 \times 10^{-16} \end{aligned}$$

Example 14

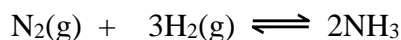
In a mixture of N_2 and H_2 initially in a mole ratio of 1:3 at 30 atm and 300°C , the percentage of ammonia by volume under the equilibrium is 17.8. Calculate the equilibrium constant (K_P) of the mixture, for the reaction



Solution

Let the initial moles of N_2 and H_2 be 1 and 3 respectively (this assumption is valid as K_P will not depend on the exact no. of moles of N_2 and H_2 . One can even start with x and $3x$).

Alternatively



Initial	1	3	0
At eqb	$1-x$	$3-3x$	$2x$

Since % by volume of a gas is same as % by mole,

$$\therefore \frac{2x}{4-2x} = 0.178$$

$$\therefore x = \frac{4 \times 0.178}{(2 + 2 \times 0.178)} = 0.302$$

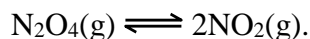
$$\therefore \text{Mole fraction of } \text{H}_2 \text{ at equilibrium} = \frac{3-3x}{4-2x} = 0.6165$$

$$\text{Mole fraction of } \text{N}_2 \text{ at equilibrium} = 1 - 0.6165 - 0.178 = 0.2055$$

$$\therefore K_P = \frac{(X_{\text{NH}_3} \times P_T)^2}{(X_{\text{N}_2} \times P_T)(X_{\text{H}_2} \times P_T)^3} = \frac{(0.178 \times 30)^2}{(0.2055 \times 30)(0.6165 \times 30)^3} = 7.31 \times 10^{-4} \text{ atm}^{-2}$$

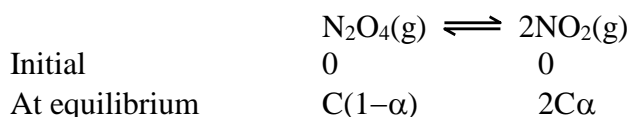
Example 15

The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm. and 348 K is 1.84 g dm^{-3} . Calculate the equilibrium constant of the reaction



Solution

Let us assume that we start with C moles of $\text{N}_2\text{O}_4(\text{g})$ initially.



Where α is the degree of dissociation of $\text{N}_2\text{O}_4(\text{g})$

$$\text{Since } = \frac{\text{Total moles at equilibrium}}{\text{Total moles initially}} = \frac{\text{Vapour density initial}}{\text{Vapour density at equilibrium}}$$

$$\text{Initial vapour density} = \frac{92}{2} = 46$$

$$\frac{C(1+\alpha)}{C} = \frac{46}{d}$$

Since vapour density and actual density are related by the equation,

$$\text{V.D.} = \frac{\rho RT}{2P} = \frac{1.84 \times 0.082 \times 348}{2} = 26.25$$

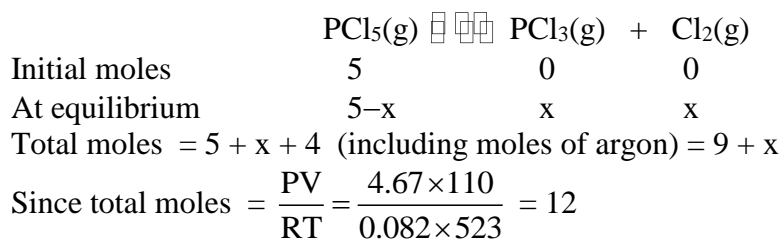
$$\therefore 1 + \alpha = \frac{46}{26.25} = 1.752 \quad \therefore \alpha = 0.752$$

$$\therefore K_p = \frac{\left(\frac{2C\alpha}{C(1+\alpha)} \times P_T \right)^2}{\frac{C(1-\alpha)}{C(1+\alpha)} \times P_T} = \frac{\left(\frac{2 \times 0.75}{1.752} \times 1 \right)^2}{\frac{0.248}{1.752} \times 1} = 5.2 \text{ atm.}$$

Example 16

In an evacuated vessel of capacity 110 litres, 4 moles of Argon and 5 moles of PCl_5 were introduced and equilibrated at a temperature of 250°C . At equilibrium, the total pressure of the mixture was found to be 4.678 atm. Calculate the degree of dissociation, of PCl_5 and K_p for the reaction $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ at this temperature.

Solution



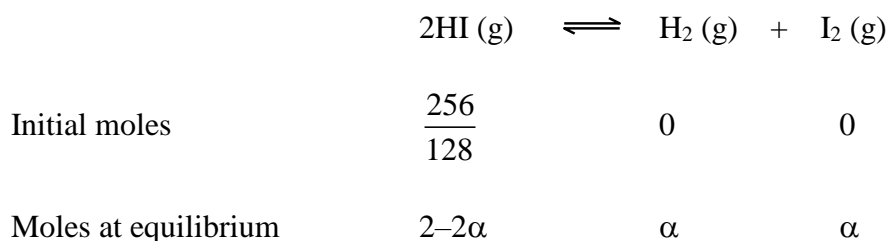
$$\therefore x = 3$$

$$\therefore \alpha = \frac{3}{5} = 0.6; K_P = \frac{\left(\frac{3}{12} \times 4.67\right)^2}{\left(\frac{2}{12} \times 4.67\right)} = 1.75$$

Example 17

256 g of HI was heated in a sealed bulb at 444°C till the equilibrium was attained. The acid was found to be 22% dissociated at equilibrium. Calculate equilibrium constants for synthesis and dissociation of HI?

Solution

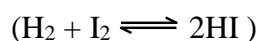


$$\text{(given } \alpha = 0.22\text{)}$$

Equilibrium constant for dissociation

$$K_C = \frac{\alpha^2}{(2-2\alpha)^2} = \frac{0.22 \times 0.22}{(2-0.44)^2} = 0.0199$$

$$\therefore \text{Equilibrium constant for synthesis} = \frac{1}{K_C} = \frac{1}{0.0199} = 50.25$$

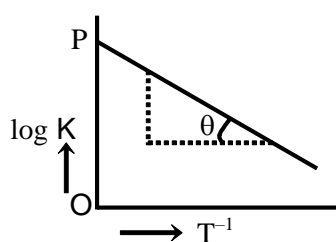


[**Note** : The equilibrium reaction considered for dissociation is $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ and not $\text{HI} \rightleftharpoons \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{I}_2$ because for synthesis, the reaction is with 1 mole each of H_2 and I_2 i.e., $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$]

Example 18

Variation of equilibrium constant K with temperature T is given by Van't Hoff equation

$$\log K = \log A - \frac{\Delta H^\circ}{2.303RT}$$



A graph between $\log K$ and T^{-1} was a straight line as shown and having $OP = 10$ and $\tan \theta = 0.5$. Calculate

- equilibrium constant at 298 K, and
- and equilibrium constant at 798 K, assuming ΔH° to be independent of temperature.

Solution

To calculate equilibrium constant, we need to know A and ΔH° , which are calculated as –

The given equation represents a straight line of slope = $\frac{-\Delta H^\circ}{2.303 R} = -\tan \theta = -0.5$

$$\therefore \Delta H^\circ = 2.303 \times 8.314 \times 0.5 = 9.574 \text{ J/mol}$$

Intercept = $\log A = OP = 10$

$$\therefore \log K = \log A - \frac{\Delta H^\circ}{2.303 RT} = 10 - \frac{9.574}{2.303 \times 8.314 \times 298}$$

$$\therefore K = 9.96 \times 10^9$$

Now, to calculate equilibrium constant at some other temperature, we will use the expression

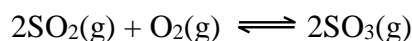
$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{K_2}{9.96 \times 10^9} = \frac{9.574}{2.303 \times 8.314} \left[\frac{500}{798 \times 298} \right]$$

$\therefore K_2$ (equilibrium constant at 798 = 9.98×10^9)

Example 19

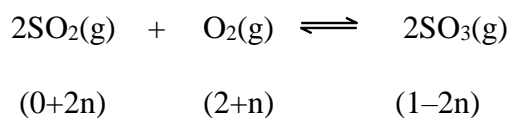
The equilibrium constant K_P of the reaction



is 900 atm^{-1} at 800°C . A mixture containing SO_3 and O_2 having initial partial pressures of 1 atm and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800°C .

Solution

It can be seen that as SO_2 is not present initially, so equilibrium cannot be established in the forward direction. Therefore it is established from reverse direction. Let n be the increase in partial pressure of O_2 . Then at equilibrium the partial pressures of SO_2 , O_2 at SO_3 are $(0+2n)$, $(2+n)$ and $(1-2n)$ in atm respectively.



$$\text{Also, } K_P = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}} = \frac{(1-2n)^2}{(0+2n)^2 (2+n)}$$

As n is small (because equilibrium constant for the reverse reaction is very small i.e., $1/900$), it can be neglected in comparison to 2 and also $1-2n$ can be taken approximately to 1.

$$\therefore 900 = \frac{1}{4n^2 \times 2}$$

Solving for n, we get $n = 0.0118$

Hence, $p_{O_2} = 2+n = 2.0118 \text{ atm}$

$$p_{SO_2} = 2n = 0.0236 \text{ atm}$$

$$p_{SO_3} = 1-2n = 1-0.0236 = 0.9764 \text{ atm}$$

Example 20

In an experiment 5 moles of HI were enclosed in a 5 litre container. At 717 K equilibrium constant for the gaseous reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ is 0.025. Calculate the equilibrium concentrations of HI, H_2 and I_2 . What is the fraction of HI that decomposes.

Solution

Let $2n$ be the number of moles of HI which is decomposed, the number of moles of H_2 and I_2 produced will be n moles each. Then molar concentrations of various species at equilibrium are –

$$[HI] = \frac{(5-2n)}{5} \text{ mol/l}, \quad [H_2] = \frac{n}{5} \text{ mol/l}, \quad [I_2] = \frac{n}{5} \text{ mol/l}$$

$$\text{Also, } K_C = \frac{[H_2][I_2]}{[HI]^2} = \frac{\frac{n}{5} \times \frac{n}{5}}{\left(\frac{5-2n}{5}\right)^2}$$

$$0.025 = \frac{n^2}{(5-2n)^2}$$

Solving for n, we get $n = 0.6$

$$\therefore [HI] = \frac{5-2 \times 0.6}{5} = \frac{3.8}{5} = 0.76 \text{ mol/l}$$

$$[\text{H}_2] = \frac{0.6}{5} = 0.12 \text{ mol / l}$$

$$[\text{I}_2] = \frac{0.6}{5} = 0.12 \text{ mol / l}$$

$$\text{Fraction of HI decomposed} = \frac{2 \times 0.6}{5} = 0.24 \text{ or } 24\%$$