# 5

CHEMICAL EQUILIBRIUM

IRREVERSIBLE REACTION

Reactions which proceed in such a way that reactants are completely converted (i. e. 100%) in to products are called irreversible reaction.

Characteristics of Irreversible Reaction :

(i) Reactions moves in one direction i.e. in forward direction only i.e. from left to right.

(ii) Products do not react together to produce reactants again i.e. no backward reaction.

(iii) Always carried out in open vessel.

(iv) In such reactions arrow ($\rightarrow$) is placed between reactant and product which shows direction of chemical change. [Reactant $\rightarrow$ Products]
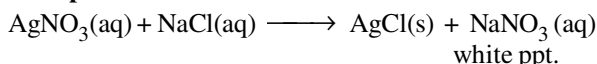
Examples of Irreversible Reaction :
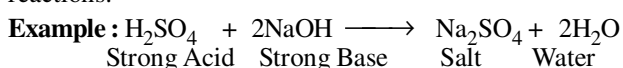
(i) **Thermal decomposition reaction :**

Example : $2\,KClO_3(s) \xrightarrow[\text{Heat}]{MnO_2} 2KCl(s) + 3O_2(g)$
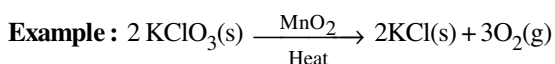
(decomposition of potassium chlorate)

(ii) **Precipitation reaction :**

Example :

$AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3\,(aq)$
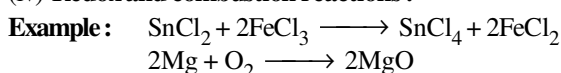<div style="text-align:right">white ppt.</div>

(iii) **Neutralisation reaction :** Reaction between strong acid and a strong base to give salt and water is called neutralisation reactions.

Example : $\underset{\text{Strong Acid}}{H_2SO_4} + \underset{\text{Strong Base}}{2NaOH} \longrightarrow \underset{\text{Salt}}{Na_2SO_4} + \underset{\text{Water}}{2H_2O}$

(iv) **Redox and combustion reactions :**

Example : $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$
$2Mg + O_2 \longrightarrow 2MgO$

REVERSIBLE REACTION

The chemical reactions which take place in both directions i.e. in the forward direction as well as in backward direction under similar conditions are called reversible reactions.

Forward direction $\Rightarrow$ Left to right ($\longrightarrow$)
Backward direction $\Rightarrow$ Right to left ($\longleftarrow$)

Reactions which proceed in both the directions and does not reach to completion are called reversible reactions.
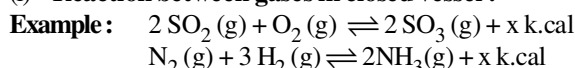
Characteristics of Reversible Reaction :

(i) In these reactions arrow ($\rightarrow$) is replaced by two half arrows ($\rightleftharpoons$) pointing the reaction in both the directions.
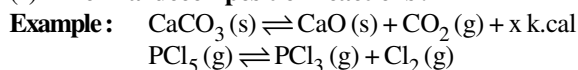
Reactants $\rightleftharpoons$ Products

(ii) Always carried out in closed vessel.

(iii) The reaction never reaches to completion.

(iv) Characterised by the establishment of equilibrium.

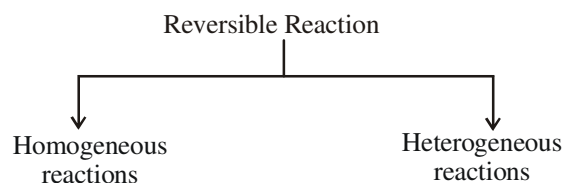(v) Reactions occurs in both the directions.

Examples of Reversible Reactions :
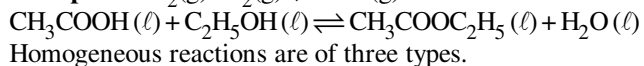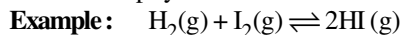
(i) **Reaction between gases in closed vessel :**

Example : $2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g) + x\text{ k.cal}$
$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2NH_3(g) + x\text{ k.cal}$

(ii) **Thermal decomposition reactions :**

Example : $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g) + x\text{ k.cal}$
$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

TYPES OF REVERSIBLE REACTIONS
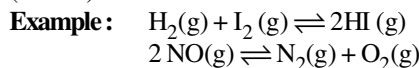
Reversible Reaction

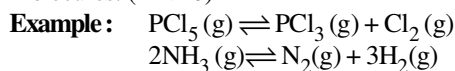Homogeneous reactions   Heterogeneous reactions

Homogeneous Reactions : The reversible reaction in which only one phase is present i.e. all the reactants and the products are in same physical state.

Example : $H_2(g) + I_2(g) \rightleftharpoons 2HI\,(g)$
$CH_3COOH\,(\ell) + C_2H_5OH\,(\ell) \rightleftharpoons CH_3COOC_2H_5\,(\ell) + H_2O\,(\ell)$

Homogeneous reactions are of three types.

(i) **First Type :** When there is no change in number of molecules ($\Delta n = 0$)

Example : $H_2(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$
$2\,NO(g) \rightleftharpoons N_2(g) + O_2(g)$

(ii) **Second Type :** When there is increase in number of molecules. ($\Delta n > 0$)

Example : $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$
$2NH_3\,(g) \rightleftharpoons N_2(g) + 3H_2(g)$

(iii) **Third Type :** When there is decrease in number of molecules. ($\Delta n < 0$)

Example : $N_2\,(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
$2SO_2\,(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
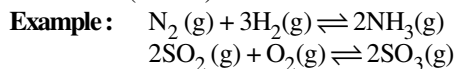
Heterogeneous Reactions : The reversible reaction in which more than one phases is present.

Example : $MgCO_3\,(s) \rightleftharpoons MgO(s) + CO_2(g)$
$3Fe\,(s) + 4\,H_2O\,(\ell) \rightleftharpoons Fe_3O_4\,(s) + 4\,H_2(g)$
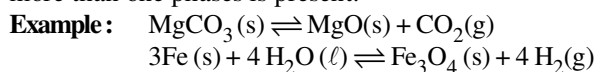
STATE OF CHEMICAL EQUILIBRIUM

It can be shown graphically.
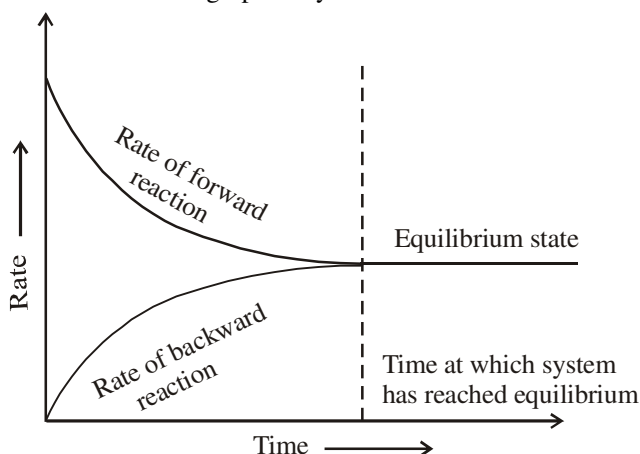
At Equilibrium state

Rate of forward reaction = Rate of backward reaction

$$R_f = R_b$$

Definition of Chemical Equilibrium : Chemical Equilibrium in a reversible reaction is a state at which both backward and forward reaction occur at the same speed.

The stage of the reversible reaction at which the concentrations of the reactants and products do not change with the time.

Characteristics of Equilibrium State : Equilibrium state can only be achieved if a reversible reaction is carried out in closed vessel. Free energy change is zero $\Delta G° = 0$.

Forward rate (R_f) = Backward rate (R_b).

Equilibrium is dynamic in nature. Chemical Equilibrium can be attained from either of the side i.e. from side of reactants or products

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

or $\quad H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
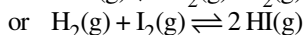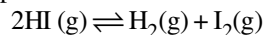
Equilibrium state can be attained in a lesser time by use of positive catalyst.

LAW OF CHEMICAL EQUILIBRIUM

Law of Mass Action : At a given temperature, the rate of reaction at a particular instant is proportional to the product of the active masses of the reactants at that instant raised to power which are numerically equal to their respective molecules in stoichiometric equation describing the reaction.

For the reaction :

$$nA + mB \rightleftharpoons zC + wD$$
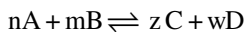
According to law of mass action

$R_f \propto [A]^n [B]^m \qquad\qquad R_b \propto [C]^z [D]^w$

$R_f = K_1 [A]^n [B]^m \qquad\quad R_b = K_2 [C]^z [D]^w$

At equilibrium : $R_f = R_b$

$K_1 [A]^n [B]^m = K_2 [C]^z [D]^w$

$$\frac{K_1}{K_2} = \frac{[C]^z [D]^w}{[A]^n [B]^m} = \frac{[Product]}{[Reactant]}$$

Finally $K_c = \dfrac{K_1}{K_2} = \dfrac{R_f}{R_b} = \dfrac{K_f}{K_b}$

EXPRESSION OF K_c :

Let 'a' moles of PCl_5 be taken in a closed vessel of volume 'v' litre. Suppose 'x' mole is dissociated at equilibrium.

	PCl_5 (g)	$\rightleftharpoons$ PCl_3(g)	+ Cl_2(g)
Initial concentration	a	0	0
At equilibrium	a – x	x	x
Active mass	$\dfrac{a-x}{v}$	$\dfrac{x}{v}$	$\dfrac{x}{v}$

According to law of mass action

$$K_c = \frac{[Product]}{[Reactant]} \;;\; K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$K_c = \frac{\dfrac{x}{v} \times \dfrac{x}{v}}{\dfrac{a-x}{v}} = \frac{x^2}{(a-x)v}$$

when a = 1, x becomes degree of dissociation

$$K_c = \frac{x^2}{(1-x)v}$$

according to ostwald dilution law $v \propto \dfrac{1}{C}$

Hence : $K_c = \dfrac{\alpha^2 C}{(1-\alpha)}$

Example 1 :

The equilibrium constant of a reaction is 20.0. At equilibrium, the rate constant of forward reaction is 10.0. Find the rate constant for backward reaction.

Sol. $K_c = 20 \quad K_f = 10, K_b = ?$

$$K_c = \frac{K_f}{K_b} \;;\; 20 = \frac{10}{K_b} \;\therefore\; K_b = \frac{10}{20} = 0.5$$

Example 2 :

At a given temperature, the equilibrium constant for the reactions : $NO\,(g) + \dfrac{1}{2} O_2\,(g) \rightleftharpoons NO_2\,(g)$ and

$2\,NO_2\,(g) \rightleftharpoons 2\,NO\,(g) + O_2\,(g)$ are K_1 and K_2 respectively. If K_1 is 4×10^{-3}, then find K_2

Sol. $NO(g) + \dfrac{1}{2} O_2(g) \rightleftharpoons NO_2(g)$

$$K_1 = \frac{[NO_2]}{[NO][O_2]^{1/2}} = 4 \times 10^{-3}$$
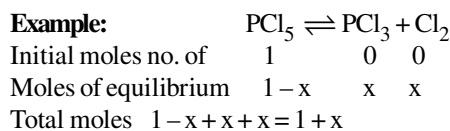
Now for reaction $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$$K_2 = \frac{[NO]^2[O_2]}{[NO_2]^2} = \frac{1}{K_1^2}$$

$$= \frac{1}{(4 \times 10^{-3})^2} = 6.25 \times 10^4$$

EQUILIBRIUM CONSTANT IN TERMS OF PRESSURE

It is denoted by K_P

$$\text{Partial pressure} = \frac{\text{no. of moles}}{\text{Total moles}} \times \text{Total pressure}$$

Example: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Initial moles no. of   1   0   0

Moles of equilibrium $1-x$ x x

Total moles $1-x+x+x = 1+x$

$$P_{PCl_5} = \frac{1-x}{1+x} \times P$$

$$P_{Cl_2} = \frac{x}{1+x} \times P \quad ; \quad P_{PCl_3} = \frac{x}{1+x} \times P$$

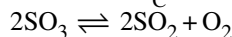$$K_P = \frac{P_{PCl_3}.P_{Cl_2}}{P_{PCl_5}}$$

Unit of equilibrium constant :

Unit of K_c = (Concentration)$^{\Delta n}$

Unit of K_p = (atm)$^{\Delta n}$

Δn = no. of moles of gaseous product

              – no. of moles of gaseous reactant

Example 3 :

The unit of K_C for the reaction

$2SO_3 \rightleftharpoons 2SO_2 + O_2$

(1) mole^2 lit^{-2} (2) mole per litre

(3) mole x litre   (4) litre per mole

Sol. (2). Unit fo K_c = $[M]^{\Delta n}$

where M = mole/litre

Δn = Number of gaseous mole of product – Number of gaseous mole of reactant

Here $\Delta n = (2+1) - 2 = 1$

$\therefore$ unit of K_c = [mole/litre]^1 = mole per litre.

SIGNIFICANCE OF EQUILIBRIUM CONSTANT

(A) High value of K_c : Denotes high concentration of the products relative to the reactants, at equilibrium

     $K_c >>> 1$ but $K_c \neq \infty$

Concentration of product > concentration of reactant

(B) Low value of K_c : Denotes high value of concentration of reactants relative to products at the equilibrium

     $K_c <<< 1$ but $K_c \neq 0$

Concentration of product < concentration of reactant

(C) Suppose there are three reaction having equilibrium constant K_1, K_2 and K_3 and $K_1 > K_2 > K_3$

Hence the order of the tendency of the reaction to proceed in forward direction (i.e. formation of product)
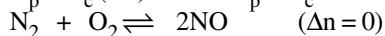
     Reaction 1 > Reaction 2 > Reaction 3

In short, $K \uparrow$, forward reaction $\uparrow$
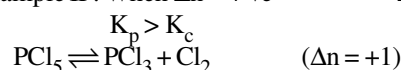
RELATION BETWEEN K_P & K_C

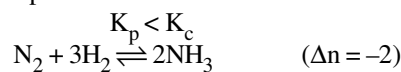 $K_P = K_C (RT)^{\Delta n}$

Example I : When $\Delta n = 0$

     $K_p = K_c (RT)^0$ $\therefore$ $K_p = K_c$

     $N_2 + O_2 \rightleftharpoons 2NO$ $(\Delta n = 0)$

Example II : When $\Delta n = +ve$ $\Delta n > 0$

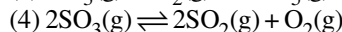 $K_p > K_c$

  $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ $(\Delta n = +1)$
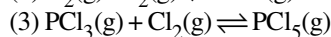
Example III : When $\Delta n = -ve$ $\Delta n < 0$

          $K_p < K_c$

  $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $(\Delta n = -2)$

Example 4 :

In which of the following reaction $K_p > K_c$

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

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

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

(4) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$
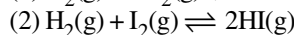
Sol. (4). Value of K_p is greater then K_c for those reaction in which $\Delta n > 0$

Here for the reaction

     $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$; $\Delta n = 3 - 2 = 1 > 0$
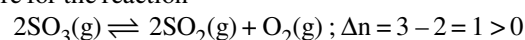
Therefore $K_p > K_c$ for this reaction

Example 5 :

At 1000K, the value of K_p for the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is 20R, then find K_c.

Sol. $K_p = 20R$ (given)

for the reaction $\Delta n = (2-1) = 1$

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

$20R = K_c (RT)^1$

$$\therefore \quad K_c = \frac{20R}{R \times 1000} = 0.02$$

STANDARD FREE ENERGY CHANGE OF A REACTION AND ITS EQUILIBRIUM CONSTANT

Let $\Delta G°$ be the difference in free energy of the reaction when all the reactants and products are in standard state (1 atm pressure and 298 K) and K_c and K_p be the thermodynamic equilibrium constant of the reaction. Both are related to each other at temperature T by following relation.

     $\Delta G° = -2.303 \, RT \log K_C$

& $\Delta G° = -2.303 \, RT \log K_p$

Equation relates equilibrium constant of a reaction to a thermochemical property.

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

here $\Delta H°$ = Standard enthalpy change

      $\Delta S°$ = Standard entropy change
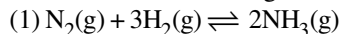
Three cases may arise :

(i) $\Delta G° = 0$ then $K_c = 1$

(ii) $\Delta G° > 0$ i.e. + ve then $K_c < 1$

In this case reverse reaction is feasible i.e. less concentration of products at equilibrium state.

(iii) $\Delta G° < 0$ i.e. –ve then $K_c > 1$

In this case forward reaction is feasible i.e. large concentration of products at equilibrium state.

In short, Free energy change Equilibrium constant Concentration of reactants and Products

$\Delta G° = 0$ $K_c = 1$ Reactants = Products

$\Delta G° > 0$ $K_c < 1$ Reactants > Products

$\Delta G° < 0$ $K_c > 1$ Reactants < Products

EQUILIBRIUM CONSTANT EXPRESSIONS FOR SOME REACTIONS

Case I :

Homogeneous gaseous equilibria when ($\Delta n = 0$)

Synthesis of hydrogen iodide

(a) Calculation of K_c : Suppose the initial concentration of H_2 and I_2 is 'a' and 'b' respectively, x is degree of dissociation and 'v' is volume in litre of container.

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

Initial conc.	a	b	0
Moles at equilibrium	a – x	b – x	2x
Active mass	$\dfrac{a-x}{v}$	$\dfrac{b-x}{v}$	$\dfrac{2x}{v}$

According to law of mass action.

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

$$K_c = \frac{[2x/v]^2}{\dfrac{a-x}{v}\dfrac{b-x}{v}} \quad ; \quad K_c = \frac{4x^2}{(a-x)(b-x)}$$

(b) Calculation of K_p : The equilibrium constant K_p, can also be calculated considering partial pressure of reactants and products at equilibrium.

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

Initial concentration   a   b   0

Moles at equilibrium   a – x   b – x   2x

Total number of moles at equilibrium

$$= (a-x) + (b-x) + 2x = (a+b)$$

Let the total pressure of the system at equilibrium be P atmosphere.

Partial pressure of H_2 $\qquad P_{H_2} = \dfrac{(a-x)}{(a+b)} P$

Partial pressure of I_2 $\qquad P_{I_2} = \dfrac{b-x}{a+b} P$

Partial pressure of HI $\qquad P_{HI} = \dfrac{2x}{a+b} P$

Therefore,

$$K_P = \frac{\left(\dfrac{2x}{a+b}\right)^2 P^2}{\dfrac{a-x}{a+b} P \times \dfrac{b-x}{a+b} P} = \frac{4x^2}{(a-x)(b-x)}$$

$$K_P = \frac{4x^2}{(a-x)(b-x)}$$

This also follows the relation $\quad K_p = K_c(RT)^{\Delta n}$

Here, $\Delta n = 0$; $K_p = K_c$

i.e. for all gaseous reaction of this type, K_p and K_c are equal and have no units.

(i) Effect of pressure : $K_c \, \alpha \, pressure^\circ$

As the equation does not include volume term, K_c is independent of pressure.

(ii) Effect of adding substances : (Reactant and products)

On adding reactant rate of forward reaction increase on adding product rate of backward reaction increase

Concentration of reactant $\uparrow$ Rate of forward reaction $\uparrow$

Concentration of product $\uparrow$ Rate of backward reaction $\uparrow$

(iii) Effect of temperature : The formation of HI from H_2 and I_2 is an exothermic reaction i.e. by increasing temperature the value of K_c decreases.

As T $\uparrow$, $K_c \downarrow$ (exothermic reaction)

Case II : Homogeneous gaseous reactions when $\Delta n > 0$

Dissociation of PCl_5

(a) Calculation of K_c : Let 'a' moles of PCl_5 be taken in a closed vessel of volume 'v' litre. Suppose 'x' mole is dissociated at equilibrium.

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

Initial concentration	a	0	0
At equilibrium	a – x	x	x
Active mass	$\dfrac{a-x}{v}$	$\dfrac{x}{v}$	$\dfrac{x}{v}$

According to law of mass action

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

$$K_c = \frac{\dfrac{x}{v} \times \dfrac{x}{v}}{\dfrac{a-x}{v}} = \frac{x^2}{(a-x)v}$$

when a = 1, x becomes degree of dissociation

$$K_c = \frac{x^2}{(1-x)v}$$

(b) Calculation of K_p : Let the total pressure at equilibrium be P. Then total number of moles at equilibrium

$$= (a-x) + x + x = a + x$$

The partial pressure of each reactant and product

$$p_{PCl_5} = \frac{a-x}{a+x} P$$

$$p_{Cl_2} = \frac{x}{a+x} P$$

$$p_{PCl_3} = \frac{x}{a+x} P$$

Applying law of mass action

$$K_P = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{\dfrac{x}{a+x} P \times \dfrac{x}{a+x} P}{\dfrac{a-x}{a+x} P}$$

$$K_p = \frac{x^2\,P}{(a-x)(a+x)}$$

when $a = 1$, $K_p = \dfrac{x^2 P}{1 - x^2}$

(i) Effect of pressure :

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

Suppose $x <<< 1$ then $1 - x^2 = 1$

$$K_p = x^2 P$$

$$x^2 \propto \frac{1}{P}$$

$$x \propto \frac{1}{\sqrt{P}} \quad P\downarrow, x\uparrow$$

Degree of dissociation of PCl_5 is inversely proportional to square root of pressure so decrease in pressure increase dissociation of PCl_5

(ii) Effect of concentration :–

Concentration of $PCl_5 \uparrow$ Rate of forward reaction $\uparrow$
Concentration of PCl_3 & $Cl_2 \uparrow$ Rate of backward reaction $\uparrow$
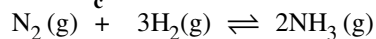
(iii) Effect of temperature : The dissociation of PCl_5 is endothermic reaction. The value of equilibrium constant increase with increase in temperature

$$K \propto T \quad \text{As } T\uparrow, K\uparrow$$

Case III : Homogeneous gaseous reaction $\Delta n < 0$

Synthesis of Ammonia

(a) Calculation of K_c :

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

Initial conc.　　a　　　　　　b　　　　　　0

Moles at eq. $a - x$　　　$b - 3x$　　　$2x$

Active mass $\dfrac{a - x}{v}$　　　$\dfrac{b - 3x}{v}$　　　$\dfrac{2x}{v}$

Applying law of mass action

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

$$K_c = \frac{[2x/v]^2}{\dfrac{a-x}{v}\;\dfrac{b-3x}{v}^{\,3}}$$

$$K_c = \frac{4x^2/v^2}{\dfrac{(a-x)}{v}\;\dfrac{b-3x}{v}^{\,3}}$$

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

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

If $x <<< 1$ then $(1-x)^4 = 1$

$$K_c = \frac{4x^2 v^2}{27} \;;\; x^2 \propto \frac{1}{v^2} \;;\; x \propto \frac{1}{v^2}$$

(b) Calculation of K_p :

Let total pressure at equilibrium be P.

Total no. of moles at equilibrium

$$= (a-x) + (b-3x) + 2x = (a+b-2x)$$

$$p_{NH_3} = \frac{2x}{(a+b-2x)} \times P$$

$$p_{N_2} = \frac{a-x}{(a+b-2x)} \times P$$

$$p_{H_2} = \frac{b-3x}{(a+b-2x)} \times P$$

$$K_p = \frac{[p_{NH_3}]^2}{[p_{N_2}][p_{H_2}]^3} = \frac{[p_{NH_3}]^2}{[p_{N_2}][p_{H_2}]^3}$$

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

$$K_p = \frac{16\,x^2(2-x)^2}{27(1-x)^4 P^2}$$

Suppose $x <<< 1$ then $(1-x)^4 = 1$; $(2-x)^2 = 4$

$$K_p = \frac{64x^2}{27P^2}$$

$$x^2 \propto P^2$$

$$x \propto P$$

(i) Effect of pressure : With increase in pressure the volume term decrease therefore x increase.

$$P\uparrow \quad V\downarrow \quad x\uparrow$$

(ii) Effect of temperature : On increasing temperature value of equilibrium constant decreases.

$$T\uparrow \quad K\downarrow \qquad \text{exothermic reaction}$$

Case IV : Homogeneous liquid system :

Formation of ethyl acetate

$$CH_3COOH\,(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5\,(\ell) + H_2O\,(\ell)$$
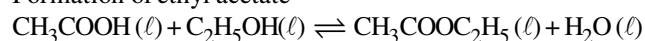
Initial conc.　　a　　　　b　　　　0　　　　0

Moles at eq.

　　$a - x$　　　$b - x$　　　x　　　x

Active mass

$\dfrac{a-x}{v}$　　　$\dfrac{b-x}{v}$　　　$\dfrac{x}{v}$　　　$\dfrac{x}{v}$

Applying law of mass action

Here V = total volume

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

$$= \frac{[x/v] \times [[x/v]}{\dfrac{a-x}{v} \times \dfrac{b-x}{v}}$$

$$K_c = \frac{x^2}{(a-x)(b-x)}$$

If $a = b = 1$ then $K_c = \frac{x^2}{(1-x)^2}$

This does not involve volume term thus K_c is not affected by change in volume e $K_c \propto V^\circ$

Case V : Heterogeneous Equilibrium

The decomposition of solid $NaHCO_3$ to produce solid Na_2CO_3, CO_2 gas and H_2O

$2\,NaHCO_3\,(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$

Applying law of mass action

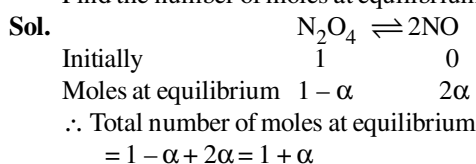$$K_c' = \frac{[Na_2CO_3][H_2O][CO_2]}{[NaHCO_3]^2}$$

It involves two pure solids, Na_2CO_3 and $NaHCO_3$. It is customary not to include concentration of pure solid in equilibrium expression.

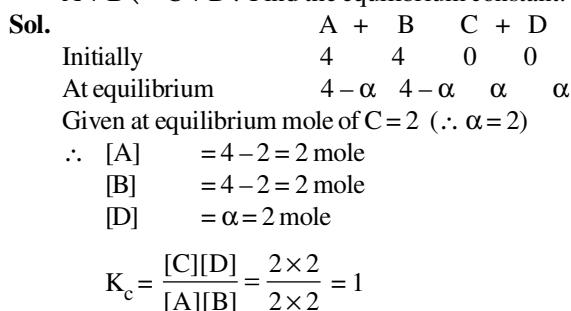$$\frac{K_c'[NaHCO_3]^2}{[Na_2CO_3]} = [CO_2]\,[H_2O]$$

$$K_c = [CO_2]\,[H_2O]$$

Example 6 :

For the reaction $N_2O_4 \rightleftharpoons 2NO$, degree of dissociation is α. Find the number of moles at equilibrium.

Sol. $N_2O_4 \rightleftharpoons 2NO$

Initially   1   0

Moles at equilibrium $1 - \alpha$ 2α

$\therefore$ Total number of moles at equilibrium

$= 1 - \alpha + 2\alpha = 1 + \alpha$

Example 7 :

4 mole of A are mixed with 4 mole of B, when 2 mole of C are formed at equilibrium according to the reaction,

$A + B \rightleftharpoons C + D$. Find the equilibrium constant.

Sol.   A + B   C + D

Initially   4   4   0   0

At equilibrium $4-\alpha$ $4-\alpha$ α α

Given at equilibrium mole of $C = 2$ $(\therefore \alpha = 2)$

$\therefore$ $[A]$ $= 4 - 2 = 2$ mole

      $[B]$ $= 4 - 2 = 2$ mole

      $[D]$ $= \alpha = 2$ mole

$$K_c = \frac{[C][D]}{[A][B]} = \frac{2 \times 2}{2 \times 2} = 1$$

LECHATELIER'S PRINCIPLE

According to this principle, "If a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shift in a direction that tends to undo the effect of the change".

(A) **Effect of change in concentration :** In a chemical equilibrium, increasing the concentration of the reactants result in shifting the equilibrium in favour of products (i.e. equilibrium shift in forward direction). Increasing concentration of the products results in shifting the equilibrium in favour of reactants (i.e in the backward direction).

| Concentration	Equilibrium shift
Concentration of reactant $\uparrow$	Forward direction
Concentration of product $\uparrow$	Backward direction

(B) **Effect of change in pressure :** According to lechatelier's principal if the pressure is increased reaction will take place in that direction, which will bring lowering of pressure or lowering in number of mole.

(i) Increase of pressure shifts the equilibrium in that direction where number of moles decreases. $(\Delta n < 0)$

eg. $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta n = 2 - 4 = -2 < 0$
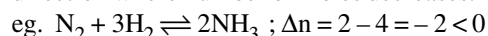
i.e. on $\uparrow$ pressure   equilibrium shift in forward direction.

(ii) Decrease of pressure shifts the equilibrium in that direction where number of mole increase. $(\Delta n > 0)$

eg. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ $\Delta n = 2 - 1 = +\,ve$
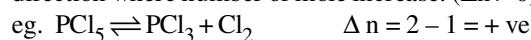
i.e. $\downarrow$ in pressure   equilibrium shift in forward direction

(iii) Change of pressure has no effect if $\Delta n = 0$

eg. $H_2 + I_2 \rightleftharpoons 2HI$ $\Delta n = 2 - 2 = 0$

(C) **Change in temperature :**

(i) **For endothermic reaction :** If we increase the temperature equilibrium shift in forward direction which proceed with absorption of heat.

(ii) **For exothermic reaction :** If we increased the temperature the equilibrium shifts in backward direction which proceed with evolution of the heat.

(D) **Role of Catalyst :** Positive catalyst increase the rate of both the forward and backward reaction equally so the equilibrium will be attained in less time. Negative catalyst decrease the rate of both forward and backward reaction so equilibrium will be attained in more time.

Application of Le Chatelier principal on physical equilibria:

(A) **Melting of Ice :**

$$H_2O\,(s) \quad \overset{0^\circ C}{\rightleftharpoons} \quad H_2O\,(\ell)$$
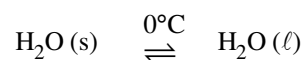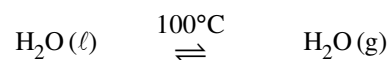
Ice   Water

(More volume)   (Less volume)

With increase in pressure melting point of ice is decreased and equilibrium will be shifted in a direction of less volume.

(B) **Vapourisation of liquid :**

$$H_2O\,(\ell) \quad \overset{100^\circ C}{\rightleftharpoons} \quad H_2O\,(g)$$

Water   Vapour

(less volume)   (more volume)

Vaporisation of liquid is endothermic process in the nature i.e. the evaporation of liquid in to its vapour is completed by absorption of heat so rise of temperature will favour vaporisation and equilibrium is shifted in forward direction. On the other hand on increasing the pressure the equilibrium will be shifted in direction of less volume means water cannot be converted in to vapour and boiling point increases.

On $\uparrow$ temperature   Vaporisation $\uparrow$ forward shift

On $\uparrow$ pressure   B.P $\uparrow$ Backward shift

(C) Melting of Sulphur :

Sulphur (s) $\rightleftharpoons$ sulphur (ℓ)
Less volume   More volume
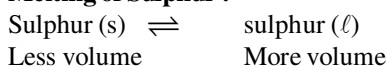
On increasing pressure the equilibrium will shift towards less volume, means solid will be not converted in to liquid, thus melting point of sulphur increases.

CALCULATION OF DEGREE OF DISSOCIATION BY DENSITY MEASUREMENT
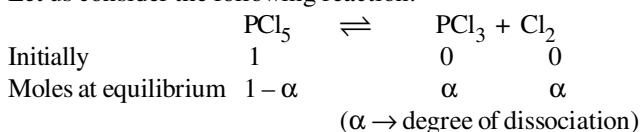
Those type of reactions in which there is change in number of moles after dissociation the extent of dissociation can be determined by vapour density measurement.

Let us consider the following reaction.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initially   1   0   0

Moles at equilibrium $1-\alpha$ α α

                  ($\alpha \rightarrow$ degree of dissociation)

Total number of moles at equilibrium

$$= (1-\alpha) + \alpha + \alpha = (1+\alpha)$$

Now, 'V' is the volume occupied by 1 mole of PCl_5 which have vapour density 'D' before dissociation and after dissociation is 'd'. So under same conditions, the volume occupied by $(1+\alpha)$ moles at equilibrium will be $(1+\alpha)$ V litre.

Since, Density $\propto \dfrac{1}{\text{Volume}}$

Therefore, $D \propto \dfrac{1}{V}$

$$d \propto \dfrac{1}{(1+\alpha)V}$$

or $\dfrac{D}{d} = 1+\alpha$ or $\alpha = \dfrac{D-d}{d}$

Note : When one mole of reactant on dissociation gives 'n' moles of gaseous products the above equation takes in the form of.

$$\alpha = \dfrac{D-d}{(n-1)d}$$

Example 8 :

At 250°C the vapour density of PCl_5 is 100 calculate the degree of dissociation at this temperature.
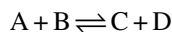
Sol. D for $PCl_5 = \dfrac{\text{Molecular mass}}{2} = \dfrac{208.5}{2} = 104.25$

d for $PCl_5 = 100$

$\alpha = \dfrac{D-d}{d} = \dfrac{104.25-100}{100} = 0.0425$

REACTION QUOTIENT AND EQUILIBRIUM CONSTANT

Consider the following reversible reaction

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

The reaction quotient (Q_c) is the ratio of the product of active masses of the products and product of active masses of the reactants.

$\therefore$ $Q_c = \dfrac{[C][D]}{[A][B]}$

The concentration are not necessarily equilibrium concentration.

    [At equilibrium $Q_c = K_c$]

Case I :

If $Q_c < K_c$ then : [Reactants] > [Products]
then the system is not at equilibrium

The value of $\dfrac{[\text{Product}]}{[\text{Reactant}]}$ is small.

$\therefore$ For establishment of equilibrium the reaction will go in forward direction. [Reactants $\rightarrow$ Products]

Case II :

If $Q_c = K_c$ then : The system is at equilibrium and the concentration of the species C, D, B, A are at equilibrium.

Case III : If $Q_c > K_c$ then : [Products] > [Reactants]
The system is not at equilibrium.

The value of $\dfrac{[\text{Product}]}{[\text{Reactant}]}$ is large

$\therefore$ For establishment of equilibrium the reaction will go in backward direction [Products $\rightarrow$ Reactants]

ADDITIONAL EXAMPLES

Example 1 :

In which case does the reaction go farthest to completion : K=1 ; K = 10^{10} ; K = 10^{-10} and why ?

Sol. The ratio $\dfrac{[\text{Product}]}{[\text{Reactant}]}$ is maximum when K = 10^{10} and thus reaction goes farthest to completion when K = 10^{10}

Example 2 :

The equilibrium constant K_c for $A_{(g)} \rightleftharpoons B_{(g)}$ is 1.1. Which gas has a molar concentration greater than 1 ?

Sol. For $A_{(g)} \rightleftharpoons B_{(g)}$; $K_c = \dfrac{[B]}{[A]} = 1.1$

$\Rightarrow$ [B] > [A]. If [B] = 1 ; [A] = 0.91

Case I $0.91 < [A] \leq 1$ Only [B] > 1
Case II   [A] > 1   Both [A] and [B] > 1

Example 3 :

0.1 mole of $N_2O_{4(g)}$ was sealed in a tube under atmospheric conditions at 25°C. Calculate the number of mole of $NO_{2(g)}$ present, if the equilibrium $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$, ($K_p = 0.14$) is reached after some time.

Sol. $N_2O_4 \rightleftharpoons 2NO_2$
    0.1   0
    $(0.1-\alpha)$ 2α

$$K_p = \frac{(2\alpha)^2}{(0.1-\alpha)} \times \frac{P}{0.1+\alpha} \quad ^1$$

or $K_p = \dfrac{40\alpha^2}{(0.1-\alpha)}$ or $\dfrac{40\alpha^2}{(0.1-\alpha)} = 0.14$

$\therefore \alpha = 0.017$ $\therefore NO_2 = 0.017 \times 2 = 0.034$ mole

Example 4 :

What concentration of CO_2 be in equilibrium with 2.5×10^{-2} mol litre^{-1} of CO at 100° C for the reaction

$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$; $K_c = 5.0$

Sol. $K_c = \dfrac{[CO_2]}{[CO]}$

$\therefore 5 = \dfrac{[CO_2]}{2.5 \times 10^{-2}}$

$\therefore [CO_2]$ at equilibrium
$= 2.5 \times 10^{-2} \times 5 = 12.5 \times 10^{-2}$ mol litre^{-1}

Example 5 :

What is the % dissociation of H_2S if 1 mole of H_2S is introduced into a 1.10 litre vessel at 1000 K ? K_c for the reaction :
$2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$ is 1×10^{-6}

Sol. $\qquad\qquad\qquad 2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$

Mole before dissociation $\quad 1 \qquad\qquad 0 \qquad\quad 0$

Mole after dissociation $\quad (1-\alpha) \qquad \alpha \qquad \dfrac{\alpha}{2}$
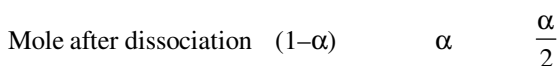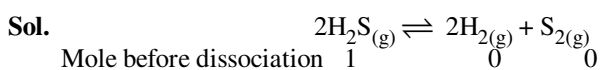
Where α is degree of dissociation of H_2S
Volume of container = 1.10 litre

$\therefore K_c = \dfrac{[H_2]^2 [S_2]}{[H_2S]^2} = \dfrac{\dfrac{\alpha}{1.1}^2 \dfrac{\alpha}{2 \times 1.1}}{\dfrac{1-\alpha}{1.1}^2} = 1 \times 10^{-6}$

Assuming $1 - \alpha = 1$ since α is small because $K_c = 10^{-6}$

$\therefore \dfrac{\alpha^3}{2(1.1)} = 10^{-6}$

$\alpha = 1.3 \times 10^{-2} = 1.3\%$

Example 6 :

In the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the equilibrium pressure is 12 atm. If 50% of CO_2 reacts, calculate K_P.

Sol. $\qquad\qquad C(s) \quad + \quad CO_2(g) \rightleftharpoons 2CO(g)$

Gaseous mole $\qquad\qquad\qquad 1 \qquad\qquad 0$
before dissociation $\quad -$

Gaseous mole after dissociation $\quad 1 - \dfrac{50}{100} \qquad \dfrac{2 \times 50}{100}$

$\qquad\qquad\qquad\qquad\qquad 0.5 \qquad\qquad 1$
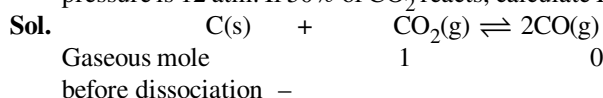
$\therefore$ Total mole = 1.5
Total pressure given at equilibrium = 12 atm

Partial pressure of $CO = \dfrac{1}{1.5} \times 12 = 8$

Partial pressure of $CO_2 = \dfrac{0.5}{1.5} \times 12 = 4$

$K_p = \dfrac{P_{CO}^2}{P_{CO_2}} = \dfrac{(8)^2}{4} = 16$ atm

QUESTION BANK

EXERCISE - 1

Q.1 Amongst the following chemical reactions the irreversible reaction is –
(A) $H_2 + I_2 \rightleftharpoons HI$
(B) $AgNO_3 + NaCl \rightleftharpoons AgCl + NaNO_3$
(C) $CaCO_3 \rightleftharpoons CaO + CO_2$
(D) $O_2 + 2SO_2 \rightleftharpoons 2SO_3$

Q.2 Which of the following conditions represents an equilibrium
(A) Freezing of ice in a open vessel, temperature of ice is constant
(B) Few drops of water is present along with air in a balloon, temperature of balloon is constant
(C) Water is boiling in an open vessel over stove, temperature of water is constant
(D) All the statements (A), (B) and (C) are correct for the equilibrium

Q.3 If a system is at equilibrium the rate of forward to the reverse reaction is –
(A) Less   (B) Equal
(C) High   (D) At equilibrium

Q.4 Which is false –
(A) The greater the concentration of the substances involved in a reaction, the lower the speed of the reaction
(B) The point of dynamic equilibrium is reached when the reaction rate in one direction just balances the reaction rate in the opposite direction
(C) The dissociation of weak electrolyte is a reversible reaction
(D) The presence of free ions facilitates chemical changes

Q.5 The equilibrium constant in a reversible reaction at a given temperature –
(A) Depends on the initial concentration of the reactants
(B) Depends on the concentration of the products at equilibrium
(C) Does not depend on the initial concentrations
(D) It is not characteristic of the reaction

Q.6 Pure ammonia is placed in a vessel at temperature where its dissociation constant (α) is appreciable. At equilibrium
(A) K_p does not change significantly with pressure
(B) α does not change with pressure
(C) Concentration of NH_3 does not change with pressure
(D) Concentration of H_2 is less than that of N_2

Q.7 Unit of equilibrium constant for the reversible reaction $H_2 + I_2 \rightleftharpoons 2HI$ is –
(A) mol^{-1} litre   (B) mol^{-2} litre
(C) mol $litre^{-1}$ (D) None of these

Q.8 In a reaction $A + B \rightleftharpoons C + D$, the concentrations of A, B, C and D (in moles/litre) are 0.5, 0.8, 0.4 and 1.0 respectively. The equilibrium constant is –
(A) 0.1   (B) 1.0
(C) 10   (D) ∞

Q.9 If in the reaction $N_2O_4 = 2NO_2, \alpha$ is that part of N_2O_4 which dissociates, then the number of moles at equilibrium will be –
(A) 3   (B) 1
(C) $(1-\alpha)^2$ (D) $(1+\alpha)$

Q.10 In a chemical equilibrium, the rate constant of the backward reaction is 7.5×10^{-4} and the equilibrium constant is 1.5. So the rate constant of the forward reaction is
(A) 5×10^{-4} (B) 2×10^{-3}
(C) 1.125×10^{-3} (D) 9.0×10^{-4}

Q.11 The equilibrium concentration of X, Y and YX_2 are 4, 2 and 2 moles respectively for the equilibrium $2X + Y \rightleftharpoons YX_2$. The value of K_c is
(A) 0.625   (B) 0.0625
(C) 6.25   (D) 0.00625

Q.12 When 3 mole of A and 1 mole of B are mixed in 1 litre vessel the following reaction takes place $A(g) + B(g) \rightleftharpoons 2C(g)$. 1.5 moles of C are formed. The equilibrium constant for the reaction is –
(A) 0.12   (B) 0.25
(C) 0.50   (D) 4.0

Q.13 In a chemical reaction equilibrium is established when –
(A) Opposing reaction ceases
(B) Concentration of reactants and products are equal
(C) Velocity of opposing reaction is the same as that of forward reaction
(D) Reaction ceases to generate heat

Q.14 For a reaction $H_2 + I_2 \rightleftharpoons 2HI$ at 721K, the value of equilibrium constant is 50. If 0.5 mols each of H_2 and I_2 is added to the system the value of equilibrium constant will be –
(A) 40   (B) 60
(C) 50   (D) 30

Q.15 In equilibrium
$$CH_3COOH + H_2O \rightleftharpoons CH_3COO + H_3^+O$$
The equilibrium constant may change when
(A) CH_3COO^- are added   (B) CH_3COOH is added
(C) Catalyst is added   (D) Mixture is heated

Q.16 The value of K_p for the following reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ is 1.2×10^{-2} at 106.5°C. The value of K_c for this reaction is –
(A) 1.2×10^{-2} (B) $< 1.2 \times 10^{-2}$
(C) 83   (D) $> 1.2 \times 10^{-2}$

Q.17 In the manufacture of ammonia by Haber's process,
$$N_2(g) + 3H_2 \rightleftharpoons 2NH_{3(g)} + 92.3kJ ,$$
which of the following conditions is unfavourable
(A) Increasing the temperature
(B) Increasing the pressure
(C) Reducing the temperature
(D) Removing ammonia as it is formed

Q.18 $NH_4COONH_{2(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$ if equilibrium pressure is 3 atm for the above reaction K_p for the reaction is –

(A) 4   (B) 27

(C) 4/27   (D) 1/27

Q.19 In a reversible reaction, the catalyst –

(A) Increases the activation energy of the backward reaction

(B) Increases the activation energy of the forward reaction

(C) Decreases the activation energy of both, forward and backward reaction

(D) Decreases the activation energy of forward reaction

Q.20 Which of the following reactions proceed at low pressure

(A) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (B) $H_2 + I_2 \rightleftharpoons 2HI$

(C) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (D) $N_2 + O_2 \rightleftharpoons 2NO$

Q.21 According to Le-chatelier principle, if heat is given to solid-liquid system, then –

(A) Quantity of solid will reduce

(B) Quantity of liquid will reduce

(C) Increase in temperature

(D) Decrease in temperature

Q.22 Following gaseous reaction is undergoing in a vessel

$C_2H_4 + H_2 \rightleftharpoons C_2H_6$; $\Delta H = -32.7$ Kcal

Which will increase the equilibrium concentration of C_2H_6

(A) Increase of temperature

(B) By reducing temperature

(C) By removing some hydrogen

(D) By adding some C_2H_6

Q.23 The endothermic reaction $(M + N \rightleftharpoons P)$ is allowed to attain an equilibrium at 25°. Formation of P can be increased by–

(A) Raising temperature

(B) Lowering temperature

(C) Keeping temperature constant

(D) Decreasing the concentration of M and N

Q.24 The equilibrium $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed container and an inert gas helium is introduced which of the following statement is correct

(A) More chlorine is formed

(B) Concentration of SO_2 is reduced

(C) More SO_2Cl_2 is formed

(D) Concentration of SO_2Cl_2, SO_2 and Cl_2 does not change

Q.25 For the reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, true condition is –

(A) $K_p = K_c$ (B) $K_p > K_c$

(C) $K_p < K_c$ (D) $K_c = 0$ but $K_p \neq 0$

Q.26 The following equilibrium exists in aqueous solution $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$. If dilute HCl is added without a change in temperature, then the

(A) Concentration of CH_3COO^- will increase

(B) Concentration of CH_3COO^- will decrease

(C) Equilibrium constant will increase

(D) Equilibrium constant will decrease

Q.27 120gm of urea are present in 5 litre solution, the active mass of urea is –

(A) 0.2   (B) 0.06

(C) 0.4   (D) 0.08

Q.28 At a given temperature, the equilibrium constant for reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. is 2.4×10^{-3}. At the same temperature, the equilibrium constant for reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ is –

(A) 2.4×10^{-3} (B) -2.4×10^{-3}

(C) 4.2×10^2 (D) 4.8×10^{-2}

Q.29 In which one of the following gaseous equilibria K_p is less than K_c

(A) $N_2O_4 \rightleftharpoons 2NO_2$ (B) $2HI \rightleftharpoons H_2 + I_2$

(C) $2SO_2 + O_2 \rightleftharpoons 2SO_3$ (D) $N_2 + O_2 \rightleftharpoons 2NO$

Q.30 In which of the following reaction $K_p > K_c$

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

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

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

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

Q.31 For the following gaseous reaction $H_2 + I_2 \rightleftharpoons 2HI$, the equilibrium constant –

(A) $K_p > K_c$ (B) $K_p < K_c$

(C) $K_p = K_c$ (D) $K_p = 1/K_c$

Q.32 The volume of a closed reaction vessel in which the equilibrium :

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

sets is halved, Now -

(A) The rates of forward and backward reactions will remain the same.

(B) The equilibrium will not shift.

(C) The equilibrium will shift to the right.

(D) The rate of forward reaction will become double that of reverse reaction and the equilibrium will shift to the right.

Q.33 The equilibrium constant for the reaction

$H_2(g) + S(s) \rightleftharpoons H_2S(g)$; is 18.5 at 935 K and 9.25 at 1000 K respectively. The change in enthalpy of the reaction will be -

(A) zero   (B) + ve

(C) – ve   (D) cannot be predicted

Q.34 The equilibrium constant K_C for the decomposition of PCl_5 is 0.0625 mole l^{-1} at 300ºC. What will be the value of K_P –

(A) 2.936 atm   (B) 1.936 atm

(C) 3.336 atm   (D) 5.123 atm

Q.35 The vapour density of N_2O_4 at a certain temperature is 30. The percentage dissociation of N_2O_4 at this temperature is-

(A) 55.5%   (B) 60%

(C) 70%   (D) 53.3%

Q.36 In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ the concentration of H_2, I_2 and HI at equilibrium are 8.0, 3.0 and 28.0 moles per litre respectively. What will be the equilibrium constant–

(A) 30.61   (B) 32.66

(C) 29.40   (D) 20.90

Q.37 A two litre flask contains 1.4 gm nitrogen and 1.0 gm hydrogen. The ratio of active mass of nitrogen and hydrogen would be -
(A) 1 : 3   (B) 1 : 5
(C) 1.4 : 1   (D) 1 : 10

Q.38 In the concentration of B is increased at fixed temperature, in the reaction $A + 2B \rightleftharpoons C + 3D$, the equilibrium constant of backward reaction –
(A) decreases
(B) increases
(C) remains unchanged
(D) first increases then decreases

Q.39 7.0g, N_2, 8.0g O_2 and 34.0g NH_3 are present in one-litre container. The active mass in g mole/litre will be respectively
(A) 0.25, 0.25, 2   (B) 0.5, 0.5, 5
(C) 1.0, 1.0, 2.0   (D) 2.0, 2.0, 16.0

Q.40 In reaction $A + 2B \rightleftharpoons 2C + D$, if concentration of A is increased four times and concentration of B is decreased to half, the rate of reaction will –
(A) become double   (B) become half
(C) remain unchanged   (D) become 1/4

Q.1 In the reaction, $A + B \rightleftharpoons C + D$, the equilibrium constant K is determined by taking 1 mole of A and 1 mole of B as initial amounts. If 2 moles of A and 3 moles of B are taken, then the equilibrium constant will be
(A) Two times
(B) Three times
(C) Six times
(D) Unchanged

Q.2 $C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g)$
What will be the effect of pressure on the above equilibrium process?
(A) Remains unaffected
(B) It will go in backward direction
(C) It will go in forward direction
(D) Unpredictable

Q.3 If pressure is increased in the following reaction
$N_2 + 3H_2 \rightleftharpoons 2NH_3$, $\Delta H = -22.4$ kcal then the equilibrium will
(A) be stable
(B) Shift towards left side
(C) Shift towards right side
(D) Shift first towards left side, then right side

Q.4 20% part of N_2O_4 is dissociated in NO_2 at 1 atmospheric pressure, then find the value of K_p.
(A) 0.27
(B) 0.24
(C) 0.38
(D) 0.17

Q.5 Vaporization of 1 mole of PCl_5 is done in a one-litre container. If 0.2 mole Cl_2 is formed at equilibrium, then what will be the value of equilibrium constant.
(A) 0.2
(B) 1.5
(C) 0.5
(D) 1.0

Q.6 For the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the partial pressures of CO_2 and CO are 2.0 and 4.0 atm respectively at equilibrium. Find the K_P for the reaction
(A) 2
(B) 8
(C) 1
(D) 4

Q.7 Consider the reaction : $XY_2(g) \rightleftharpoons XY(g) + Y(g)$
If the initial pressure of XY_2 is 500 torr and equilibrium pressure is 600 torr, the equilibrium constant K_p in terms of torr is –
(A) 20
(B) 50
(C) 25
(D) 100

Q.8 For a chemical reaction ;
$A(g) + B(\ell) \rightleftharpoons D(g) + E(g)$
Hypothetically at what temperature, $K_p = K_c$
(when, $R = 0.08$ ℓ-atm/mole-K)
(A) T = 0 K
(B) T = 1 K
(C) T = 12.5 K
(D) T = 273 K

Q.9 5 mole of NH_4HS (s) start to decompose at a particular temperature in a closed vessel. If pressure of $NH_3(g)$ in the vessel is 2 atm then K_p for the reaction :
$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ will be –
(A) 2
(B) 4
(C) 0.4
(D) 0.8

Q.10 $S(s) + O_2(g) \rightleftharpoons SO_2(g)$, 25% of O_2 converts to SO_2. If the pressure at equilibrium is 12 atm, K_p for the given reaction will be –
(A) 3
(B) 1
(C) 1/3
(D) None of these

Q.11 PCl_5 is dissociating 50% at 250°C at a total pressure of P atm. If equilibrium constant is K_p then which of the following relation is numerically correct –
(A) $K_p = 3P$
(B) $P = 3K_p$
(C) $P = \dfrac{2K_p}{3}$
(D) $K_p = \dfrac{2P}{3}$

Q.12 For the reaction, $A + B \rightleftharpoons 3C$ at 25°C, a 3L vessel contains 1, 2, 4 mole of A, B and C respectively. Predict the direction of reaction.
(A) Forward if K_C for the reaction is 14
(B) Backward if K_C for the reaction is 14
(C) Forward if K_C for the reaction is 8
(D) Backward if K_C for the reaction is 9

Q.13 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
When 46g of I_2 and 1g of H_2 are heated at equilibrium at 450ºC, the equilibrium mixture contained 1.9g of I_2. How many moles of I_2 and HI are present at equilibrium –
(A) 0.0075 & 0.147 moles
(B) 0.0050 & 0.147 moles
(C) 0.0075 & 0.347 moles
(D) 0.0052 & 0.347 moles

Q.14 One mole of ammonium carbamate dissociate as shown below at 500 K.
$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$
If the pressure exerted by the released gases is 3.0 atm, the value of K_P is -
(A) 7 atm
(B) 3 atm
(C) 4 atm
(D) 8 atm

Q.15 At 700 K, the equilibrium constant K_P, for the reaction
$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$
is 1.8×10^{-3} kPa. What is the numerical value of K_C for this reaction at the same temperature –
(A) 3.09×10^{-7} mole litre^{-1}
(B) 9.03×10^{-7} mole litre^{-1}
(C) 5.05×10^{-9} mole litre^{-1}
(D) 5.05×10^{-5} mole litre^{-1}

Q.16 K_P for the reaction $A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g)$; is 0.05 atm. What will be its K_C at 1000 K in terms of R –
(A) $\dfrac{5 \times 10^{-5}}{R}$
(B) $\dfrac{R}{5 \times 10^{-5}}$
(C) $5 \times 10^{-5} R$
(D) None of these

Q.17 If PCl_5 is 80% dissociated at 523 K. Calculate the vapour density of the equilibrium mixture at 523 K –
(A) 75.9
(B) 57.9
(C) 97.5
(D) 95.7

Q.18 For a gas reaction, $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$, the partial pressures of H_2 and N_2 are 0.4 and 0.8 atmosphere, respectively. The total pressure of the entire system is 2.8 atmosphere. What will be the value of K_P if all the concentration are given in atmosphere ?
(A) 32 atm^{-2}
(B) 20 atm^{-2}
(C) 50 atm^{-2}
(D) 80 atm^{-2}

Q.19 In the reaction : $A + B \rightleftharpoons C + D$
the initial concentration of A is double the initial concentration of B. At equilibrium the concentration of B was found to be one third of the concentration of C. The value of equilibrium constant is –
(A) 1.8   (B) 1.008
(C) 0.0028   (D) 0.08

Q.20 The value of K_C for the reaction :
$A + 3B \rightleftharpoons 2C$ at $400°C$. Calculate the value of K_P
(A) 1.64×10^{-4} (B) 1.64×10^{-6}
(C) 1.64×10^{-5} (D) 1.64×10^{-3}

Q.21 4.0 gms of hydrogen react with 9.023×10^{23} molecules of chlorine to form HCl gas. The total pressure after the reaction was found to be 700 mm. The partial pressure of HCl will be –
(A) 3900 mm   (B) 600 mm
(C) 700 mm   (D) 350 mm

Q.22 The equilibrium constant 'K' for the reaction
$N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 16. What would be value of equilibrium constant 'K' for the reaction :

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

(A) 0.25   (B) 0.4
(C) 2   (D) 0.625

Q.23 1.0 mole of $PCl_3(g)$ and 2.0 moles of Cl_2 (g) were placed in a 3 litre flask and heated to 400 K. When equilibrium was established , only 0.70 mole of PCl_3 (g) remained . What is the value of equilibrium constant for the reaction :
$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ at 400 K ?
(A) 0.25   (B) 1.31
(C) 0.76   (D) 2.6

Q.24 For the reaction $N_2 \rightleftharpoons 2NH_3$, $N_2 : H_2$ were taken in the ratio of 1 : 3 . Up to the point of equilibrium 50% each reactant has been reacted. If total pressure at equilibrium is P. The partial pressure of ammonia would be –
(A) P/3   (B) P/6
(C) P/4   (D) P/8

Q.25 In a reaction vessel of 2 litre capacity 3 moles of N_2 reacts with 2 moles of O_2 to produce 1 mole of NO. What is the molar concentration of N_2 at equilibrium ?
(A) 1.25   (B) 1.50
(C) 0.75   (D) 2.0

Q.26 In a reversible reaction $K_c > K_p$ and $\Delta H = + 40$ Kcal. The product will be obtained in less amount on –
(A) decreasing pressure and temperature
(B) increasing pressure and temperature
(C) decreasing pressure and increasing temperature
(D) decreasing temperature and increasing pressure

Q.27 Which of the following conditions will be helpful for obtaining maximum yield of SO_3 according to Le Chatelier principle ?
$2SO_2(g) + O_2 (g) \rightleftharpoons 2SO_3 (g)$ $(\Delta H = -0.95$ K. cal.)
(A) Low pressure
(B) High temperature
(C) Low temperature, high pressure, high concentration of SO_2 and O_2
(D) High pressure

Q.28 Which of the following conditions should be more favourable for increasing the rate of forward reaction in the equilibrium given below.
$H_2 \rightleftharpoons H + H$ $(\Delta H = $ positive)
(A) $2000°C$ temperature and 760 mm pressure
(B) $3500°C$ temperature and 100 cm pressure
(C) $3500°C$ temperature and 1 mm pressure
(D) All are wrong

Q.29 In the reaction, $x_2 (g) + 4y_2(g) \rightleftharpoons 2xy_4 (g)$, $\Delta H < 0$. Which of the following factors will be favourable for better yield of the product –
(A) low temperature and high pressure
(B) high temperature and low pressure
(C) low temperature and low pressure
(D) high temperature and high pressure

PREVIOUS YEAR AIEEE QUESTIONS

Q.1 For the reaction $CO + \frac{1}{2} O_2 \longrightarrow CO_2$, the value of

$\frac{K_P}{K_C}$ is - **[AIEEE-2002]**

(A) $\frac{1}{RT}$ (B) $\sqrt{RT}$

(C) $\frac{1}{\sqrt{RT}}$ (D) RT

Q.2 Which of the following equilibria is not affected by change in volume of the flask – **[AIEEE-2002]**
(A) $PCl_5 (g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
(B) $N_2(g) + 3H_2 (g) \rightleftharpoons 2NH_3(g)$
(C) $N_2 (g) + O_2 (g) \rightleftharpoons 2NO(g)$
(D) $SO_2Cl_2 (g) \rightleftharpoons SO_2(g) + Cl_2(g)$

Q.3 For the reaction equilibrium $N_2O_4 (g) \rightleftharpoons 2NO_2 (g)$ the concentrations of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol L^{-1} respectively. The value of K_C for the reaction is – **[AIEEE-2003]**
(A) 3×10^{-3} mol L^{-1} (B) 3×10^3 mol L^{-1}
(C) 3.3×10^2 mol L^{-1} (D) 3×10^{-1} mol L^{-1}

Q.4 Consider the reaction equilibrium
$2SO_2(g) + O_2 (g) \rightleftharpoons 2 SO_3 (g) ; \Delta H^\circ = -198 kJ$
On the basis of Le Chatelier's principle, the condition favourable for the forward reaction is - **[AIEEE-2003]**
(A) Lowering the temperature and increasing the pressure
(B) Any value of temperature and pressure
(C) Lowering of temperature as well as pressure
(D) Increasing temperature as well as pressure

Q.5 What is the equilibrium expression for the reaction
$P_{4(S)} + 5O_{2(g)} \rightleftharpoons P_4O_{10(s)}$? **[AIEEE-2004]**
(A) $K_C = [P_4O_{10}] / [P_4] [O_2]^5$ (B) $K_C = [P_4O_{10}] / 5 [P_4] [O_2]$
(C) $K_C = [O_2]^5$ (D) $K_C = 1/ [O_2]^5$

Q.6 For the reaction $CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$ the K_p/K_c is equal to - **[AIEEE-2004]**

(A) $\frac{1}{RT}$ (B) RT

(C) $\sqrt{RT}$ (D) 1.0

Q.7 The equilibrium constant for the reaction

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ at temperature T is 4×10^{-4}. The value of K_C for the reaction

$NO_{(g)} \rightleftharpoons \frac{1}{2} N_{2(g)} + \frac{1}{2} O_{2(g)}$ at the same temperature is

- **[AIEEE-2004]**
(A) 2.5×10^2 (B) 50
(C) 4×10^{-4} (D) 0.02

Q.8 For the reaction : $2 NO_{2(g)} \rightleftharpoons 2 NO_{(g)} + O_{2(g)}$, $(K_c = 1.8 \times 10^{-6}$ at 184ºC) $(R = 0.0831 kJ/(mol.K))$
When K_p and K_c are compared at 184ºC it is found that **[AIEEE-2005]**
(A) K_p is less than K_c
(B) K_p is greater than K_c
(C) Whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure
(D) $K_p = K_c$

Q.9 The exothermic formaton of ClF_3 is represented by the equation -
$Cl_{2(g)} + 3F_{2(g)} \rightleftharpoons 2 ClF_{3(g)} ; \Delta_r H = -329 kJ$
Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3 ? **[AIEEE-2005]**
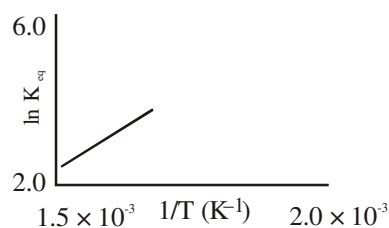
(A) Removing Cl_2
(B) Increasing the temperature
(C) Adding F_2
(D) Increasing the volume of the container

Q.10 A schematic plot of $\ell n K_{eq}$ versus inverse of temperature for a reaction is shown below **[AIEEE-2005]**

The reaction must be
(A) endothermic (B) exothermic
(C) highly spontaneous at ordinary temperature
(D) one with negligible enthalpy change

Q.11 An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm ? The equilibrium constant for NH_4HS decomposition at this temperature is– **[AIEEE-2005]**
(A) 0.18 (B) 0.30
(C) 0.11 (D) 0.17

Q.12 Phosphorus pentachloride dissociates as follows, is a closed reaction vessel, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be – **[AIEEE 2006]**
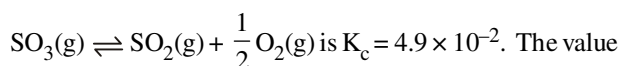
(A) $\frac{2x}{1-x} P$ (B) $\frac{x}{x-1} P$

(C) $\frac{x}{1-x} P$ (D) $\frac{x}{x+1} P$

Q.13 The equilibrium constant for the reaction

$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2} O_2(g)$ is $K_c = 4.9 \times 10^{-2}$. The value

of K_c for the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ will
be **[AIEEE 2006]**
(A) 2.40×10^{-3} (B) 9.8×10^{-2}
(C) 4.9×10^{-2} (D) 416

Q.14 For the following three reactions a, b and c, equilibrium
constants are given - **[AIEEE 2008]**
(a) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$; K_1
(b) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$; K_2
(c) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$; K_3

Which of the following relations is correct ?
(A) $K_2 K_3 = K_1$ (B) $K_3 = K_1 K_2$
(C) $K_3 K_2{}^3 = K_1{}^2$ (D) $K_1 \sqrt{K_2} = K_3$

Q.15 The equilibrium constants Kp_1 and Kp_2 for the reactions
$X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in the ratio of
1 : 9. If the degree of dissociation of X and Z be equal then
the ratio of total pressures at these equilibria is - **[AIEEE 2008]**
(A) 1 : 1 (B) 1 : 3
(C) 1 : 9 (D) 1 : 36

ANSWER KEY

EXERCISE - 1

Q	1	2	3	4	5	6	7	8	9	10	11
A	B	B	B	A	C	A	D	B	D	C	B
Q	12	13	14	15	16	17	18	19	20	21	22
A	D	C	C	D	B	A	B	C	C	A	B
Q	23	24	25	26	27	28	29	30	31	32	33
A	A	D	C	B	C	C	C	D	C	D	C
Q	34	35	36	37	38	39	40				
A	A	D	B	D	C	A	C				

EXERCISE - 2

Q	1	2	3	4	5	6	7	8	9	10	11
A	D	B	C	D	C	B	C	C	B	C	B
Q	12	13	14	15	16	17	18	19	20	21	22
A	B	C	C	A	A	B	C	A	A	B	A
Q	23	24	25	26	27	28	29				
A	C	A	A	A	C	C	A				

EXERCISE - 3

Q	1	2	3	4	5	6	7	8	9	10	11
A	C	C	A	A	D	A	B	B	C	B	C
Q	12	13	14	15							
A	D	D	B	D							