8

Chemical Equilibrium

TOPIC 1

The Chemical Equilibrium, Basic Law of Mass Action and Equilibrium Constant

A 20 litre container at 400 K contains CO₂(g) at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO₂ attains its maximum value, will be [NEET 2017] (Given that:

$$SrCO_3(s) \Longrightarrow SrO(s) + CO_2(g),$$
 $K_p = 1.6 \text{ atm})$
(a) 5 L (b) 10 L (c) 4 L (d) 2 L

Ans. (a)

For the reaction,

$$SrCO_{3}(s) \Longrightarrow SrO(s) + CO_{2}(q), \\ K_{p} = 1.6 \text{ atm} = p_{CO_{2}} = \text{maximum} \\ \text{pressure of CO}_{2} \\ \text{Given, } p_{1} = 0.4 \text{ atm, } V_{1} = 20 \text{ L, } T_{1} = 400 \text{ K} \\ p_{2} = 1.6 \text{ atm, } V_{2} = ?, T_{2} = 400 \text{ K} \\ \text{At constant temperature, } p_{1}V_{1} = p_{2}V_{2} \\ 0.4 \times 20 = 1.6 \times V_{2} \\ V_{2} = \frac{0.4 \times 20}{1.6} = 5 \text{ L} \\ \end{cases}$$

02 For a given exothermic reaction, K_p and K_p' are the equilibrium constants at temperatures T_1 and T_2 , respectively. Assuming that heat of reaction is constant in temperature range between T_1 and T_2 , it is readily observed that

[CBSE AIPMT 2014]

(a)
$$K_p > K'_p$$
 (b) $K_p < K'_p$ (c) $K_p = K'_p$ (d) $K_p = \frac{1}{K'_p}$

Ans. (a)

The equilibrium constant at two different temperatures for a thermodynamic process is given by

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

$$\begin{split} & \text{Here,} K_1 \text{ and } K_2 \text{ are replaced by } K_p \text{ and } K'_p. \\ & \text{Therefore,} \log \frac{K'_p}{K_p} = \frac{\Delta H^\circ}{2.303R} \Bigg[\frac{1}{T_1} - \frac{1}{T_2} \Bigg] \end{split}$$

For exothermic reaction,

$$T_2 > T_1$$
 and $H = -ve$
 $\Rightarrow K_p > K'_p$

- **03** If the value of an equilibrium constant for a particular reaction is 1.6×10^{12} , then at equilibrium the system will contain
 - (a) all reactants [CBSE AIPMT 2015]
 - (b) mostly reactants
 - (c) mostly products
 - (d) similar amounts of reactants and products

Ans. (c)

For a reaction,

A
$$\longrightarrow$$
 B

Reactant Product

$$K = \frac{[B]_{eq}}{[A]_{eq}}$$

$$1.6 \times 10^{12} = \frac{[B]_{eq}}{[A]_{eq}}$$

So, mostly the product will be present in

 $[B]_{eq} \gg [A]_{eq}$

the equilibrium mixture.

If the equilibrium constant for $N_2(g)+O_2(g) \longrightarrow 2NO(g)$ is K, the equilibrium constant for $\frac{1}{2}N_2(g)+\frac{1}{2}O_2(g) \longrightarrow NO(g)$ will be, [CBSE AIPMT 2015]

(a)
$$K^{1/2}$$
 (b) $\frac{1}{2}K$ (c) K (d) K^2

Ans. (a)

Plan As we can see the reaction for which we have to find out equilibrium constant is different only in stoichiometric coefficient as compared to the given reaction. Hence, we can find equilibrium constant for the required reaction with the help of mentioned equilibrium constant in the problem.

Given, equilibrium constant for the reaction,

i.e.
$$\begin{aligned} N_{22}(g) + O_2(g) & \longrightarrow 2NO(g) \text{ is } K \\ K &= \frac{[NO]^2}{[N_2][O_2]} & ...(i) \end{aligned}$$

Let equilibrium constant for the reaction

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \xrightarrow{} NO(g) \text{ is } K'$$
 i.e.
$$K' = \frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}}$$

On squaring both sides

$$K'^2 = \frac{[NO]^2}{[N_2][O_2]}$$
 ...(ii)

On comparing Eqs. (i) and (ii), we get

$$K = K^{\prime 2}$$

$$K^{\prime} = \sqrt{K}$$

05 Using the Gibbs energy change, $\Delta G^{\circ} = +63.3 \text{ kJ}$ for the following reaction,

$$Ag_2CO_3(s) \longrightarrow 2Ag^+(aq) + CO_3^{2-}(aq)$$

the $K_{\rm sp}$ of ${\rm Ag}_2$ ${\rm CO}_3({\rm s})$ in water at 25°C is

(R = 8.314 JK⁻¹mol⁻¹)
[CBSE AIPMT 2014]

(a)
$$3.2 \times 10^{-26}$$
 (b) 8.0×10^{-12} (c) 2.9×10^{-3} (d) 7.9×10^{-2}

Ans. (b)

or

 ΔG° is related to $K_{\rm sp}$ by the equation, $\Delta G^{\circ} = -2.303 RT \log K_{\rm sp}$

Given,
$$\Delta G^{\circ} = +63.3 \text{ kJ}$$

 $=63.3 \times 10^{3} \text{ J}$
Thus, substitute $\Delta G^{\circ} = 63.3 \times 10^{3} \text{ J}$,
 $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \text{ and } T = 298 \text{ K}[25 + 273 \text{ K}] \text{ from the above equation we get,}$
 $63.3 \times 10^{3} = -2.303 \times 8.314 \times 298 \log K_{\text{sp}}$
 $\therefore \log K_{\text{sp}} = -11.09$
 $\Rightarrow K_{\text{sp}} = \text{antilog}(-11.09)$
 $K_{\text{sp}} = 8.0 \times 10^{-12}$

06 For the reaction,

 $N_2(g) + O_2(g) \Longrightarrow 2NO(g)$, the equilibrium constant is K_1 . The equilibrium constant is K_2 for the reaction,

N₂ for the reaction,

 $2NO(g)+O_2(g) \longrightarrow 2NO_2(g)$. What is K for the reaction,

$$NO_2(g) \longrightarrow \frac{1}{2}N_2(g) + O_2(g)$$
?

[CBSE AIPMT 2011]

(a) $1/(4 K_1 K_2)$ (b) $[1/K_1 K_2]^{1/2}$ (c) $1/(K_1 K_2)$ (d) $1/(2 K_1 K_2)$

Ans. (b)

$$\begin{array}{c} \mathrm{N_2(\,g)} + \mathrm{O_2(\,g)} & \Longrightarrow \mathrm{2NO(\,g)}; K_1 & \dots \text{(i)} \\ \mathrm{2NO(\,g)} + \mathrm{O_2(\,g)} & \Longrightarrow \mathrm{2NO_2(\,g)}; K_2 & \dots \text{(ii)} \\ \mathrm{On\,adding\,Eqs.\,(i)\,and\,(ii)} \end{array}$$

$$N_2(g) + 2O_2(g) \Longrightarrow 2NO_2(g); K = K_1 \times K_2$$
...(iii)

On dividing (iii) by $\frac{1}{2}$ and on reversing we get,

NO₂(g)
$$\rightleftharpoons \frac{1}{2} N_2(g) + O_2(g);$$

So, $K = \frac{(N_2)^{1/2}(O_2)}{(NO_2)}$
 $K = \left[\frac{1}{K K_2}\right]^{1/2}$

07 In which of the following equilibrium K_c and K_p are not equal? [CBSE AIPMT 2010]

$$\begin{split} \text{(a)} 2\text{NO}(g) & \longrightarrow \text{N}_2(g) + \text{O}_2(g) \\ \text{(b)} \text{SO}_2(g) + \text{NO}_2(g) & \longrightarrow \text{SO}_3(g) + \text{NO}(g) \\ \text{(c)} \text{H}_2(g) + \text{I}_2(g) & \longrightarrow 2\text{HI}(g) \\ \text{(d)} 2\text{C}(s) + \text{O}_2(g) & \longrightarrow 2\text{CO}_2(g) \end{split}$$

Ans. (d)

Key Idea The reaction for which the number of moles of gaseous products (n_p) is not equal to the number of moles of gaseous reactants (n_R) , has different value of K_c and K_p .

From the equation, $K_p = K_C \times (RT)^{\Delta n_g}$

where,
$$[\Delta n_g \text{ gaseous} = n_p - n_R]$$

(a) $n_P = n_R = 2$, thus, $K_p = K_C$
(b) $n_P = n_R = 2$, thus, $K_p = K_C$
(c) $n_P = n_R = 2$, thus, $K_p = K_C$
(d) $n_P = 2$, $n_R = 1$, thus, $K_p \neq K_C$

08 The dissociation constants for acetic acid and HCN at 25° C are 1.5×10^{-5} and 4.5×10^{-10} ,

respectively. The equilibrium constant for the equilibrium,

$$CN^- + CH_3COOH \longrightarrow HCN + CH_3COO^-$$
 would be

[CBSE AIPMT 2009]

(a) 3.0×10^5

(b) 3.0×10^{-5}

(c) 3.0×10^{-4}

(d) 3.0×10^4

Ans. (d)

Given,
$$CH_3COOH \longrightarrow CH_3COO^- + H^+$$
,
$$K_{\sigma} = 1.5 \times 10^{-5} \quad ...(i)$$

$$HCN \longrightarrow H^+ + CN^-$$
,
$$K_{\sigma_1} = 4.5 \times 10^{-10} \quad ...(ii)$$

For $CN^- + CH_3COOH \longrightarrow HCN + CH_3COO^-$ K = ?

On subtracting Eq. (ii) from Eq. (i), we get

CH₃C00H + CN⁻
$$\Longrightarrow$$
 HCN+ CH₃C00⁻

$$K = \frac{K_a}{K_{a_1}} = \frac{1.5 \times 10^{-5}}{4.5 \times 10^{-10}}$$

$$= \frac{10^5}{7} = 3.33 \times 10^4 \approx 3 \times 10^4$$

09 If the concentration of OH⁻ ions in the reaction,

$$Fe(OH)_3(s) \Longrightarrow Fe^{3+}(aq) + 3OH^-(aq)$$

is decreased by 1/4 times, then equilibrium concentration of Fe³⁺ will increase by [CBSE AIPMT 2008]

(a) 8 times (c) 64 times (b) 16 times (d) 4 times

Ans. (c)

Fe(OH)₃(s)
$$\Longrightarrow$$
 Fe³⁺ (aq) + 3OH⁻(aq)

$$K = \frac{[Fe^{3+}][OH^{-}]^{3}}{[Fe(OH)_{3}]} ...(i$$

To maintain equilibrium constant, let the concentration of Fe³⁺ is increased x times, on decreasing the concentration of OH by $\frac{1}{4}$ times

$$K = \frac{[xFe^{3+}][\frac{1}{4} \times OH^{-}]^{3}}{[Fe(OH)_{\pi}]}$$
...(ii)

By dividing eq. (ii) by (i) we get $\frac{1}{64} \times x = 1$

10 The value of equilibrium constant of the reaction,

$$HI(g) \longrightarrow \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$$
 is 8.0.

The equilibrium constant of the reaction,

$$H_2(g) + I_2(g) \Longrightarrow 2HI(g)$$
 will be [CBSE AIPMT 2008]

(a)
$$\frac{1}{16}$$
 (b) $\frac{1}{64}$ (c) 16 (d) $\frac{1}{8}$

Ans. (b)

$$\begin{split} &\text{HI(}g\text{)} \Longrightarrow \frac{1}{2} \text{H}_{2}(g) + \frac{1}{2} \text{I}_{2}(g) \\ & \text{K} = \frac{[\text{I}_{2}]^{1/2} [\text{H}_{2}]^{1/2}}{[\text{HI}]} \qquad ...(i) \end{split}$$

$$H_{2}(g) + I_{2}(g) \Longrightarrow 2HI(g)$$

$$K' = \frac{[HI]^{2}}{[H_{2}][I_{2}]} \qquad ...(ii)$$

From Eqs. (i) and (ii)

$$K \times \sqrt{K'} = 1$$

$$K' = \frac{1}{K^2} = \frac{1}{(8)^2} = \frac{1}{64}$$

11 The equilibrium constants of the following are

[NEET 2017, CBSE AIPMT 2007]

$$N_2 + 3H_2 \Longrightarrow 2NH_3;$$
 K_1
 $N_2 + 0_2 \Longrightarrow 2N0;$ K_2
 $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O;$ K_3

The equilibrium constant (K) of the reaction

$$2NH_3 + \frac{5}{2}O_2 \xrightarrow{K} 2NO + 3H_2O$$
, will

be

(a)
$$K_1 K_3^3 / K_2$$
 (b) $K_2 K_3^3 / K_1$ (c) $K_2 K_3 / K_1$ (d) $K_2^3 K_3 / K_1$

Ans. (b)

Given,
$$N_2 + 3H_2 \Longrightarrow 2NH_3$$
, K_1 ...(i)
 $N_2 + 0_2 \Longrightarrow 2NO$, K_2 ...(ii)
 $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$, K_3 ...(iii)

To calculate,

$$2NH_3 + \frac{5}{2} O_2 \xrightarrow{K} 2NO + 3H_2O$$
,
 $K = ?$...(iv)

On reversing the equation (i) and multiplying the equation (iii) by 3, we get

$$2NH_2 \Longrightarrow N_2 + 3H_2, \frac{1}{K_1} \qquad ...(v)$$

$$3H_2 + \frac{3}{2}O_2 \longrightarrow 3H_2O, K_3^3$$
 ...(vi

Now, add equation. (ii), (v) and (vi), we get the resultant equation. (iv).

$$2NH_3 + \frac{5}{2}O_2 \stackrel{\longleftarrow}{\longleftarrow} 2NO + 3H_2O$$

$$K = \frac{K_2K_3^3}{K_3}$$

12 For the reaction,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(I),$$

$$\Delta_r H = -170.8 \,\text{kJ mol}^{-1}$$

Which of the following statement is not true? [CBSE AIPMT 2006]

- (a) At equilibrium, the concentrations of $CO_{2}(g)$ and $H_{2}O(I)$ are not equal
- The equilibrium constant for the reaction is given by $K_p = \frac{[CO_2]}{[CH_4][O_2]}$
- (c) Addition of $CH_4(g)$ or $O_2(g)$ at equilibrium will cause a shift to the right
- (d) The reaction is exothermic

Ans. (b)

For the reaction,

$$CH_4(g) + 2O_2(g) \iff CO_2(g) + 2H_2O(I)$$

 $\Delta H_r = -170.8 \text{ k J mol}^{-1}$

This equilibrium is an example of heterogeneous chemical equilibrium. Hence, for it

$$K_c = \frac{[CO_2]}{[CH_4][O_2]^2}$$
 ...(i)

(equilibrium constant on the basis of concentration)

and

$$K_p = \frac{p_{\text{CO}_2}}{p_{\text{CH}_4} \times p_{\text{O}_2^2}}$$
 ...(ii)

(equilibrium constant according to partial pressure)

Thus, in this concentration of $CO_2(g)$ and H_2O (I) are not equal at equilibrium.

The equilibrium constant

$$(K_p) = \frac{[CO_2]}{[CH_4][O_2]} \text{ is not correct}$$

expression.

On adding $CH_4(g)$ or $O_2(g)$ at equilibrium, K_{c} will be decreased according to expression (i) but K_{c} remains constant at constant temperature for a reaction, so for maintaining the constant value of K_{C} , the concentration of CO₂ will increased in same order. Hence, on addition of CH₄ or O_2 equilibrium will cause to the right. Combustion reaction is an example of exothermic reaction.

13 In the two gaseous reactions (i) and (ii) at 250°C

(i)
$$NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g), K_1$$

(ii) $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)_1K_2$ the equilibrium constants K_1 and K_2 are related as

(a)
$$K_2 = \frac{1}{K_1}$$

(b)
$$K_2 = K_1^{1/2}$$

(a)
$$K_2 = \frac{1}{K_1}$$
 (b) $K_2 = K_1^{1/2}$ (c) $K_2 = \frac{1}{K_1^2}$ (d) $K_2 = K_1^2$

(d)
$$K_2 = K_1^2$$

Ans. (c)

For equation (i),

$$NO(g) + \frac{1}{2}O_2(g) \Longrightarrow NO_2(g)$$

$$K_1 = \frac{[NO_2]}{[NO][O_2]^{1/2}} \qquad ...(i)$$

For equation (ii),

$$2NO_{2}(g) \xrightarrow{} 2NO(g) + O_{2}(g)$$

$$K_{2} = \frac{[NO]^{2}[O_{2}]}{[NO_{2}]^{2}} \qquad ...(ii)$$

Now, on reversing equation (i), we get, $\frac{1}{K_1} = \frac{1}{\left[NO_2\right]} \frac{1}{\left[NO_2\right]^{1/2}}$

$$= \frac{[N0][O_2]^{1/2}}{[NO_2]}$$

$$= \frac{[N0][O_2]^{1/2}}{[NO_2]}$$

$$= \frac{1}{[N0]} = \frac{[N0][O_2]^{1/2}}{[NO_2]}$$

$$= \frac{[N0]^2[O_2]}{[NO_2]^2} = K_2$$

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

14 Reaction,

BaO₂(s)
$$\Longrightarrow$$
 BaO(s)+O₂(g),
 $\Delta H = +ve$

In equilibrium condition, pressure of O₂ depends on

[CBSE AIPMT 2002]

- (a) increased mass of BaO₂
- (b) increased mass of BaO
- (c) increased temperature of equilibrium
- (d) increased mass of BaO2 and BaO both

Ans. (c)

$$BaO_2(s) \xrightarrow{r_1} BaO(s) + O_2(g), \Delta H = + ve$$

According to law of mass action, the rate of forward reaction = r_1

$$r_1 \propto [BaO_2]$$

or
$$r_1 = k_1 [BaO_2]$$

 BaO_2 is solid substance in pure state concentration = 1m

then,
$$r_1 = k_1$$

Similarly the rate of backward reaction

$$r_2 \propto [BaO][O_2]$$

or
$$r_2 = k_2 [Ba0][0_2]$$

: Concentration of solid [BaO] = 1 $[O_2(g)]$

$$\therefore \qquad r_2 = k_2 \left[O_2 \right]$$

At equilibrium,

$$\begin{aligned} & r_1 = r_2 \\ & K_1 = K_2 \left[O_2 \right] \\ & \text{or } & K_1 = K_2 \cdot p_{O_2} \\ & \text{where,} & p_{O_2} = \text{partial pressure of } O_2 \\ & \text{or} & \frac{K_1}{K_2} = p_{O_2} \end{aligned} \qquad \text{(equilibrium)}$$

constant)

$$\frac{K_1}{K_2} = K$$
or
$$K = p_{0_2}$$

So, from the above it is clear that pressure of O_2 does not depend upon the concentration of reactants. The given equation is an endothermic reaction. If the temperature of such reaction is increased, then dissociation of BaO₂ would increase and more O_2 is produced.

15 For the equilibrium,

 $MgCO_3(s) \stackrel{\Delta}{\longleftrightarrow} MgO(s) + CO_2(g)$ which of the following expressions is correct? [CBSE AIPMT 2000]

(a)
$$K_p = p_{\text{CO}_2}$$

(b) $K_p = \frac{[\text{MgO}][\text{CO}_2]}{[\text{MgCO}_3]}$
(c) $K_p = \frac{p_{\text{MgO}} \cdot p_{\text{CO}_2}}{p_{\text{MgCO}_3}}$
(d) $K_p = \frac{p_{\text{MgO}} + p_{\text{CO}_2}}{p_{\text{MgCO}_3}}$

Ans. (a)

In heterogeneous system, K_0 and K_0 are not depend upon the concentration or pressure of solid substance. Hence, at equilibrium their concentration or pressure are assumed as one.

$$\mathsf{MgCO_3}(s) \ensuremath{ \Longleftrightarrow} \mathsf{MgO}(s) + \mathsf{CO_2}(g)$$

$$\ensuremath{ :} \ensuremath{ :} \ensuremath{ \in} \ensuremath{ \mathsf{K}_p} = p_{\mathsf{CO}_2}$$

16 If K_1 and K_2 are the respective equilibrium constants for the two reactions,

$$XeF_6(g) + H_2O(g) \longrightarrow XeOF_4(g)$$

 $+ 2HF(g)$
 $XeO_4(g) + XeF_6(g) \longrightarrow XeOF_4(g)$
 $+XeO_3 F_2(g)$

The equilibrium constant of the reaction,

$$XeO_4(g) + 2HF(g) \Longrightarrow XeO_3F_2(g) + H_2O(g)$$

will be [CBSE AIPMT 1998]
 $(a)K_1/(K_2)^2$ $(b)K_1\cdot K_2$
 $(c)K_1/K_2$ $(d)K_2/K_1$

Ans. (d)

$$\begin{split} \operatorname{XeF_6}(g) + \operatorname{H_2O}(g) & \Longrightarrow \operatorname{XeOF_4}(g) + 2\operatorname{HF}(g) \\ K_1 &= \frac{[\operatorname{XeOF_4} \mathbb{I} \operatorname{HF}]^2}{[\operatorname{XeF_6} \mathbb{I} \operatorname{H_2O}]} & ...(i) \end{split}$$

$$\begin{split} \operatorname{XeO_4}(g) + \operatorname{XeF_6}(g) & \longrightarrow \operatorname{XeOF_4}(g) \\ & + \operatorname{XeO_3F_2}(g) \\ \operatorname{K_2} &= \frac{[\operatorname{XeOF_4}][\operatorname{XeO_3F_2}]}{[\operatorname{XeO_4}][\operatorname{XeF_6}]} \quad ...(ii) \end{split}$$

For the reaction,

$$XeO_4(g) + 2HF(g) \xrightarrow{} XeO_3F_2(g)$$

 $K = \frac{[XeO_3F_2][H_2O]}{[XeO_4][HF]^2} + H_2O(g)$
...(iii)

By dividing eq. (ii) by (i) we get,

$$K = \frac{K_2}{K_1}$$

17 The equilibrium constants for the reaction, $A_2 \longleftrightarrow 2A$ at 500 K and 700 K are 1×10^{-10} and 1×10^{-5} . The given reaction is **[CBSE AIPMT 1996]** (a) exothermic (b) slow

Ans. (b)

For the reaction,

(c) endothermic

$$A_2 \rightleftharpoons 2A$$

$$K = \frac{[A]^2}{[A_2]}$$

(d) fast

The value of equilibrium constant is very less and hence, the product concentration is also very less. So, the reaction is slow.

18 If α is the fraction of HI dissociated at equilibrium in the reaction, $2HI(g) \Longrightarrow H_2(g)+I_2(g)$ starting with the 2 moles of HI, then the

total number of moles of reactants and products at equilibrium are

[CBSE AIPMT 1996]

$$\begin{array}{cccc} (a)2+2\alpha & & (b)2 \\ (c)1+\alpha & & (d)2-\alpha \\ \hline & \textbf{Ans. (b)} & & & \\ & & 2\text{HI(g)} & & & \text{H}_2(g) & +\text{I}_2(g) \\ \text{In initial} & 2 \text{ mol} & 0 \text{ mol} & 0 \text{ mol} \\ \text{At equilibrium} & (2-2\alpha) & \alpha \text{ mol} & \alpha \text{ mol} \\ & & & \text{mol} & \end{array}$$

So, at equilibrium total moles = $2-2\alpha + \alpha + \alpha$

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

19 The rate constants for forward and backward reaction of hydrolysis of ester are 1.1×10^{-2} and 1.5×10^{-3} per minute. Equilibrium constant for the reaction, [CBSE AIPMT 1995] $CH_3COOC_2H_5 + H^+ \Longrightarrow$

$$CH_3COOH + C_2H_5OHis$$

(a) 4.33 (b) 5.33 (c) 6.33 (d) 7.33

Ans. (d)

Equilibrium constant, $K = \frac{k_f}{k_b}$ $= \frac{\text{Forward rate constant}}{\text{Backward rate constant}}$ $K = \frac{1.1 \times 10^{-2}}{1.5 \times 10^{-3}} = \frac{1.1 \times 10}{1.5} = \frac{11}{1.5} = 7.33$

20 K_1 and K_2 are equilibrium constant for reactions (i) and (ii) $N_2(g) + O_2(g) \Longrightarrow 2NO(g)$...(i

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$
 ...(i)
 $NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$...(ii)

Then, [CBSE AIPMT 1989]

(a)
$$K_1 = \left[\frac{1}{K_2}\right]^2$$
 (b) $K_1 = K_2^2$
(c) $K_1 = \frac{1}{K_2}$ (d) $K_1 = (K_2)^0$

Ans. (a)

Consider reaction (i),

$$N_2(g) + O_2(g) \Longrightarrow 2NO(g)$$
 ...(i)
 $K_1 = \frac{[NO]^2}{[N_2][O_2]}$

Now, consider reaction (ii),

NO(g)
$$\rightleftharpoons \frac{1}{2} N_2(g) + \frac{1}{2} O_2(g)$$
 ...(ii)

$$K_2 = \frac{[N_2]^{1/2} [O_2]^{1/2}}{[NO]}$$

$$\frac{1}{K_2} = \frac{1}{\frac{[N_2]^{1/2}[O_2]^{1/2}}{[NO]}} = \frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}}$$

$$\left(\frac{1}{K_2}\right)^2 = \left\{\frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}}\right\}^2$$

$$= \frac{[NO]^2}{[N_2][O_2]} = K_1$$

TOPIC 2

Factors Affecting Equilibrium and Le-Chatelier's Principles

Which one of the following conditions will favour maximum formation of the product in the reaction, [NEET 2018]

$$A_2(g) + B_2(g) \Longrightarrow X_2(g);$$

$$\Delta_r H = -X \text{ kJ}?$$

- (a) High temperature and high pressure
- (b) Low temperature and low pressure
- (c) Low temperature and high pressure
- (d) High temperature and low pressure

Ans. (c)

Key Concept The given question is based upon Le-Chatelier's principle. According to this principle, if a stress is applied to a reaction mixture at equilibrium, reaction proceeds in such a direction that relieves the stress.

The given reaction is

 $A_2(g) + B_2(g) \Longrightarrow X_2(g)$: $\Delta_r H = - X k J$ According to Le-Chatelier's principle, with increase in temperature the equilibrium shifts in the direction of endothermic reaction (i.e., heat is absorbed).

Alternatively, the decrease in temperature shifts the equilibrium towards the direction of exothermic reaction (i.e. heat is produced).

$$\therefore A_2(g) + B_2(g) \xrightarrow{\text{Endothermic}} X_2(g)$$
Exothermic

Similarly, an increase in pressure will shifts the equilibrium to that direction which leads to decrease in total number of gaseous moles. Whereas, a decrease in the pressure will shift the equilibrium to that direction which leads to an increase in total number of gaseous moles.

For,
$$A_2(g) + B_2(g) \Longrightarrow X_2(g)$$

$$\Delta n_g = 1 - 2 = -1$$

Thus, low temperature and high pressure will favour maximum formation of the product in the given reaction.

- 22 For the reversible reaction, $N_2(g) + 3H_2(g) \Longrightarrow 2NH_3(g) + heat$ the equilibrium shifts in forward
 - direction [CBSE AIPMT 2014] (a) by increasing the concentration of $NH_{z}(q)$
 - (b) by decreasing the pressure
 - (c) by decreasing the concentrations of $N_2(g)$ and $H_2(g)$
 - (d) by increasing pressure and decreasing temperature

Any change in the concentration, pressure and temperature of the reaction results in change in the direction of equilibrium. This change in the direction of equilibrium is governed by Le-Chatelier's principle. According to this equilibrium shifts in the opposite direction to undo the change.

$$N_2(g) + 3H_2(g) \Longrightarrow 2NH_3(g) + Heat$$

- (a) Increasing the concentration of NH₃(g) On increasing the concentration of $NH_3(g)$, the equilibrium shifts in the backward direction where concentration of $NH_3(g)$ decreases.
- (b) Decreasing the pressure Since, $p \propto n$ (number of moles), therefore, equilibrium shifts in the backward direction where number of moles are increasing.
- (c) Decreasing the concentration of $N_2(g)$ and $H_2(g)$ Equilibrium shifts in the backward direction when concentration of $N_2(g)$ and $H_2(g)$ decreases.
- (d) Increasing pressure and decreasing temperature On increasing pressure, equilibrium shifts in the forward direction where number of moles decreases. It is an example of exothermic reaction therefore decreasing temperature favours the forward direction.
- 23 KMnO₄ can be prepared from K₂MnO₄ as per reaction, $3Mn0_4^{2-} + 2H_20 \Longrightarrow$

 $2MnO_4^- + MnO_2^- + 40H^-$

The reaction can go to completion by removing OH⁻ ions by adding [NEET 2013]

(a) HCI (b) KOH

(c)CO₂ $(d) SO_2$

Ans. (c)

Since, OH⁻ are generated from weak acid (H_2O) , and a weak acid (like CO_2) should be used to remove it. Because if we add strong acid like (HCI) it reverse the reaction. KOH increases the concentration of OH⁻, thus again shifts the reaction in backward side.

CO₂ combines with OH⁻ to give carbonate which is easily removed.

SO₂ reacts with water to give strong acid, so it cannot be used.

24 The value of ΔH for the reaction,

 $X_2(g) + 4Y_2(g) \Longrightarrow 2XY_4(g)$ is less than zero. Formation of

 $XY_4(g)$ will be favoured at [CBSE AIPMT 2011]

- (a) low pressure and low temperature
- (b) high temperature and low pressure
- (c) high pressure and low temperature
- (d) high temperature and high pressure

Ans. (c)

 $X_2(g) + 4Y_2 \rightleftharpoons 2XY_4(g)$; where

and $\Delta n < 0 [\Delta n = n_P - n_R]$

- .. The forward reaction is favoured at high pressure and low temperature. (According to Le-Chatelier's principle)
- 25 The reaction quotient (Q) for the reaction,

 $N_2(g) + 3H_2(g) \Longrightarrow 2NH_3(g)$ is

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

The reaction will proceed towards right side, if [CBSE AIPMT 2003]

(a) $Q > K_c$

(b) 0 = 0

(c) $Q = K_c$

(d) $Q < K_c$

where, K_c is the equilibrium constant.

Ans. (a)

For the reaction,

$$\begin{aligned} &\mathsf{N_2}(g) + 3\mathsf{H_2}(g) & \Longrightarrow 2\mathsf{NH_3}(g) \\ & \mathcal{O}(\mathsf{Quotient}) = \frac{[\mathsf{NH_3}]^2}{[\mathsf{N_2}\,\mathbb{I}\,\mathsf{H_2}\,]^3}, \end{aligned}$$

$$\Delta n_a = 2 - 4 = -2$$

At equilibrium Q is equal to K_c but for the progress of reaction towards right side,

26 For a reversible reaction, if the concentrations of the reactants are doubled, the equilibrium constant

will be [CBSE AIPMT 2000]

(a) one-fourth (c) doubled

(b) halved (d) the same

Ans. (d)

Consider a hypothetical change,

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

For this reaction, $K_{eq} = \frac{[C][D]}{[A][B]}$

For the above reaction if concentration of reactants are doubled then the rate of forward reaction increases for a short time but after sometime equilibrium will established. So, concentration has no effect on equilibrium constant. It remains unchanged after increasing the concentration of reactants.

27 According to Le-Chatelier's principle, adding heat to a solid → liquid equilibrium will cause

[CBSE AIPMT 1993]

- (a) temperature to increase
- (b) temperature to decrease
- (c) amount of liquid to decrease
- (d) amount of solid to decrease

Ans. (d)

When we add heat to the equilibrium between solid and liquid, then the equilibrium shifts towards liquid and hence, the amount of solid decrease and amount of liquid increase.

28 Which one of the following information can be obtained on the basis of Le-Chatelier's principle?

[CBSE AIPMT 1992]

- (a) Dissociation constant of a weak acid
- (b) Entropy change in a reaction
- (c) Equilibrium constant of a chemical reaction
- Shift in equilibrium position on changing value of a constant

Ans. (d)

Le-Chatelier's and Braun French chemists made certain generalisations to explain the effect of changes in concentrations, temperature or pressure on the state of system in equilibrium. When a system is subjected to a change in one of these factors, the equilibrium gets disturbed and the system re-adjusts itself until it return to equilibrium.