18. *For the equilibrium* $AB(g) \rightleftharpoons A(g) + B(g)$ *at a given temperature, the pressure at which one-third of AB is dissociated is numerically equal to*

(A) 8 *times* K_p **(B)** 16 *times* K_p **(C)** 4 *times* K_p **(D)** 9 *times* K_p

19. *In a revesible reaction, if the concentration of reactants are doubled, the equilibrium constant K will* :

(A) *change to* 1/4 *K* **(B)** *change to* 1/2 *K*

(C) *change to* 2 *K* **(D)** *remain the same*

20. *For the equilibrium* $AB(g) \rightleftharpoons A(g) + B(g)$, K_p *is equal to four times the total pressure. Calculate the number of moles of A formed if one mol of AB is taken initially.*

(A) 0.45 **(B)** 0.30 **(C)** 0.60 **(D)** 0.90

***21.** *When two reactants, A and B are mixed to give products C and D, the reaction quotient Q, at the initial stages of the reaction*

(A) *is zero* **(B)** *increase with time*

(C) *rate of change of Q decreases with time* **(D)** *rate of change of Q increases with time*

22. *At equilibrium,* $X + Y \rightleftharpoons 3Z$, *1 mole of X,* 2 *mole of Y and* 4 *moles of Z are contained in a* 3.0 *L vessel. Comment on the status of equilibrium system, if at a particular time instant, the value of reaction coefficient Q is found to be* 15 :

(A) *at equilibrium* **(B)** *in forward direction*

(C) *in backward direction* **(D)** *None of these*

LE-CHATELIER'S PRINCIPLE Section - 2

How an equilibrium state relieves the external stress ?

How a state in equilibrium (*a stable state*) adjusts to the ***external stress*** (*change in Temperature, pressure or concentration of reactants/products*) is generalised in Le Chatelier's principle.

Le Chatelier's Principle states that :

> *If a stress is applied to a system in equilibrium, the equilibrium condition is upset; A net reaction occurs in that direction which tends to relieve the external stress and finally a new equilibrium is attained.*

To understand its application to a system, let us consider following example:

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

$\Delta H = -92$ kJ for *Forward Reaction*

$\Delta H = +92$ kJ for *Backward Reaction*

Note : ΔH : Enthalpy Change is a measure of heat evolved or heat absorbed in a chemical reaction. It is negative when heat is evolved and positive when heat is absorbed during a chemical change. You will learn details of it later in the Chapter on Chemical Energetics.

Note that in the above reaction :

(a) Forward reaction is exothermic (favours formation of NH_3) and backward reaction is endothermic (favours decomposition of NH_3)

(b) Formation of NH_3 results in decrease in number of moles (from 4 total moles of N_2 and H_2 to 2 total moles of NH_3) is a decrease in volume to right (in forward reaction)

(c) Both reactants and products are gases and they will be influenced by changes in P, T and changing concentrations.

Effect of Temperature

Temperature can be increased by adding heat and can be decreased by taking out heat from the system.

- Increase the temperature by supplying heat: According to Le Chatelier's principle the disturbed equilibrium state will move in that direction where heat is being absorbed (*where stress is relieved*) i.e. in endothermic direction. In case of given situation, reverse direction will be favoured (*that being endothermic*) till whole of extra heat in consumed. So NH_3 will decompose on increasing temperature.
- Decrease the temperature by extracting heat: According to Le Chatelier's principle, the system will go in the direction where heat is evolved i.e. in exothermic direction. In given situation, forward reaction will be favoured (i.e. formation of NH_3) till the new equilibrium is again established.

Note : *The new equilibrium state has a new value of equilibrium constant K on changing the temperature.*

Effect of Pressure

- Increase in pressure would result in decrease in volume thereby increasing the concentration (mol/L). The system will shift in a direction where number of moles decreases (decreasing concentration). In given situation, there is decrease in number of moles in forward direction, so increasing pressure favours forward reaction (i.e., formation of NH_3).
- Decreasing the pressure would mean lower number of moles/L. The system will shift in a direction which will produce more moles. In given situation, there is increase is number of moles in reverse direction, so decreasing pressure favours backward reaction (i.e., decomposition of NH_3)

Effect of Concentration

The Concentration can be changed in two ways :

(a) By removing some of a component or **(b)** By adding some more of a component.

According to Le Chatelier's principle :

- The addition of any component to a side (reactants and products) of a reaction in equilibrium shifts the equilibrium in the direction away from that side or one can say that equilibrium shifts in that direction which consumes the increased concentration.
- In given situation ;
  Increasing amount of pure N_2 and H_2 would favour formation of NH_3.
  Increasing amount of NH_3 would favour decomposition of NH_3

- The removal of any component from a side (reactants and products) of a reaction in equilibrium shifts the equilibrium in the direction towards that side, or one can say the equilibrium shifts in that direction which produces the decreased concentration.
- In given situation :
  Decreasing the amount of NH_3 from right side drives the equilibrium to forward direction i.e.,favours formation of NH_3. Decreasing amount of N_2 or H_2 from left drives the equilibrium to reverse direction i.e.,favours decomposition of NH_3.

Effect of Catalyst

- Catalyst increases the rate of both forward and backward reactions simultaneously and to the same extent in a reversible reaction. By increasing both rates, ***catalyst reduces the time to reach equilibrium state***.
- Catalyst does not change the relative amounts of either reactants or products, hence it has no effect on equilibrium constant

Evaluation of K_{eq} at different temperatures :

If K_1 be the equilibrium constant at T_1 (in Kelvin) and K_2 be the equilibrium constant at T_2 (in Kelvin) $(T_2 > T_1)$, the two constants are related by Van't Hoff equation as follows :

$$\log_{10}\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303\,R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$ where *R* is gas constant and ΔH° is the standard heat of reaction.

Note : The value of ΔH is negative for exothermic reaction and is positive for endothermic reaction.

Le Chatelier's principle and Physical equilibrium :

Consider the physical equilibrium of change of state :

$$\text{solid} \rightleftharpoons \text{liquid}$$

Effect of pressure on melting

When a solid melts, there is a decrease in volume for some solids (ice, diamond, carborundum, magnesium nitride, quartz etc.) and there is an increase in volume for some solids (sulphur, iron, copper, silver, gold etc.).

When ice melts, there is a decrease in volume. On this kind of system where there is a decrease in volume due to melting, increasing pressure will reduce the melting point of the system. Thus, increasing the pressure will favor the melting of ice.

Similarly, when sulphur melts, there is an increase in volume. On this kind of system where there is an increase in volume due to melting, decreasing pressure will reduce the melting point of the system. Thus, decreasing the pressure will favor the melting of sulphur.

Vapour pressure of liquids

Consider liquid $\rightleftharpoons$ vapour equilibrium :

This is an endothermic reaction in forward direction. Hence rise in temperature will favour evaporation. This means, increase in temperature results in increase in vapour pressure of the system.

Effect of pressure on boiling point

As we increase pressure on the system : Liquid $\rightleftharpoons$ vapour ; vapours condenses lowering the vapour pressure of system. This means boiling point rises on increasing pressure as to reach the pressure required for the liquid to start boiling, needs to be increased.

Effect of temperature on solubility

In most cases, formation of solution (*solute in solvent*) is an endothermic process. In such cases, increasing temperature, increases the solubility of solutes. In cases, where dissolution of solute is followed by evolution of heat ; increasing temperature lowers the solubility of solutes.

Solubility of gases in liquid : As the temperature increases, the solubility of a gas decreases. This means that more gas is present in a solution with a lower temperature as compared to a solution with higher temperature.

Effect of pressure on solubility

When a gas dissolves in liquid, there is a decrease in volume of the gas $\left(X(g) \rightleftharpoons X(aq)\right)$. Thus, increase of pressure will favour the dissolution of gas in liquid.

Illustration - 7 *For the reaction :* $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$, K_{eq} *is* 0.63 *at* 727°C *and* 1.26 *at* 927°C.

(a) *What is the average* ΔH *for the temperature range considered ?* [*Use* $\log_{10} 2 = 0.3$]

(b) *What is the value of* K_{eq} *at* 1227°C ?

SOLUTION :

(a) $T_1 = 1000\text{ K}, T_2 = 1200\text{ K}$,

$K_1 = 0.63, K_2 = 1.26$

Using the Vant' Hoff equation :

$$\log_{10}\frac{K_2}{K_1} = \frac{\Delta H°}{2.303\,R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\Rightarrow \quad \log_{10}\left(\frac{1.26}{0.63}\right) = \frac{\Delta H}{2.303(2)}\left(\frac{1200-1000}{1200\times1000}\right)$$

$$\Rightarrow \quad \Delta H = 8.32\text{ kcal/mol}$$

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

(b) Let K_2 be the equilibrium constant at $T_2 = 1500\text{K}$

$T_1 = 1000\text{ K}$ and then $K_1 = 0.63$

$$\Rightarrow \quad \log_{10}\left(\frac{K_2}{0.63}\right) = \frac{8.32\times10^3}{2.303(2)}\left(\frac{1500-1000}{1500\times1000}\right)$$

$$\Rightarrow \quad \log_{10}\frac{K_2}{0.63} \approx 0.6 = \log_{10} 4$$

$$\Rightarrow \quad K_2 = 0.63\times4 = 2.52$$

Illustration - 8 *What would be the effect of increasing the volume of each of the following systems at equilibrium ?*

(i) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

(ii) $Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$

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

SOLUTION :

Increasing volume (at constant temperature) will result in a decrease in the concentration of all the gases. As per Le-Chatelier's Principle, the reaction should move in a direction of increase in total number of gaseous moles (thereby increasing concentration). Thus, shift is in a direction of $\Delta n_g > 0$

(i) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$ [Backward direction $\because (\Delta n_g)_{\text{Backward direction}} > 0$]

(ii) $Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$ [Backward direction $\because (\Delta n_g)_{\text{Backward direction}} > 0$]

(iii) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ [Forward direction $\because (\Delta n_g)_{\text{forward direction}} > 0$]

Illustration - 9

What happens when an inert gas is added to

(i) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ **(ii)** $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

at equilibrium at : **(a)** *constant pressure and temperature,* **(b)** *constant volume and temperature.*

SOLUTION :

Lets discuss what happens when an inert gas is added to the following reaction at equilibrium stage :

$$mA(g) + nB(g) \rightleftharpoons pC(g) + qD(g)$$

If the reaction is at equilibrium, we have :

$$K_{eq} = Q \qquad \text{....(i)}$$

Any factor (e.g. change in conc. of Reactants/Products or both) can have impact (in terms of change in the conc. of reactants/products) on that reaction at equilibrium only if that factor changes the equations (i) so that $K_{eq} \neq Q$

Two cases occur :

(a) Inert gas addition at constant pressure :

$$K_{eq} = Q = \frac{p_C^p \; p_D^q}{p_A^m \; p_B^n} \quad \text{(at equilibrium)}$$

and partial pressure $(p) = \chi P_{Total}$

$$\left[\text{where } \chi = \frac{n}{n_{Total}} = \text{Mole fraction}\right]$$

Thus, when an inert gas is added, χ of each of the gas decreases and since P_{Total} is constant, partial pressure decreases leading to a new equation :

$$Q > K_{eq} \text{ or } Q < K_{eq}$$

which will depend on whether

$\Delta n_g = \Sigma(n_g)_P - \Sigma(n_g)_R < 0$ or > 0 respectively.

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

$$\Delta n_g = 1 > 0 \Rightarrow Q < K_{eq}$$

(Reaction will move in forward direction)

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

$$\Delta n_g = -1 < 0 \Rightarrow Q > K_{eq}$$

(Reaction will move in the backward direction)

(b) Inert gas addition at constant volume :

$$K_{eq} = Q = \frac{p_C^p \; p_D^q}{p_A^m \; p_B^n} \quad \text{(at equilibrium)}$$

and partial pressure $(p) = \chi P_{Total}$

$$\left[\text{where } \chi = \frac{n}{n_{Total}} = \text{Mole fraction}\right]$$

Now, when inert gas is added at constant volume, $P_{Total} \uparrow$ and $\chi \downarrow$ but partial pressure of each gas remains same, since :

Partial pressure $(p) = \frac{n}{n_{Total}} \cdot P_{Total}$ and using Dalton's Law and ideal gas equation :

$$P_{Total} \cdot V = n_{Total} RT$$

$$\left[\text{Check : } \frac{P_{Total}}{n_{Total}} = \frac{RT}{V} = \text{const.}\right]$$

Thus, $K_{eq} = Q$ even on adding inert gas at constant volume Thus, adding inert gas at constant volume has no effect on a reaction at equilibrium.

Degree of Dissociation and Density :

When a gas decomposes (dissociates), its volume increases in accordance with increase in the total number of moles (at constant pressure). As the total mass remains same, its density decreases in the same proportion.

$\Rightarrow$ Initial mass of gas mixture = mass of gas mixture at any time $= \rho_i V_i = \rho_f V_f$ [mass = density × volume]

$= n_i M_{mix,i} = n_f M_{mix,f}$ [mass = moles × Mol. mass]

where ρ_i = Initial density of the mixture ; ρ_f = Final density of the mixture ; V_i and V_f = Initial and final volumes of the system

$M_{mix,\,i} \equiv$ Initial molecular weight of the mixture and $M_{mix,\,f} \equiv$ Final molecular weight of the mixture.

$$\Rightarrow \quad \frac{n_f}{n_i} = \frac{M_{mix,\,i}}{M_{mix,f}} = \frac{d_i}{d_f}$$

where $d_i \equiv$ Initial vapour density of the mixture and $d_f \equiv$ Final vapour density of the mixture.

Consider the dissociation of PCl_5 to clearly understand the concept.

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

Moles	PCl_5	PCl_3	Cl_2
Initial	a	0	0
At equilibrium	$a - a\alpha$	$a\alpha$	$a\alpha$

where α = degree of dissociation = x/a

Total moles = $a + a\alpha$

$$\Rightarrow \quad \frac{a}{a + a\alpha} = \frac{d_{mix}}{d_0} = \frac{d_{mix}}{d_{PCl_5}}$$

d_{mix} = density of mixture of PCl_5, PCl_3, Cl_2

Using the correlation for vapour density and moles, we have : $\dfrac{M_{mix,\,i}}{M_{mix,\,f}} \equiv \dfrac{M_{PCl_5}}{M_{mix,\,f}} = \dfrac{1+\alpha}{1}$

$M_{mix,\,f}$ can be found out by experiments. Thus, α can be calculated.

Illustration - 10 *When PCl_5 is heated, it dissociates into PCl_3 and Cl_2. The vapor density of the gas mixture at 200°C and at 250°C is 70 and 58 respectively. Find the degree of dissociation at two temperatures.*

SOLUTION :

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

Moles	PCl_5	PCl_3	Cl_2
Initial Moles	a	0	0
At equilibrium	$a - a\alpha$	$a\alpha$	$a\alpha$

Total moles = a + aα Using the result $= \left[\dfrac{d_0}{d_{mix}} = \dfrac{a + a\alpha}{a}\right]$

d_0 = density of PCl_5

At T = 200°C (v.d. ≡ vapour density)

$$\Rightarrow \quad \frac{d_0}{d_{mix}} = \frac{v.d._{PCl_5}}{v.d._{mix}} = \frac{M_0/2}{70} = \frac{a + a\alpha}{a}$$

$$= \frac{208.5/2}{70} = 1 + \alpha \quad \Rightarrow \quad \alpha = 0.49$$

At T = 250°C

$$\frac{d_0}{d_{mix}} = \frac{v.d._{PCl_5}}{v.d._{mix}} = \frac{M_0/2}{58} = \frac{a + a\alpha}{a}$$

$$= \frac{208.5/2}{58} = 1 + \alpha \quad \Rightarrow \quad \alpha = 0.80$$

Illustration - 11 *K_P for the reaction $PCl_5\,(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ 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 = $1 - x + x + x = 1 + x$

$P = 5$ atm and $K_p = 0.82$

$$p_{PCl_5} = \left(\frac{1-x}{1+x}\right)P \quad ; \quad p_{PCl_3} = \frac{x}{1+x}P$$

and $\quad p_{Cl_2} = \dfrac{x}{1+x}P$

Now, $\quad K_p = \dfrac{(p_{PCl_3})(p_{Cl_2})}{(p_{PCl_5})} \Rightarrow K_p = \dfrac{x^2}{1-x^2}P = 0.82$

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

$x = 0.375$ (or 37.5%)

Now the new pressure $P = 10$ atm.

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

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

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

Note :

- By increasing pressure, degree of dissociation has decreased, i.e., the system shifts to reverse direction. Compare the result by applying Le Chatelier's principle.
- Read the following example very carefully, In the following example, the volume is suddenly doubled, so first the initial concentration of all species at equilibrium will be halved and a new equilibrium will be re-established.

Illustration - 12 *At a given temperature and a total pressure of 1.0 atm for the homogenous gaseous reaction $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$, the partial pressure of NO_2 is 0.5 atm.*

(a) *Find the value of K_P.*

(b) *If the volume of the vessel is decreased to half of its original volume, at constant temperature, what are the partial pressures of the components of the equilibrium mixture ?*

SOLUTION :

For equilibrium system, $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$, the total pressure is 1.0 atm.

$\Rightarrow$ The total pressure = $p_{N_2O_4} + p_{NO_2} = 1.0$

$\Rightarrow$ $p_{N_2O_4} = 0.5$ atm and $p_{NO_2} = 0.5$ atm

(i) $\quad K_P = \dfrac{(p_{NO_2})^2}{p_{N_2O_4}} = \dfrac{0.5^2}{0.5} = 0.5\,\text{atm}$

(ii) As volume is decreased to half its original volume, equilibrium is disturbed and the new initial conditions for the re-establishment of new equilibrium are :

$$p_{N_2O_4} = 1.0 \text{ atm} \quad \text{and} \quad p_{NO_2} = 1.0 \text{ atm}$$

[$\because$ P is doubled as V is halved at constant T]

According to Le Chatelier principle, when volume is decreased, the system moves in that direction where there is decrease in number of moles. Hence, the system (here) will move in reverse direction, as there is a decrease in mole ($\Delta n_g = 2 - 1 = 1$) i.e, the NO_2 will be converted to N_2O_4.

Let the decrease in pressure of NO_2 be x atm.

Pressure	N_2O_4	NO_2
Initial	1.0	1.0
At equilibrium	$1 + x/2$	$1 - x$

$$\Rightarrow \quad K_P = \frac{(1-x)^2}{(1+x/2)} = 0.5$$

$$\Rightarrow \quad 4x^2 - 9x + 2 = 0$$

$$\Rightarrow \quad x = 2 \quad \text{or} \quad 0.25 \qquad (x \neq 2, \text{ as initial pressure} = 1.0)$$

$$\Rightarrow \quad x = 0.25$$

$$p_{N_2O_4} = 1 + \frac{x}{2} = 1.125 \text{ atm}$$

$$\text{and} \quad p_{NO_2} = 1 - x = 0.75 \text{ atm}$$

Illustration - 13 *1 mole of N_2 and 3 moles of PCl_5 are placed in a 82.1L container heated to 127° C. The equilibrium pressure is 2.0 atm. Assuming ideal behaviour, Calculate the degree of dissociation of PCl_5 and value of K_p for its dissociation.*

SOLUTION :

Dissociation of PCl_5 is written as :

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

Let x be the no. of moles of PCl_5 decomposed at equilibrium.

Moles	PCl_5	PCl_3	Cl_2
Initial	3	0	0
At equilibrium	$3 - x$	x	x

Now total gaseous moles in the container = n_T

$\Rightarrow \quad n_T$ = moles of $(PCl_5 + PCl_3 + Cl_2)$ + moles of N_2

$\Rightarrow \quad n_T = 3 - x + x + x + 1 = 4 + x$

The mixture behaves ideally, hence $PV = n_T RT$

Let us calculate no. of moles by using gas equation

$$\Rightarrow \quad n_T = \frac{PV}{RT} = \frac{2.0 \times 82.1}{0.082 \times 400} \quad \Rightarrow \quad n_T = 5$$

Now, equating the two values of n_T, we have :

$$4 + x = 5 \qquad \Rightarrow \qquad x = 1.$$

$\Rightarrow$ Degree of dissociation = 1/3 = 0.333

$$K_P = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

Now $p_{PCl_5} = \frac{3-x}{4+x} P$ $\qquad$ P = equilibrium pressure

$$= \frac{2}{5} \times 2.0 = 0.8 \text{atm}$$

$$p_{Cl_2} = p_{PCl_3} = \frac{x}{4+x} P = \frac{1}{5} \times 2.0 = 0.4 \text{ atm}$$

$$\Rightarrow \quad K_p = \frac{0.4 \times 0.4}{0.8} = 0.20 \text{ atm}$$

Note :

- The inert gases like N_2 or noble gases (He, Ne etc) though do not take part in the reaction, but still they affect the degree of dissociation and equilibrium concentrations for the reactions in which $\Delta n_g \neq 0$. They add to the total pressure of the equilibrium mixture ($p \alpha n$).

Illustration - 14 *At temperature T, a compound $AB_2(g)$ dissociates according to the reaction :*

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

with a degree of dissociation α which is small compared to the unity. Deduce the expression for α in terms of the equilibrium constant K_p and the total pressure P.

SOLUTION :

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

Moles	AB_2	AB	B_2
Initial	a	0	0
At equilibrium	$a - a\alpha$	$a\alpha$	$a\alpha/2$

$$\Rightarrow \quad \text{Total moles} = n_T = a + \frac{a\alpha}{2}$$

$$K_p = \frac{(p_{AB})^2 (p_{B_2})}{(p_{AB_2})^2}$$

$$p_{AB} = \frac{a\alpha}{a + a\alpha/2} . P \; ; \; p_{AB_2} = \frac{a - a\alpha}{a + a\alpha/2} P \; ; \; p_{B_2} = \frac{a\alpha/2}{a + a\alpha/2} . P$$

$$\text{As } \alpha << 1 \quad a + \frac{a\alpha}{2} \approx a$$

$$a - a\alpha \approx a$$

$$\Rightarrow \quad p_{AB} \approx \alpha P \; ; \; p_{AB_2} \approx P \; ; \; p_{B_2} = \frac{\alpha}{2} P$$

$$\Rightarrow \quad K_p = \frac{(\alpha P)^2 \cdot \left(\frac{\alpha}{2} P\right)}{(P)^2} = \frac{\alpha^3}{2} P \Rightarrow \alpha = \sqrt[3]{\frac{2K_p}{P}}$$

Illustration - 15 *The equilibrium constant K_p of the reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is 900 at 800 K. A mixture containing SO_3 and O_2 having initial partial pressures of 1 and 2 atm. respectively heated at constant volume is allowed to equilibrate. Calculate the partial pressures of each gas at 800 K.*

SOLUTION :

$$\text{Now}: \; 2\,SO_2(g) + O_2 \rightleftharpoons 2\,SO_3(g) \qquad K_p = 900$$

$$\Rightarrow \quad 2\,SO_3(g) \rightleftharpoons 2\,SO_2\,(g) + O_2(g) \quad K_p = 1/900$$

and initial pressure of $SO_3 = 1$ and $O_2 = 2$ atm.

Let x be the decrease in partial pressure of SO_3 at equilibrium.

Partial pressure	SO_3	SO_2	O_2
Initial	1	0	2
At equilibrium	$1 - x$	x	$2 + x/2$

$$\Rightarrow K_p = \frac{(p_{SO_2})^2 \times p_{O_2}}{(p_{SO_3})^2} \quad \Rightarrow K_p = \frac{x^2 \times \left(2 + \frac{x}{2}\right)}{(1-x)^2} = \frac{1}{900}$$

$$\Rightarrow \frac{x^2(4+x)}{2(1-x)^2} = \frac{1}{900}$$

Assume that x is very small (as K_p <<1 and O_2 is already present at the time of dissociation).

$$\Rightarrow \quad (4+x) \sim 4 \text{ and } (1-x) \sim 1$$

$$\Rightarrow \quad \frac{x^2(4)}{2(1)^2} = \frac{1}{900} \quad \Rightarrow \quad x = \frac{1}{30\sqrt{2}} = 0.023$$

$$\Rightarrow \quad p_{SO_2} = x = 0.023 \text{ atm}$$

$$\text{and} \quad p_{SO_3} = 1 - x = 0.977 \text{ atm}$$

$$\text{and} \quad p_{O_2} = 2 + \frac{x}{2} = 2.0115 \text{ atm}$$

Note : Check the correctness of your approximation.
$(4+x) = (4 + 0.023) \sim 4$ and $(1-x) = (1 - 0.023) \sim 1$

IN-CHAPTER EXERCISE - B

1. *Find the value of K_P for the reaction : $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, if the partial pressures of SO_2, O_2, and SO_3 are 0.60 atm, 0.10 atm and 0.30 atm respectively. What will be the partial pressure of O_2 gas if at equilibrium, equal amounts (in moles) of SO_2 and SO_3 are observed ?*

2. *Calculate the volume percent of chlorine gas at equilibrium in the dissociation of $PCl_{5(g)}$ under a total pressure of 1.5 atm. The K_P for its dissociation = 0.3*

Choose the correct alternative. Only one choice is correct. However, question marked '*' may have more than one correct option.

3. *Pressure is doubled in each of the following equilibriums. In which case yield is maximum ?*

(A) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$ **(B)** $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$

(C) $2Fe(s) + 3H_2O(g) \rightleftharpoons Fe_2O_3(s) + 3H_2(g)$ **(D)** $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

4. *Increase in the pressure for the equilibrium :* $H_2O(\ell) \rightleftharpoons H_2O(g)$ *results in the :*

I : *formation of more $H_2O(\ell)$* II : *formation of more $H_2O(g)$*

III : *increase in b.p. of $H_2O(\ell)$* IV : *decrease in b.p. of $H_2O(\ell)$*

Hence, correct choice is :

(A) *I, II* **(B)** *II, III* **(C)** *I, III* **(D)** *I, IV*

5. *In presence of a catalyst, what happens to the chemical equilibrium ?*

(A) *Energy of activation of the forward and backwards reactions are lowered by the same amount*

(B) *Equilibrium amount is not disturbed*

(C) *Rates of forward and reverse reactions increase by the same factor*

(D) *All of the above*

6. *NH_3 at 10 atm and CO_2 at 30 atm pressure are introduced in an evacuated chamber. If K_p for the reaction :*

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

is 2000 atm^3 at 400 K, then the final pressure in the reaction chamber will be :

(A) *less than 40 atm* **(B)** *more than 40 atm*

(C) *equal to 40 atm* **(D)** *can not be predicted*

7. *During thermal dissociation, the observed vapour density of $N_2O_4(g)$ is 26.0. The extent of dissociation of $N_2O_4(g)$ is :*

(A) 50% **(B)** 87% **(C)** 77% **(D)** 23%

8. *The equilibrium constant K_p for the reaction* $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ *changes if :*

(A) *the total pressure changes* **(B)** *a catalyst is used*

(C) *the amounts of H_2 and I_2 change* **(D)** *the temperature changes*

9. *To the system* $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

in equilibrium, some N_2 gas was added at constant volume. Then,

(A) *K_p will remain constant and K_c will change* **(B)** *K_c will remain constant and K_p will change*

(C) *Both K_p and K_c will remain constant* **(D)** *Both K_p and K_c will change*

10. *When pressure is applied to the equilibrium system*

$$\text{Ice} \rightleftharpoons \text{Water}$$

Which of the following phenomenon will happen ?

(A) *More ice will be formed* **(B)** *Water will evaporate*

(C) *More water will be formed* **(D)** *Equilibrium will not be shifted*

11. *For the reaction :*

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

the forward reaction at constant temperature is favoured by

(A) *introducing an inert gas at constant volume*

(B) *introducing chlorine gas at constant volume*

(C) *introducing an inert gas at constant pressure*

(D) *decreasing the volume of the container*

***12.** *In which of the following reactions, the yield of the products increase by the increase in the pressure ?*

(A) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ **(B)** $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(C) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ **(D)** $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

13. *For the reaction* $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, *the value of* K_p *is* 1.7×10^3 *at* 500 *K and* 1.78×10^4 *at* 600 *K. Which of the following is correct ?*

I. *The proportion of* NO_2 *in the equilibrium mixture is increased by decreasing the pressure*

II. *The standard enthalpy change for the forward reaction is negative*

III. *units of* K_p *are atm*

IV. *at* 500 *K, the degree of dissociation* N_2O_4 *decreases by* 50% *by increasing the pressure by* 100%.

The correct choice is :

(A) *I, III* **(B)** *I* **(C)** *II, IV* **(D)** *III*

14. *The equilibrium constant for the reaction* $N_2(g)+O_2(g) \rightleftharpoons 2NO(g)$ *is* 4×10^{-4} *at* 2000*K. In presence of a catalyst, equilibrium is attained ten times faster. Therefore, the equilibrium constant in presence of the catalyst at* 2000*K is :*

(A) 4×10^{-5} **(B)** 4×10^{-4} **(C)** 4×10^{-3}

(D) *Difficult to compute without more data*

15. *The equilibrium concentration of* C_2H_4 *in the gas phase reaction*

$$C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g) \; ; \; \Delta H = -32.7\,\text{kcal};$$ *can be increased by*

I. *removal of* C_2H_6 II. *removal of* H_2 III. *decreasing temperature* IV. *increasing pressure*

The correct choice is :

(A) *I, II* **(B)** *I, III* **(C)** *II, III* **(D)** *None of these*

16. *When KOH is dissolved in water, heat is evolved. If the temperature is raised, the solubility of KOH.*

(A) *Increases* **(B)** *Decreases* **(C)** *Remains the same* **(D)** *Cannot be predicted*