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Chemical Equilibrium

Reversible Reactions

"The reactions in which reactants combine together or dissociate to form products and under similar conditions of temperature and pressure, products recombine or dissociate to give back the reactants are called reversible reactions."

These reactions are represented by sign of reversibility (⇋). Here, the reaction occurring from left to right is called forward reaction, while that occurring from right to left is called backward or reverse reaction. For example,

$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g) + \text{Heat}$ (Haber's process)

$2SO_2(g) + O_2(g) \leftrightharpoons 2SO_3(g) + \text{Heat}$ (Contact process)

$N_2(g) + O_2(g) \leftrightharpoons 2NO(g) - \text{Heat}$

$PCl_5(g) \leftrightharpoons PCl_3(g) + Cl_2(g) - \text{Heat}$

Reversible reactions involve the state of chemical equilibrium and it is the reason why these reactions are never completed.

The State of Chemical Equilibrium

If a reversible reaction is carried out in a closed vessel, after some time a state comes when the rate of forward reaction becomes equal to the rate of backward reaction and concentration of any reactant or product in reaction mixture does not change with time. This state of reversible reactions is called the state of chemical equilibrium. Thus,

"The state of a reversible reactions when the rate of forward reaction becomes equal to the rate of backward reaction and concentration of any reactant or product does not change with time is called the state of chemical equilibrium."

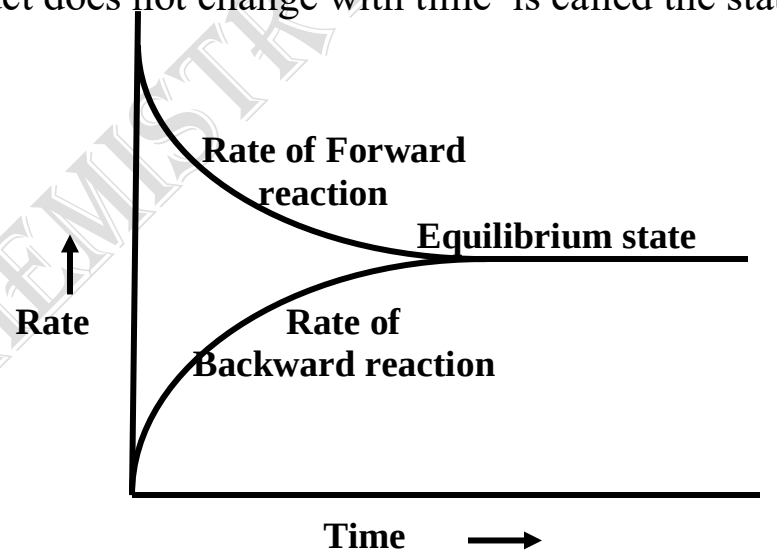


Fig.- Expression of Equilibrium state

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In fact, the rate of a chemical reaction depends upon the concentration of reactants. When a reversible reaction is carried out in a closed vessel, the concentration of reactants goes on decreasing, while that of products goes on increasing with time. Hence, the rate of forward reaction goes on decreasing, while that of backward reaction goes on increasing with time. At equilibrium state these two rates become equal.

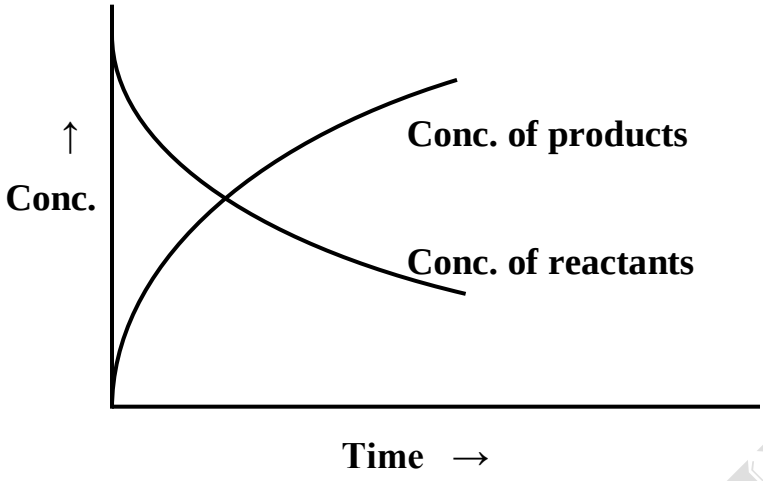


Fig. – Variation of conc. with time

Characteristics of Equilibrium State

(1) At equilibrium state, the rate of forward reaction becomes equal to the rate of backward reaction.

(2) At equilibrium, both reactants and products remain present in reaction mixture, but the concentration of any species does not change with time.

(3) At equilibrium state, all the visible properties of the system such as temperature, pressure, colour, composition, density etc. become constant. Hence, it seems that, the reaction has stopped, but the reaction actually does not stop, but occurs both in forward and backward directions with equal rates. Thus, the equilibrium state seems to be static but it is actually dynamic in nature.

(4) If any of the reactants or products is gaseous, then equilibrium is always established in closed vessel and is never established in open vessel. However, if all the reactants and products are solids or liquids, then it can be established in open vessel.

(5) Equilibrium state depends upon temperature, pressure and conc. and therefore gets changed with change of these parameters.

(6) Catalysts have no effect on equilibrium. In fact, catalysts increase both forward and backward reactions for same extent and help in quick establishment of the equilibrium but they do not affect the equilibrium state. If catalyst is not used then

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also same equilibrium is established, but it takes relatively longer time.

(7) The equilibrium state can be attained from either of the directions i.e. it can be achieved by carrying out the reaction either taking reactants or taking products. In both the cases same equilibrium state is achieved.

(8) At equilibrium state, the change in free energy of the system (ΔG) is equal to zero.

Laws of Chemical Equilibrium

Following are two laws of chemical equilibrium –

(1) Law of mass action

(2) Le-Chatelier's principle

These laws are only applicable when equilibrium state has attained and are applicable on both physical and chemical equilibrium.

Law of Mass Action

This law was for the first time proposed by Guldberg and Waage. It gives quantitative relationship between the rate of the reaction and the active mass (molar concentration) of the reactants. According to this law,

"At constant temperature, in the equilibrium of a reversible reaction, the rate of the reaction of a reactant is directly proportional to its active mass (molar concentration) and the rate of the entire reaction is proportional to the product of the active masses of the reactants."

Let us consider following reversible reaction-

$$A + B \leftrightharpoons C + D$$

Applying law of mass action on forward reaction-

Rate of the reaction of reactant A α [A]

Rate of the reaction of reactant B α [B]

Rate of forward reaction, $r_f \alpha [A][B]$

or $r_f = k_f [A][B]$ ---------- (1)

Where, k_f is a proportionality constant called rate constant for forward reaction.

Similarly for backward reaction-

Rate of the reaction of reactant C α [C]

Rate of the reaction of reactant D α [D]

Rate of backward reaction, $r_b \alpha [C][D]$

or $r_b = k_b [C][D]$ ---------- (2)

Where, k_b is rate constant for backward reaction.

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At the equilibrium of the reaction-

$$r_f = r_b$$

$$\therefore \quad k_f [A] [B] = k_b [C] [D]$$

$$\text{or} \quad \frac{k_f}{k_b} = \frac{[C] [D]}{[A] [B]}$$

$$\text{or} \quad \frac{[C] [D]}{[A] [B]} = K_C \qquad \text{---------- (3)}$$

Where, K_C is a new constant called equilibrium constant of the reaction in terms of molar concentration.

Thus,

" At constant temperature, in the equilibrium of a reversible reaction, the ratio of the product of the molar conc. of products to the product of the molar conc. of reactants is constant, which is called equilibrium constant of the reaction."

For a chemical reaction of type,

$$aA + bB \leftrightharpoons cC + dD$$

We get following form of equation (3)-

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad \text{---------- (4)}$$

Thus, "At constant temperature, in the equilibrium of a reversible reaction, the ratio of the product of the molar conc. of products to the product of the molar conc. of reactants with each concentration terms raised to the power equal to the number of moles represented in balanced chemical equation is constant, which is called equilibrium constant of the reaction."

From ideal gas equation,

$$PV = nRT$$

$$\text{or} \quad P = \frac{n}{V} RT$$

$$\text{or} \quad P = CRT$$

Where, C = molar conc.

Thus, for gaseous reactions, the molar conc. of the different species in eq. (4) can be replaced by their partial pressure. In such case, the equilibrium constant K_C is represented by K_P. Here,

$$K_P = \frac{[p_C]^c [p_D]^d}{[p_A]^a [p_D]^d} \qquad \text{---------- (5)}$$

Where, K_P is equilibrium constant of the reaction in terms of partial pressure.

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Relation Between K_C and K_P

Let us consider following general reversible reaction,

$$aA + bB \leftrightharpoons cC + dD$$

Applying law of mass action, equilibrium constant of the reaction in terms of molar conc. -

$$K_C = \frac{[c_C]^c [c_D]^d}{[c_A]^a [c_B]^b} \quad \text{----------} \quad (1)$$

Where, $[c_A]$, $[c_B]$, $[c_C]$, and $[c_D]$ are the molar conc. of species A, B, C, and D at equilibrium.

If the reaction is gaseous, then the equilibrium constant in terms of partial pressure-

$$K_P = \frac{[p_C]^c [p_D]^d}{[p_A]^a [p_B]^b} \quad \text{----------} \quad (2)$$

Where, $[P_A]$, $[P_B]$, $[P_C]$, and $[P_D]$ are the partial pressure of species A, B, C, and D at equilibrium.

From ideal gas equation,

$$PV = nRT$$

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

or $$P = CRT$$

Where, C = molar conc.

Thus, $[P_A] = [C_A RT]$ $[P_B] = [C_B RT]$

$[P_C] = [C_C RT]$ $[P_D] = [C_D RT]$

Putting these values of $[P_A]$, $[P_B]$, $[P_C]$, and $[P_D]$ in eq. (2) we get,

$$K_P = \frac{[C_C RT]^c [C_D RT]^d}{[C_A RT]^a [C_B RT]^b}$$

or $$K_P = \frac{[c_C]^c [c_D]^d}{[c_A]^a [c_B]^b} \times (RT)^{(c+d)-(a+b)} \quad \text{---------} \quad (3)$$

From eq. (1) and (3) we get,

$$K_P = K_C \times (RT)^{(c+d)-(a+b)}$$

or $$K_P = K_C \times (RT)^{\Delta n_g} \quad \text{---------} \quad (4)$$

Where, $\Delta n_g = \Sigma n_g(\text{products}) - \Sigma n_g(\text{reactants})$

This expression gives the relation between K_P and K_C for the gaseous reactions.

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Applications

(1) The reactions in which the number of gaseous moles remains unchanged. For example,

$$H_2(g) + I_2(g) \leftrightharpoons 2HI(g)$$
$$N_2(g) + O_2(g) \leftrightharpoons 2NO(g)$$

Here, $\Delta n_g = 2 - 2$

$= 0$

$\therefore \quad K_P = K_C (RT)^0$

or $\quad K_P = K_C$

Thus, for the reactions in which the total the number of gaseous moles of products is equal to that of reactants, the value of K_P is equal to that of K_C.

(2) The reactions in which the number of gaseous moles increases. For example,

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

Here, $\Delta n_g = 2 - 1$

$= 1$

$\therefore \quad K_P = K_C (RT)^1$

or $\quad K_P = K_C RT$

or $\quad K_P > K_C$

Thus, for the reactions in which the total the number of gaseous moles of products is greater than that of reactants, the value of K_P is greater than that of K_C.

(3) The reactions in which the number of gaseous moles decreases. For example,

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

Here, $\Delta n_g = 2 - 4$

$= -2$

$\therefore \quad K_P = K_C (RT)^{-2}$

or $\quad K_P = \frac{KC}{(RT)^2}$

or $\quad K_P < K_C$

Thus, for the reactions in which the total the number of gaseous moles of products is lesser than that of reactants, the value of K_P is lesser than that of K_C.

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Factors Affecting Equilibrium Constant

(1) Temperature- The equilibrium constant of a reaction is the characteristic of the reaction at a given temperature but it get changed with change of temperature. For example, for following reaction,

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

At 717K temperature, equilibrium constant,

$$K_C = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$
$$= 48$$

This value of K_C remains constant as long as temperature is constant, but gets changed with change of temperature.

(2) Mode of writing the reaction-Let us consider following equilibrium-

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

Here, equilibrium constant,

$$K_C = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} \quad \text{---------- (1)}$$

If the same reaction is written in opposite direction-

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

Then, equilibrium constant,

$$K_C' = \frac{[H_2(g)][I_2(g)]}{[HI(g)]^2} \quad \text{---------- (2)}$$

Comparing eq. (1) and (2) we get,

$$K_C' = \frac{1}{K_C}$$

or $$K_{backward} = \frac{1}{K_{forward}} \quad \text{--------- (3)}$$

Thus, the equilibrium constant for backward reaction is equal to the reciprocal of that for forward reaction.

(2) Stoichiometry of the reaction- Let us consider following equilibrium-

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

Here, equilibrium constant,

$$K_C = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} \quad \text{---------- (1)}$$

If the stoichiometry of the reaction is halved, then-

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

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Then, equilibrium constant,

$$K_C' = \frac{[HI(g)]}{[H_2(g)]^{1/2}[I_2(g)]^{1/2}} \quad \text{---------- (2)}$$

Comparing eq. (1) and (2) we get,

$$K_C' = \sqrt{K_C}$$

Thus, if the stoichiometry of a reaction is halved, the equilibrium constant of the reaction becomes equal to the squire root of the original value.

Factors which do not affect Equilibrium Constant

(1) Initial conc. of the reactants-If the initial conc. of the reactants is changed, the conc. of the products in the equilibrium mixture gets changed in same proportion, but the value of K_C remains unchanged provided that the temperature remains unchanged at the equilibrium.

(2) Pressure

(3) Presence or absence of catalyst

Representation of Equilibrium Constant

(1) For Homogeneous Equilibria– For homogeneous equilibria, the equilibrium constants are simply represented following law of mass action. For example for following equilibrium-

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

Here, equilibrium constant,

$$K_C = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

and

$$K_P = \frac{[P_{HI(g)}]^2}{[P_{H_2}(g)][P_{I_2}(g)]}$$

Similarly for following equilibrium-

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

Here, equilibrium constant,

$$K_C = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

and

$$K_P = \frac{[P_{NH_3}(g)]^2}{[P_{N_2}(g)][P_{H_2}(g)]^3}$$

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(2) For Heterogeneous Equilibria – For these equilibria, the molar conc. of solid and liquid phases are by conventions, taken to be constant and are not represented in the expression of equilibrium constants. For example for following equilibrium-

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Here, conc. quotient,

$$Q = \frac{[CaO(s)]\,[CO_2(g)]}{[CaCO_3(s)]}$$

By convention, $[CaO(s)] = [CaCO_3(s)] = 1$

$\therefore$ $K_C = [CO_2(g)]$

and $K_P = [P_{CO_2}(g)]$

Similarly for following equilibrium-

$$H_2O(l) \rightleftharpoons H_2O(g)$$

Equilibrium constant,

$K_C = [H_2O(g)]$

and $K_P = [P_{H_2O}(g)]$

Unit of Equilibrium Constant

(1) Unit of $K_C = (\text{mole-litre}^{-1})^{\Delta ng}$

(2) Unit of $Kp = (\text{atm})^{\Delta ng}$

Where, $\Delta n_g = \Sigma\, n_g(\text{products}) - \Sigma\, n_g(\text{reactants})$

(1) For the reactions in which the number of gaseous moles remains unchanged. For example,

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

Here, $\Delta n_g = 2 - 2$

$= 0$

$\therefore$ Unit of $K_C = (\text{mole-litre}^{-1})^{\Delta ng}$

$= (\text{mole-litre}^{-1})^0$

= No unit (Dimensionless)

Similarly, Unit of $Kp = (\text{atm})^{\Delta ng}$

$= (\text{atm})^0$

= No unit (Dimensionless)

Thus, the reactions in which total the number of gaseous moles of products is

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equal to that of reactants, the equilibrium constants K_C and K_P have no unit i.e. are dimensionless.

(2) For the reactions in which the number of gaseous moles changes, the equilibrium constants K_C and K_P have some definite unit. For example, for the reaction,

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

Here, $\Delta n_g = 2 - 1$

$= 1$

$\therefore$ Unit of $K_C = (\text{mole-litre}^{-1})^{\Delta ng}$

$= (\text{mole-litre}^{-1})^1$

$= \text{mole-litre}^{-1}$

Similarly, Unit of $Kp = (\text{atm})^{\Delta ng}$

$= (\text{atm})^1$

$= \text{atm}$

Similarly, for the reaction,

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

Here, $\Delta n_g = 2 - 4$

$= -2$

$\therefore$ Unit of $K_C = (\text{mole-litre}^{-1})^{\Delta ng}$

$= (\text{mole-litre}^{-1})^{-2}$

$= \text{mole}^{-2}\text{-litre}^2$

Similarly, Unit of $Kp = (\text{atm})^{\Delta ng}$

$= (\text{atm})^{-2}$

$= \text{atm}^{-2}$

Mathematical Expression of Equilibrium Constant

(1) Synthesis of HI

Let, a moles of H_2 (g) and b moles of I_2 (g) are taken in a closed container of volume V litre and are subjected to the reaction. At equilibrium x moles each of H_2 and I_2 combine together to form 2x moles of HI, then-

$H_2(g)$ +	$I_2(g)$	$\rightleftharpoons$ $2HI(g)$	
a	b	0	initial no. of moles
(a-x)	(b-x)	2x	no. of moles at equilibrium
$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{2x}{V}$	molar conc. at equilibrium

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Applying law of mass action, the equilibrium constant,

$$K_C = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

$$= \frac{[\frac{2x}{V}]^2}{[\frac{(a-x)}{V}][\frac{(b-x)}{V}]}$$

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

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

This is the mathematical expression of K_C for the formation of HI by combination of H_2 and I_2. Since, this expression does not involve volume term, the equilibrium constant K_C for this reaction is independent of the volume of the container and therefore, it does not change with the change of the volume of the container.

(2) Dissociation of HI

Let, a moles of HI (g) are taken in a closed container of volume V litre and are subjected to dissociation. At equilibrium x moles of HI get dissociated to give x/2 moles each of H_2 and I_2, then-

$2HI(g)$	$\leftrightharpoons$	$H_2(g)$	+	$I_2(g)$	
a		0		0	initial no. of moles
(a-x)		$\frac{x}{2}$		$\frac{x}{2}$	no. of moles at equilibrium
$\frac{(a-x)}{V}$		$\frac{x}{2V}$		$\frac{x}{2V}$	molar conc. at equilibrium

Applying law of mass action, the equilibrium constant,

$$K_C = \frac{[H_2(g)][I_2(g)]}{[HI(g)]^2}$$

$$= \frac{[\frac{x}{2V}][\frac{x}{2V}]}{[\frac{(a-x)}{V}]^2}$$

$$= \frac{x^2}{4V^2} \times \frac{V^2}{(a-x)^2}$$

or $$K_C = \frac{x^2}{4(a-x)^2}$$

This is the mathematical expression of K_C for the dissociation of HI. Since, this expression does not involve volume term, the equilibrium constant K_C for this

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reaction is independent of the volume of the container and therefore, it does not change with the change of the volume of the container.

(3) Dissociation of PCl_5

Let, a moles of PCl_5 (g) are taken in a closed container of volume V litre and are subjected to dissociation. At equilibrium x moles of PCl_5 get dissociated to give x moles each of PCl_3 and Cl_2, then-

PCl_5 (g)	⇋	PCl_3 (g)	+	Cl_2 (g)	
a		0		0	initial no. of moles
(a-x)		x		x	no. of moles at equilibrium
$\frac{(a-x)}{V}$		$\frac{x}{V}$		$\frac{x}{V}$	molar conc. at equilibrium

Applying law of mass action, the equilibrium constant,

$$K_C = \frac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$$

$$= \frac{[\frac{x}{V}][\frac{x}{V}]}{\frac{(a-x)}{V}}$$

$$= \frac{x^2}{V^2} \times \frac{V}{(a-x)}$$

or $$K_C = \frac{x^2}{V(a-x)}$$

This is the mathematical expression of K_C for the dissociation of PCl_5. From this expression it is clear that, the equilibrium constant K_C for this reaction is inversely proportional to the volume of the container and therefore, it will decrease with the increase of the volume of the container and vice versa.

(4) Expression of K_P for dissociation of PCl_5

Let, 1 mole of PCl_5 (g) is taken in a closed container and is subjected to dissociation. At equilibrium α moles of PCl_5 get dissociated to give α moles each of PCl_3 and Cl_2, then-

PCl_5 (g)	⇋	PCl_3 (g)	+	Cl_2 (g)	
1		0		0	initial no. of moles
(1- α)		α		α	no. of moles at equilibrium

Thus, total no. of moles at equilibrium = (1- α) + α + α
= (1+ α)

If P is the total pressure at equilibrium, then-

Partial pressure of PCl_5 (g), $[P_{PCl_5}] = \frac{(1-\alpha)}{(1+\alpha)} \times P$

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Partial pressure of PCl_3 (g), $[P_{PCl_3}] = \frac{\alpha}{(1+\alpha)} \times P$

Partial pressure of Cl_2 (g), $[P_{Cl_2}] = \frac{\alpha}{(1+\alpha)} \times P$

Applying law of mass action, the equilibrium constant,

$$K_P = \frac{[\frac{\alpha}{(1+\alpha)} \times P]\,[\frac{\alpha}{(1+\alpha)} \times P]}{[\frac{(1-\alpha)}{(1+\alpha)} \times P]}$$

or $$K_P = \frac{\alpha^2 P}{(1-\alpha^2)}$$

This is the mathematical expression of K_P for the dissociation of PCl_5. From this expression it is clear that, the equilibrium constant K_P for this reaction is directly proportional to the total pressure of the gaseous mixture and therefore, it will increase with increase of the total pressure of the gaseous mixture.

Q. Derive expression of K_P for the following equilibrium-

$$N_2O_4(g) \leftrightharpoons 2NO_2\,(g)$$

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