

$$\theta_A = \frac{K_1 P_A}{1 + K_1 P_A + K_2 P_B}$$

So when both gases are strongly adsorbed then extent of adsorption of gas is strongly affected by the presence of the other.

6.8 CATALYTIC REACTION OF TWO GASES ON SOLID SURFACE

Generally following steps are involved in catalytic reaction of two gases on solid surface.

- (i) Diffusion of reactant towards solid surface
- (ii) Adsorption of reactant on solid surface
- (iii) Product formation after interaction of reactants
- (iv) Desorption of product
- (v) Diffusion of product towards gas phase

Catalytic reaction of two gases on a solid surface can take place by one of the following mechanisms: Langmuir Hinshelwood mechanism or Eley-Rideal mechanism

6.8.1 Langmuir-Hinshelwood Mechanism

Langmuir Hinshelwood mechanism involves the following steps

- (i) Diffusion of reactant gases towards solid surface of catalyst.
- (ii) Interaction of adsorbed reactant gases on catalyst surface.
- (iii) Product formed after interaction of reactants.
- (iv) Desorption of product occurs, which is followed by diffusion of product towards gas phase.

Steps of Langmuir Hinshelwood Mechanism in the Form of Chemical Equations



According to Langmuir Hinshelwood mechanism, the rate of reaction is proportional to fraction of surface covered by A and B i.e.

$$\text{Rate of reaction} \propto \theta_A \theta_B \quad (6.71)$$

$$\text{Rate of reaction} \propto \theta_B \quad (6.72)$$

Combining equation (6.71) and (6.72), we get

$$\text{Rate of reaction} = k_r \theta_A \theta_B \quad (6.73)$$

(6.73) From equation (6.68) and (6.70) by putting values of θ_A and θ_B in equation

$$R_{\text{rex}} = k_r \frac{(aP_A)(bP_B)}{(1 + aP_A + bP_B)^2}$$

$$R_{\text{rex}} = k_r \frac{abP_A P_B}{(1 + aP_A + bP_B)^2} \quad (6.74)$$

Equation (6.74) is the rate expression for the catalytic reaction of two gases on solid following Langmuir-Hinshelwood mechanism.

Depending upon value of adsorption coefficients of gas A and B, following approximations are concluded

- (i) When both gases are weakly adsorbed then, $1 + aP_A + bP_B \approx 1$ by putting this approximation in equation (6.74), we get

$$R_{\text{rex}} = k_r abP_A P_B$$

$$R_{\text{rex}} \propto P_A P_B$$

It is the equation for second order reaction.

- (ii) When gas A is strongly adsorbed then, $1 + aP_A + bP_B \approx aP_A$. Putting this approximation in equation (6.74), we get

$$R_{\text{rex}} = k_r (ab) \frac{P_A P_B}{(aP_A)^2}$$

$$R_{\text{rex}} = k_r \frac{(ab) P_A P_B}{a^2 P_A^2}$$

$$R_{\text{rex}} = k_r \frac{b P_B}{a P_A}$$

So, overall order of reaction is zero because order of reaction with respect to A is -1 while order of reaction with respect to B is 1.

The increase in pressure of gas A will decrease the rate of reaction when A is strongly adsorbed. This reduction in rate of reaction is known as "retardation by reactants". Retardation is not only caused by strong adsorption of one reactant gas, high pressure of one of the reactant gases can also cause retardation. For example at constant value of P_B , rate of reaction increases with the increase of P_A upto a certain value. But further increase in pressure of gas A causes reduction in rate of reaction i.e.

If $P_B = \text{constant}$ and $P_A = \text{variable}$ then

- (i) When P_A is very low then, $1 + aP_A + bP_B \approx 1 + bP_B$ equation (6.74) will be

$$R_{\text{rex}} = k_r \frac{abP_A P_B}{(1 + bP_B)^2}$$

So, rate of reaction increases with P_A within low range value of P_A

- (ii) When P_A is very high then, $1 + aP_A + bP_B \approx aP_A$ the equation (6.74) will be

$$R_{\text{rex}} = k_r (ab) \frac{P_A P_B}{(aP_A)^2}$$

$$R_{\text{rex}} = k_r \frac{b P_B}{a P_A} \quad (\text{Retardation by reactants})$$

So, rate of reaction decreases with high value of P_A .

The value of P_A for which rate of reaction is maximum is called $P_{A(\text{max})}$. After $P_{A(\text{max})}$, retardation by reactant starts as shown in Fig. 6.23.

Differentiating equation (6.74) with respect to " P_A "

$$\frac{d[\text{Rate}]}{dP_A} = k_r abP_B \frac{d}{dP_A} \left[\frac{P_A}{(1 + aP_A + bP_B)^2} \right]$$

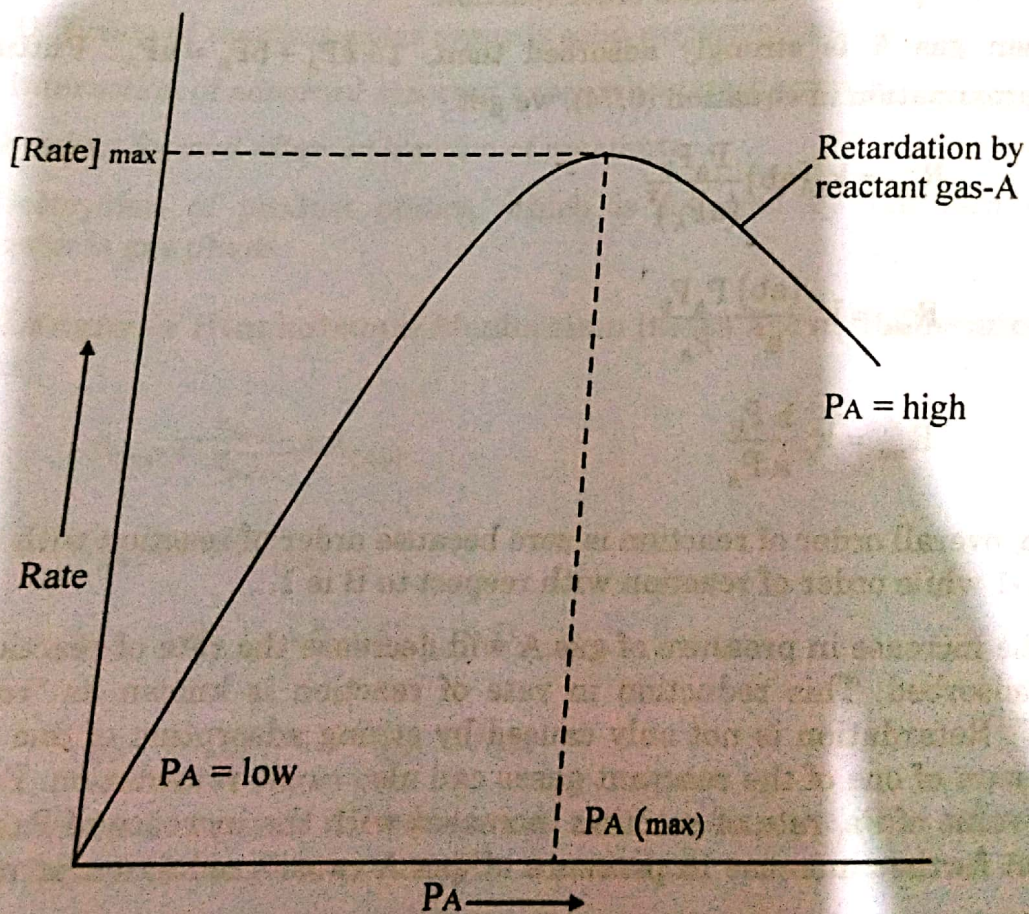


Fig. 6.23 Plot of rate of reaction versus pressure of gas A

$$\frac{d[\text{Rate}]}{dP_A} = k_r abP_B \frac{d}{dP_A} \left[P_A (1 + aP_A + bP_B)^{-2} \right]$$

By applying product rule,

$$\frac{d[\text{Rate}]}{dP_A} = k_r abP_B \left[P_A \frac{d(1 + aP_A + bP_B)^{-2}}{dP_A} + (1 + aP_A + bP_B)^{-2} \frac{dP_A}{dP_A} \right]$$

$$\frac{d[\text{Rate}]}{dP_A} = k_r abP_B \left[P_A (-2)(1 + aP_A + bP_B)^{-3} \frac{d}{dP_A} (1 + aP_A + bP_B) + (1 + aP_A + bP_B)^{-2} (1) \right]$$

$$\frac{d[\text{Rate}]}{dP_A} = k_r abP_B \left[\frac{-2P_A}{(1 + aP_A + bP_B)^3} \left(\frac{d}{dP_A} (1) + a \frac{dP_A}{dP_A} + b \frac{dP_B}{dP_A} \right) + (1 + aP_A + bP_B)^{-2} \right]$$

The derivative of constant is zero. Hence, above equation become,

$$\frac{d[\text{Rate}]}{dP_A} = k_r abP_B \left[\frac{-2aP_A}{(1 + aP_A + bP_B)^3} + \frac{1}{(1 + aP_A + bP_B)^2} \right]$$

At $[\text{Rate}]_{\text{max}}$, the slope of graph is zero and $P_A = P_{A(\text{max})}$

$$0 = k_r abP_B \left[\frac{-2aP_{A(\text{max})}}{(1 + aP_{A(\text{max})} + bP_B)^3} + \frac{1}{(1 + aP_{A(\text{max})} + bP_B)^2} \right] \quad (6.75)$$

Equation (6.75) is a product of two quantities which is equal to zero. One quantity on L.H.S must be zero, constant $k_r abP_B$ can't be zero. So,

$$0 = \left[\frac{1}{(1 + aP_{A(\text{max})} + bP_B)^2} - \frac{2aP_{A(\text{max})}}{(1 + aP_{A(\text{max})} + bP_B)^3} \right]$$

$$\frac{2aP_{A(\text{max})}}{(1 + aP_{A(\text{max})} + bP_B)^3} = \frac{1}{(1 + aP_{A(\text{max})} + bP_B)^2}$$

$$2aP_{A(\text{max})} = \frac{(1 + aP_{A(\text{max})} + bP_B)^3}{(1 + aP_{A(\text{max})} + bP_B)^2}$$

$$2aP_{A(\text{max})} = (1 + aP_{A(\text{max})} + bP_B)$$

$$2aP_{A(\text{max})} - aP_{A(\text{max})} = 1 + bP_B$$

$$aP_{A(\text{max})} = 1 + bP_B$$

$$P_{A(\text{max})} = \frac{1 + bP_B}{a} \quad (6.76)$$

Afeeta Mahesh

Using equation (6.76), we can calculate the value of pressure of gas A at which rate of reaction is maximum. The retardation caused by high pressure of gas A is not much significant, %age decline in rate of reaction from $P_{A(\max)}$ to $2P_{A(\max)}$ is only 11.1%. It can be proved mathematically as

Rate of Reaction at $P_A = P_{A(\max)}$

$$[\text{Rate}]_{P_A = P_{A(\max)}} = k_r ab \left[\frac{P_{A(\max)} P_B}{(1 + aP_{A(\max)} + bP_B)^2} \right] \quad (6.77)$$

Putting value of $P_{A(\max)}$ from equation (6.76) into equation (6.77), we get

$$[\text{Rate}]_{P_A = P_{A(\max)}} = k_r ab \left[\frac{\left(\frac{1 + bP_B}{a} \right) P_B}{\left(1 + a \left(\frac{1 + bP_B}{a} \right) + bP_B \right)^2} \right]$$

$$[\text{Rate}]_{P_A = P_{A(\max)}} = k_r \frac{ab}{a} \left[\frac{(1 + bP_B) P_B}{(1 + (1 + bP_B) + bP_B)^2} \right]$$

$$[\text{Rate}]_{P_A = P_{A(\max)}} = k_r b \left[\frac{(1 + bP_B) P_B}{(2 + 2bP_B)^2} \right]$$

$$[\text{Rate}]_{P_A = P_{A(\max)}} = \frac{k_r b}{4} \left[\frac{(1 + bP_B) P_B}{(1 + bP_B)^2} \right]$$

$$[\text{Rate}]_{P_A = P_{A(\max)}} = \frac{k_r b}{4} \left[\frac{P_B}{(1 + bP_B)} \right] \quad (6.78)$$

Rate of Reaction at $P_A = 2P_{A(\max)}$

$$[\text{Rate}]_{P_A = 2P_{A(\max)}} = k_r ab \left[\frac{2P_{A(\max)} P_B}{(1 + a2P_{A(\max)} + bP_B)^2} \right] \quad (6.79)$$

Putting value of $P_{A(\max)}$ from equation (6.76) into equation (6.79), we get

$$[\text{Rate}]_{P_A = 2P_{A(\max)}} = k_r ab \left[\frac{2 \left(\frac{1 + bP_B}{a} \right) P_B}{\left(1 + 2a \left(\frac{1 + bP_B}{a} \right) + bP_B \right)^2} \right]$$

$$[\text{Rate}]_{P_A = 2P_{A(\max)}} = 2k_r b \left[\frac{(1 + bP_B) P_B}{(1 + 2(1 + bP_B) + bP_B)^2} \right]$$

$$[\text{Rate}]_{P_A = 2P_{A(\text{max})}} = 2k_r b \left[\frac{(1 + bP_B)P_B}{(1 + 2 + 2bP_B + bP_B)^2} \right]$$

$$[\text{Rate}]_{P_A = P_{A(\text{max})}} = 2k_r b \left[\frac{(1 + bP_B)P_B}{(3 + 3bP_B)^2} \right]$$

$$[\text{Rate}]_{P_A = 2P_{A(\text{max})}} = \frac{2}{9} k_r b \frac{(1 + bP_B)P_B}{(1 + bP_B)^2}$$

$$[\text{Rate}]_{P_A = 2P_{A(\text{max})}} = \frac{2k_r b}{9} \frac{P_B}{(1 + bP_B)} \tag{6.80}$$

Percentage of rate at $P_A = 2P_{A(\text{max})}$

$$\% \text{age Rate} = \frac{[\text{Rate}]_{P_A = 2P_{A(\text{max})}}}{[\text{Rate}]_{P_A = P_{A(\text{max})}}} \times 100 \tag{6.81}$$

Substituting values of $[\text{Rate}]_{P_A = 2P_{A(\text{max})}}$ and $[\text{Rate}]_{P_A = P_{A(\text{max})}}$

$$\% \text{age Rate} = \frac{\frac{2 k_r b (P_B)}{9 (1 + bP_B)}}{\frac{k_r b \left(\frac{P_B}{1 + bP_B} \right)}{4}} \times 100$$

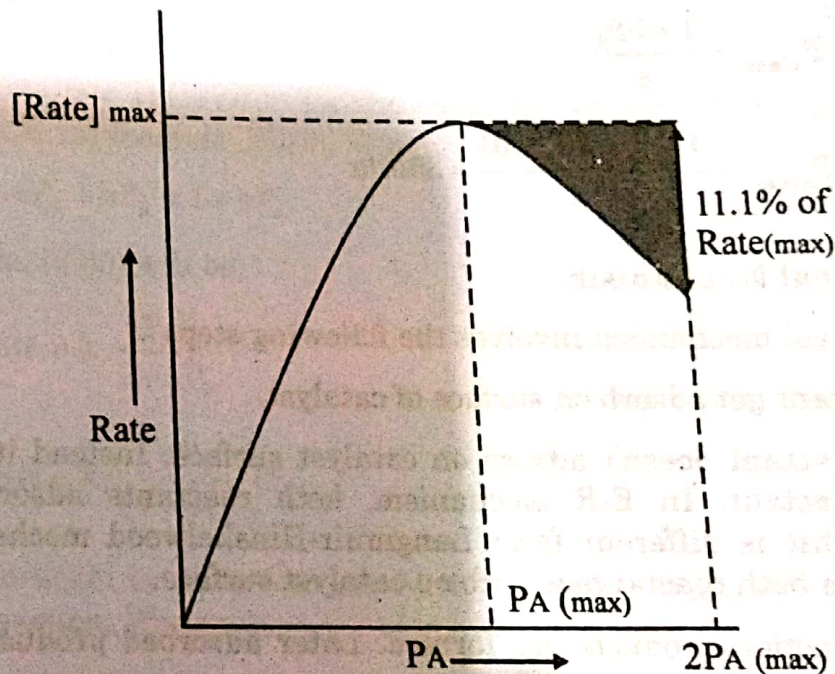


Fig. 6.24 Rate of reaction as a function of P_A showing decline rate at $2P_{A(\text{max})}$

When pressure of gas A is very high then, $1 + aP_A \approx aP_A$. So, equation (6.84) will be,

$$\text{Rate} = k \frac{aP_A P_A}{aP_A}$$

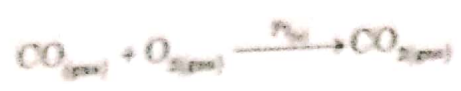
$$\text{Rate} = k P_A$$

Above equation shows, when P_A is very high, then reaction will be 1st order. It also shows that, when P_A is very high then rate of reaction is independent of extent of adsorption of gas A.

6.9 CATALYTIC INORGANIC REACTIONS

6.9.1 Catalytic Oxidation of Carbon Monoxide (CO)

Carbon monoxide can be converted into carbon dioxide by heterogeneous catalysis i.e.



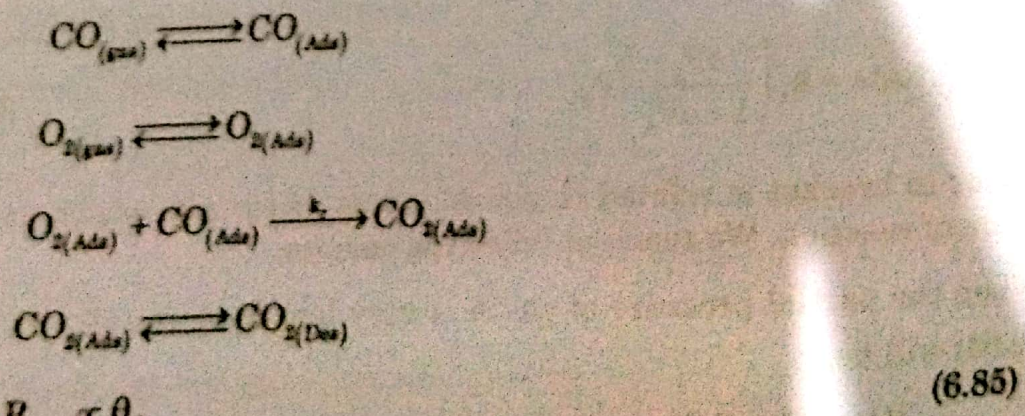
Important features of reaction are as follows

It is a heterogenous catalytic reaction because catalyst is in solid form and reactants are in gaseous phase. It is a simple reaction and can be considered as an example of double system. In this case both reactants are diatomic molecules. One reactant is a homonuclear i.e. O_2 having non polar nature while, CO is heteronuclear as having two different atoms having slightly polar nature. CO is strongly adsorbed on platinum surface because it is π acceptor ligand and has polar nature. O_2 is weakly adsorbed as it is non polar and has no π acceptor ligand ability. So, it can't easily form strong bond with catalyst, e.g. Pt, Pd etc.

The experimental rate law computed by earlier studies is

$$\text{Rate} \propto \frac{P_{\text{O}_2}}{P_{\text{CO}}}$$

According to Langmuir Hinshelwood mechanism, the reaction scheme can be written as



$$R_{\text{rxn}} \propto \theta_{\text{CO}} \tag{6.86}$$

By combining equations (6.85) and (6.86)

$$R_{\text{rez}} \propto \theta_{\text{O}_2} \theta_{\text{CO}}$$

$$R_{\text{rez}} = k_r \theta_{\text{O}_2} \theta_{\text{CO}} \quad (6.87)$$

Putting values of θ_{O_2} and θ_{CO} in equation (6.87),

$$R_{\text{rez}} = k_r \frac{(aP_{\text{O}_2})(bP_{\text{CO}})}{(1 + aP_{\text{O}_2} + bP_{\text{CO}})^2} \quad (6.88)$$

As CO is strongly adsorbed, so $b \gg \gg a$. Then $1 + aP_{\text{O}_2} + bP_{\text{CO}} \approx bP_{\text{CO}}$. By putting this approximation in equation (6.88), we get

$$R_{\text{rez}} = k_r \frac{abP_{\text{O}_2} P_{\text{CO}}}{(bP_{\text{CO}})^2}$$

$$R_{\text{rez}} = k_r \frac{a}{b} \left(\frac{P_{\text{O}_2}}{P_{\text{CO}}} \right)$$

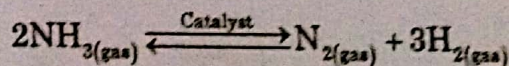
As k_r and a/b are constants. So,

$$\text{Rate} \propto \frac{P_{\text{O}_2}}{P_{\text{CO}}}$$

Hence rate of formation of CO_2 is first order with respect to P_{O_2} and negative first order with respect to P_{CO} . So it is a zero order reaction.

6.9.2 Catalytic Decomposition of Ammonia (NH_3)

Ammonia is commercially produced by Haber's process which is a catalytic process. Its synthesis reaction is reversible. Nitrogen gas (N_2) and hydrogen gas (H_2) are produced o decomposition of ammonia.



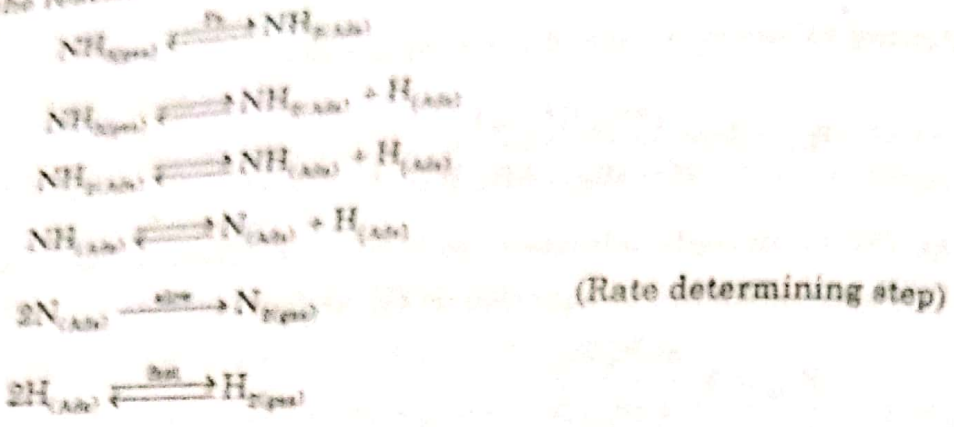
Important features of reaction are as follows .

It is a catalytic reaction which is an example of heterogeneous catalysis because catalyst is in solid state and reactant is in gaseous state. Catalyst used in this reaction may be Pt, Pd, and Fe. But Pt and Pd are expensive, so Fe is used on industrial scale. It is a reversible process, so catalyst increases rate of formation as well as rate of decomposition of NH_3 .

It is experimentally proved that the rate of decomposition of ammonia is directly related to pressure of ammonia and inversely proportional to pressure of hydrogen by the expression give below.

$$\text{Rate of decomposition of } \text{NH}_3 \propto \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^2} \quad (6.89)$$

One of the suggested mechanisms for catalytic decomposition of NH_3 on the iron (Fe) surface is stepwise removal of hydrogen atom from NH_3 molecule. The scheme of the reaction is given below.



Desorption of nitrogen is rate determining step. So, rate of decomposition of ammonia depends upon this step.

Tempkin Adsorption Isotherm for Decomposition of NH_3

Tempkin gave an adsorption isotherm to explain the adsorption-desorption of nitrogen on iron surface. According to this isotherm, rate of adsorption and desorption are exponentially related to fractional surface coverage.

$$R_{Ads} \propto P_{N_2}$$

$$R_{Ads} \propto \frac{1}{e^{\theta_N}}$$

Where, " g " is a roughness factor which indicates heterogeneity of surface of adsorbent and related to activation energy of adsorption. θ_N is fractional surface coverage of nitrogen gas.

$$R_{Ads} = k_1 \frac{P_{N_2}}{e^{\theta_N}}$$

$$R_{Ads} = k_1 P_{N_2} e^{-\theta_N} \quad (6.90)$$

By increasing P_{N_2} , R_{Ads} increases. But by increasing θ_N , R_{Ads} decreases exponentially.

Rate of desorption of nitrogen is

$$R_{Des} \propto e^{\theta_N}$$

$$R_{Des} = k_2 e^{\theta_N} \quad (6.91)$$

Rate of desorption of nitrogen is exponentially related to fractional surface coverage of nitrogen (θ_N).

At equilibrium stage, rate of adsorption becomes equal to rate of desorption of nitrogen as

$$R_{Ads} = R_{Des}$$

$$k_a P_{N_2} e^{-\epsilon \theta_N} = k_d e^{h \theta_N}$$

$$\frac{k_a}{k_d} P_{N_2} = \frac{e^{h \theta_N}}{e^{-\epsilon \theta_N}}$$

As, $a = \frac{k_a}{k_d}$ so, above equation becomes

$$a P_{N_2} = e^{h \theta_N} e^{\epsilon \theta_N}$$

$$a P_{N_2} = e^{\theta_N (h + \epsilon)}$$

Let, $h + \epsilon = f$

$$a P_{N_2} = e^{f \theta_N}$$

Taking natural logarithm of above equation

$$\ln(a P_{N_2}) = \ln(e^{f \theta_N})$$

$$\ln(a P_{N_2}) = f \theta_N$$

$$\theta_N = \frac{\ln(a P_{N_2})}{f} \quad (6.92)$$

From equation (6.92) putting the value of θ_N into equation (6.91), we get

$$R_{Des} = k_d e^{h \left(\frac{1}{f} \ln(a P_{N_2}) \right)}$$

$$R_{Des} = k_d e^{\frac{\ln(a P_{N_2}) h}{f}}$$

$$R_{Des} = k_d (a P_{N_2})^{\frac{h}{f}} \quad (6.93)$$

As, $(R_{Des})_{N_2} = (R_{Decomposition})_{NH_3}$

Then, equation (6.93) will be,

$$(R_{Decomposition})_{NH_3} = k_d (a P_{N_2})^{\frac{h}{f}} \quad (6.94)$$

As we know that, $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

$$K = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$$

Where, K is the equilibrium constant

$$P_{NH_3} = \frac{P_{NH_3}^2}{P_{N_2}^2} \cdot K \tag{6.95}$$

Putting the value of P_{NH_3} from equation (6.95) into equation (6.94)

$$(R_{\text{decomposition}})_{NH_3} = k_d \left(a \frac{P_{NH_3}^2}{P_{N_2}^2} \cdot K \right)^{\frac{1}{2}}$$

$$(R_{\text{decomposition}})_{NH_3} = k_d \left(\frac{a}{K} \right)^{\frac{1}{2}} \left(\frac{P_{NH_3}^2}{P_{N_2}^2} \right)^{\frac{1}{2}} \tag{6.96}$$

a, h and f are constants. The value of h/f may be 0 to 1.

- (i) When value of h/f is equal to 0 then, equation (6.96) will be,

$$(R_{\text{decomposition}})_{NH_3} = k_d$$

Hence, the rate of decomposition of ammonia is independent of pressure of NH_3 and H_2 .

- (ii) When the value of h/f is equal to 1 then equation (6.96) will be,

$$(R_{\text{decomposition}})_{NH_3} = k_d \left(\frac{a}{K} \right) \left(\frac{P_{NH_3}^2}{P_{N_2}^2} \right)$$

$$(R_{\text{decomposition}})_{NH_3} \propto \left(\frac{P_{NH_3}^2}{P_{N_2}^2} \right)$$

Hence, the rate of decomposition of ammonia is dependent on pressure of NH_3 and H_2 at maximum value of h/f.

6.10 CATALYSIS OR USE OF CATALYST IN INDUSTRY

80% of reactions in world are catalytic reactions. Out of this, more than 90 % reactions in industry are also catalytic reactions.

(1) Fertilizer Industry

The 1st step of urea synthesis in Haber's process is catalytic in which the synthesis of ammonia can be done. The reaction is reversible and catalytic as given below

