

Lecture 8

Reaction mechanism and kinetic study

Reaction mechanism and rate equations

For irreversible gas phase reaction $A(g) \rightarrow B(g)$, global rate for catalyst particles is expressed in terms of temperature and concentration of A in bulk gas stream which can be measured or specified directly. Global rates of catalytic reactions are usually expressed per unit mass of catalyst.

Power law model

For homogeneous reaction, power law form of rate equation is used where rate is function of concentration and rate is determined by fitting data to the equation. The exponents on the concentration is the apparent order of the reaction and 'k' is the kinetic constant or reaction rate constant which is independent of concentration and depends on temperature.

For reactions $A+B \rightarrow C+D$

$$r_a = -\frac{dC_a}{dt} = kC_A^\alpha C_B^\beta$$

Here α is the order with respect to A and β is the order with respect to B

This power law approach can also be used for solid catalytic reactions. This analysis is simple. The major disadvantage of this method is that it ignores all the factors associated with adsorption and reaction mechanism on surface of solid catalyst. Hence, power law kinetics fails to adequately describe any solid catalytic process and the rate equation derived from mechanistic model is more preferred. Power law kinetics is preferred as a mode of obtaining preliminary value of rate parameters for solid catalyzed reactions.

Langmuir-Hinshelwood –Hougen-Watson(LHHW) model

The rate equation derived from mechanistic model that simulates the actual surface phenomenon during the process is preferred for reactions involving solid catalysts. The Langmuir-Hinshelwood–Hougen-Watson(LHHW) approach is one of the most commonly used way of deriving rate expressions for fluid solid catalytic reactions. The advantages of this method are that :

- (1) Rate derived by this method takes into account the adsorption-desorption process occurring over the surface along with the surface reaction.
- (2) Rate equation derived can be extrapolated more accurately to concentrations lying beyond the experimentally measured values.

During this method of derivation of rate expression, all the physical transport steps like mass transfer from bulk phase to catalyst surface or diffusion of reactants from pore mouth to interior pore (intraparticle diffusion) are excluded. Thus, it is assumed that the external and internal mass transport processes are very rapid relative to the chemical rate process occurring on or within the catalyst particle. The chemical rate depends on :

- (1) chemisorption steps
- (2) surface reaction steps
- (3) desorption steps

This simple kinetic model assumes isothermal condition about and within catalyst that is temperature gradient is zero.

In LHHW model development, the rate equation is first derived in terms of surface concentration of adsorbed species and vacant sites. Then, these surface concentrations are related to the fluid or bulk concentration that is directly measurable.

For the reaction $A + B \rightleftharpoons C + D$

Let r_a = rates of adsorption (g mol/s.gm of catalyst)

r_s = rates of surface reaction	(g mol/s.gm of catalyst)
r_d = rates of desorption	(g mol/s.gm of catalyst)
C_{AS} = concentration of adsorbed A on surface	(g mol/gm of catalyst)
C_{BS} = concentration of adsorbed B on surface	(gmol/gm of catalyst)
C_{CS} = concentration of adsorbed C on surface	(g mol/gm of catalyst)
C_{DS} = concentration of adsorbed D on surface	(g moles/gm of catalyst)
C_O = total concentration of active sites on surface	(g mol/gm of catalyst)
C_V = concentration of vacant sites on surface	(g mol/gm of catalyst)
C_A = concentration of A in bulk gas phase	(g mol/cm ³)

Similarly C_B, C_C, C_D are the concentrations of B,C,D in the bulk gas phase, respectively.

Let the reaction follows the mechanism given below ;

- (1) $A + S \rightleftharpoons A.S$ --- Adsorption of reactant A on surface vacant site S
- (2) $B + S \rightleftharpoons B.S$ --- Adsorption reactant B on surface vacant site S
- (3) $A.S + B.S \rightleftharpoons C.S + D.S$ --- Surface reaction between adsorbed A and B
- (4) $C.S \rightleftharpoons C + S$ --- Desorption of product C from surface creating a vacant site
- (5) $D.S \rightleftharpoons D + S$ --- Desorption of product D from surface creating a vacant site

Among the various steps described, the slowest step controls the overall rate of reaction and the other remaining steps are assumed to be at near equilibrium conditions. This approach greatly simplifies the overall rate expression, reducing the number of rate constants and equilibrium constants to be determined from experimental data. Further

each step in this method is assumed to be elementary and the number of sites is conserved in each step.

Therefore, the controlling step can be either of the following:

- (1) Surface reaction
- (2) Adsorption
- (3) Desorption

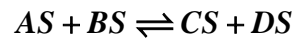
Now total concentration of active sites on surface, C_o , will be the summation concentrations of all sites on which either reactants or products are adsorbed and the concentration of vacant sites.

$$\therefore C_o = C_v + C_{AS} + C_{BS} + C_{CS} + C_{DS}$$

Where, C_v is the concentration of vacant sites.

Case 1 : Rate is surface reaction controlling

The surface reaction is the slowest step and is the rate controlling. According to the mechanism, surface reaction occurs between adsorbed A and adsorbed B producing adsorbed C & adsorbed D.



The rate of surface reaction is given as

$$r_s = k_s C_{AS} C_{BS} - k'_s C_{CS} C_{DS} \quad k_s = \text{rate constant for forward surface reaction}$$

$$k'_s = \text{rate constant for reverse surface reaction}$$

$$\begin{aligned} &= k_s \left[C_{AS} C_{BS} - \frac{k'_s}{k_s} C_{CS} C_{DS} \right] \\ &= k_s \left[C_{AS} C_{BS} - \frac{1}{K_s} C_{CS} C_{DS} \right] \quad \because K_s = \frac{k_s}{k'_s} \end{aligned} \quad (1)$$

Now, since all the other steps are considered to be in equilibrium, therefore concentration of adsorbed species can be obtained as follows.

For adsorption steps and desorption steps :

$$\text{From step (1)} \quad K_A = \frac{C_{AS}}{C_A \cdot C_V} \qquad \text{From step (4)} \quad K_C = \frac{C_{CS}}{C_C \cdot C_V}$$

$$\text{From step (2)} \quad K_B = \frac{C_{BS}}{C_B \cdot C_V} \qquad \text{From step (5)} \quad K_D = \frac{C_{DS}}{C_D \cdot C_V}$$

K_A, K_B, K_C, K_D are adsorption equilibrium constants.

Then, the adsorbed phase concentrations can be written as

$$C_{AS} = K_A C_A C_V \quad C_{CS} = K_C C_C C_V$$

$$C_{BS} = K_B C_B C_V \quad C_{DS} = K_D C_D C_V$$

Substituting all these value in equation (1)

$$r_s = k_s \left[C_{AS} C_{BS} - \frac{1}{K_S} C_{CS} C_{DS} \right] = k_s \left[K_A C_A C_V \cdot K_B C_B C_V - \frac{K_C}{K_S} C_C C_V \cdot K_D C_D C_V \right]$$

$$\text{or, } r_s = k_s \left[K_A K_B C_A C_B C_V^2 - \frac{K_C K_D}{K_S} C_C C_D C_V^2 \right]$$

$$\text{or } r_s = k_s K_A K_B \left[C_A C_B - \frac{K_C K_D}{K_S K_A K_B} C_C C_D \right] C_V^2 \qquad (2)$$

$$\text{Now, } C_o = C_{AS} + C_{BS} + C_{CS} + C_{DS} + C_V$$

$$C_o = K_A C_A C_V + K_B C_B C_V + K_C C_C C_V + K_D C_D C_V + C_V$$

$$= C_V [1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D]$$

$$C_V = \frac{C_O}{1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D} \quad (3)$$

For the reaction $A+B \rightleftharpoons C+D$, at equilibrium, the overall equilibrium constant is

$$K = \frac{C_C C_D}{C_A C_B}$$

All concentrations correspond to the equilibrium conditions in gas phase.

$$K = \frac{(C_{CS} / K_C C_V)(C_{DS} / K_D C_V)}{(C_{AS} / K_A C_V)(C_{BS} / K_B C_V)} = \frac{C_{CS} C_{DS}}{C_{AS} C_{BS}} \cdot \frac{K_A K_B C_V^2}{K_C K_D C_V^2}$$

$$\text{Or, } K = \frac{K_A K_B}{K_C K_D} \cdot K_S \quad \therefore K_S = \frac{C_{CS} C_{DS}}{C_{AS} C_{BS}} \quad (4)$$

Substituting (3) &(4) in equation (2),

$$r_s = k_s K_A K_B \left[C_A C_B - \frac{1}{K} C_C C_D \right] \frac{C_O^2}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D)^2}$$

$$r_s = k_s K_A K_B C_O^2 \frac{C_A C_B - \frac{1}{K} C_C C_D}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D)^2} \quad (5)$$

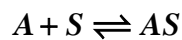
The above rate expression can also be derived in terms of bulk partial pressure.

Case 2: Rate is adsorption control

(a) Adsorption of A controlling

Let adsorption of A be the slowest step so that adsorption of B, surface reaction and desorption of C are at equilibrium.

Adsorption of A is given as



Rate of adsorption $r_a = k_a C_A C_V - k_d C_{AS}$

$$r_a = k_a \left[C_A C_V - \frac{k_d}{k_a} C_{AS} \right]$$

$$\text{Or, } r_a = k_a \left[C_A C_V - \frac{1}{K_A} C_{AS} \right] \quad K_A = \frac{k_a}{k_d} \text{ (adsorption equilibrium constant for A)}$$

$$r_a = k_a C_V \left[C_A - \frac{1}{K_A} \frac{C_{AS}}{C_V} \right] \quad (6)$$

Now as other steps are in equilibrium :

$$K_S = \frac{C_{CS} C_{DS}}{C_{AS} C_{BS}}$$

$$K_B = \frac{C_{BS}}{C_B C_V} \quad K_C = \frac{C_{CS}}{C_C C_V} \quad K_D = \frac{C_{DS}}{C_D C_V}$$

$$C_{BS} = K_B C_B C_V \quad C_{CS} = K_C C_C C_V \quad C_{DS} = K_D C_D C_V$$

Then ,

$$C_{AS} = \frac{C_{CS} C_{DS}}{K_S C_{BS}} = \frac{K_C C_C C_V \cdot K_D C_D C_V}{K_S K_B C_B C_V} = \frac{K_C K_D}{K_S K_B} \frac{C_C C_D C_V}{C_B}$$

Substituting value in equation (6)

$$r_a = k_a C_V \left[C_A - \frac{1}{K_A C_V} \frac{K_C K_D}{K_S K_B} \frac{C_C C_D C_V}{C_B} \right]$$

$$r_a = k_a C_V \left[C_A - \frac{K_C K_D}{K_S K_A K_B} \frac{C_C C_D}{C_B} \right]$$

$$r_a = k_a C_V \left[C_A - \frac{1}{K} \frac{C_C C_D}{C_B} \right] \quad (7)$$

$$K = \frac{K_S K_A K_B}{K_C K_D} = \text{Overall equilibrium constant.}$$

$$\begin{aligned}
\text{Now } C_0 &= C_V + C_{AS} + C_{BS} + C_{CS} + C_{DS} \\
&= C_V + \frac{K_C K_D}{K_S K_B} \cdot \frac{C_C C_D C_V}{C_B} + K_B C_B C_V + K_C C_C C_V + K_D C_D C_V \\
&= C_V \left[1 + \frac{K_C K_D K_A}{K_S K_A K_B} \left(\frac{C_C C_D}{C_B} \right) + K_B C_B + K_C C_C + K_D C_D \right] \\
&= C_V \left[1 + \frac{K_A C_C C_D}{K C_B} + K_B C_B + K_C C_C + K_D C_D \right] \\
C_V &= \frac{C_0}{1 + \frac{K_A C_C C_D}{K C_B} + K_B C_B + K_C C_C + K_D C_D} \quad \because K = \frac{K_S K_A K_B}{K_C K_D}
\end{aligned}$$

Substituting value of C_V in equation (7)

$$r_a = k_a C_0 \frac{C_A - \left[\frac{C_C C_D}{K C_B} \right]}{1 + \frac{K_A C_C C_D}{K C_B} + K_B C_B + K_C C_C + K_D C_D} \quad (8)$$

For a given catalyst C_0 is constant.

Similarly expression when desorption of product is the rate controlling step can be derived. For desorption of C controlling the whole reaction, the rate expression can be derived as

$$r_d = k_d C_0 K \frac{C_A C_B - \left[\frac{C_C C_D}{K} \right]}{1 + K_A C_A + K_B C_B + K_C K C_A C_B + K_D C_D}$$

Eley Rideal model

Apart from power law and Langmuir-Hinshelwood models, other kinetic models are also used to fit the data. EleyRideal model depicts the reaction mechanism in which one reactant species (say A) is adsorbed while the second reactant species (say B) is not adsorbed on the catalyst surface. The reaction then occurs when the passing gas molecules of B in gas phase directly reacts with the adsorbed species A. The schematic representation is shown in Fig. 1.

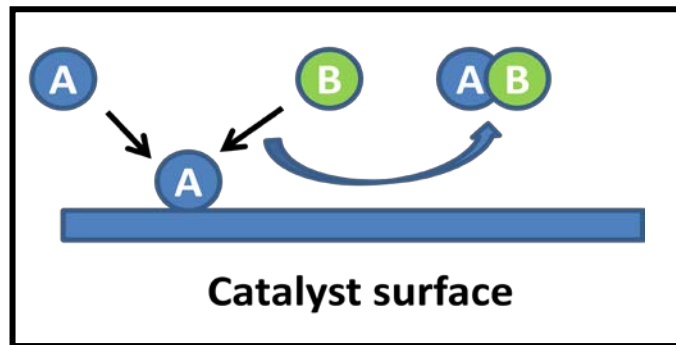


Fig. 1. Eley Rideal mechanism for reaction of adsorbed A with gas phase B producing product AB

- (1) $A + S \rightleftharpoons AS$
- (2) $AS + B (g) \rightarrow P$

Assuming that step 2, the reaction between adsorbed A and gas phase B is irreversible and the rate determining step, then the rate of reaction can be written as

$$r = k C_{AS} C_B \quad (9)$$

The concentration of adsorbed A can be given as $C_{AS} = K_A C_A C_V$

Now, $C_0 = C_{AS} + C_V = K_A C_A C_V + C_V = C_V (1 + K_A C_A)$

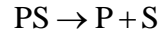
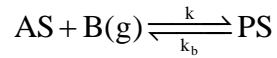
$$C_V = \frac{C_0}{1 + K_A C_A}$$

$$C_{AS} = \frac{K_A C_A C_0}{1 + K_A C_A}$$

Substituting value of C_{AS} in equation (9)

$$r = k C_{AS} C_B = \frac{k C_O K_A C_A C_B}{1 + K_A C_A}$$

If the products are chemisorbed then the reaction may become reversible as shown below.



Then the rate expression can be written as

$$r = k C_{AS} C_B - k_b C_{PS}$$

The concentration of adsorbed product is $C_{PS} = K_P C_P C_V$

$$C_O = C_{AS} + C_{PS} + C_V = K_A C_A C_V + K_P C_P C_V + C_V = C_V (1 + K_A C_A + K_P C_P)$$

$$C_V = \frac{C_O}{1 + K_A C_A + K_P C_P}$$

$$C_{AS} = K_A C_A C_V = \frac{K_A C_A C_O}{1 + K_A C_A + K_P C_P}$$

$$C_{PS} = K_P C_P C_V = \frac{K_P C_P C_O}{1 + K_A C_A + K_P C_P}$$

Substituting C_{AS} and C_{PS} in rate expression,

$$r = k C_{AS} C_B - k_b C_{PS} = k \left(C_{AS} C_B - \frac{1}{K} C_{PS} \right) \quad \because K = \frac{k}{k_b}$$

$$r = k \left(\frac{K_A C_A C_O}{(1 + K_A C_A + K_P C_P)} C_B - \frac{1}{K} \frac{K_P C_P C_O}{(1 + K_A C_A + K_P C_P)} \right)$$

$$r = kC_O \frac{\left(K_A C_A C_B - \frac{K_P}{K} C_P \right)}{1 + K_A C_A + K_P C_P}$$

Estimation of model parameters

The various parameters in the kinetic models such as rate constants, reaction orders, and equilibrium constants are derived by fitting the experimental data. The optimal values of the parameters in the rate equation of a heterogeneous reaction are determined traditionally by using gradient or direct search methods. For success of this method, a very good initial estimate of the parameters is required. This proves to be difficult in most cases. If the initial estimates are far from the global optima, then it is likely that the gradient or direct search method will not converge at all or will converge to local optima. Recently genetic algorithm (GA) is increasingly applied in estimation of kinetic parameters. The major advantage of this method is that it is not dependent on the initial estimate of the parameters. GA performs a multi-directional search.
