

Rate equations for fluid-solid reactions (kinetic models)

Book: *Elements of Chemical Reaction Engineering*, H.S. Fogler, 4th Edition (Chapter 10)

Adsorption

- Adsorption is the first step of the reaction process
- When species A adsorbs on site S (eg. CO adsorbs on site S as a whole unit) it is known as **molecular** or **non-dissociated adsorption**

$$\text{Rate of attachment} = k_A p_A C_v$$

$$\text{Rate of detachment} = k_{-A} C_{A.S}$$

$$\text{Net rate of adsorption, } r_A = k_A p_A C_v - k_{-A} C_{A.S} = k_A \left[p_A C_v - \frac{C_{A.S}}{K_A} \right]$$

$$\text{At equilibrium, } r_A = 0 \quad \text{and} \quad k_A p_A C_v = k_{-A} C_{A.S}$$

$K_A =$ adsorption equilibrium constant

$$\text{or, } C_{A.S} = K_A p_A C_v \quad \left(\because K_A = \frac{k_A}{k_{-A}} \right)$$

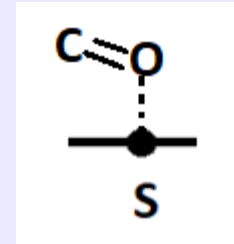
$$\text{As } C_t = C_v + C_{A.S} = C_v + K_A p_A C_v$$

$$\text{or, } C_t = C_v (1 + K_A p_A)$$

$$\text{Replacing we have, } \boxed{C_{A.S} = \frac{K_A p_A C_t}{1 + K_A p_A}} \quad \text{or} \quad \boxed{\theta = \frac{K_A p_A}{1 + K_A p_A}}$$

$$\text{or, } \theta = \frac{v}{v_m} = \frac{K_A p_A}{1 + K_A p_A} \quad \text{Rearranging gives, } \frac{K_A p_A}{v} = \frac{1 + K_A p_A}{v_m}$$

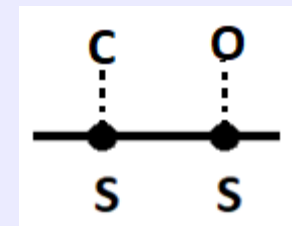
$$\text{or, } \boxed{\frac{p_A}{v} = \frac{1}{K_A v_m} + \frac{1}{v_m} p_A}$$



- In case of **dissociated adsorption**, the molecule (say CO) dissociates and adsorbs on two vacant sites instead of one
- The **rate** of adsorption is **proportional** to the
 - (i) **partial pressure of A** (as this is governed by number of collisions of gas A with surface)
 - (ii) **the square of the concentration of vacant sites** (as two adjacent vacant sites are required when a molecule dissociates and adsorbs, and the probability of the two vacant sites occurring adjacent to one another is proportional to the square of the concentration of vacant sites)
- The rate of desorption is proportional to the product of the occupied site concentration
- Therefore, net rate of adsorption is

$$r_A = k_A p_{CO} C_v^2 - k_{-A} C_{C.S} C_{O.S}$$

$$r_A = k_A \left[p_{CO} C_v^2 - \frac{C_{C.S} C_{O.S}}{K_A} \right]$$



At equilibrium $r_A = 0$ and $k_A p_{CO} C_v^2 = k_{-A} C_{C.S} C_{O.S}$

For $C_{C.S} = C_{O.S}$, $K_A p_{CO} C_v^2 = C_{O.S}^2$

or, $C_{O.S} = C_v \sqrt{K_A p_{CO}}$

Now $C_t = C_v + C_{C.S} + C_{O.S}$

or, $C_t = C_v + C_v\sqrt{K_A p_{CO}} + C_v\sqrt{K_A p_{CO}} = C_v[1 + 2\sqrt{K_A p_{CO}}]$

$$C_v = \frac{C_t}{1+2\sqrt{K_A p_{CO}}}$$

Replacing this value of C_v , we get

$$C_{O.S} = \frac{\sqrt{K_A p_{CO}} C_t}{1+2\sqrt{K_A p_{CO}}}$$

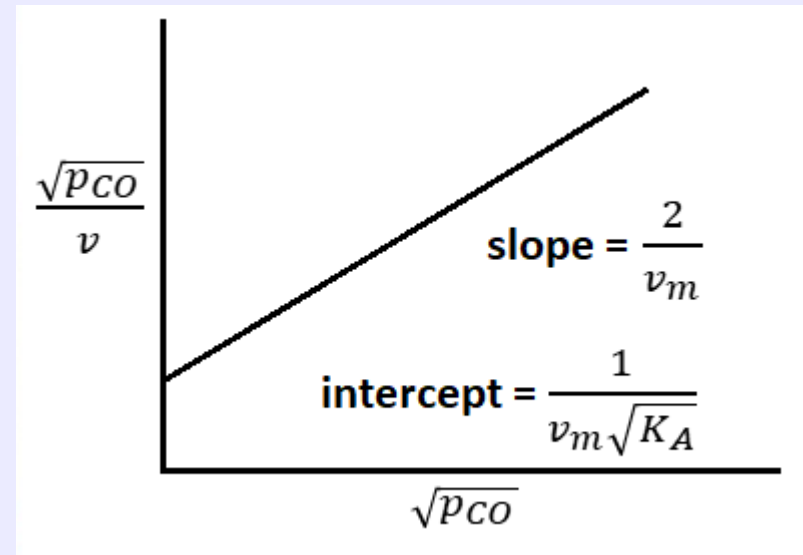
or, $\theta = \frac{C_{O.S}}{C_t} = \frac{\sqrt{K_A p_{CO}}}{1+2\sqrt{K_A p_{CO}}}$

Similar to non-dissociative adsorption, $\theta = \frac{v}{v_m}$

Therefore, $\frac{v}{v_m} = \frac{\sqrt{K_A p_{CO}}}{1+2\sqrt{K_A p_{CO}}}$

or, $\frac{v_m}{v} = \frac{1+2\sqrt{K_A p_{CO}}}{\sqrt{K_A p_{CO}}}$

or, $\frac{\sqrt{p_{CO}}}{v} = \frac{1}{v_m\sqrt{K_A}} + \frac{2}{v_m}\sqrt{p_{CO}}$



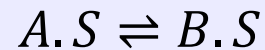
Surface Reaction

Once the reactant is adsorbed onto the surface it is capable of reacting in a number of ways to form the product

Three such ways are:

(a) Single site mechanism

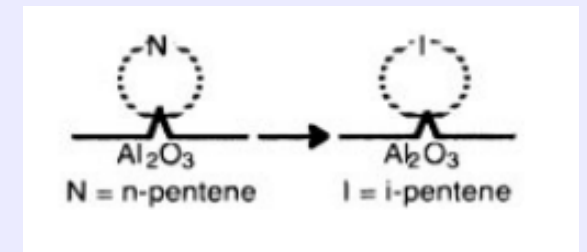
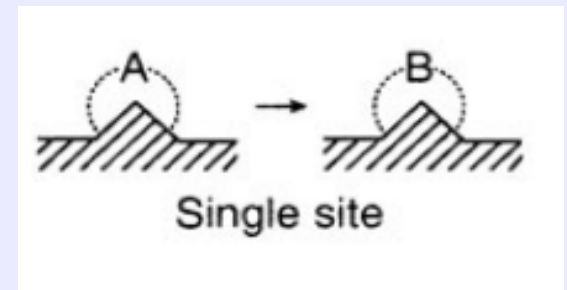
Here, only the site on which the reactant is adsorbed is involved in the reaction (eg., for the isomerization of *n*-pentene to *i*-pentene, the adsorbed *n*-pentene molecule is converted directly on the site to form *i*-pentene)



Both the forward and backward reaction rates are elementary and the surface reaction rate law is given by ,

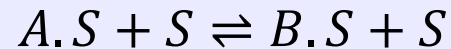
$$r_s = k_s \left[C_{A.S} - \frac{C_{B.S}}{K_s} \right]$$

where $K_s = \frac{k_s}{k_{-s}}$ = surface reaction equilibrium constant



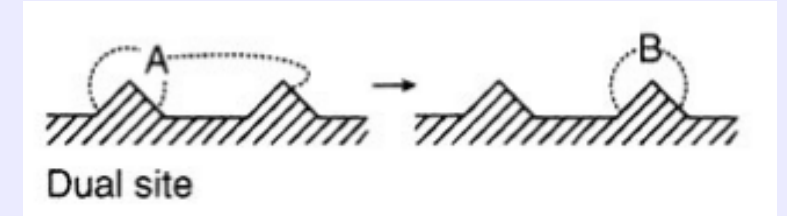
(b) Dual site mechanism

- (i) Adsorbed molecule interacts with another site (either occupied or unoccupied) to form the product. The adsorbed molecule A may react with an adjacent vacant site to yield a vacant site and a site with adsorbed B

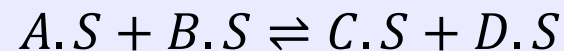


The surface reaction rate law is given by,

$$r_s = k_s \left[C_{A.S} C_v - \frac{C_{B.S} C_v}{K_s} \right]$$

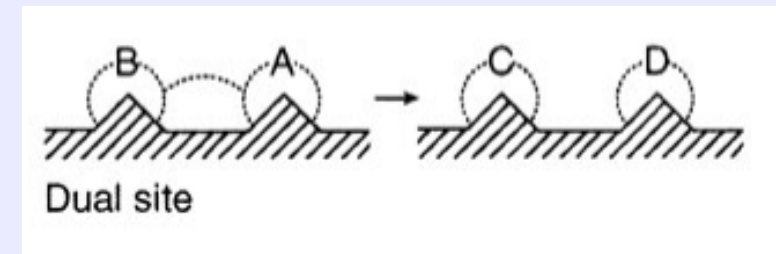


- (ii) When reaction takes place between two adsorbed species

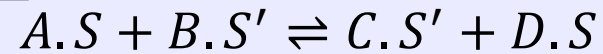


The surface reaction rate law is given by,

$$r_s = k_s \left[C_{A.S} C_{B.S} - \frac{C_{C.S} C_{D.S}}{K_s} \right]$$

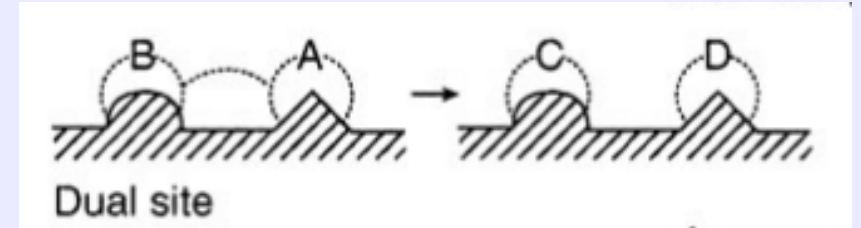


(iii) When reaction takes place between two species adsorbed on two different sites, S and S'



The surface reaction rate law is given by,

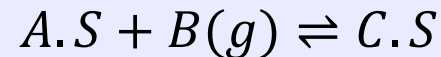
$$r_s = k_s \left[C_{A.S} C_{B.S'} - \frac{C_{C.S'} C_{D.S}}{K_s} \right]$$



All the above mentioned single site and dual site mechanism reactions are said to follow **Langmuir-Hinshelwood kinetics**

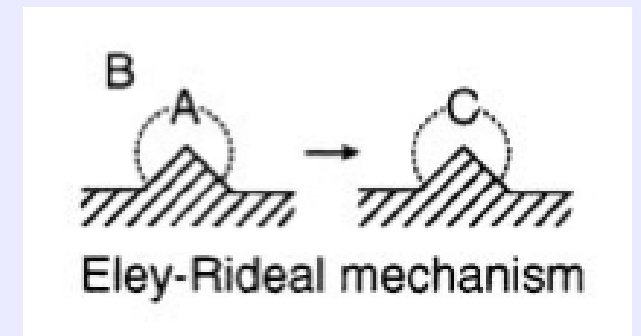
(c) Eley-Rideal mechanism

(ii) When reaction takes place between an adsorbed molecule and a molecule in the gas phase



The surface reaction rate law is given by,

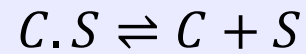
$$r_s = k_s \left[C_{A.S} p_B - \frac{C_{C.S}}{K_s} \right]$$



This type of mechanism is referred to as **Eley-Rideal mechanism**

Desorption

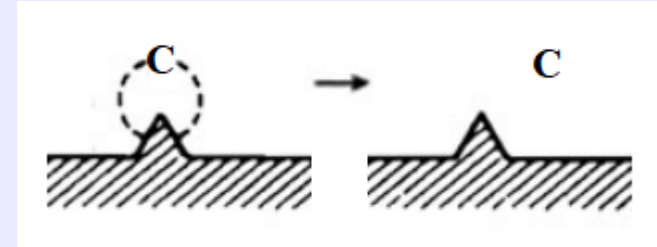
The products of the surface reaction adsorbed on the surface is subsequently desorbed into the gas phase



The rate of desorption is given by,

$$r_D = k_D \left[C_{C.S} - \frac{p_C C_v}{K_{DC}} \right]$$

where K_{DC} = desorption equilibrium constant



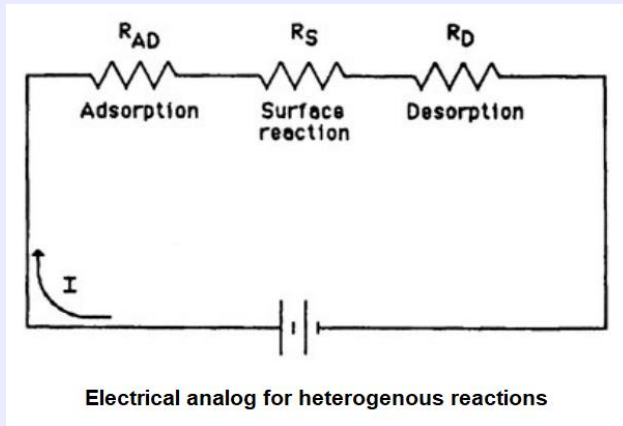
Important: Desorption equilibrium constant (K_{DC}) is just the reciprocal of the adsorption equilibrium constant (K_{AC}) for C $\left[K_{DC} = \frac{1}{K_{AC}} \right]$

Adsorption - $C + S \rightleftharpoons C.S$

Rate of adsorption is, $r_a = k_A \left[p_C C_v - \frac{C_{C.S}}{K_{AC}} \right]$ where $K_{AC} = \frac{k_A}{k_{-A}}$

Rate limiting step

- At steady state, the rate of adsorption, surface reaction and desorption are equal to one another
- However, one particular step in the series is usually found to be **rate limiting**, i.e., if this step is somehow made faster, the entire reaction would proceed at an accelerated rate



- Current (I) is analogous to $(-r_A)$

$$I = \frac{V}{R_{total}} = \frac{V}{R_A + R_S + R_D}$$

- It is important to know which resistance among the three is the largest and is limiting (controlling) the overall reaction

The way to do this is known as the **Langmuir-Hinshelwood-Hougen-Watson** approach

- First a sequence of steps is assumed for the reaction
- Rate laws are written for the individual steps assuming each one of them is reversible
- A rate limiting step is postulated and steps that are not rate limiting are used to eliminate the adsorbed species and vacant sites