

The type of adsorption that affects the rate of a chemical reaction is *chemisorption*. Here, the adsorbed atoms or molecules are held to the surface by valence forces of the same type as those that occur between bonded atoms in molecules. Like physical adsorption, chemisorption is an exothermic process, but the heats of adsorption are generally of the same magnitude as the heat of a chemical reaction (i.e., 10 to 100 kcal/g mol). If a catalytic reaction involves chemisorption, it must be carried out within the temperature range where chemisorption of the reactants is appreciable.

In a landmark contribution to catalytic theory, Taylor³ suggested that a reaction is not catalyzed over the entire solid surface but only at certain *active sites* or centers. He visualized these sites as unsaturated atoms in the solids that resulted from surface irregularities, dislocations, edges of crystals, and cracks along grain boundaries. Other investigators have taken exception to this definition, pointing out that other properties of the solid surface are also important. However, for our purposes we will define an *active site as a point on the catalyst surface that can form strong chemical bonds with an adsorbed atom or molecule*.

One parameter used to quantify the activity of a catalyst is the *turnover frequency*, N . It is the number of molecules reacting per active site per second at the conditions of the experiment. When a metal catalyst such as platinum is deposited on a support, the metal atoms are considered active sites. The *dispersion*, D , of the catalyst is the fraction of the metal atoms deposited that are on the surface.

Example 6-1 A Turnover Frequency in Fisher-Tropsch Synthesis



The Fisher-Tropsch synthesis was studied using a commercial 0.5 wt % Ru on $\gamma\text{-Al}_2\text{O}_3$.⁴ The catalyst dispersion percentage of atoms exposed, determined from hydrogen chemisorption, was found to be 49%. At a pressure of 988 kPa and a temperature of 574K, a turnover frequency of 0.1607 s^{-1} was reported for methane. What is the rate of formation of methane in mol/s·g of catalyst (metal plus support)?

Solution

$$\begin{aligned} -r_A' &= N_{\text{C114}} D \left(\frac{1}{\text{MW}_{\text{Ru}}} \right) \frac{\% \text{Ru}}{100} \\ &= \frac{0.1607 \text{ molecule}}{(\text{surface atoms Ru}) \cdot \text{s}} \times \frac{1 \text{ mol CH}_4}{6.02 \times 10^{23} \text{ molecules}} \\ &\quad \times \frac{0.49 \text{ surface atom}}{\text{total atoms Ru}} \times \frac{6.02 \times 10^{23} \text{ atoms Ru}}{\text{g atom (mol) Ru}} \\ &\quad \times \frac{\text{g atoms Ru}}{101.1 \text{ g Ru}} \times \frac{0.005 \text{ g Ru}}{\text{g total}} \\ &= 3.89 \times 10^{-6} \text{ mol/s} \cdot \text{g catalyst} \end{aligned} \quad (\text{E6-1.1})$$

³ H. S. Taylor, *Proc. R. Soc. (Lond.)*, A108, 105 (1928).

⁴ R. S. Dixit and L. L. Tavlarides, *Ind. Eng. Chem. Process Des. Dev.*, 22, 1 (1983).

6.2 Steps in a Catalytic Reaction

A schematic diagram of a tubular reactor packed with catalytic pellets is shown in Figure 6-2(a). The overall process by which heterogeneous catalytic reactions proceed can be broken down into the sequence of individual steps shown in Table 6-1 and pictured in Figure 6-3 for an isomerization.

The overall rate of reaction is equal to the rate of the slowest step in the mechanism. When the diffusion steps (1, 2, 6, and 7 in Table 6-1) are very fast compared with the reaction steps (3, 4, and 5), the concentrations in the immediate vicinity of the active sites are indistinguishable from those in the bulk fluid. In this situation, the transport or diffusion steps do not affect the overall rate of the reaction. In other situations, if the reaction steps are very fast compared with the diffusion steps, mass transport does affect

A reaction takes place on the surface, but the species involved in the reaction must get to and from the surface

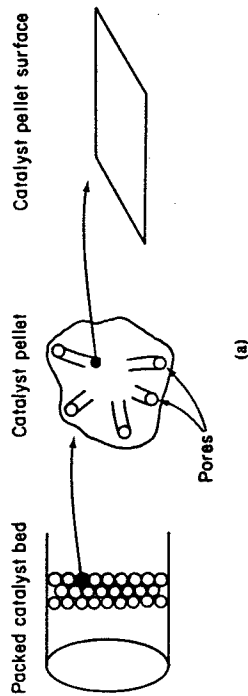


Figure 6-2 (a) Catalytic packed-bed reactor—schematic. (b) different shapes and sizes of catalyst. (Courtesy of the Engelhard Corp.)

Chemisorption on active sites is what catalyzes the reaction

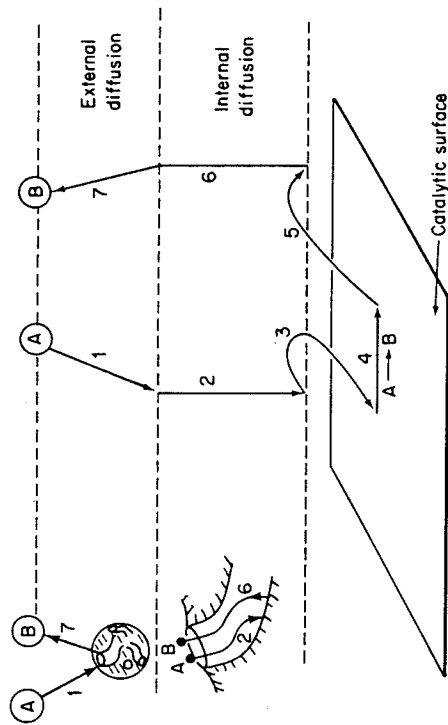


Figure 6-3 Steps in a heterogeneous catalytic reaction.

TABLE 6-1. STEPS IN A CATALYTIC REACTION

1. Mass transfer (diffusion) of the reactant(s) (e.g., species A) from the bulk fluid to the external surface of the catalyst pellet
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface
3. Adsorption of reactant A onto the catalytic surface
4. Reaction on the surface of the catalyst (e.g., $A \rightarrow B$)
5. Desorption of the products (e.g., B) from the surface
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface
7. Mass transfer of the products from the external pellet surface to the bulk fluid

the reaction rate. In systems where diffusion from the bulk gas or liquid to the catalyst surface or to the mouths of catalyst pores affects the rate, changing the flow conditions past the catalyst should change the overall reaction rate. In porous catalysts, on the other hand, diffusion within the catalyst pores may limit the rate of reaction. Under these circumstances, the overall rate will be unaffected by external flow conditions even though diffusion affects the overall reaction rate.

There are many variations of the situation described in Table 6-1. Sometimes, of course, two reactants are necessary for a reaction to occur, and both of these may undergo the steps listed above. Other reactions between two substances have only one of them adsorbed.

With this introduction, we are ready to individually treat the steps involved in catalytic reactions. In this chapter only the steps of adsorption, surface reaction, and desorption will be considered [i.e., it is assumed that the diffusion steps (1, 2, 6, and 7) are very fast, such that the overall reaction

In this chapter we focus on:

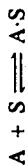
3. Adsorption
4. Surface reaction
5. Desorption

rate is not affected by mass transfer in any fashion]. Further treatment of the effects involving diffusion limitations is provided in Chapters 10 and 11.

In the following analysis, adsorption will be discussed first, with emphasis on chemisorption. Adsorption can occur without reaction, and the mathematical treatment of nonreactive adsorption will lead naturally to the analysis of simultaneous adsorption, reaction, and desorption.

6.2.1 Adsorption Isotherms

Since chemisorption is usually a necessary part of a catalytic process, we shall discuss it before treating catalytic reaction rates. The letter S will represent an active site; alone it will denote a vacant site, with no atom, molecule, or complex adsorbed on it. The combination of S with another letter (e.g., A-S) will mean that one unit of A will be adsorbed on the site S, and A can be an atom, molecule, or some other atomic combination, depending on the circumstances. Consequently, the adsorption of A on a site S is represented by



The total molar concentration of active sites per unit mass of catalyst is equal to the number of active sites per unit mass divided by Avogadro's number, and will be labeled C_s (mol/g cat). The molar concentration of vacant sites, C_v , is the number of vacant sites per unit mass of catalyst divided by Avogadro's number. In the absence of catalyst deactivation we assume that the total concentration of active sites remains constant. Some further definitions include:

- P_i partial pressure of species i in the gas phase, atm
- C_i surface concentration of sites occupied by species i , g mol/g cat
- S_a surface area per unit mass of catalyst, m^2/g cat
- C_i^s surface concentration of sites occupied by species i based on the surface area, g mol i/m^2

The last definition means that

$$C_i^s = \frac{C_i}{S_a} \quad (6-1)$$

A conceptual model depicting species A and B on two sites is shown in Figure 6-4.

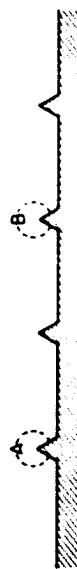


Figure 6-4 Vacant and occupied sites

For the system shown, the total concentration of sites is

$$C_s = C_v + C_A + C_B \quad (6-2)$$

Site balance

This equation is referred to as a *site balance*.

Now consider the adsorption of a nonreacting gas onto the surface of a catalyst. Adsorption data are frequently reported in the form of adsorption isotherms. Isotherms portray the amount of a gas adsorbed on a solid at different pressures but at one temperature. A typical adsorption isotherm, shown in Figure 6-5, is taken from the classic study of Ward,⁵ who adsorbed hydrogen on powdered copper at 25°C (see Table 6-2). The data appear to be quite precise. Only one point is slightly off a smooth curve, and there is

TABLE 6-2. ADSORPTION OF H₂ ON CU POWDER AT 25°C

Increasing Pressure, P _{H₂} (torr) ^a	C _{H₂,S} × 10 ² (g mol/g Cu)	Decreasing Pressure, P _{H₂} (torr) ^a	C _{H₂,S} × 10 ² (g mol/g Cu)
3.25	0.559	45.1	1.160
8.90	0.761	21.5	0.995
17.65	0.941	10.65	0.800
36.2	1.212	5.40	0.659
74.5	1.281	2.95	0.564
204.8	1.471	1.70	0.464

^a 1 torr = 1 mmHg = 0.133 kPa = 0.00132 atm.

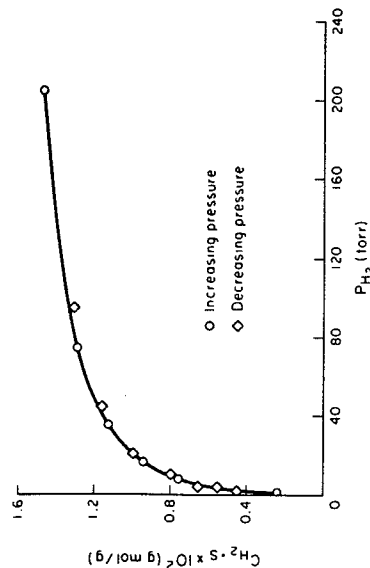


Figure 6-5 Adsorption of hydrogen on copper.

⁵ R. F. H. Ward, *Proc. R. Soc. (Lond.)*, A133, 506.

no hysteresis, since the points taken while the pressure was being gradually increased lie on the same curve as those taken while the pressure was decreased.

This isotherm can be used to gain insight into the adsorption process. An equation for the curve in Figure 6-5 will be derived, and the derivation will reveal significant properties of the hydrogen-copper system. First, a model system is proposed and then the isotherm obtained from the model is compared with the experimental data shown on the curve. If the curve predicted by the model agrees with the experimental one, the model may reasonably describe what is occurring physically in the real system. If the predicted curve does not agree with that obtained experimentally, the model fails to match the physical situation in at least one important characteristic, and perhaps more. To describe Ward's data, two models will be postulated—one in which hydrogen is adsorbed as molecules, H₂, on copper powder, and the other in which hydrogen is adsorbed as atoms, H, instead of molecules.

The adsorption of hydrogen molecules will be considered first. Since the hydrogen does not react further after being adsorbed, we need only to consider the adsorption process:



In obtaining a rate law for the rate of adsorption, the reaction in Equation (6-3) can be treated as an *elementary reaction*. The rate of attachment of the hydrogen molecules to the surface is proportional to the number of collisions that these molecules make with the surface per second. In other words, a specific fraction of the molecules that strike the surface become adsorbed. The collision rate is, in turn, directly proportional to the hydrogen partial pressure, P_{H₂}. Since hydrogen molecules can adsorb only on vacant sites, and not on sites already occupied by other hydrogen molecules, the rate of attachment is also directly proportional to the concentration of vacant sites, C_v. Combining these two facts means that the rate of attachment of hydrogen molecules to the surface is directly proportional to the product of the partial pressure of H₂ and the concentration of vacant sites; i.e.,

$$\text{rate of attachment} = k_A P_{\text{H}_2} C_v$$

The rate of detachment of molecules from the surface can be a first-order process; that is, the detachment of hydrogen molecules from the surface is usually directly proportional to the concentration of sites occupied by the molecules, C_{H₂,S}:

$$\text{rate of detachment} = k_A' C_{\text{H}_2, \text{S}}$$

The net rate of adsorption is equal to the rate of molecular attachment to the surface minus the rate of detachment from the surface. If k_A and k_A' are the constants of proportionality for the attachment and detachment processes, then

$$r_{\text{AD}} = k_A P_{\text{H}_2} C_v - k_A' C_{\text{H}_2, \text{S}} \quad (6-4)$$

$$A + S \rightleftharpoons A \cdot S$$

$$k_A = \frac{1}{\text{atm} \cdot \text{s}} \times \left(\frac{P_A C_v - C_{A \cdot S}}{K_A} \right)$$

The ratio $K_A = k_A/k_{-A}$ is the *adsorption equilibrium constant*. Using it to rearrange Equation (6-4) gives

$$r_{AD} = k_A \left(P_{H_2} C_v - \frac{C_{H_2 \cdot S}}{K_A} \right) \quad (6-5)$$

The parameters k_A , k_{-A} , and K_A are all functions of temperature, exhibiting an exponential temperature dependence. The forward and reverse specific reaction rates, k_A and k_{-A} , increase with increasing temperature, while the adsorption equilibrium constant, K_A , decreases with increasing temperature. At a single temperature, in this case 25°C, they are, of course, constant in the absence of any catalyst deactivation.

Since hydrogen is the only material adsorbed on the catalyst, the site balance gives

$$C_t = C_v + C_{H_2 \cdot S} \quad (6-6)$$

The points plotted in Figure 6-5 were taken at equilibrium conditions. The experimental details present in the original work support this fact, and the absence of hysteresis confirms it. At equilibrium, the net rate of adsorption equals zero. Setting the right-hand side of Equation (6-5) equal to zero and solving for the concentration of H_2 adsorbed on the surface, we get

$$C_{H_2 \cdot S} = K_A C_t P_{H_2}$$

Using Equation (6-6) to give C_t in terms of $C_{H_2 \cdot S}$ and the total number of sites C_t , we can solve for $C_{H_2 \cdot S}$ in terms of constants and the pressure of hydrogen; i.e.,

$$C_{H_2 \cdot S} = K_A C_t P_{H_2} = K_A P_{H_2} (C_t - C_{H_2 \cdot S})$$

Rearranging gives us

$$C_{H_2 \cdot S} = \frac{K_A P_{H_2} C_t}{1 + K_A P_{H_2}} \quad (6-7)$$

This equation thus gives $C_{H_2 \cdot S}$ as a function of the partial pressure of hydrogen, and so is an equation for the adsorption isotherm. This particular type of isotherm equation is called a *Langmuir isotherm*.⁶

A quick look shows that this equation shares many properties with the curve in Figure 6-5. The curve is concave downward, since the second derivative $[d^2 C_{H_2 \cdot S} / (dP_{H_2})^2]$ is negative everywhere. The slope $(dC_{H_2 \cdot S} / dP_{H_2})$ is always positive and it decreases steadily as P_{H_2} increases, approaching zero as P_{H_2} becomes very large. However, merely sharing properties does not mean that curves display identical behavior. As was shown in Chapter 5, one method of checking whether a model predicts the behavior of some experimental data is to linearize the model's equation and then plot the indicated variables against one another. For example, Equation (6-7)

⁶ Named after Irving Langmuir (1881–1957), who first proposed it. He received the Nobel prize in 1932 for his discoveries in surface chemistry.

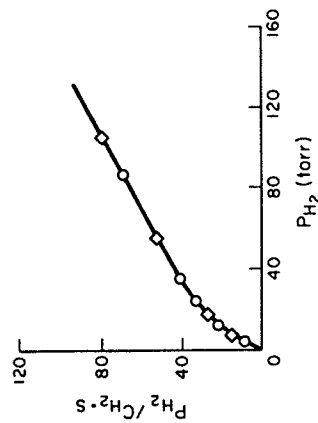


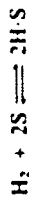
Figure 6-6 Adsorption of molecular hydrogen.

may be arranged in the form

$$\frac{P_{H_2}}{C_{H_2 \cdot S}} = \frac{1}{K_A C_t} + \frac{P_{H_2}}{C_t} \quad (6-8)$$

and the linearity of a plot of $P_{H_2}/C_{H_2 \cdot S}$ as a function of P_{H_2} will determine if the data conform to a Langmuir single-site isotherm. The data in Figure 6-5 are replotted in Figure 6-6 in the form suggested by Equation (6-8). The data indicate a slight but definite curvature. Thus there is a significant question as to whether these data really conform to a model of hydrogen adsorbing as molecules.

Next, the isotherm for hydrogen adsorbing as atoms is derived:



When a molecule dissociates upon adsorption, it is referred to as *dissociative adsorption*. As in the case of molecular adsorption, the rate of adsorption here is proportional to the pressure of hydrogen in the system, because this rate governs the number of gaseous collisions with the surface. For a molecule to dissociate as it adsorbs however, two adjacent vacant active sites are required, rather than the single site needed when a substance adsorbs in its molecular form. The probability of two vacant sites occurring adjacent to one another is proportional to the square of the concentration of vacant sites. These two observations mean that the rate of adsorption is proportional to the product of the hydrogen partial pressure and the square of the vacant-site concentration, $P_{H_2} C_v^2$.

For desorption to occur, two occupied sites must be adjacent, meaning that the rate of desorption is proportional to the square of the occupied-site concentration, $(C_{H \cdot S})^2$. The net rate of adsorption can then be expressed as

$$r_{AD} = k_A P_{H_2} C_v^2 - k_{-A} C_{H \cdot S}^2 \quad (6-9)$$

Factoring out k_A , the equation for *dissociative adsorption* is

$$r_{AD} = k_A \left(P_{H_2} C_v^2 - \frac{C_{H \cdot S}^2}{K_A} \right)$$

Rate of dissociative adsorption

On this particular catalyst the data show that hydrogen does not adsorb as molecules (H_2)

Langmuir isotherm for adsorption of molecular hydrogen

where

$$K_A = \frac{k_A}{k_{-A}}$$

At equilibrium, $r_{AD} = 0$, and

$$K_A P_{H_2} C_v^2 = C_{H_2S}^2 \quad (6-10)$$

or

$$(K_A P_{H_2})^{1/2} C_v = C_{H_2S}$$

From Equation (6-2),

$$C_v = C_t - C_{H_2S}$$

This value may be substituted into Equation (6-10) to give an expression that can be solved for C_{H_2S} . The resulting isotherm equation is

$$C_{H_2S} = \frac{(K_A P_{H_2})^{1/2} C_t}{1 + (K_A P_{H_2})^{1/2}} \quad (6-11)$$

Taking the inverse of both sides of the equation, then multiplying through by $(P_{H_2})^{1/2}$, yields

$$\frac{(P_{H_2})^{1/2}}{C_{H_2S}} = \frac{1}{C_t (K_A)^{1/2}} + \frac{(P_{H_2})^{1/2}}{C_t} \quad (6-12)$$

This equation is the linearized Langmuir isotherm for dissociative adsorption. It says that if the hydrogen is dissociatively adsorbed on the copper, a straight line should result when $(P_{H_2})^{1/2}/C_{H_2S}$ is plotted as a function of $P_{H_2}^{1/2}$.

The data in Figure 6-5 are replotted in Figure 6-7 in the form suggested by Equation (6-12). An excellent straight line is obtained, giving support to

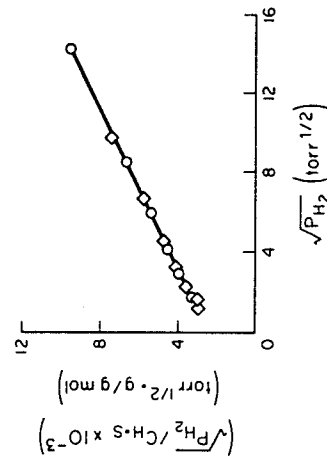


Figure 6-7 Dissociative adsorption of hydrogen.

The dissociative adsorption of H_2 model fits the experimental data for this catalyst

the postulate of hydrogen being dissociatively adsorbed on the copper powder.

A comparison of the results of the models indicates that hydrogen is adsorbed on the copper as atoms rather than as molecules. Hydrogen-deuterium tracer studies have confirmed this interpretation. Some comments seem deserved here. The data presented seemed very precise. If they had not been so, and there had been significant scatter, it would have been impossible to distinguish between the two models. The curvature in Figure 6-6 is slight, so the difference between the two mechanisms in discerning eye is necessary to distinguish between the two mechanisms in this situation. This subtle difference is one reason why this type of agreement between a model and the behavior of experimental data usually requires supporting spectroscopic and tracer experiments.

When more than one substance is present, the adsorption isotherm equations are somewhat more complex. The principles are the same, though, and the isotherm equations are easily derived. It is left as an exercise to show that the adsorption isotherm of A in the presence of adsorbent B is given by the relationship

$$C_{A,S} = \frac{K_A P_A C_t}{1 + K_A P_A + K_B P_B} \quad (6-13)$$

When the adsorption of both A and B are first-order processes, the desorptions are also first-order, and both A and B are adsorbed as molecules. The derivations of other Langmuir isotherms are given as exercises.

In obtaining the Langmuir isotherm equation, several aspects of the adsorption system were presupposed in the derivations. The most important of these, and the one that has been subject to the greatest doubt, is that a uniform surface is assumed. In other words, any active site has the same attraction for an impinging molecule as does any other site. Isotherms different from the Langmuir types may be derived based on various assumptions concerning the adsorption system, including different types of non-uniform surfaces.

Note assumptions in the model and check their validity

6.2.2 Surface Reaction

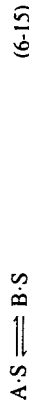
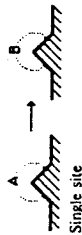
The rate of adsorption of species A onto a solid surface is given by

$$r_{AD} = k_A \left(P_A C_t - \frac{C_{A,S}^2}{K_A} \right) \quad (6-14)$$

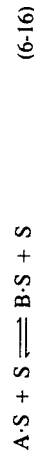
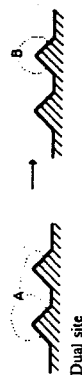
Surface reaction models

Once a reactant has been adsorbed onto the surface, it is capable of reacting in a number of ways to form the reaction product. Three of these ways are:

1. The surface reaction may be a single-site mechanism in which only the site on which the reactant is adsorbed is involved in the reaction. For example, an adsorbed molecule of A may isomerize (or perhaps decompose) directly on the site to which it is attached; i.e.,



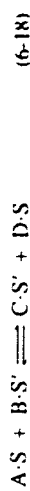
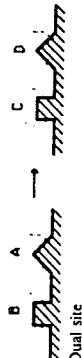
2. The surface reaction may be a dual-site mechanism in which the adsorbed reactant interacts with another site (either unoccupied or occupied) to form the product. For example, adsorbed A may react with an adjacent vacant site to yield a vacant site and a site on which the product is adsorbed; i.e.,



Another example of a dual-site mechanism is the reaction between two adsorbed species:



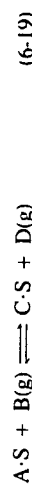
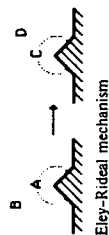
A third dual-site mechanism is the reaction of two species adsorbed on different types of sites S and S':



Langmuir-Hinshelwood kinetics

Reactions involving either single- or dual-site mechanisms described above are sometimes referred to as following *Langmuir-Hinshelwood kinetics*.

3. A third mechanism is the reaction between an adsorbed molecule and a molecule in the gas-phase:



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

6.2.3 Desorption

In each of the cases above, the products of the surface reaction adsorbed on the surface are subsequently desorbed into the gas phase. Recalling equations (6-3) through (6-5), we see that the rate of desorption of a species A,



is opposite in sign to the rate of adsorption of species A.

6.2.4 The Rate-Limiting Step

When heterogeneous reactions are carried out at steady state, the rates of each of the three reaction steps in series (adsorption, surface reaction, and desorption) are equal to one another:

$$-r'_A = r_{AD} = r_S = r_D$$

However, one particular step in the series is usually found to be *rate-limiting* or *rate-controlling*. That is, if we could make this particular step go faster, the entire reaction would proceed at an accelerated rate. Consider the analogy to the electrical circuit shown in Figure 6-8. A given concentration of reactants is analogous to a given driving force or electromotive force (EMF). The current I (with units of C/s) is analogous to the rate of reaction. r'_A (mols/g cat), and a resistance R , is associated with each step in the series. Since the resistances are in series, the total resistance is just the sum of the individual resistances, so the current I is

$$I = \frac{E}{R_{\text{tot}}} = \frac{E}{R_{AD} + R_S + R_D} \quad (6-21)$$

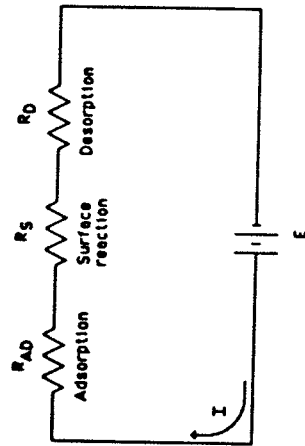


Figure 6-8 Electrical analog to heterogeneous reactions.

The concept of a rate-limiting step

Since we observe only the total resistance, R_{tot} , it is our task to find which resistance is much larger (say, 100 Ω), than the other two (say, 0.1 Ω). Thus, if we could lower the largest resistance, the current I ($=r_A$) would be larger for a given E . Analogously, we want to know which step in the adsorption–reaction–desorption series is limiting the overall rate of reaction.

The approach in determining catalytic and heterogeneous mechanisms is usually termed the *Langmuir–Hinshelwood approach*, since it is derived from ideas proposed by Hinshelwood⁷ based on Langmuir's principles for adsorption. It consists of first assuming a sequence of steps in the reaction. In writing this sequence a choice must be made between such mechanisms as molecular or atomic adsorption, and single- or dual-site reaction. Next, rate laws are written for the individual steps as shown in the preceding section, assuming all steps are reversible. Finally, a rate-limiting step is postulated and steps that are not rate-limiting are used to eliminate all coverage-dependent terms. The Langmuir–Hinshelwood approach was popularized by Hougen and Watson⁸ and occasionally includes their names. The most questionable assumption in using this technique to obtain a rate law is the hypothesis that the activity of the surface toward adsorption, desorption, or surface reaction is independent of coverage; that is, the surface is essentially uniform as far as the various steps in the reaction are concerned.

An algorithm to determine the rate-limiting step

6.3 Synthesizing a Rate Law, Mechanism, and Rate-limiting Step

We now wish to develop rate laws for catalytic reactions that are not diffusion-limited. In developing the procedure to obtain a mechanism, a rate-limiting step, and a rate law consistent with experimental observation, we shall discuss a particular catalytic reaction, the decomposition of cumene to form benzene and propylene. The overall reaction is



A conceptual model depicting the sequences of steps in this platinum-catalyzed reaction is shown in Figure 6-9a. Figure 6-9a is only a schematic representation of the adsorption of cumene; probably a more realistic model is the formation of a complex of the π orbitals of benzene with the catalytic surface, as shown in Figure 6-9b.

The following nomenclature will be used to denote the various species

⁷ C. N. Hinshelwood, *The Kinetics of Chemical Change* (Oxford: Clarendon Press, 1940).

⁸ O. A. Hougen and K. M. Watson, *Ind. Eng. Chem.*, 35, 529 (1943).

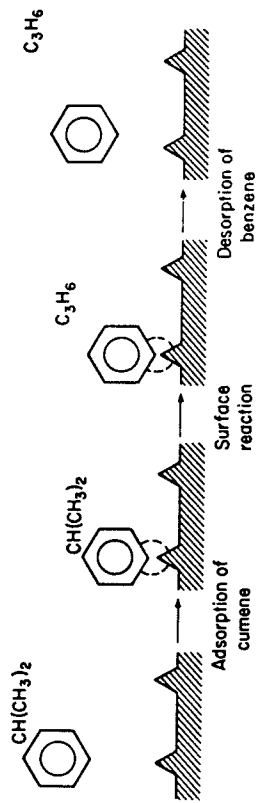


Figure 6-9 (a) Sequence of steps in reaction-limited catalytic reaction.

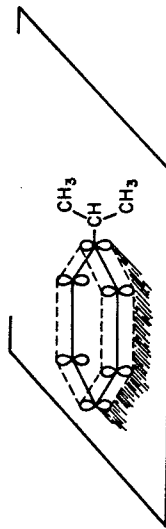
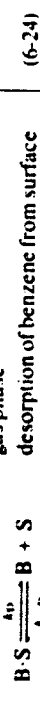
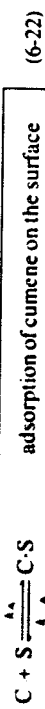


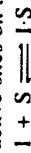
Figure 6-9 (b) π -orbital complex on surface.

in this reaction: C = cumene, B = benzene, P = propylene, and I = inhibitor. The reaction sequence for this decomposition is:



These three steps represent the mechanism for cumene decomposition

Equations (6-22) through (6-24) represent the proposed mechanism for this reaction. We may also have an inhibitor present that does not participate in the reaction but does occupy active sites on the surface:



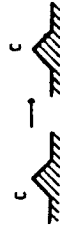
When writing rate laws for these steps, we treat each step as an elementary reaction; the only difference is that the species concentrations in the gas phase are replaced by their respective partial pressures:



The rate expression for the adsorption of cumene as given in Equation (6-22) is

$$r_{\text{AD}} = k_A P_C - k_{-A} C_{\text{C}\cdot\text{S}}$$

$$\text{Adsorption: } r_{\text{AD}} = k_A \left(P_C C_{\text{S}} - \frac{C_{\text{C}\cdot\text{S}}}{K_A} \right) \quad (6-25)$$



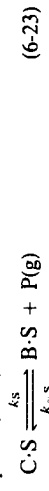
If r_{AD} has units of mol/g cat·h, and $C_{C,S}$ has units of mol cumene adsorbed/g cat, typical units of k_A , k_{-A} and K_A would be

$$[k_A] \equiv (\text{kPa}\cdot\text{s})^{-1} \text{ or } (\text{atm}\cdot\text{h})^{-1}$$

$$[k_{-A}] \equiv \text{h}^{-1} \text{ or } \text{s}^{-1}$$

$$[K_A] \equiv \left[\frac{k_A}{k_{-A}} \right] \equiv \text{kPa}^{-1}$$

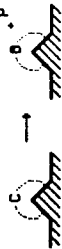
The rate law for the surface reaction step producing adsorbed benzene and propylene in the gas phase; i.e.,



is

$$r_s = k_s C_{C,S} - k_{-s} P_P C_{B,S}$$

$$\text{Surface reaction: } r_s = k_s \left(C_{C,S} - \frac{P_P C_{B,S}}{K_S} \right) \quad (6-26)$$



with the *surface reaction equilibrium constant* being

$$K_S = \frac{k_s}{k_{-s}}$$

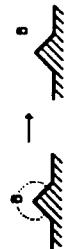
Typical units for k_s and K_S are s^{-1} and atm, respectively.

Propylene is not adsorbed on the surface. Consequently, its concentration on the surface is zero.

$$C_{P,S} = 0$$

The rate of benzene desorption [see Equation (6-24)] is

$$r_D = k_D C_{B,S} - k_{-D} P_B C_C \quad (6-27)$$



$$\text{Desorption: } r_D = k_D \left(C_{B,S} - \frac{P_B C_C}{K_D} \right) \quad (6-28)$$

Typical units of k_D and K_D are s^{-1} and kPa, respectively. Since the reaction is carried out at steady-state conditions, the rates of each of the steps in the sequence are equal:

$$-r'_C = r_{AD} = r_s = r_D \quad (6-29)$$

The rate of adsorption of the inhibitor I is

$$r_I = k_I \left(P_I C_v - \frac{C_{I,S}}{K_I} \right) \quad (6-30)$$

At steady-state operation the net rate of adsorption of the inhibitor is zero (i.e., $r_I = 0$), and the equilibrium surface concentration of the inhibitor is

$$C_{I,S} = K_I P_I C_v \quad (6-31)$$

We note that the system may contain inert gases which do not adsorb on the surface and so do not act as inhibitors.

For the mechanism postulated in the sequence given by equations (6-22) through (6-24), we wish to determine which step is rate-limiting. We first

assume one of the steps to be rate-limiting (rate-controlling) and then formulate the reaction rate law in terms of the partial pressures of the species present. From this expression we can determine the variation of the initial reaction rate with the initial total pressure. If the predicted rate varies with pressure in the same manner as the rate observed experimentally, the implication is that the assumed mechanism and rate-limiting step are correct.

6.3.1 Is the Adsorption of Cumene Rate-limiting?

To answer this question we shall assume that the adsorption of cumene is indeed rate-limiting, derive the corresponding rate law, and then check to see if it is consistent with experimental observation. By assuming that this (or any other) step is rate-limiting, we are considering that the reaction rate constant of this step (in this case k_A) is small with respect to the specific rates of the other steps (in this case k_S and k_D). The rate of adsorption is

$$-r'_C = r_{AD} = k_A \left(P_C C_v - \frac{C_{C,S}}{K_A} \right) \quad (6-25)$$

Since we cannot measure either C_v or $C_{C,S}$, we must replace these variables in the rate equation with measurable quantities for the equation to be meaningful.

For steady-state operation we have

$$-r'_C = r_{AD} = r_s = r_D \quad (6-32)$$

For adsorption-limited reactions, k_A is small and k_S and k_D are large. Consequently, the ratios r_s/k_S and r_D/k_D are very small (approximately zero), whereas the ratio r_A/k_A is relatively large. The surface reaction rate expression is

$$r_s = k_S \left(C_{C,S} - \frac{C_{B,S} P_P}{K_S} \right) \quad (6-33)$$

For adsorption-limited reactions the surface specific reaction rate k_S is large by comparison and we can set

$$\frac{r_s}{k_S} \approx 0$$

and solve Equation (6-33) for $C_{C,S}$:

$$C_{C,S} = \frac{C_{B,S} P_P}{K_S} \quad (6-34)$$

To be able to express $C_{C,S}$ solely in terms of the partial pressures of the species present, we must evaluate $C_{B,S}$. The rate of desorption is

$$r_D = k_D \left(C_{B,S} - \frac{P_B C_C}{K_D} \right) \quad (6-28)$$

However, for adsorption-limited reactions, k_D is large by comparison and

we can set

Using $\frac{r_S}{k_S} = 0 = \frac{r_D}{k_D}$ to find $C_{B,S}$ and $C_{C,S}$ in terms of partial pressures

$$\frac{r_D}{k_D} = 0$$

and then solve Equation (6-28) for $C_{B,S}$:

$$C_{B,S} = \frac{P_B C_v}{K_D} \quad (6-35)$$

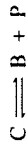
After combining equations (6-34) and (6-35), we have

$$C_{C,S} = \frac{P_B P_P C_v}{K_D K_S} \quad (6-36)$$

Replacing $C_{C,S}$ in the rate equation by Equation (6-36), and then factoring C_v , we obtain

$$r_{AD} = k_A \left(P_C - \frac{P_B P_P}{K_S K_D K_A} \right) C_v = k_A \left(P_C - \frac{P_B P_P}{K_r} \right) C_v \quad (6-37)$$

Observe that by setting $r_{AD} = 0$, the product $K_S K_D K_A$ is simply the overall equilibrium constant K_r for the reaction



$$K_A K_S K_D = K_r \quad (6-38)$$

The equilibrium constant can be determined from thermodynamic data and is related to the change in the Gibbs free energy, ΔG° , by the equation (see Appendix C)

$$RT \ln K = -\Delta G^\circ \quad (6-39)$$

where R is the ideal gas constant and T is the absolute temperature.

The concentration of vacant sites, C_v , can now be eliminated from Equation (6-37) by utilizing the equation to give the total concentration of sites, C_t , which is assumed constant:⁹

$$\text{total sites} = \text{vacant sites} + \text{occupied sites}$$

Since cumene, benzene, and the inert inhibitor are all adsorbed on the sur-

⁹ Some prefer to write the surface reaction rate in terms of the fraction of the surface or sites covered i.e., f_A , rather than the number of sites C_A , covered. The difference being the multiplication factor of the total site concentration, C_t . In any event, the final form of the rate law is the same because C_t , K_A , k_r , etc. are all lumped into the specific reaction rate k .

face, the concentration of occupied sites is $(C_{C,S} + C_{B,S} + C_{I,S})$, and the total concentration of sites is

$$C_t = C_v + C_{C,S} + C_{B,S} + C_{I,S} \quad (6-40)$$

Substituting equations (6-31), (6-35), and (6-36) into Equation (6-40), we have

$$C_t = C_v + \frac{P_B P_P C_v}{K_D K_S} + \frac{P_B C_v}{K_D} + P_I K_I C_v$$

Solving for C_v , we have

$$C_v = \frac{C_t}{P_B P_P / K_D K_S + P_B / K_D + P_I K_I + 1} \quad (6-41)$$

Combining equations (6-41) and (6-37), we find that the rate law for the catalytic decomposition of cumene, assuming that the adsorption of cumene is the rate-limiting step, is

$$-r_C = r_{AD} = \frac{C_t k_A (P_C - P_P P_B / K_r)}{1 + P_P P_B / K_S K_D + P_B / K_D + K_I P_I} \quad (6-42)$$

Cumene reaction rate law if adsorption were the limiting step

We now wish to sketch a plot of the initial rate as a function of the total pressure P_{T0} . Initially, no products are present; consequently, $P_P = P_B = 0$. The initial rate is given by

$$-r_{C0} = -r_0 = \frac{k_A y_{C0} P_{T0} C_t}{1 + y_{I0} K_I P_{T0}} \quad (6-43)$$

where y_{C0} and y_{I0} are, respectively, the initial mole fractions of cumene and inert. At low pressures, we can neglect the second term in the denominator of Equation (6-43) with respect to 1,

$$y_{I0} K_I P_{T0} \ll 1$$

and observe that the initial rate increases linearly with pressure.

$$-r_0 \sim P_{T0}$$

At high pressures,

$$y_{I0} K_I P_{T0} \gg 1$$

and we see that the initial rate is independent of the total pressure,

$$-r_0 = \frac{k_A y_{C0} C_t}{y_{I0} K_I}$$

In Figure 6-10, $-r_0$ is shown as a function of P_{T0} for a system initially containing 80% cumene and 20% inhibitor. In Equation (6-43), when no inhibitors are present, $y_{I0} = 0$ and $y_{C0} = 1$; then

$$-r_0 = k_A P_{T0} C_t$$

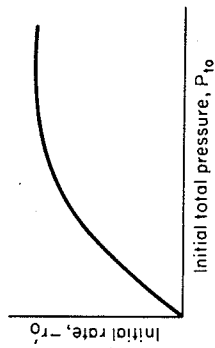


Figure 6-10 Adsorption-limited reaction with adsorbing inerts.

Observe that the initial rate increases linearly with total pressure (Figure 6-11). Before checking to see if Figure 6-11 is consistent with experimental

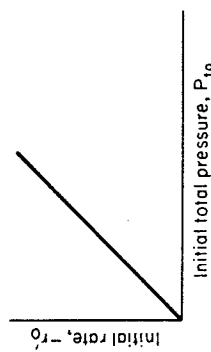


Figure 6-11 Uninhibited adsorption-limited reaction.

If adsorption were rate-limiting, the data should show $-r_0$ increasing linearly with P_{10}

observation, we shall derive the corresponding rate laws and initial rate plots when the surface reaction is rate-limiting and then when the desorption of benzene is rate-limiting.

6.3.2 Is the Surface Reaction Rate-limiting?

The rate of surface reaction is

$$r_s = k_s \left(C_{C-S} - \frac{P_B C_{B-S}}{K_S} \right) \quad (6-26)$$

Single-site mechanism

Since we cannot readily measure the concentrations of the adsorbed species, we must utilize the adsorption and desorption steps to eliminate C_{C-S} and C_{B-S} from this equation.

From the adsorption rate expression in Equation (6-25) and the condition that k_A is large by comparison when surface reaction is controlling (i.e., $r_{AD}/k_A \approx 0$), we obtain a relationship for the surface concentration for adsorbed cumene:

$$C_{C-S} = K_A P_C C_v$$

In a similar manner, the surface concentration of adsorbed benzene can be evaluated from the desorption rate expression [Equation (6-28)] together

with the approximation:

$$\text{when } \frac{r_D}{k_D} \approx 0 \quad \text{then } C_{B-S} = \frac{P_B C_v}{K_D}$$

Substituting for C_{B-S} and C_{C-S} in Equation (6-26) gives us

$$r_s = k_s \left(P_C K_A - \frac{P_B P_P}{K_D K_S} \right) C_v = k_s K_A \left(P_C - \frac{P_B P_P}{K_C} \right) C_v \quad (6-44)$$

The only variable left to eliminate is C_v . Using Equation (6-40),

$$C_t = C_v + C_{B-S} + C_{C-S} + C_{I-S}$$

and substituting for concentrations of the adsorbed species, C_{i-S} [Equation (6-31)], C_{B-S} , and C_{C-S} yields

$$C_v = \frac{C_t}{1 + P_B/K_D + K_A P_C + P_I K_I}$$

Letting $K_B = 1/K_D$, the final form of the rate law is

$$-r'_C = \frac{k_s C_t K_A (P_C - P_B P_P / K_C)}{1 + P_B K_B + K_A P_C + P_I K_I} \quad (6-45)$$

Cumene rate law for surface-reaction-limiting

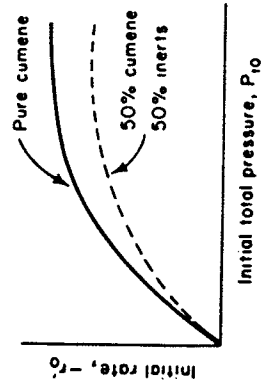
For an initial mixture of 50% C and 50% I, $P_P = P_B = 0$ and the initial rate can be determined from the equation

$$-r'_0 = \frac{k_s C_t K_A (0.5 P_{10})}{1 + (0.5 K_A + 0.5 K_I) P_{10}} \quad (6-46)$$

For pure cumene, the initial rate equation is also obtained from Equation (6-45):

$$-r'_0 = \frac{k_s C_t K_A P_{10}}{1 + K_A P_{10}} = \frac{k P_{10}}{1 + K_A P_{10}}$$

The rates for the cumene mixture and for pure cumene are plotted in Figure 6-12.



If surface reaction were rate-limiting, the data would show this behavior

Initial total pressure, P_{10}

Figure 6-12 Surface-reaction-limited.

6.3.3 Is the Desorption of Benzene Rate-limiting?

The rate expression for the desorption of benzene is

$$r_D = k_D \left(C_{B,S} - \frac{P_B C_v}{K_D} \right) \tag{6-28}$$

From the rate expression for surface reaction, Equation (6-26), we set

$$\frac{r_S}{k_S} \approx 0$$

to obtain

$$C_{B,S} = K_S \left(\frac{C_{C,S}}{P_P} \right) \tag{6-47}$$

Similarly, for the adsorption step, Equation (6-25), we set

$$\frac{r_{AD}}{k_A} \approx 0 \quad \text{to obtain}$$

$$C_{C,S} = K_A P_C C_v$$

then substitute for $C_{C,S}$ in Equation (6-47):

$$C_{B,S} = \frac{K_A K_S P_C C_v}{P_P} \tag{6-48}$$

Combining equations (6-28) and (6-48) gives us

$$r_D = k_D K_A K_S \left(\frac{P_C}{P_P} - \frac{P_B}{K_r} \right) C_v \tag{6-49}$$

where K_A and K_S are the adsorption and surface reaction equilibrium constants and K_r is the gas-phase equilibrium constant for the reaction. To obtain an expression for C_v , we again perform a site balance:

$$\text{Site balance: } C_t = C_{C,S} + C_{B,S} + C_{I,S} + C_v$$

After substituting for the respective surface concentrations, we solve the site balance for C_v :

$$C_v = \frac{C_t}{1 + K_A K_S P_C / P_P + K_A P_C + K_I P_I} \tag{6-50}$$

Replacing C_v in Equation (6-49) by Equation (6-50) and multiplying the numerator and denominator by P_P , we obtain the rate expression for desorption control:

$$r_D = \frac{k_D C_t K_S K_A (P_C - P_B P_P / K_r)}{P_P + P_C K_A K_S + K_A P_P P_C + K_I P_I P_P} \tag{6-51}$$

To determine the dependence of the initial rate on total pressure, we

Cumene decomposition rate law if desorption were limiting

again set $P_P = P_B = 0$; and, for the case of no inhibitor ($P_I = 0$), the rate law reduces to

$$-r_0 = k_D C_t$$

with the corresponding plot of $-r_0$ shown in Figure 6-13. If desorption were controlling, we would see that the initial rate would be independent of the initial pressure.

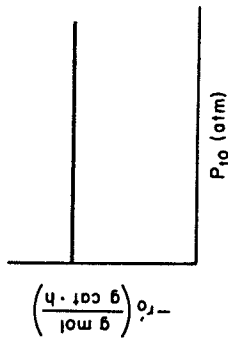


Figure 6-13 Desorption-limited reaction.

6.3.4 Summary of the Cumene Decomposition

The experimental observations of $-r_0$ as a function of P_{T0} are shown in Figure 6-14. From the plot in Figure 6-14 we can clearly see that desorption

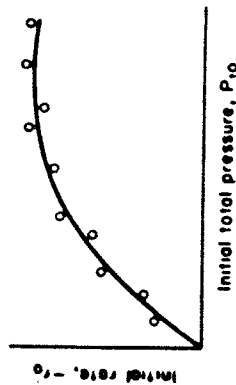


Figure 6-14 Actual initial rate as a function of total pressure for cumene decomposition.

Cumene decomposition is surface-reaction-limited

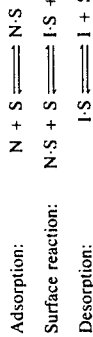
is not the controlling step. However, to determine whether adsorption or surface reaction is controlling, we must use either pure cumene or at least a feed containing no inhibitors in our initial rate experiments. If we carried out these experiments in the laboratory, we would find that the surface reaction is indeed the rate-limiting step, with the rate law being

$$-r_0 = \frac{k(P_C - P_B P_P / K_r)}{1 + K_B P_B + K_A P_C + K_I P_I} \tag{6-45}$$

TABLE 6-3. ALGORITHM FOR DETERMINING REACTION MECHANISM AND RATE-LIMITING STEP
Isomerization of *n*-pentene (N) to *i*-pentene (I) over alumina



1. Select a mechanism:



Treat each reaction step as an elementary reaction when writing rate laws.

2. Assume a rate-limiting step: Choose the surface reaction first, since more than 75% of all heterogeneous reactions that are not diffusion-limited are surface-reaction-limited. The rate law for the surface reaction step is

$$-r_N = r_S = k_S \left(C_N C_{\text{N}\cdot\text{S}} - \frac{C_{\text{I}\cdot\text{S}} C_{\text{S}}}{K_S} \right)$$

3. Find the expression for concentration of the adsorbed species $C_{\text{I}\cdot\text{S}}$: Use the other steps that are not limiting to solve for $C_{\text{I}\cdot\text{S}}$ (e.g., $C_{\text{N}\cdot\text{S}}$ and C_{S}). For this reaction,

$$\text{From } \frac{r_{\text{AD}}}{k_{\text{AD}}} = 0: \quad C_{\text{N}\cdot\text{S}} = P_N K_N C_{\text{S}}$$

$$\text{From } \frac{r_{\text{D}}}{k_{\text{D}}} = 0: \quad C_{\text{I}\cdot\text{S}} = \frac{P_I C_{\text{S}}}{K_I} = K_I P_I C_{\text{S}}$$

4. Write a site balance:

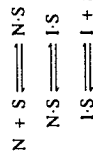
$$C_{\text{S}} = C_{\text{S}} + C_{\text{N}\cdot\text{S}} + C_{\text{I}\cdot\text{S}}$$

5. Derive the rate law: Combine steps 2, 3, and 4 to arrive at the rate law:

$$-r_N = r_S = \frac{k_S C_{\text{S}} \left(P_N K_N C_{\text{S}} - \frac{P_I C_{\text{S}}}{K_I} \right)}{(1 + K_N P_N + K_I P_I)}$$

6. Compare with data: Compare the rate law derived in Step 5 with experimental data. If they agree, there is a good chance that you have found the correct mechanism and rate-limiting step. If your derived rate law (i.e., model) does not agree with the data:

- Assume a different rate-limiting step and repeat steps 2 through 6.
- If, after assuming that each step is rate-limiting, none of the derived rate laws agree with the experimental data, select a different mechanism, e.g., Mechanism II:



and then proceed through steps 2 through 6. Mechanism II turns out to be the correct one.

- If two or more models agree, statistical tests (e.g., comparison of residuals) should be used to discriminate between them (see the Supplementary Reading).

It should be reinforced at this point that since the adsorption is exothermic, the higher the reaction temperature, the smaller the equilibrium constant. Consequently, at high temperatures, the denominator of catalytic rate laws approaches 1. For example, for a surface-reaction-limited irreversible isomerization



in which both A and B are adsorbed on the surface, the rate law is

$$-r_A' = \frac{K P_A}{1 + K_A P_A + K_B P_B}$$

At high temperatures

$$1 \gg (P_A K_A + P_B K_B)$$

The rate law could then be approximated as

$$-r_A' \approx k P_A$$

or for a reversible isomerization we would have

$$-r_A' \approx k \left(P_A - \frac{P_B}{K_r} \right)$$

The algorithm we can use as a start in postulating a reaction mechanism and rate-limiting step is shown in Table 6-3. We can never really prove a mechanism by comparing the derived rate law with experimental data. An independent spectroscopic or tracer experiment is usually needed to confirm the mechanism. We can, however, prove that a proposed mechanism is inconsistent with the experimental data by following the algorithm in Table 6-3. Rather than taking all the experimental data and then trying to build a model from the data, Box et al.¹⁰ describe techniques of sequential data-taking and model building.

6.4 Design of Reactors for Gas-Solid Reactions

6.4.1 Basic Guidelines

Designing or analyzing a reactor in which a fluid reaction is promoted by a solid catalyst differs little from designing or analyzing a reactor for homogeneous reactions. The principles presented in the first four chapters of this book remain valid. The kinetic rate law is often more complex for a catalytic reaction than for a homogeneous one, and this complexity can make the fundamental design equation more difficult to solve analytically. Nu-

¹⁰ G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statistics for Engineers* (New York: Wiley, 1978).

merical solution of the reactor design equation thus is encountered rather frequently when designing reactors for catalytic reactions.

The principal difference between reactor design calculations involving homogeneous reactions and those involving fluid-solid heterogeneous reactions is that for the latter, the reaction rate is based on mass of solid, W rather than on reactor volume V . For a fluid-solid heterogeneous system, the rate of reaction of a substance A is defined as

$$-r'_A = \text{g mol } A \text{ reacted/s/g catalyst}$$

The mass of solid is used because the amount of the catalyst or the amount of the solid reactant present is what is important to the rate of reaction. The reactor volume that contains the catalyst or other solid is of secondary significance.

6.4.2 The Design Equation

Three idealized types of reactors have been treated in this book: the perfectly mixed batch reactor, the plug-flow tubular reactor, and the perfectly mixed continuous-stirred tank reactor (CSTR). For these three types, design equations were developed based on reactor volume. To arrive at the analogous design equations for heterogeneous reactions, we simply replace the generation term $r_A V$ with $r'_A W$:

$$G = r'_A W = \frac{\text{g mol}}{(\text{time})(\text{mass of cat.})} \cdot (\text{mass of catalyst})$$

For an ideal batch reactor, the differential form of the design equation is

$$N_{A0} \frac{dX}{dt} = -r'_A V \quad (2-6)$$

The analogous equation based on weight of catalyst or solid is

$$N_{A0} \frac{dX}{dt} = -r'_A W \quad (6-52)$$

From this equation, the integral form of the design equation for a batch catalytic or fluid-solid reactor follows directly:

$$t = N_{A0} \int_0^X \frac{dX}{-r'_A W} \quad (6-53)$$

Batch design equation

If catalyst activity is decaying with time, it is necessary to separate the time-dependent terms before integrating.

For a tubular reactor, the differential form of the design equation is

$$F_{A0} \frac{dX}{dV} = -r'_A \quad (2-15)$$

and the corresponding equation for a tubular reactor that has a fluid-solid

or catalytic reaction occurring in it is

$$F_{A0} \frac{dX}{dW} = -r'_A \quad (6-54)$$

The derivation of the design equation for a catalytic reactor will be carried out in a manner analogous to the development of the tubular reactor design equation. To accomplish this derivation, we simply replace the volume coordinate in Equation (1-8) with the catalyst weight coordinate W (see Figure 6-15). The generalized mole balance on species A over catalyst weight ΔW results in the equation

$$\begin{array}{l} \text{in} \quad - \quad \text{out} \quad + \text{generation} = \text{accumulation} \\ F_A(W) - F_A(W + \Delta W) + r'_A \Delta W = 0 \end{array} \quad (6-55)$$

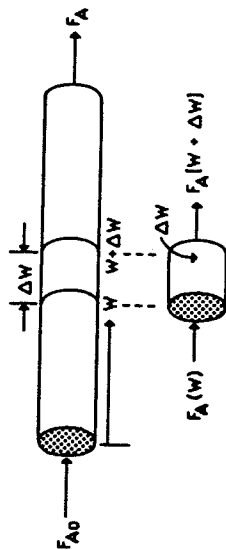


Figure 6-15 Packed-bed reactor schematic.

The dimensions of the left-hand side of Equation (6-55) are

$$(r'_A) \Delta W = \frac{\text{moles } A}{(\text{time})(\text{mass catalyst})} \cdot (\text{mass catalyst}) = \frac{\text{moles } A}{\text{time}}$$

After dividing by ΔW , and taking the limit as $\Delta W \rightarrow 0$,

$$- \frac{dF_A}{dW} = -r'_A \quad (6-56)$$

we substitute for F_A in terms of the conversion and the molar feed rate entering the reactor, F_{A0} :

$$F_{A0} \frac{dX}{dW} = -r'_A \quad (6-54)$$

When the pressure drop through the reactor (see Section 4.4) and catalyst decay (see Section 6.7) are neglected, the integral form of the packed-bed design equation is

$$W = F_{A0} \int_0^X \frac{dX}{-r'_A} \quad (6-57)$$

The design equation for a perfectly mixed "fluidized" catalytic reactor can be replaced by that of a CSTR.

Use differential form of design equation for catalyst decay and pressure drop

Packed-bed (FBR) design equation

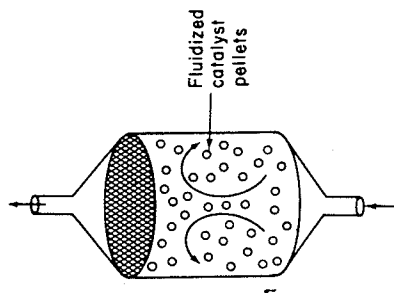


Figure 6-16 Fluidized CSTR reactor.

Tank reactors for solid-catalyzed gaseous or liquid reactions are seen much less frequently than tubular reactors because of the difficulty in separating the phases and in agitating a fluid phase in the presence of solid particles. One type of CSTR for catalytic reactions is the spinning basket reactor, which has the catalyst embedded in the blades of the spinning agitator.¹¹ Another is the Berty reactor, which uses an internal recycle stream to achieve perfectly mixed behavior.¹² These reactors are frequently used in industry to evaluate reaction mechanisms and determine reaction kinetics.

For the ideal CSTR, the design equation based on volume is

$$V = \frac{F_{A0}X}{-r_A} \quad (2-13)$$

and the equivalent equation for a catalytic or fluid-solid reactor (Figure 6-16) with the rate based on mass of solid is

$$W = \frac{F_{A0}X}{-r_A} \quad (6-58)$$

Fluidized CSTR design equation

Better models and design equations exist for fluidized-bed reactors and they should be used. One commonly used model is the bubbling bed model of Kunii and Levenspiel.¹³

All the design equations for ideal catalytic or fluid-solid reactors can thus be obtained from their homogeneous reactor analogs merely by substituting the catalyst or solid weight, W , for the reactor volume, V . The

¹¹ J. J. Carberry, *Ind. Eng. Chem.*, 56(11), 39 (1964).

¹² J. Berty, *Chem. Eng. Prog.*, 70(5), 78 (1974).

¹³ D. Kunii and O. Levenspiel, *Fluidization Engineering* (Huntington, N.Y.: Krieger, 1977).

reactor volume is merely the catalyst weight W divided by the bulk density of the catalyst, ρ_B . In the catalytic or fluid-solid reactor design equation, r_A , based on catalyst mass, must of course be used.

The preceding four sections conclude our discussion of elementary heterogeneous catalysis mechanisms and design equations. In the following section we shall work through an example problem using experimental data to (1) deduce a rate law, (2) determine a mechanism consistent with experimental data, (3) evaluate the rate law parameters, and (4) design a CSTR and packed-bed reactor.

6.5 Heterogeneous Data Analysis for Reactor Design

In this section we focus on four operations that reactor engineers need to be able to accomplish: (1) developing an algebraic rate law consistent with experimental observations, (2) linearizing the rate law in such a manner that the rate law parameters (e.g., k , K_A) can be readily extracted from the experimental data, (3) finding a mechanism and rate-limiting step consistent with the experimental data, and (4) designing a catalytic reactor to achieve a specified conversion. We shall use the hydrodemethylation of toluene to illustrate these four operations.

Hydrogen and toluene are reacted over a solid mineral catalyst containing clinoptilolite (a crystalline silica-alumina) to yield methane and benzene:¹⁴



We wish to design tubular (packed-bed) and CSTR (fluidized-bed) reactors to produce 10 mol of benzene per minute from a feed consisting of 20% toluene, 40% hydrogen, and 40% inerts at 600°C and 10 atm (1013 kPa). To achieve this goal we must first determine the rate law from the differential reactor data presented in Table 6-4. In this table we find the rate of reaction of toluene as a function of the partial pressures of hydrogen (H), toluene (T), benzene (B), and methane (M). In the first two runs, methane was introduced into the feed together with hydrogen and toluene, while the other product, benzene, was fed to the reactor together with the reactants only in runs 3, 4, and 6. In runs 5 and 16 both methane and benzene were introduced in the feed. In the remaining runs, neither of the products were present in the feedstream; consequently, since the conversion was less than 1% in the differential reactor, the partial pressures of methane and benzene in these runs were essentially zero, and the reaction rates were equivalent to initial rates of reaction.

Differential
Rate law
 F_{ind}
Mechanism
Evaluation
Rate law
parameters
 D_{-100}
PBR
CSTR

¹⁴ J. Papp, D. Kallo, and G. Schay, *J. Catal.*, 23, 168 (1971).

TABLE 6-4

Run	$r_T^* \times 10^{10}$ (g mol toluene) (g cat·s)	Partial Pressure (atm)			
		Toluene, P_T	Hydrogen (H ₂), P_{H_2}	Methane, P_M	Benzene, P_B
Set A					
1	71.0	1	1	1	0
2	71.3	1	1	4	0
Set B					
3	41.6	1	1	0	1
4	19.7	1	1	0	4
5	42.0	1	1	1	1
6	17.1	1	1	0	5
Set C					
7	71.8	1	1	0	0
8	142.0	1	2	0	0
9	284.0	1	4	0	0
Set D					
10	47.0	0.5	1	0	0
11	71.3	1	1	0	0
12	117.0	5	1	0	0
13	127.0	10	1	0	0
14	131.0	15	1	0	0
15	133.0	20	1	0	0
16	41.8	1	1	1	1

* $P_H = P_{H_2}$.

Unscramble the data to find the rate law

6.5.1 Deducing a Rate Law from the Experimental Data

Assuming that the reaction is essentially irreversible (which is reasonable after comparing runs 3 and 5), we ask what qualitative conclusions can be drawn from the data about the dependence of the rate of disappearance of toluene, $-r_T^*$, on the partial pressures of toluene, hydrogen, methane, and benzene.

1. *Dependence on methane:* If the methane were adsorbed on the surface, the partial pressure of methane would appear in the denominator of the rate expression and the rate would vary inversely with methane concentration; i.e.,

$$r_T^* \sim \frac{[]}{1 + K_M P_M + \dots} \quad (6-59)$$

However, from runs 1 and 2 we observe that a fourfold increase in the pressure of methane has little effect on r_T^* . Consequently, we can conclude that methane is either very weakly adsorbed (i.e., $K_M P_M \ll 1$) or goes directly into the gas phase in a manner similar to propylene in the cumene decomposition.

2. *Dependence on benzene:* In runs 3 and 4, we observe that for fixed concentrations (partial pressures) of hydrogen and toluene the rate decreases with increasing concentration of benzene. A rate expression in which the benzene partial pressure appears in the denominator could explain this dependency; i.e.,

$$-r_T^* \sim \frac{1}{1 + K_B P_B + \dots} \quad (6-60)$$

The type of dependence of $-r_T^*$ on P_B given by Equation (6-60) suggests that benzene is adsorbed on the clinoptilolite surface.

3. *Dependence on toluene:* At low concentrations of toluene (runs 10 and 11), the rate increases with increasing partial pressure of toluene, while at high toluene concentrations (runs 14 and 15), the rate is essentially independent of the toluene partial pressure.

A form of the rate expression that would describe this behavior is

$$-r_T^* \sim \frac{P_T}{1 + K_T P_T + \dots} \quad (6-61)$$

A combination of equations (6-60) and (6-61) suggests that the rate law may be of the form

$$-r_T^* \sim \frac{P_T}{1 + K_T P_T + K_B P_B + \dots} \quad (6-62)$$

4. *Dependence on hydrogen:* When we examine runs 7, 8, and 9 in Table 6-4, we see that the rate increases linearly with increasing hydrogen concentration and we conclude that the reaction is first-order in H₂. In light of this fact, it is doubtful that hydrogen is first-adsorbed on the surface. If it were adsorbed, $-r_T^*$ would have a dependence on P_{H_2} analogous to the dependence of $-r_T^*$ on the partial pressure of toluene, P_T [see Equation (6-61)]. For first-order dependence on H₂,

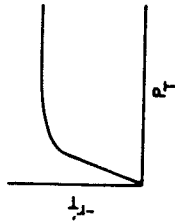
$$-r_T^* \propto P_{H_2} \quad (6-63)$$

Combining equations (6-59) through (6-63), we find that the rate law

$$-r_T^* = \frac{k P_{H_2} P_T}{1 + K_B P_B + K_T P_T}$$

is in qualitative agreement with the data shown in Table 6-4

If it is in the denominator, it is probably on the surface



6.5.2 Finding a Mechanism Consistent with Experimental Observations

We now propose a mechanism for the hydrodemethylation of toluene. We assume that toluene is adsorbed on the surface and then reacts with hydrogen in the gas phase to produce benzene adsorbed on the surface and methane in the gas phase. Benzene is then desorbed from the surface. Since approximately 75% of all heterogeneous reaction mechanisms are surface-reaction-limited rather than adsorption- or desorption-limited, we begin by assuming the reaction between adsorbed toluene and gaseous hydrogen to be reaction-rate-limited. Symbolically, this mechanism and associated rate laws for each elementary step are:

Adsorption: $T(g) + S \rightleftharpoons T \cdot S$

$$r_{AD} = k_A \left(C_T P_T - \frac{C_{T \cdot S}}{K_T} \right) \quad (6-64)$$

Surface reaction: $H_2(g) + T \cdot S \rightleftharpoons B \cdot S + M(g)$

$$r_S = k_S \left(P_{H_2} C_{T \cdot S} - \frac{C_{B \cdot S} P_M}{K_S} \right) \quad (6-65)$$

Desorption: $B \cdot S \rightleftharpoons B(g) + S$

$$r_D = k_D \left(C_{B \cdot S} - \frac{P_B C_B}{K_B} \right) \quad (6-66)$$

For surface-reaction-limited mechanisms,

$$r_S = k_S \left(P_{H_2} C_{T \cdot S} - \frac{C_{B \cdot S} P_M}{K_S} \right) \quad (6-65)$$

we see that we need to replace $C_{T \cdot S}$ and $C_{B \cdot S}$ in Equation (6-65) by quantities that we can measure.

For surface-reaction-limited mechanisms, we use the adsorption rate Equation (6-64) to obtain $C_{T \cdot S}$:

$$\frac{r_{AD}}{k_A} \approx 0$$

Then

$$C_{T \cdot S} = K_T P_T C_T \quad (6-67)$$

and we use the desorption rate Equation (6-66) to obtain $C_{B \cdot S}$:

$$\frac{r_D}{k_D} \approx 0$$

Approximately 75% of all heterogeneous reaction mechanisms are surface-reaction-limited

Proposed mechanism

Then

$$C_{B \cdot S} = \frac{P_B C_B}{K_B} \quad (6-68)$$

The total concentration of sites is

$$C_T = C_v + C_{T \cdot S} + C_{B \cdot S} \quad (6-69)$$

Substituting equations (6-67) and (6-68) into Equation (6-69) and rearranging, we obtain

$$C_v = \frac{C_T}{1 + P_T K_T + P_B / K_B} \quad (6-70)$$

Next, substitute for $C_{T \cdot S}$ and $C_{B \cdot S}$ and then substitute for C_v in Equation (6-65) to obtain the rate law for the case of surface-reaction control:

$$-r_T' = r_S = \frac{C_T k_S K_T (P_{H_2} P_T - P_B P_M / K_S)}{1 + P_T K_T + P_B / K_B} \quad (6-71)$$

Neglecting the reverse reaction and letting $K_B = 1/K_B'$, and $k = k_S C_T$, we have

Rate law for surface-reaction-limited mechanism

$$-r_T' = \frac{k K_T P_{H_2} P_T}{1 + K_B P_B + K_T P_T} \quad (6-72)$$

Note that the equilibrium constant for adsorption of a given species is exactly the reciprocal of the equilibrium constant for the desorption of that species ($K_B = 1/K_B'$).

6.5.3 Evaluation of the Rate Law Parameters

In the original work on this reaction by Papp et al.,¹⁵ over 25 models were tested against experimental data, and it was concluded that the mechanism and rate-limiting step above (i.e., the surface reaction between adsorbed toluene and H₂ gas) is the correct one. Assuming that the reaction is essentially irreversible, the rate law for the reaction on clinoptilolite is

$$-r_T' = k K_T \frac{P_{H_2} P_T}{1 + K_B P_B + K_T P_T} \quad (6-72)$$

We now wish to determine how best to analyze the data to extract the rate law parameters, k , K_T , and K_B . This analysis is referred to as *parameter estimation*.¹⁶ We must now rearrange our rate law to obtain a linear relationship between our measured variables. For the rate law given by Equation

¹⁵ Ibid.

¹⁶ See the Supplementary Reading for a variety of techniques for estimating the rate law parameters.

(6-72), we see that if both sides of Equation (6-72) are divided by $P_{H_2}P_T$ and the equation is then inverted; i.e.,

$$\frac{P_{H_2}P_T}{-r_T} = \frac{1}{kK_T} + \frac{K_B}{kK_T} \frac{P_B}{P_T} + \frac{P_T}{k} \quad (6-73)$$

Linearize the rate equation to extract the rate law parameters

The multiple regression techniques described in Chapter 5 could be used to determine the rate law parameters by using the equation

$$Y = a_0 + a_1X_1 + a_2X_2 \quad (5-22)$$

In the example that follows we shall use graphical techniques, as well as linear regression techniques, to evaluate the rate law parameters.

Example 6-2 Determining the Rate Law Parameters k , K_T , and K_B

Use the data in Table 6-4 together with Equation (6-73) to evaluate the rate law parameters.

Solution

The calculations are shown in Table E6-2.1. A plot of $(P_{H_2}P_T/(-r_T))$ versus P_T at constant P_B will be linear with slope $1/k$ (see Figure E6-2.1).

$$\text{slope} = \frac{1}{k} = \frac{15.0 - 0.8}{20} \times 10^6 = 0.71 \times 10^6$$

$$k = 1.408 \times 10^{-6} \frac{\text{g mol}}{\text{g cat} \cdot \text{s} \cdot \text{atm}}$$

TABLE E6-2.1

Run	$-r_T \times 10^{10}$ (g mol/g cat·s)	P_T (atm)	P_{H_2} (atm)	$\frac{P_T P_{H_2}}{-r_T} \times 10^6$ (g cat·s·atm ² /mol)	P_B (atm)
3	41.6	1	1	2.40	1
4	19.7	1	1	5.07	4
6	17.1	1	1	5.85	5
7	71.8	1	1	1.39	0
9	284.0	1	4	1.41	0
10	47.0	0.5	1	1.06	0
12	117.0	5	1	4.27	0
13	127.0	10	1	7.87	0
14	131.0	15	1	11.45	0
15	133.0	20	1	15.04	0

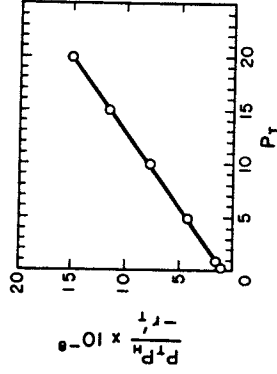


Figure E6-2.1

Rearranging Equation (6-73) for $P_B = 0$, we have

$$\frac{P_T P_{H_2}}{-r_T} = \frac{P_T}{k} + \frac{1}{kK_T} \quad (E6-2.1)$$

From Figure E6-2.1,

$$\frac{P_T P_{H_2}}{-r_T} = 10^6 \text{ when } P_T = 13.1 \text{ atm}$$

Substituting these values into Equation (E6-2.1), we find that

$$10^6 = \frac{13.1}{1.408 \times 10^{-6}} = 0.7 \times 10^6 = \frac{1}{kK_T} \quad (E6-2.2)$$

$$K_T = 1.01 \text{ atm}^{-1} = 0.01 \text{ kPa}^{-1}$$

The constant K_B can be evaluated from the slope of the plot of $(P_{H_2}P_T/(-r_T))$ versus P_B for constant P_T . From Figure E6-2.2,

$$K_B = \text{slope} \cdot kK_T$$

$$= (0.88 \times 10^6)(1.41 \times 10^{-6})(1.01)$$

$$= 1.26 \text{ atm}^{-1} = 0.0125 \text{ kPa}^{-1}$$

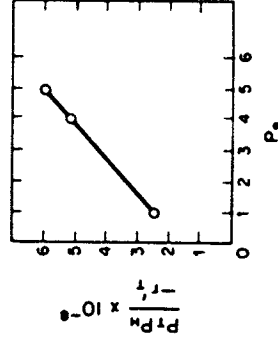


Figure E6-2.2

In addition to the graphical determination, we can use linear regression to determine the rate law parameters. We will use equations (5-33) through (5-35) along with Table E6-2.2 to determine k , K_T , and K_B in equations (6-73) and (5-22).

Recalling Equation (6-73)

$$\frac{P_{12}P_T}{-r'_T} = \frac{1}{kK_T} + \frac{K_B}{kK_T} P_B + \frac{P_T}{k} \quad (6-73)$$

and Equation (5-22)

$$Y = a_0 + a_1 X_1 + a_2 X_2 \quad (5-22)$$

where

$$Y = P_{12}P_T / -r'_T, \quad a_0 = 1/kK_T, \quad a_1 = K_B/kK_T, \quad a_2 = 1/k, \quad X_1 = P_B, \quad \text{and} \quad X_2 = P_T$$

Next, recalling the linear regression equations and applying them for the 16 runs of this example

$$\sum_{j=1}^{16} Y_j = 16a_0 + a_1 \sum_{j=1}^{16} X_{1j} + a_2 \sum_{j=1}^{16} X_{2j} \quad (E6-2.3)$$

$$\sum_{j=1}^{16} X_{1j} Y_j = a_0 \sum_{j=1}^{16} X_{1j} + a_1 \sum_{j=1}^{16} X_{1j}^2 + a_2 \sum_{j=1}^{16} X_{1j} X_{2j} \quad (E6-2.4)$$

$$\sum_{j=1}^{16} X_{2j} Y_j = a_0 \sum_{j=1}^{16} X_{2j} + a_1 \sum_{j=1}^{16} X_{1j} X_{2j} + a_2 \sum_{j=1}^{16} X_{2j}^2 \quad (E6-2.5)$$

If we were to use a software package such as POLYMATH, we would simply enter Y , X_1 , and X_2 for each run and the parameters a_0 , a_1 , and a_2 would be displayed in a few seconds. Alternatively we can form Table E6-2.2 and carry out the numerical operations ourselves to determine the rate law parameters. We can either form the table using a calculator, or by using a spreadsheet such as Excel or Lotus 123.

TABLE E6-2.2

Run	$P(P_T/P_T)$	$X_1(P_B)$	$X_2(P_T)$	X_1^2	X_2^2	$X_1 X_2$	Y
1	1.41E+08	0.0	1.0	0.00E+00	1.41E+08	0.0	0.0
2	1.40E+08	0.0	1.0	0.00E+00	1.40E+08	0.0	1.0
3	2.40E+08	1.0	1.0	2.40E+08	2.40E+08	1.0	1.0
4	5.08E+08	4.0	1.0	2.03E+09	5.08E+08	16.0	4.0
5	2.38E+08	1.0	1.0	2.38E+08	2.38E+08	1.0	1.0
6	5.83E+08	5.0	1.0	2.92E+09	5.83E+08	25.0	5.0
7	1.39E+08	0.0	1.0	0.00E+00	1.39E+08	0.0	1.0
8	1.41E+08	0.0	1.0	0.00E+00	1.41E+08	0.0	1.0
9	1.06E+08	0.0	1.0	0.00E+00	1.06E+08	0.0	1.0
10	1.40E+08	0.0	1.0	0.00E+00	1.40E+08	0.0	1.0
11	4.27E+08	9.0	1.0	0.00E+00	4.27E+08	0.0	1.0
12	7.87E+08	0.0	1.0	0.00E+00	7.87E+08	0.0	1.0
13	1.14E+09	0.0	1.0	0.00E+00	1.14E+09	0.0	1.0
14	1.50E+09	0.0	1.0	0.00E+00	1.50E+09	0.0	1.0
15	2.39E+08	1.0	1.0	2.39E+08	2.39E+08	1.0	1.0
16	6.62E+09	12.0	61.5	5.67E+09	6.00E+10	44.0	761.25
Sum							12.0
(i = 1 to 16)							

Equation (E6-2.3) becomes

$$6.62 \times 10^9 = 16a_0 + 12a_1 + 61.5a_2 \quad (E6-2.6)$$

Equation (E6-2.4) becomes

$$5.67 \times 10^9 = 12a_0 + 44a_1 + 12a_2 \quad (E6-2.7)$$

Equation (E6-2.5) becomes

$$6.0 \times 10^{10} = 61.5a_0 + 12a_1 + 761.25a_2 \quad (E6-2.8)$$

Solving these three equations simultaneously, we obtain $a_0 = 7.12 \times 10^7$, $a_1 = 9.0 \times 10^7$, and $a_2 = 7.16 \times 10^7$. The corresponding rate law parameters are:

$$k = 1.4 \times 10^{-8} \text{ gmol/gcat} \cdot \text{s} \cdot \text{atm}, \quad K_T = 1.0/\text{atm}, \quad \text{and} \quad K_B = 1.26/\text{atm}.$$

Using POLYMATH, we obtain

$$Y = 7.12 \times 10^7 + 9.0 \times 10^7 X_1 + 7.16 \times 10^7 X_2$$

with, of course, the parameter values being the same as those obtained from Table E6-2.2 and Equation (E6-2.5).

After substituting the numerical values of k , K_B , and K_T into Equation (6-72), the rate law at 600°C for hydromethylation of toluene



is given by the equation

$$-r'_T = \frac{1.4 \times 10^{-8} P_{12} P_1}{1 + 1.26 P_B + 1.0 P_T} \quad \frac{\text{mol toluene}}{\text{g cat} \cdot \text{s}} \quad (6-74)$$

where P_i is in atm.

6.5.4 Reactor Design

Our next step is to express the partial pressures P_T , P_B , and P_{H_2} as a function of X . combine the partial pressures with the rate law $-r'_T$ as a function of conversion, and carry out the integration of the packed-bed design equation

$$W = F_{A0} \int_0^X \frac{dX}{-r'_T(X)} \quad (6-57)$$

Design equation neglecting pressure drop and catalyst decay

Example 6-3 Fixed (i.e., Packed)-Bed Reactor Design

Determine the catalyst weight necessary to achieve 89.5% conversion of toluene in a packed-bed reactor with a bulk density of 2.3 g/cm³. Use the same

reaction and initial conditions as described at the beginning of Section 6.5 with an entering volumetric flow rate of 400 dm³/min. Also determine the catalyst weight in a CSTR with a bulk density of 0.4 gm/cm³.



Solution

1. Design equation:

$$\frac{dF_T}{dW} = r_T'$$

$$F_{T0} \frac{dX}{dW} = -r_T'$$

Neglecting pressure drop and catalyst decay we can integrate to obtain

$$W = F_{T0} \int_0^X \frac{dX}{-r_T'} \quad (E6-3.1)$$

2. Rate law:

$$-r_T' = \frac{kK_T P_{H_2} P_T}{1 + K_B P_B + K_T P_T} \quad (E6-3.2)$$

3. Stoichiometry:

$$P_T = C_T RT = C_{T0} RT_0 \left(\frac{1-X}{1+\epsilon X} \right) = P_{T0} \left(\frac{1-X}{1+\epsilon X} \right) \quad (E6-3.3)$$

$$\epsilon = y_{T0} \delta = 0.2(0) = 0$$

$$P_{T0} = y_{T0} P_0 = (0.2)(10) = 2 \text{ atm}$$

$$P_T = 2(1-X)$$

$$P_{H_2} = P_{T0}(\Theta_{H_2} - X)$$

$$\Theta_{H_2} = \frac{0.4}{0.2} = 2$$

$$P_{H_2} = 2(2-X)$$

$$P_B = C_B RT = C_{B0} RT_0(\Theta_B + X) = P_{B0}(\Theta_B + X) \quad (E6-3.4)$$

$$\Theta_B = 0$$

$$P_B = 2X \quad (E6-3.5)$$

Note that P_{T0} designates initial toluene pressure. In this example, initial total pressure is designated P_0 to avoid any confusion.

4. Combining gives us

$$W = F_{T0} \int_0^X \frac{dX}{-r_T'} = F_{T0} \int_0^X \frac{1 + P_{T0} K_B X + P_{T0} K_T (1-X)}{k K_T P_{T0}^2 (1-X)(\Theta_{H_2} - X)} dX$$

Stoichiometry plus rate law

5. Parameter evaluation: Substituting for P_B , P_{H_2} , and P_T in Equation (6-74) yields

$$-r_T' = \frac{5.64 \times 10^{-9} (1-X)(2-X) \text{ g mol T}}{1 + 2.52(X) + 2.02(1-X) \text{ g cat s}} \quad (E6-3.6)$$

Expressing $-r_T'$ in kg of catalyst and min, we have

$$\begin{aligned} -r_T' &= \frac{5.64 \times 10^{-9} (1-X)(2-X) \text{ g mol T}}{3.02 + 0.5X} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{60 \text{ s}}{1 \text{ min}} \\ &= \frac{3.38 \times 10^{-7} (1-X)(2-X) \text{ g mol T}}{3.02 + 0.5X} \text{ kg cat min} \end{aligned} \quad (E6-3.7)$$

The next task to be done is to calculate the conversion for a specified molar flow rate of benzene from the reactor. The molar feed rate of toluene is

$$F_{T0} = C_{T0} v_0 = \left(\frac{P_{T0}}{RT_0} \right) v_0 = \frac{2}{(0.082)(873)} 400$$

$$= 11.175 \text{ g mol toluene/min}$$

The exiting molar feed of benzene is given in the example requirements by

$$F_B = F_{T0} X = 10 \frac{\text{g mol}}{\text{min}}$$

The corresponding desired conversion is

$$X = \frac{F_B}{F_{T0}} = \frac{10.0}{11.175} = 0.895$$

We can now proceed to solve for the catalyst weight necessary to obtain this conversion by using Equation (E6-3.7)

$$-r_T' = \frac{3.38 \times 10^{-7} (1-X)(2-X) \text{ g mol T}}{3.02 + 0.5X} \text{ kg cat min} \quad (E6-3.7)$$

6. Numerical techniques: The calculations for X versus $(1/r_T')$ are displayed in Table E6-3.1 and plotted in Figure E6-3.1.

TABLE E6-3.1

X	$-r_T'$	$1/r_T'$
0.0	2.24×10^{-7}	$f_1 = 446$
0.2	1.52×10^{-7}	$f_2 = 656$
0.4	9.63×10^{-8}	$f_3 = 1038$
0.6	5.34×10^{-8}	$f_4 = 1872$
0.8	2.18×10^{-8}	$f_5 = 4585$
0.895	1.03×10^{-8}	$f_6 = 9708$

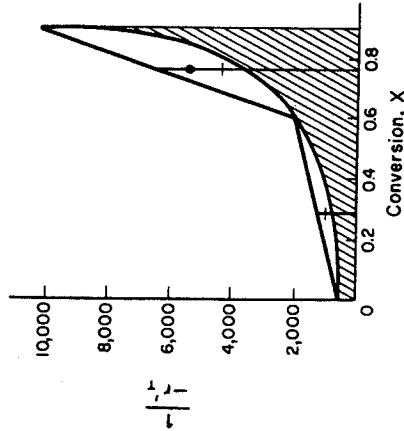


Figure E6-3.1

$$W = F_{T0} \int_0^{0.895} \frac{dX}{-r_1'} = \left(11.175 \frac{\text{g mol T}}{\text{min}} \right) (\text{area under the curve})$$

Using the graphical form of Simpson's rule, we find

$$\text{area} = 1957 \frac{\text{kg cat}\cdot\text{min}}{\text{g mol T}}$$

$$W = (11.175)(1957)$$

$$W = 2.19 \times 10^4 \text{ kg of catalyst}$$

Using numerical integration (Appendix A.5), after dividing the area under the curve into two parts: $X = 0$ to $X = 0.8$ with $h_1 = 0.2$ and $X = 0.8$ to $X = 0.895$ with $h_2 = 0.095$, we have

$$\begin{aligned} W &= F_{T0} \left[\frac{h_1}{3} (f_1 + 4f_2 + 2f_3 + 4f_4 + f_5) + \frac{h_2}{2} (f_5 + f_6) \right] \\ &= F_{T0} \left[\frac{0.2}{3} (446 + 4(656) + 2(1038) + 4(1872) + 4585) \right. \\ &\quad \left. + F_{T0} \left[\frac{0.095}{2} (4585 + 9708) \right] \right] \end{aligned}$$

$$= 11.175(1148 + 679) = 2.04 \times 10^4 \text{ kg of catalyst}$$

Since the bulk catalyst density is $2.3 \text{ g/cm}^3 = 2.3 \text{ kg/liter}$, the reactor necessary volume is

$$V = 9.51 \times 10^3 \text{ liters}$$

Since the reciprocal of the rate of reaction increases sharply as the conversion approaches unity, the numerical integration probably should have included a greater number of integrals than the six used in the calculation.

Graphical evaluation

Numerical evaluation

We will now calculate the fluidized CSTR catalyst weight necessary to achieve the same conversion as in the packed-bed reactor at the same operating conditions. The bulk density in the fluidized reactor is 0.4 g/cm^3 . The design equation is

$$W = \frac{F_{T0}X}{-r_1'} \quad (6-58)$$

at $X = 0.895$ we have

$$\begin{aligned} -r_1' &= 1.03 \times 10^{-4} \frac{\text{g mol T}}{\text{kg cat}\cdot\text{min}} \\ W &= \frac{F_{T0}X}{-r_1'} = \frac{10 \text{ g mol T/min}}{1.03 \times 10^{-4} \text{ g mol T/kg cat}\cdot\text{min}} \end{aligned}$$

$$W = 9.70 \times 10^4 \text{ kg of catalyst}$$

$$V = \frac{9.70 \times 10^4 \text{ kg}}{0.4 \text{ kg/liter}} = 2.42 \times 10^5 \text{ liters}$$

Note that the resulting single CSTR volume would have been too large—try to increase the temperature and/or use a series of CSTRs.

These values of the catalyst weight and reactor volume are quite high, especially for the low feed rates given. Consequently, the temperature of

How can the weight of catalyst be reduced?

An algorithm

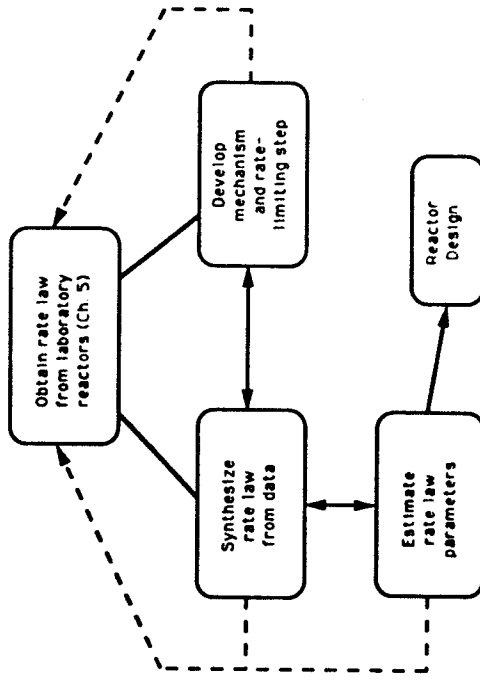


Figure 6-17 Collecting information for catalytic reactor design.

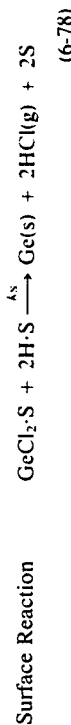
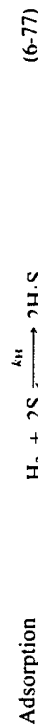
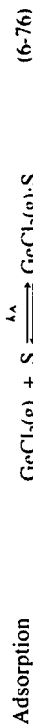
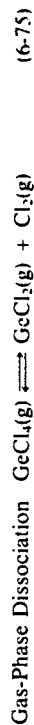
the reacting mixture should be increased to reduce the catalyst weight, provided that side reactions do not become a problem at higher temperatures.

Example 6-3 illustrated the major activities pertinent to catalytic reactor design. These activities are shown in Figure 6-17. In this example the rate law was extracted directly from the data and then a mechanism was found that was consistent with experimental observation. However, developing a feasible mechanism may guide one in the synthesis of the rate law. The dashed lines represent feedback to obtain new data in specific regions to evaluate more precisely the parameters or to differentiate between mechanisms.

6.6 Chemical Vapor Deposition (CVD)

We now extend the principle of the preceding sections to one of the emerging technologies in chemical engineering. Chemical engineers are now playing an important role in the electronics industry. Specifically they are becoming more involved in the manufacturing of electronic and photonic devices and recording materials. In the formation of microcircuits, electrically interconnected films are laid down by chemical reactions (see Section 11.8). One method by which these films are made is Chemical Vapor Deposition (CVD). The mechanisms by which CVD occur are very similar to the mechanisms of heterogeneous catalysis discussed earlier in this chapter. The reactant(s) adsorb on the surface and then react on the surface to form a new surface. This process may be followed by a desorption step, depending on the particular reaction.

The application of a germanium epitaxial film as an interlayer between a gallium arsenide layer and a silicon layer and as a contact layer is receiving increasing attention in the microelectronics industry.¹⁷ Epitaxial germanium is also an important material in the fabrication of tandem solar cells. The growth of germanium films can be accomplished by CVD. A proposed mechanism is:



At first it may appear that a site has been lost when comparing the r.h.s. and l.h.s. of the surface reaction step. However, the newly-formed germanium atom on the r.h.s. is a site for the future adsorption of $\text{H}_2(\text{g})$ or

¹⁷ Ishii, H. and Y. Takahashi, *J. Electrochemical Society* 135, p. 1539, (1988).

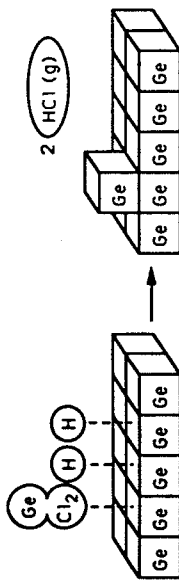


Figure 6-18

$\text{GeCl}_2(\text{g})$ and there are three sites on both the r.h.s. and l.h.s. of Equation (6-78). These sites are shown schematically in Figure 6-18.

The surface reaction between adsorbed molecular hydrogen and germanium dichloride is believed to be rate-limiting:

$$r_{\text{Dep}}^{\text{Ge}} = k_S f_{\text{GeCl}_2} f_{\text{H}}^2 \quad (6-79)$$

where $r_{\text{Dep}}^{\text{Ge}}$ = deposition rate (nm/s)

k_S = surface specific reaction rate (nm/s)

f_{v} = fraction of the surface that is vacant

f_{GeCl_2} = fraction of the surface occupied by germanium dichloride

f_{H} = fraction of the surface covered by molecular hydrogen

The deposition rate (film growth rate) is usually expressed in Angstroms per second and is easily converted to a molar rate (moles/m²·s) by multiplying by the molar density of germanium.

The difference between developing CVD rate laws and rate laws for catalysis is that the site concentration, e.g., C_v , is replaced by the fractional surface area coverage, e.g., f_v . The total fraction of surface available for adsorption should, of course, add up to 1.0.

Area balance

$$f_v + f_{\text{GeCl}_2} + f_{\text{H}} = 1 \quad (6-80)$$

We will first focus our attention on the adsorption of GeCl_2 . The rate of jumping on the surface is proportional to the partial pressure of GeCl_2 . The net rate of GeCl_2 adsorption is

$$r_{\text{Ad}} = k_A \left[f_v P_{\text{GeCl}_2} - \frac{f_{\text{GeCl}_2}}{K_A} \right] \quad (6-81)$$

Since the surface reaction is rate-limiting, in a manner analogous to catalysis reactions, we have for the adsorption of GeCl_2 ,

$$\frac{r_{\text{Ad}}}{k_A} = 0$$

Solving Equation (6-81) for the fractional surface coverage of GeCl_2 gives

$$f_{\text{GeCl}_2} = f_v K_A P_{\text{GeCl}_2} \quad (6-82)$$

For the dissociative adsorption of hydrogen on the Ge surface, the equation analogous to (6-81) is

$$r_{\text{H}_2} = k_{\text{H}} \left[P_{\text{H}_2} f_{\text{H}}^2 - \frac{f_{\text{H}}^2}{K_{\text{H}}} \right] \quad (6-83)$$

Since surface reaction is rate-limiting

$$\frac{r_{\text{H}_2}}{k_{\text{H}}} \approx 0$$

Then

$$f_{\text{H}} = f_{\text{v}} \sqrt{K_{\text{H}} P_{\text{H}_2}} \quad (6-84)$$

Recalling the rate of deposition of germanium we substitute for f_{GeCl_2} and f_{H} in Equation (6-79) to obtain

$$r_{\text{Dep}}^{\text{v}} = f_{\text{v}}^3 k_{\text{S}} K_{\text{A}} P_{\text{GeCl}_2} K_{\text{H}} P_{\text{H}_2} \quad (6-85)$$

We solve for f_{v} in an identical manner to that for C_{v} in heterogeneous catalysis. Substituting equations (6-82) and (6-84) into Equation (6-80) gives

$$f_{\text{v}} + f_{\text{v}} \sqrt{K_{\text{H}} P_{\text{H}_2}} + f_{\text{v}} K_{\text{A}} P_{\text{GeCl}_2} = 1 \quad (6-86)$$

Rearranging yields

$$f_{\text{v}} = \frac{1}{1 + K_{\text{A}} P_{\text{GeCl}_2} + \sqrt{K_{\text{H}} P_{\text{H}_2}}} \quad (6-87)$$

Finally, substituting for f_{v} in Equation (6-85) we find

$$r_{\text{Dep}}^{\text{v}} = \frac{k_{\text{S}} K_{\text{H}} K_{\text{A}} P_{\text{GeCl}_2} P_{\text{H}_2}}{[1 + K_{\text{A}} P_{\text{GeCl}_2} + \sqrt{K_{\text{H}} P_{\text{H}_2}}]^3} \quad (6-88)$$

and lumping, K_{A} , K_{H} , and k_{S} into a specific reaction rate k' ,

$$r_{\text{Dep}}^{\text{v}} = \frac{k' P_{\text{GeCl}_2} P_{\text{H}_2}}{[1 + K_{\text{A}} P_{\text{GeCl}_2} + \sqrt{K_{\text{H}} P_{\text{H}_2}}]^3} \quad (6-89)$$

If it is assumed Reaction (6-75) is in equilibrium, then the partial pressure of GeCl_4 varies linearly with the partial pressure of GeCl_2 , i.e.,

$$P_{\text{GeCl}_4} \approx P_{\text{GeCl}_2}$$

And, if hydrogen is weakly adsorbed, we obtain the rate law given by Ishii and Takahashi,¹⁸

$$r_{\text{Dep}}^{\text{v}} = \frac{k P_{\text{GeCl}_2} P_{\text{H}_2}}{[1 + K_1 P_{\text{GeCl}_4}]^3} \quad (6-90)$$

¹⁸ Ibid.

We leave it as an exercise to determine if the constants k and K_1 depend on the concentration of any other species.

6.7 Catalyst Deactivation

In designing fixed and ideal fluidized-bed catalytic reactors, we have assumed up to now that the activity of the catalyst remains constant throughout the catalyst's life. That is, the total concentration of active sites, C_t , accessible to the reaction does not change with time. Unfortunately, Mother Nature is not so kind as to allow this behavior to be the case in most industrially significant catalytic reactions. One of the most insidious problems in catalysis is the loss of catalytic activity that occurs as the reaction takes place on the catalyst. A wide variety of mechanisms have been proposed by Butt and Petersen,¹⁹ to explain and model catalyst deactivation.

Catalytic deactivation adds another level of complexity to sorting out the reaction rate law parameters and pathways. In addition, we need to make adjustments for the decay of the catalysts in the design of catalytic reactors. This adjustment is usually made by a quantitative specification of the catalyst's activity, $a(t)$. In analyzing reactions over decaying catalysts we divide the reactions into two categories: *separable kinetics* and *non-separable kinetics*. In separable kinetics, we separate the rate law and activity, i.e.,

$$\text{Separable Kinetics: } r_A = a(\text{past history}) \times r_A(\text{present condition}).$$

When the kinetics and activity are separable it is possible to study catalyst decay and reaction kinetics independently. However, non-separability, i.e.,

$$\text{Non-Separable Kinetics: } r_A = r_A(\text{past history, present conditions})$$

must be accounted for by assuming the existence of a non-ideal surface or by describing deactivation by a mechanism composed of several elementary steps.²⁰

In this section we shall consider only separable kinetics and define the activity of the catalyst at time t , $a(t)$, as the ratio of the rate of reaction on a catalyst that has been used for a time t , to the rate of reaction on a fresh catalyst.

$$a(t) = \frac{\text{catalyst activity}}{\text{catalyst activity}}$$

$$a(t) = \frac{-r_A'(t)}{-r_A(t) \quad (t=0)} \quad (6-91)$$

Combining equations (6-91) and (3-1), the rate of disappearance of reactant

¹⁹ J. B. Butt, and E. E. Petersen, *Activation, Deactivation and Poisoning of Catalysts* (New York: Academic Press, 1988).

²⁰ D. T. Lynch and G. Emig, "On the Separability of Catalyst Activity and Kinetic Behavior," *Chemical Engineering Science*, Vol. 44, No. 6, pp. 1275-1280, 1989.

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