Catalysis and Catalytic Reactors 10

It isn't that they can't see the solution. It is that they can't see the problem.

—G. K. Chesterton

Overview. The objectives of this chapter are to develop an understanding of catalysts, reaction mechanisms, and catalytic reactor design. Specifically, after reading this chapter one should be able to

- Define a catalyst and describe its properties.
- Describe the steps in a catalytic reaction and in chemical vapor deposition (CVD).
- Suggest a mechanism and apply the concept of a rate-limiting step to derive a rate law.
- Use nonlinear regression to determine the rate law and rate-law parameters that best fit the data.
- Use the rate law parameters to design PBRs and fluidized CSTRs.
- Describe the analogy between catalytic steps and CVD in microelectronic fabrication.
- Analyze catalyst decay and reactors that can be used to help offset decay.

The various sections of this chapter roughly correspond to these objectives.

10.1 Catalysts

Catalysts have been used by humankind for over 2000 years.[1] The first observed uses of catalysts were in the making of wine, cheese, and bread. It was found that it was always necessary to add small amounts of the previous

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[1] S. T. Oyama and G. A. Somorjai, *J. Chem. Educ.*, 65, 765 (1986).

batch to make the current batch. However, it wasn't until 1835 that Berzelius began to tie together observations of earlier chemists by suggesting that small amounts of a foreign substance could greatly affect the course of chemical reactions. This mysterious force attributed to the substance was called *catalytic.* In 1894, Ostwald expanded Berzelius's explanation by stating that catalysts were substances that accelerate the rate of chemical reactions without being consumed during the reaction. During the 180 years since Berzelius's work, catalysts have come to play a major economic role in the world market. In the United States alone, sales of process catalysts will reach over $20 billion by 2018, the major uses being in petroleum refining and in chemical production.

10.1.1 Definitions

A *catalyst* is a substance that affects the rate of a reaction but emerges from the process unchanged. A catalyst usually changes a reaction rate by promoting a different molecular path ("mechanism") for the reaction. For example, gaseous hydrogen and oxygen are virtually inert at room temperature, but react rapidly when exposed to platinum. The reaction coordinate (cf. Chapter 3) shown in Figure 10-1 is a measure of the progress along the reaction path as H_2 and O_2 approach each other and pass over the activation energy barrier to form H_2O. *Catalysis is the occurrence, study, and use of catalysts and catalytic processes.* Commercial chemical catalysts are immensely important. Approximately one-third of the material gross national product of the United States involves a catalytic process somewhere between raw material and finished product.[2] The development and use of catalysts is a major part of the constant search for new ways of increasing product yield and selectivity from chemical reactions. Because a catalyst makes it possible to obtain an end product by a different pathway with a lower energy barrier, it can affect both the yield and the selectivity.

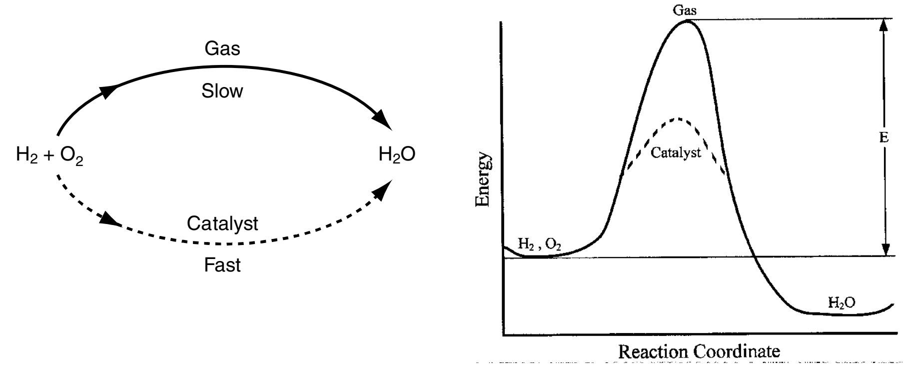

Figure 10-1 Different reaction paths.

Catalysts can accelerate the reaction rate but cannot change the equilibrium.

Normally when we talk about a catalyst, we mean one that speeds up a reaction, although strictly speaking, a catalyst can either accelerate or slow the formation of a particular product species. *A catalyst changes only the rate of a reaction; it does not affect the equilibrium.*

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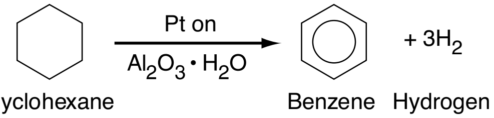
[2] V. Haensel and R. L. Burwell, Jr., *Sci. Am.*, 225(10), 46.

The 2007 Nobel Prize for Chemistry was awarded to Gerhard Ertl for his pioneering work on heterogeneous catalytic reactions. A *heterogeneous catalytic reaction* involves more than one phase; usually the catalyst is a solid and the reactants and products are in liquid or gaseous form. One example is the production of benzene, which is mostly manufactured today from the dehydrogenation of cyclohexane (obtained from the distillation of petroleum crude oil) using platinum-on-alumina as the catalyst:



The simple and complete separation of the fluid product mixture from the solid catalyst makes heterogeneous catalysis economically attractive, especially because many catalysts are quite valuable and their reuse is demanded.

A heterogeneous catalytic reaction occurs at or very near the fluid–solid interface. The principles that govern heterogeneous catalytic reactions can be applied to both catalytic and noncatalytic fluid–solid reactions. The two other types of heterogeneous reactions involve gas–liquid and gas–liquid–solid systems. Reactions between gases and liquids are usually mass-transfer limited.

10.1.2 Catalyst Properties

Ten grams of this catalyst possess more surface area than a U.S. football field

Catalyst types:
- Porous
- Molecular sieves
- Monolithic
- Supported
- Unsupported

Typical zeolite catalyst

High selectivity to para-xylene

Because a catalytic reaction occurs at the fluid–solid interface, a large interfacial area is almost always essential in attaining a significant reaction rate. In many catalysts, this area is provided by an inner porous structure (i.e., the solid contains many fine pores, and the surface of these pores supplies the area needed for the high rate of reaction), see Figures 10-4(b) and 10-9. The area possessed by some porous catalysis materials is surprisingly large. A typical silica-alumina cracking catalyst has a pore volume of 0.6 cm^3/g and an average pore radius of 4 nm. The corresponding surface area is 300 m^2/g of these *porous catalysts*. Examples include the Raney nickel used in the hydrogenation of vegetable and animal oils, platinum-on-alumina used in the reforming of petroleum naphthas to obtain higher octane ratings, and promoted iron used in ammonia synthesis. Sometimes pores are so small that they will admit small molecules but prevent large ones from entering. Materials with this type of pore are called *molecular sieves*, and they may be derived from natural substances such as certain clays and zeolites, or they may be totally synthetic, such as some crystalline aluminosilicates (see Figure 10-2). These sieves can form the basis for quite selective catalysts; the pores can control the residence time of various molecules near the catalytically active surface to a degree that essentially allows *only* the desired molecules to react. One example of the high selectivity of zeolite catalysts is the formation of para-xylene from toluene and methane shown in Figure 10-2(b).[3] Here, benzene and toluene enter through the zeolite pore and react on the interior surface to form a mixture of ortho-, meta-, and para-xylenes. However, the size of the pore mouth is such that only

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[3] R. I. Masel, *Chemical Kinetics and Catalysis* (New York: Wiley Interscience, 2001), p. 741.

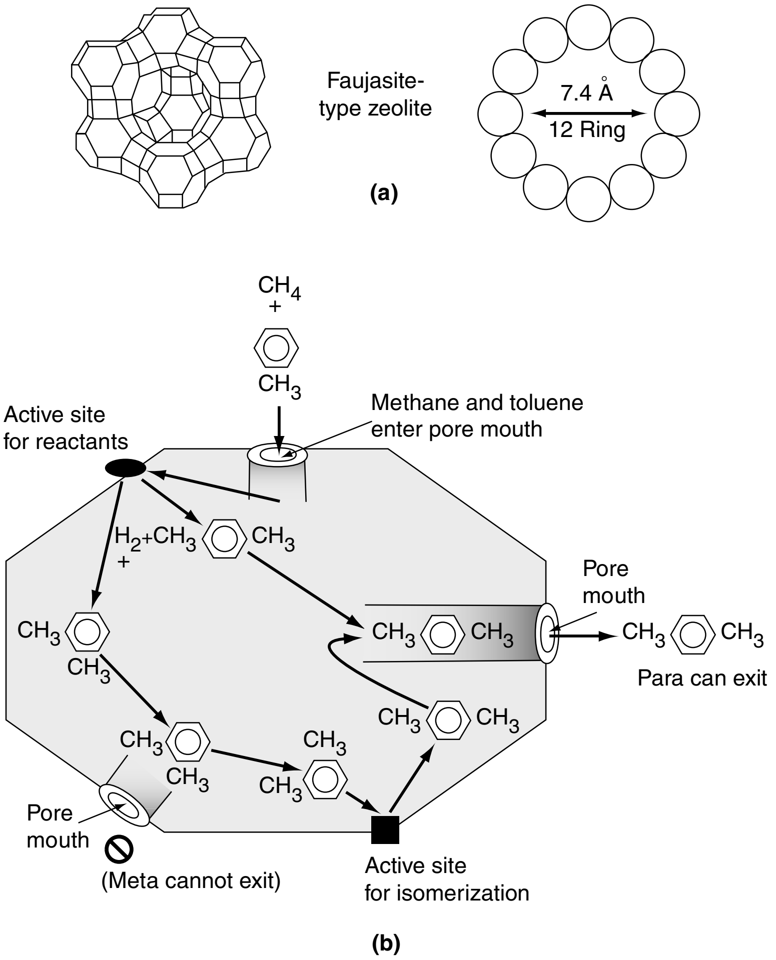

Figure 10-2 (a) Framework structures and (b) pore cross sections of two types of zeolites. (a) Faujasite-type zeolite has a three-dimensional channel system with pores at least 7.4 Å in diameter. A pore is formed by 12 oxygen atoms in a ring. (b) Schematic of reaction CH_4 and $C_6H_5CH_3$. (Note that the size of the pore mouth and the interior of the zeolite are not to scale.) [(a) from N. Y. Chen and T. F. Degnan, *Chem. Eng. Prog.*, *84*(2), 33 (1988). Reproduced by permission of the American Institute of Chemical Engineers. Copyright © 1988 AIChE. All rights reserved.]

para-xylene can exit through the pore mouth, as meta- and ortho- xylene with their methyl group on the side cannot fit through the pore mouth. There are interior sites that can isomerize ortho-xylene and meta-xylene to para-xylene. Hence, we have a very high selectivity to form para-xylene.

In some cases a catalyst consists of minute particles of an active material dispersed over a less-active substance called a *support*. The active material is frequently a pure metal or metal alloy. Such catalysts are called *supported catalysts*, as distinguished from *unsupported catalysts*. Catalysts can also have small amounts of active ingredients added called *promoters*, which increase their activity. Examples of supported catalysts are the packed-bed catalytic converter in an automobile, the platinum-on-alumina catalyst used in petroleum reforming, and the vanadium pentoxide on silica used to oxidize sulfur dioxide in manufacturing sulfuric acid. On the other hand, platinum gauze for ammonia oxidation, promoted iron for ammonia synthesis, and the silica–alumina dehydrogenation catalyst used in butadiene manufacture typify unsupported catalysts.

10.1.3 Catalytic Gas-Solid Interactions

For the moment, let us focus our attention on gas-phase reactions catalyzed by solid surfaces. For a catalytic reaction to occur, at least one and frequently all of the reactants must become attached to the surface. This attachment is known as *adsorption* and takes place by two different processes: physical adsorption and chemisorption. *Physical adsorption* is similar to condensation. The process is exothermic, and the heat of adsorption is relatively small, being on the order of 1 to 15 kcal/mol. The forces of attraction between the gas molecules and the solid surface are weak. These van der Waals forces consist of interaction between permanent dipoles, between a permanent dipole and an induced dipole, and/or between neutral atoms and molecules. The amount of gas physically adsorbed decreases rapidly with increasing temperature, and above its critical temperature only very small amounts of a substance are physically adsorbed.

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. As a result, the electronic structure of the chemisorbed molecule is perturbed significantly, causing it to be extremely reactive. Interaction with the catalyst causes bonds of the adsorbed reactant to be stretched, making them easier to break.

Figure 10-3 shows the bonding from the adsorption of ethylene on a platinum surface to form chemisorbed ethylidyne. Like physical adsorption, chemisorption is an exothermic process, but the heats of adsorption are

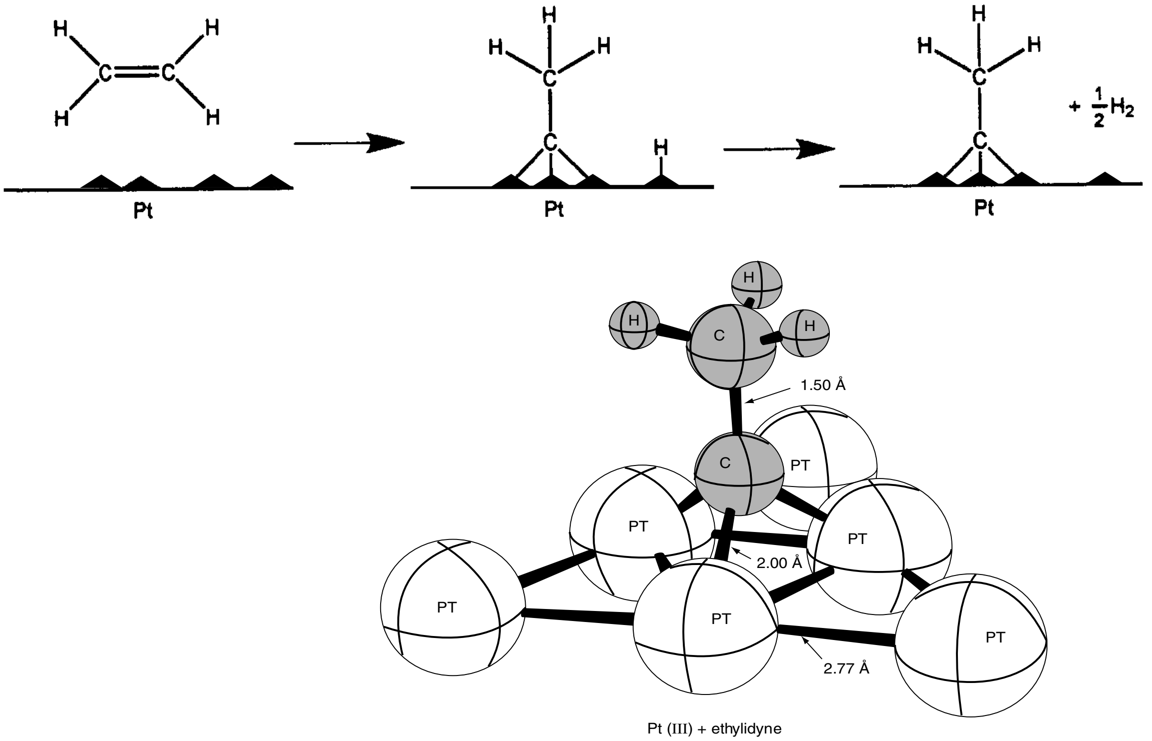

Figure 10-3 Ethylidyne chemisorbed on platinum. (Adapted from G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*. © 1994 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.)

generally of the same magnitude as the heat of a chemical reaction (i.e., 40 to 400 kJ/mol). If a catalytic reaction involves chemisorption, it must be carried out within the temperature range where chemisorption of the reactants is appreciable.

Chemisorption on active sites is what catalyzes the reaction.

In a landmark contribution to catalytic theory, Taylor suggested that a reaction is not catalyzed over the entire solid surface but only at certain *active sites* or *centers*.[4] 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. The active sites can also be thought of as places where highly reactive intermediates (i.e., chemisorbed species) are stabilized long enough to react. This stabilization of a reactive intermediate is key in the design of any catalyst. Consequently, 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* (*TOF*), *f*. 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 TOFs for a number of reactions are shown in *Professional Reference Shelf R10.1*. The *dispersion, D*, of the catalyst is the fraction of the metal atoms deposited on a catalyst that are *on* the surface.

10.1.4 Classification of Catalysts

One common way to classify catalysts is in terms of the type of reaction they catalyze.

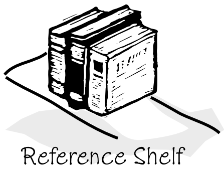

Table 10-1 gives a list of representative reactions and their corresponding catalysts. Further discussion of each of these reaction classes and the materials that catalyze them can be found on the CRE Web site's *Professional Reference Shelf R10.1*.

TABLE 10-1 TYPES OF REACTIONS AND REPRESENTATIVE CATALYSTS

Reaction	*Catalysts*
1. Halogenation–dehalogenation	$CuCl_2$, AgCl, Pd
2. Hydration–dehydration	Al_2O_3, MgO
3. Alkylation–dealkylation	$AlCl_3$, Pd, Zeolites
4. Hydrogenation–dehydrogenation	Co, Pt, Cr_2O_3, Ni
5. Oxidation	Cu, Ag, Ni, V_2O_5
6. Isomerization	$AlCl_3$, Pt/Al_2O_3, Zeolites

If, for example, we were to form styrene from an equimolar mixture of ethylene and benzene, we could first carry out an alkylation reaction to form

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[4] H. S. Taylor, *Proc. R. Soc. London*, *A108*, 105 (1928).

ethyl benzene, which is then dehydrogenated to form styrene. We need both an alkylation catalyst and a dehydrogenation catalyst:

$$C_2H_4 + C_6H_6 \xrightarrow[\text{trace HCl}]{\text{AlCl}_3} C_6H_5C_2H_5 \xrightarrow{\text{Ni}} C_6H_5CH{=}CH_2 + H_2$$

10.2 Steps in a Catalytic Reaction

A photograph of different types and sizes of catalysts is shown in Figure 10-4a. A schematic diagram of a tubular reactor packed with catalytic pellets is shown in Figure 10-4b. The overall process by which heterogeneous catalytic reactions proceed can be broken down into the sequence of individual steps shown in Table 10-2 and pictured in Figure 10-5 for an isomerization reaction.

Figure 10-4a Catalyst particles of different shapes (spheres, cylinders) and sizes (0.1 cm to 1 cm). (Photo courtesy of the Engelhard Corporation.)

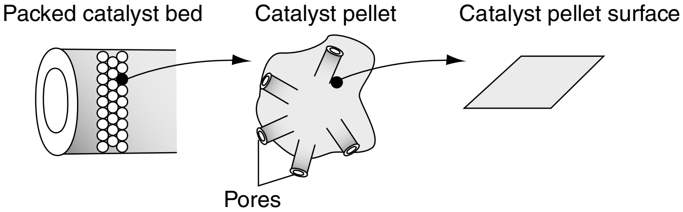

Figure 10-4b Catalytic packed-bed reactor—schematic.

Each step in Table 10-2 is shown schematically in Figure 10-5.

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

The overall rate of reaction is limited by the rate of the slowest step in the sequence. When the diffusion steps (1, 2, 6, and 7 in Table 10-2) are very fast compared with the surface reaction-rate 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 the reaction rate. In systems where diffusion from the bulk gas or liquid to the external catalyst surface or to the mouths of catalyst pores affects the rate, i.e., steps 1 and 7, changing the flow conditions past the catalyst should change the overall reaction rate (see Chapter 14). Once inside the porous catalysts, on the other hand, diffusion within the catalyst pores, i.e., steps 2 and 6, may limit the rate of reaction and, as a result, the overall rate will be unaffected by external flow conditions even though diffusion affects the overall reaction rate (see Chapter 15).

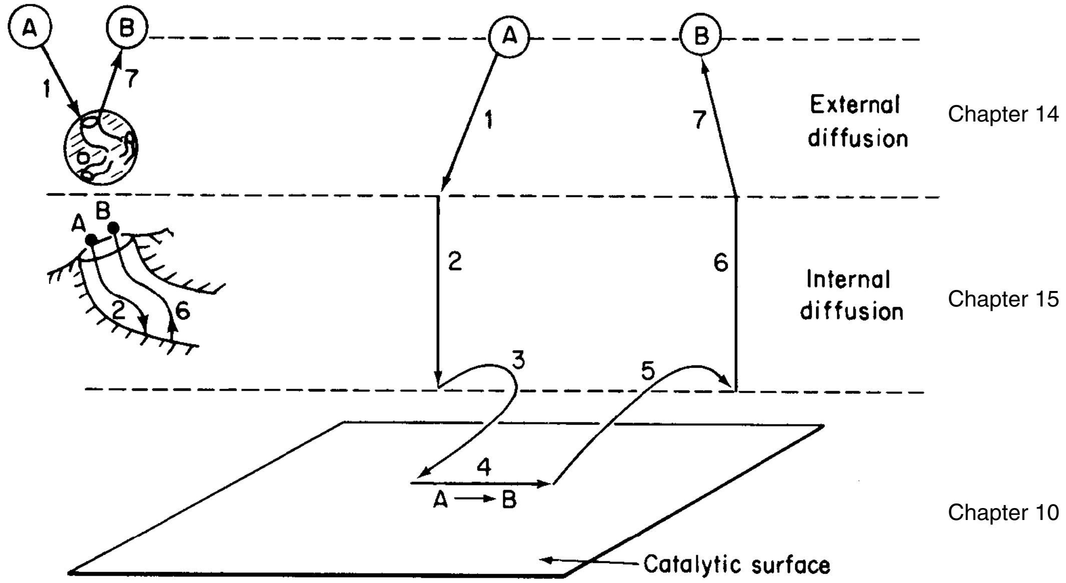

Figure 10-5 Steps in a heterogeneous catalytic reaction.

TABLE 10-2 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 catalyst surface
4. Reaction on the surface of the catalyst (e.g., $A \longrightarrow B$)
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

There are many variations of the situation described in Table 10-2. 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 may have only one of them adsorbed.

In this chapter we focus on:
3. Adsorption
4. Surface reaction
5. Desorption

With this introduction, we are ready to treat individually the steps involved in catalytic reactions. In this chapter, only steps 3, 4, and 5—i.e., adsorption, surface reaction, and desorption—are considered as we assume that the diffusion steps (1, 2, 6, and 7) are very fast so that the overall reaction rate is not affected by mass transfer in any fashion. Further treatment of the effects involving diffusion limitations is provided in Chapters 14 and 15.

Where Are We Heading?[†] As we saw in Chapter 7, one of the tasks of a chemical reaction engineer is to analyze rate data and to develop a rate law that can be used in reactor design. Rate laws in heterogeneous catalysis seldom

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[†] "If you don't know where you are going, you'll probably wind up someplace else." Yogi Berra

follow power-law models and hence are inherently more difficult to formulate from the data. To develop an in-depth understanding and insight as to how the rate laws are formed from heterogeneous catalytic data, we are going to proceed in somewhat of a reverse manner than what is normally done in industry when one is asked to develop a rate law. That is, we will postulate catalytic mechanisms and *then* derive rate laws for the various mechanisms. The mechanism will typically have an adsorption step, a surface reaction step, and a desorption step, one of which is usually rate-limiting. Suggesting mechanisms and rate-limiting steps is not the first thing we normally do when presented with data. However, by deriving equations for different mechanisms, we will observe the various forms of the rate law one can have in heterogeneous catalysis. Knowing the different forms that catalytic rate equations can take, it will be easier to view the trends in the data and deduce the appropriate rate law. This deduction is usually what is done first in industry before a mechanism is proposed. Knowing the form of the rate law, one can then numerically evaluate the rate-law parameters and postulate a reaction mechanism and rate-limiting step that are consistent with the rate data. Finally, we use the rate law to design catalytic reactors. This procedure is shown in Figure 10-6. The dashed lines represent feedback to obtain new data in specific regions (e.g., concentrations, temperature) to evaluate the rate-law parameters more precisely or to differentiate between reaction mechanisms.

An algorithm

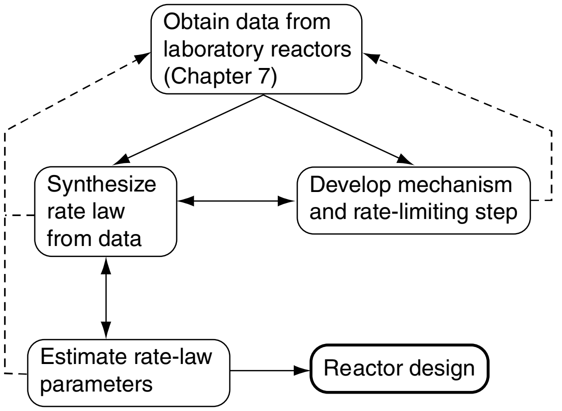

Figure 10-6 Collecting information for catalytic reactor design.

We will discuss each of the steps shown in Figure 10-5 and Table 10-2. As mentioned earlier, this chapter focuses on Steps 3, 4, and 5 (the adsorption, surface reaction and desorption steps) by assuming that Steps 1, 2, 6, and 7 are very rapid. Consequently, to understand when this assumption is valid, we shall give a quick overview of Steps 1, 2, 6, and 7. These steps involve diffusion of the reactants to and within the catalyst pellet. While these diffusion steps are covered in detail in Chapters 14 and 15, it is worthwhile to give a brief description of these two mass-transfer steps to better understand the entire sequence of steps. If you have had the core course in *Mass Transfer* or *Transport Phenomena* you can skip Sections 10.2.1 and 10.2.2, and go directly to Section 10.2.3.

Chance Card:
Do not pass go
proceed directly to
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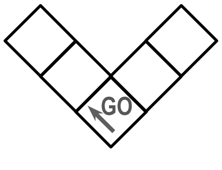


10.2.1 Step 1 Overview: Diffusion from the Bulk to the External Surface of the Catalyst

External and internal mass transfer in catalysis are covered in detail in Chapters 14 and 15.

For the moment let's assume that the transport of A from the bulk fluid to the external surface of the catalyst is the slowest step in the sequence. We lump all the resistance to transfer from the bulk fluid to the surface in the mass-transfer boundary layer surrounding the pellet. In this step the reactant A, which is at a bulk concentration C_{Ab} must travel (diffuse) through the boundary layer of thickness δ to the external surface of the pellet where the concentration is C_{As}, as shown in Figure 10-7. The rate of transfer (and hence rate of reaction, $-r'_A$) for this slowest step is

$$\text{Rate} = k_C\,(C_{Ab} - C_{As})$$

where the mass-transfer coefficient, k_C, is a function of the hydrodynamic conditions, namely the fluid velocity, U, and the particle diameter, D_p.

External mass transfer

"The thick and thin of it."

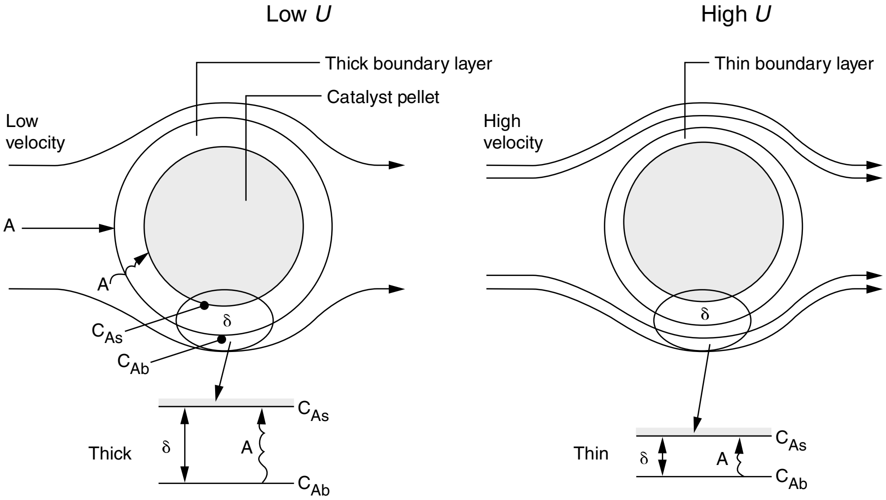


Figure 10-7 Diffusion through the external boundary layer (also see Figure 14-3).

As we see (Chapter 14), the mass-transfer coefficient is inversely proportional to the boundary layer thickness, δ, and directly proportional to the diffusion coefficient (i.e., the diffusivity D_{AB}).

$$k_C = \frac{D_{AB}}{\delta}$$

At low velocities of fluid flow over the pellet, the boundary layer across which A and B must diffuse is thick, and it takes a long time for A to travel to the surface, resulting in a small mass-transfer coefficient k_C. As a result, mass transfer across the boundary layer is slow and limits the rate of the overall reaction. As the velocity over the pellet is increased, the boundary layer becomes thinner and the mass-transfer rate is increased. At very high velocities, the boundary layer thickness, δ, is so small it no longer offers any resistance to the diffusion across the boundary layer. As a result, external mass transfer no longer limits the rate of reaction. This external resistance also decreases as the particle size is decreased. As the fluid velocity increases and/or the particle diameter decreases, the mass-transfer coefficient increases until a plateau is reached, as shown in Figure 10-8. On this plateau, $C_{Ab} \approx C_{As}$, and one of the other steps in the sequence, i.e., Steps 2 through 6, is the slowest step and limits the overall reaction rate. Further details on external mass transfer are discussed in Chapter 14.

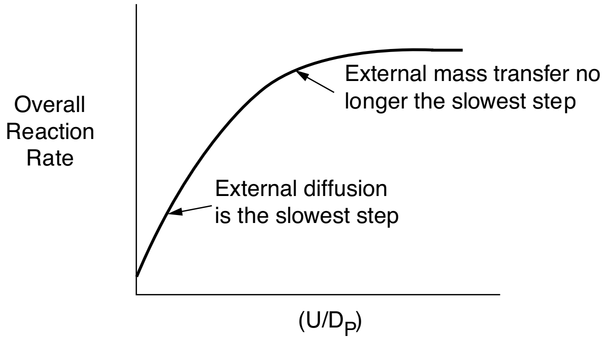


Figure 10-8 Effect of particle size and fluid velocity on the overall reaction rate.

10.2.2 Step 2 Overview: Internal Diffusion

Now consider that we are operating at a fluid velocity where external diffusion is no longer the rate-limiting step and that internal diffusion is the slowest step. In Step 2 the reactant A diffuses from the external pellet surface at a concentration C_{As} into the pellet interior, where the concentration is C_A. As A diffuses into the interior of the pellet, it reacts with catalyst deposited on the sides of the catalyst pellet's pore walls.

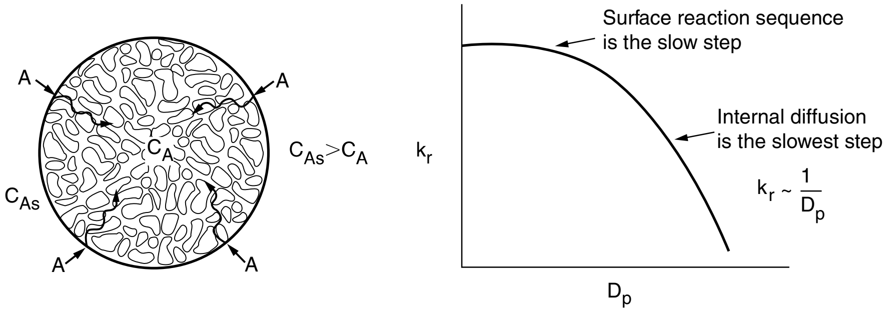
For large pellets, it takes a long time for the reactant A to diffuse into the interior, compared to the time that it takes for the reaction to occur on the interior pore surface. Under these circumstances, the reactant is only consumed near the exterior surface of the pellet and the catalyst near the center of the pellet is wasted catalyst. On the other hand, for very small pellets it takes very little time to diffuse into and out of the pellet interior and, as a result, internal diffusion no longer limits the rate of reaction. When internal mass transfer no longer limits the rate of reaction, the rate law can be expressed as

$$\text{Rate} = k_r\, C_{As}$$

where C_{As} is the concentration at the external pellet surface and k_r is an overall rate constant, which is a function of particle size. The overall rate constant, k_r, increases as the pellet diameter decreases. In Chapter 15, we show that Figure 15-5 can be combined with Equation (15-34) to arrive at the plot of k_r as a function of D_P, shown in Figure 10-9(b).

We see in Figure 10-9 that at small particle sizes, internal diffusion is no longer the slow step and that the surface reaction sequence of adsorption, surface reaction, and desorption (Steps 3, 4, and 5 in Figure 10-5) limit the overall rate

Internal mass transfer



(a) (b)

Figure 10-9 Effect of particle size on the overall reaction-rate constant. (a) Branching of a single pore with deposited metal; (b) decrease in rate constant with increasing particle diameter. (See the CRE Web site, Chapter 12.)

of reaction. Consider now one more important point about internal diffusion and surface reaction. These steps (2 through 6) are **not at all** affected by flow conditions external to the pellet.

In the material that follows, we are going to choose our pellet size and external fluid velocity such that neither external diffusion nor internal diffusion is limiting as discussed in Chapters 14 and 15. Instead, we assume that either Step 3 (adsorption), Step 4 (surface reaction), or Step 5 (desorption), or a combination of these steps, limits the overall rate of reaction.

10.2.3 Adsorption Isotherms

Because 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 species A will be chemically adsorbed on the site S. Species 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

$$A + S \rightleftarrows A \cdot S$$

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_t (mol/g-cat). The molar concentration of vacant sites, C_v (mol/g-cat), 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, C_t, remains constant. Some further definitions include

P_i = partial pressure of species i in the gas phase, (atm or kPa)
$C_{i \cdot S}$ = surface concentration of sites occupied by species i, (mol/g-cat)

A conceptual model depicting species A and B adsorbed on two different sites is shown in Figure 10-10.

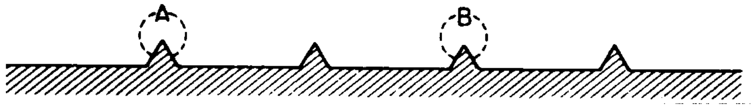


Figure 10-10 Vacant and occupied sites.

For the system shown in Figure 10-10, the total concentration of sites is

Site balance

$$C_t = C_v + C_{A\cdot S} + C_{B\cdot S} \tag{10-1}$$

This equation is referred to as a *site balance*. A typical value for the total concentration of sites could be the order of 10^{22} sites/g-cat.

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 at a given temperature.

Postulate models; then see which one(s) fit(s) the data.

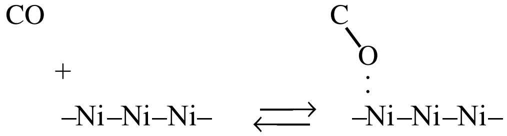
First, an adsorption mechanism is proposed, and then the isotherm (see Figure 10-11, page 413) obtained from the mechanism is compared with the experimental data. If the isotherm predicted by the model agrees with the experimental data, the model may reasonably describe what is occurring physically in the real system. If the predicted curve does not agree with the experimental data, the model fails to match the physical situation in at least one important characteristic and perhaps more.

We will consider two types of adsorption: molecular adsorption and dissociative adsorption. To illustrate the difference between molecular adsorption and dissociative adsorption, we will postulate two models for the adsorption of carbon monoxide on metal surfaces. In the molecular adsorption model, CO is adsorbed as molecules, CO,

$$CO + S \rightleftarrows CO\cdot S$$

as is the case on nickel

Two models:
1. Adsorption as CO
2. Adsorption as C and O

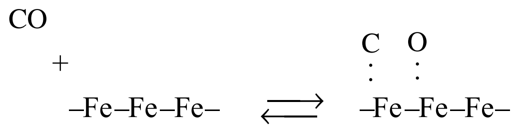


$$\begin{matrix} CO \\ + \\ \text{–Ni–Ni–Ni–} \end{matrix} \rightleftarrows \begin{matrix} C \\ \diagdown O \\ \vdots \\ \text{–Ni–Ni–Ni–} \end{matrix}$$

In the dissociative adsorption model, carbon monoxide is adsorbed as oxygen and carbon atoms instead of molecular CO

$$CO + 2S \rightleftarrows C\cdot S + O\cdot S$$

as is the case on iron[5]



$$\begin{matrix} CO \\ + \\ \text{–Fe–Fe–Fe–} \end{matrix} \rightleftarrows \begin{matrix} C \quad O \\ \vdots \quad \vdots \\ \text{–Fe–Fe–Fe–} \end{matrix}$$

---

[5] R. I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces* (New York: Wiley, 1996).

The former is called *molecular* or *nondissociated adsorption* (e.g., CO) and the latter is called *dissociative adsorption* (e.g., C and O). Whether a molecule adsorbs nondissociatively or dissociatively depends on the surface.

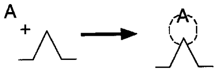
The adsorption of carbon monoxide molecules will be considered first. Because the carbon monoxide does not react further after being adsorbed, we need only to consider the adsorption process:

Molecular Adsorption

$$\text{CO} + \text{S} \rightleftarrows \text{CO}\cdot\text{S} \tag{10-2}$$

In obtaining a rate law for the rate of adsorption, the reaction in Equation (10-2) can be treated as an *elementary reaction.* The rate of attachment of the carbon monoxide molecules to the active site on the surface is proportional to the number of collisions that these molecules make with a surface active site 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 carbon monoxide partial pressure, P_{CO}. Because carbon monoxide molecules adsorb only on vacant sites and not on sites already occupied by other carbon monoxide 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 carbon monoxide molecules to the surface is directly proportional to the product of the partial pressure of CO and the concentration of vacant sites; that is,

$\boxed{P_{\text{CO}} = C_{\text{CO}}RT}$

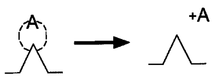


$\text{A} + \text{S} \longrightarrow \text{A}\cdot\text{S}$

$$\text{Rate of attachment} = k_{\text{A}}P_{\text{CO}}C_v$$

The rate of detachment of molecules from the surface can be a first-order process; that is, the detachment of carbon monoxide molecules from the surface is usually directly proportional to the concentration of sites occupied by the adsorbed molecules (e.g., $C_{\text{CO}\cdot\text{S}}$):

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



$\text{A}\cdot\text{S} \longrightarrow \text{A} + \text{S}$

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 $k_{-\text{A}}$ are the constants of proportionality for the attachment and detachment processes, then

$$r_{\text{AD}} = k_{\text{A}}P_{\text{CO}}C_v - k_{-\text{A}}C_{\text{CO}\cdot\text{S}} \tag{10-3}$$

The ratio $K_{\text{A}} = k_{\text{A}}/k_{-\text{A}}$ is the *adsorption equilibrium constant.* Using K_{A} to rearrange Equation (10-3) gives

Adsorption

$\text{A} + \text{S} \rightleftarrows \text{A}\cdot\text{S}$

$r_{\text{AD}} = k_{\text{A}}\left(P_{\text{A}}C_v - \frac{C_{\text{A}\cdot\text{S}}}{K_{\text{A}}}\right)$

$$\boxed{r_{\text{AD}} = k_{\text{A}}\left(P_{\text{CO}}C_v - \frac{C_{\text{CO}\cdot\text{S}}}{K_{\text{A}}}\right)} \tag{10-4}$$

The adsorption rate constant, k_{A}, for molecular adsorption is virtually independent of temperature, while the desorption constant, $k_{-\text{A}}$, increases exponentially with increasing temperature. Consequently, *the equilibrium adsorption constant K_{A} decreases exponentially with increasing temperature.*

Because carbon monoxide is the only material adsorbed on the catalyst, the site balance gives

$$C_t = C_v + C_{\text{CO}\cdot\text{S}} \tag{10-5}$$

$-r'_A = r_{\mathrm{AD}} = \left(\frac{\mathrm{mol}}{\mathrm{g\text{-}cat}\cdot \mathrm{s}}\right)$

$k_{\mathrm{A}} = \left(\frac{1}{\mathrm{atm}\cdot \mathrm{s}}\right)$

$P_{\mathrm{A}} = (\mathrm{atm})$

$C_v = \left(\frac{\mathrm{mol}}{\mathrm{g\text{-}cat}}\right)$

$K_{\mathrm{A}} = \left(\frac{1}{\mathrm{atm}}\right)$

$C_{\mathrm{A}\cdot\mathrm{S}} = \left(\frac{\mathrm{mol}}{\mathrm{g\text{-}cat}}\right)$

At equilibrium, the net rate of adsorption equals zero, i.e., $r_{\mathrm{AD}} \equiv 0$. Setting the left-hand side of Equation (10-4) equal to zero and solving for the concentration of CO adsorbed on the surface, we get

$$C_{\mathrm{CO}\cdot\mathrm{S}} = K_{\mathrm{A}} C_v P_{\mathrm{CO}} \tag{10-6}$$

Using Equation (10-5) to give C_v in terms of $C_{\mathrm{CO}\cdot\mathrm{S}}$ and the total number of sites C_t, we can solve for the equilibrium value of $C_{\mathrm{CO}\cdot\mathrm{S}}$ in terms of constants and the pressure of carbon monoxide

$$C_{\mathrm{CO}\cdot\mathrm{S}} = K_{\mathrm{A}} C_v P_{\mathrm{CO}} = K_{\mathrm{A}} P_{\mathrm{CO}}(C_t - C_{\mathrm{CO}\cdot\mathrm{S}})$$

Rearranging gives us

$$\boxed{C_{\mathrm{CO}\cdot\mathrm{S}} = \frac{K_{\mathrm{A}} P_{\mathrm{CO}} C_t}{1 + K_{\mathrm{A}} P_{\mathrm{CO}}}} \tag{10-7}$$

This equation thus gives the equilibrium concentration of carbon monoxide adsorbed on the surface, $C_{\mathrm{CO}\cdot\mathrm{S}}$, as a function of the partial pressure of carbon monoxide, and is an equation for the adsorption isotherm. This particular type of isotherm equation is called a *Langmuir isotherm.*[6] **Figure 10-11(a)** shows the Langmuir isotherm for the amount of CO adsorbed per unit mass of catalyst as a function of the partial pressure of CO. For the case of dissociative adsorption, Equation (10-11), **Figure 10-11(b)**, shows the concentration of the atoms C and O adsorbed per unit mass of catalyst.

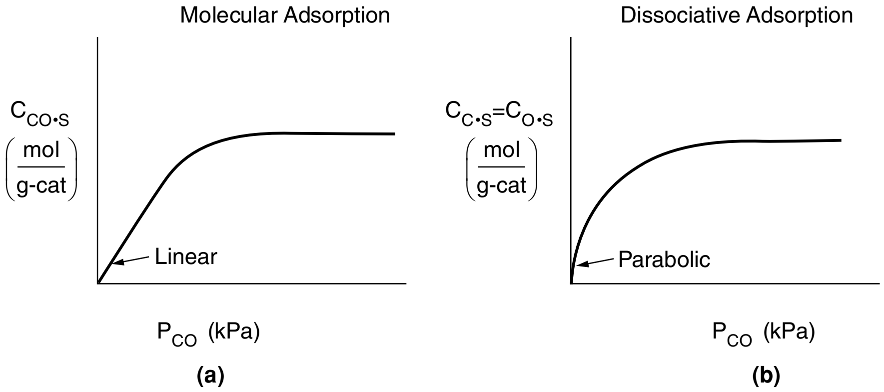


Figure 10-11 Langmuir isotherms for **(a)** molecular adsorption **(b)** dissociative adsorption of CO.

One method of checking whether a model (e.g., molecular adsorption versus dissociative adsorption) predicts the behavior of the experimental data is to linearize the model's equation and then plot the indicated variables against one another. For example, the molecular adsorption isotherm, Equation (10-7), may be arranged in the form

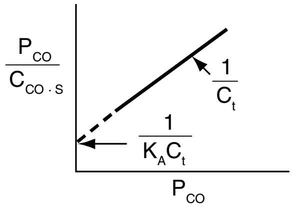
$$\frac{P_{\mathrm{CO}}}{C_{\mathrm{CO}\cdot\mathrm{S}}} = \frac{1}{K_{\mathrm{A}} C_t} + \frac{P_{\mathrm{CO}}}{C_t} \tag{10-8}$$

---

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

and the linearity of a plot of $P_{CO}/C_{CO\cdot S}$ as a function of P_{CO} will determine if the data conform to molecular adsorption, i.e., a Langmuir single-site isotherm.

Molecular Adsorption



Next, we derive the isotherm for carbon monoxide disassociating into separate atoms as it adsorbs on the surface, i.e.,

Dissociative adsorption

$$\mathrm{CO} + 2\mathrm{S} \rightleftarrows \mathrm{C\cdot S} + \mathrm{O\cdot S}$$

When the carbon monoxide molecule dissociates upon adsorption, it is referred to as the *dissociative adsorption* of carbon monoxide. As in the case of molecular adsorption, the rate of adsorption is proportional to the pressure of carbon monoxide in the system because this rate is governed by 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 carbon monoxide partial pressure and the square of the vacant-site concentration, $P_{CO}C_v^2$.

For desorption to occur, two occupied sites must be adjacent, meaning that the rate of desorption is proportional to the product of the occupied-site concentration, (C·S) × (O·S). The net rate of adsorption can then be expressed as

$$r_{AD} = k_A P_{CO} C_v^2 - k_{-A} C_{O\cdot S} C_{C\cdot S} \tag{10-9}$$

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

Rate of dissociative adsorption

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

where

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

For dissociative adsorption, both k_A and k_{-A} increase exponentially with increasing temperature, while the *adsorption equilibrium constant* K_A decreases with increasing temperature.

At equilibrium, $r_{AD} \equiv 0$, and

$$k_A P_{CO} C_v^2 = k_{-A} C_{C\cdot S} C_{O\cdot S}$$

For $C_{C\cdot S} = C_{O\cdot S}$

$$(K_A P_{CO})^{1/2} C_v = C_{O\cdot S} \tag{10-10}$$

Substituting for $C_{C\cdot S}$ and $C_{O\cdot S}$ in a site balance equation (10-1), Site balance:

$$C_t = C_v + C_{\mathrm{O\cdot S}} + C_{\mathrm{C\cdot S}}$$

$$= C_v + (K_{\mathrm{CO}}P_{\mathrm{CO}})^{1/2}C_v + (K_{\mathrm{CO}}P_{\mathrm{CO}})^{1/2}C_v = C_v(1 + 2(K_{\mathrm{CO}}P_{\mathrm{CO}})^{1/2})$$

Solving for C_v

$$C_v = C_t \,/ (1 + 2(K_{\mathrm{CO}}P_{\mathrm{CO}})^{1/2})$$

This value may be substituted into Equation (10-10) to give an expression that can be solved for the equilibrium value of $C_{\mathrm{O\cdot S}}$. The resulting equation for the isotherm shown in Figure 10-11(**b**) is

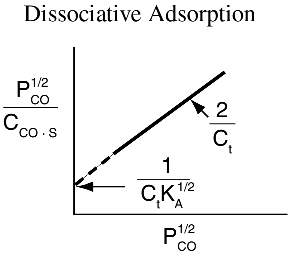
Langmuir isotherm for carbon monoxide dissociative adsorption as atomic carbon and oxygen

$$\boxed{C_{\mathrm{O\cdot S}} = \frac{(K_{\mathrm{A}}P_{\mathrm{CO}})^{1/2}C_t}{1 + 2(K_{\mathrm{A}}P_{\mathrm{CO}})^{1/2}}} \tag{10-11}$$

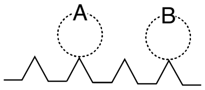
Taking the inverse of both sides of the equation, then multiplying through by $(P_{\mathrm{CO}})^{1/2}$, yields

$$\frac{(P_{\mathrm{CO}})^{1/2}}{C_{\mathrm{O\cdot S}}} = \frac{1}{C_t(K_{\mathrm{A}})^{1/2}} + \frac{2(P_{\mathrm{CO}})^{1/2}}{C_t} \tag{10-12}$$

If dissociative adsorption is the correct model, a plot of $(P_{\mathrm{CO}}^{1/2}/C_{\mathrm{O\cdot S}})$ versus $P_{\mathrm{CO}}^{1/2}$ should be linear with slope $(2/C_t)$.



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 another adsorbate B is given by the relationship



$C_t = C_v + C_{\mathrm{A\cdot S}} + C_{\mathrm{B\cdot S}}$

$$C_{\mathrm{A\cdot S}} = \frac{K_{\mathrm{A}}P_{\mathrm{A}}C_t}{1 + K_{\mathrm{A}}P_{\mathrm{A}} + K_{\mathrm{B}}P_{\mathrm{B}}} \tag{10-13}$$

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 relatively easy.

In obtaining the Langmuir isotherm equations, 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 active site. Isotherms different from the Langmuir isotherm, such as the Freundlich isotherm, may be derived based on various assumptions concerning the adsorption system, including different types of nonuniform surfaces.

Note assumptions in the model and check their validity.

10.2.4 Surface Reaction

The rate of adsorption of species A onto a solid surface

$$A + S \rightleftarrows A \cdot S$$

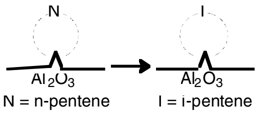
is given by

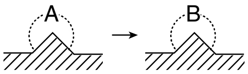
$$\boxed{r_{AD} = k_A \left(P_A C_v - \frac{C_{A \cdot S}}{K_A} \right)} \qquad (10\text{-}14)$$

Surface reaction models

After a reactant has been adsorbed onto the surface, i.e., A · S, it is capable of reacting in a number of ways to form the reaction product. Three of these ways are:

1. ***Single site.*** 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, such as





Single site

The pentane isomerization can be written in generic form as

$$A \cdot S \rightleftarrows B \cdot S$$

Each step in the reaction mechanism is elementary, so the surface reaction rate law is

Single Site

$$k_S = \left(\frac{1}{s} \right)$$

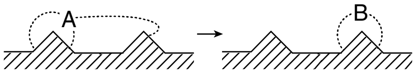
$$\boxed{r_S = k_S C_{A \cdot S} - k_{-S} C_{B \cdot S} = k_S \left(C_{A \cdot S} - \frac{C_{B \cdot S}}{K_S} \right)} \qquad (10\text{-}15)$$

K_s = (dimensionless)

where K_S is the surface-reaction equilibrium constant $K_S = k_S / k_{-S}$

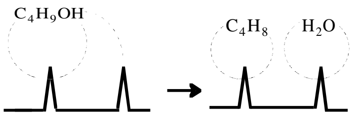
2. ***Dual site.*** The surface reaction may be a dual-site mechanism in which the adsorbed reactant interacts with another site (either unoccupied or occupied) to form the product.

First type of dual-site mechanism



Dual site

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, or as in the case of the dehydration of butanol, the products may adsorb on two adjacent sites.



$$C_4H_9OH\cdot S + S \rightarrow C_4H_g\cdot S + H_2O\cdot S$$

$$r_S = k_S\left[(C_{C_4H_9OH\cdot S})(C_\upsilon) - \frac{(C_{C_4H_g\cdot S})(C_{H_2O\cdot S})}{K_S}\right]$$

For the generic reaction

$$\mathrm{A\cdot S + S} \rightleftarrows \mathrm{B\cdot S + S}$$

Dual Site

$$r_S = \left(\frac{\text{mol}}{\text{g-cat}\cdot\text{s}}\right)$$

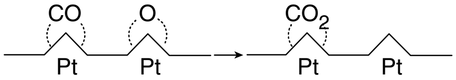
$$k_S = \left(\frac{\text{g-cat}}{\text{mol}\cdot\text{s}}\right)$$

K_S = (dimensionless)

the corresponding surface-reaction rate law is

$$\boxed{r_S = k_S\left(C_{A\cdot S}C_v - \frac{C_{B\cdot S}C_v}{K_S}\right)} \tag{10-16}$$

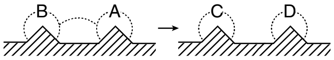
A second dual-site mechanism is the reaction between two adsorbed species, such as the reaction of CO with O.



$$CO\cdot S + O\cdot S \rightleftarrows CO_2\cdot S + S$$

$$r_S = k_S\left[(C_{CO\cdot S})(C_{O\cdot S}) - \frac{(C_{CO_2\cdot S})(C_\upsilon)}{K_S}\right]$$

For the generic reaction



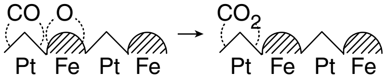
Dual site

$$\mathrm{A\cdot S + B\cdot S} \rightleftarrows \mathrm{C\cdot S + D\cdot S}$$

the corresponding surface-reaction rate law is

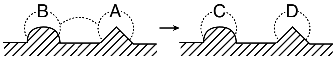
$$\boxed{r_S = k_S\left(C_{A\cdot S}C_{B\cdot S} - \frac{C_{C\cdot S}C_{D\cdot S}}{K_S}\right)} \tag{10-17}$$

A third dual-site mechanism is the reaction of two species adsorbed on different types of sites S and S′, such as the reaction of CO with O.



$$CO\cdot S + O\cdot S' \rightarrow CO_2\cdot S + S'$$

For the generic reaction



Dual site

$$A\cdot S + B\cdot S' \rightleftarrows C\cdot S' + D\cdot S$$

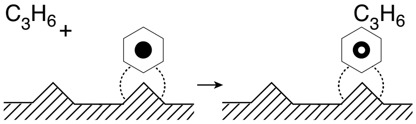
the corresponding surface-reaction rate law is

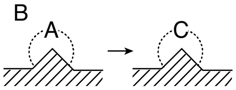
$$\boxed{r_S = k_S\left(C_{A\cdot S}C_{B\cdot S'} - \frac{C_{C\cdot S'}C_{D\cdot S}}{K_S}\right)} \tag{10-18}$$

Langmuir–Hinshelwood kinetics

Reactions involving either single- or dual-site mechanisms, which were described earlier, are sometimes referred to as following *Langmuir–Hinshelwood kinetics*.

3. ***Eley–Rideal.*** A third mechanism is the reaction between an adsorbed molecule and a molecule in the gas phase, such as the reaction of propylene and benzene (cf. the reverse reaction in Figure 10-13)





Eley–Rideal mechanism

For the generic reaction

$$A\cdot S + B(g) \rightleftarrows C\cdot S$$

the corresponding surface-reaction rate law is

$$k_s = \left(\frac{1}{\text{atm}\cdot\text{s}}\right)$$

$$K_S = \left(\frac{1}{\text{atm}}\right)$$

$$\boxed{r_S = k_S\left(C_{A\cdot S}P_B - \frac{C_{C\cdot S}}{K_S}\right)} \tag{10-19}$$

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

10.2.5 Desorption

K_{DC} = (atm)

$$k_D = \left(\frac{1}{s}\right)$$

In each of the preceding cases, the products of the surface reaction adsorbed on the surface are subsequently desorbed into the gas phase. For the desorption of a species (e.g., C)

$$\text{C}\cdot\text{S} \rightleftarrows \text{C} + \text{S}$$

the rate of desorption of C is

$$\boxed{r_{DC} = k_D\left(C_{C\cdot S} - \frac{P_C C_v}{K_{DC}}\right)} \tag{10-20}$$

where K_{DC} is the desorption equilibrium constant with units of atm. Now let's look at the above adsorption from right to left. We note that the desorption step for C is just the reverse of the adsorption step. Consequently, the rate of desorption of C, r_{DC}, is just opposite in sign to the rate of adsorption of C, r_{ADC}

$$r_{DC} = -r_{ADC}$$

In addition, we see that the desorption equilibrium constant K_{DC} is just the reciprocal of the adsorption equilibrium constant for C, K_C

K_{DC} = (atm)

$$K_C = \left(\frac{1}{\text{atm}}\right)$$

$$K_{DC} = \frac{1}{K_C}$$

in which case the rate of desorption of C can be written

$$\boxed{r_{DC} = k_D(C_{C\cdot S} - K_C P_C C_v)} \tag{10-21}$$

In the material that follows, the form of the equation for the desorption step that we will use to develop our rate laws will be similar to Equation (10-21).

10.2.6 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

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

However, one particular step in the series is usually found to be *rate-limiting* or *rate-controlling*. That is, if we could make that particular step go faster, the entire reaction would proceed at an accelerated rate. Consider the analogy to the electrical circuit shown in Figure 10-12. A given concentration of reactants is analogous to a given driving force or electromotive force (EMF). The current I (with units of Coulombs/s) is analogous to the rate of reaction, $-r'_A$ (mol/s·g-cat), and a resistance R_i is associated with each step in the series. Because the resistances are in series, the total resistance R_{tot} is just the sum of the individual resistances, for adsorption (R_{AD}), surface reaction (R_S), and desorption (R_D). The current, I, for a given voltage, E, is

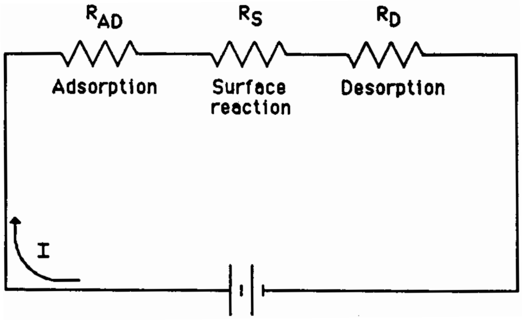


Figure 10-12 Electrical analog to heterogeneous reactions.

$$I = \frac{E}{R_{tot}} = \frac{E}{R_{AD}+R_S+R_D}$$

The concept of a rate-limiting step

Who is slowing us down?

Because 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 resistances (say, 0.1 Ω). Thus, if we could lower the largest resistance, the current I (i.e., $-r'_A$) , would be larger for a given voltage, 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 Hinshelwood based on Langmuir's principles for adsorption.[7] The Langmuir–Hinshelwood approach was popularized by Hougen and Watson and occasionally includes their names.[8] It consists of first assuming a sequence of steps in the reaction. In writing this sequence, one must choose among 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

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[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).

preceding section, assuming that 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 most questionable assumption in using this technique to obtain a rate law is the hypothesis that the activity of the surface is essentially uniform as far as the various steps in the reaction are concerned.

Industrial Example of Adsorption-Limited Reaction

An example of an adsorption-limited reaction is the synthesis of ammonia from hydrogen and nitrogen

$$3H_2 + N_2 \rightleftarrows 2NH_3$$

over an iron catalyst that proceeds by the following mechanism:[9]

Dissociative adsorption of N_2 is rate-limiting

$$\begin{array}{ll} H_2 + 2S \rightleftarrows 2H\cdot S \} & \text{Rapid} \\ N_2 + 2S \rightleftarrows 2N\cdot S \} & \text{Rate-limiting} \\ \left.\begin{array}{l} N\cdot S + H\cdot S \rightleftarrows HN\cdot S + S \\ NH\cdot S + H\cdot S \rightleftarrows H_2N\cdot S + S \\ H_2N\cdot S + H\cdot S \rightleftarrows NH_3\cdot S + S \\ NH_3\cdot S \rightleftarrows NH_3 + S \end{array}\right\} & \text{Rapid} \end{array}$$

The rate-limiting step is believed to be the adsorption of the N_2 molecule as an N atom.

Industrial Example of Surface-Limited Reaction

An example of a surface-limited reaction is the reaction of two noxious automobile exhaust products, CO and NO

$$CO + NO \longrightarrow CO_2 + \tfrac{1}{2}N_2$$

carried out *over a copper catalyst* to form environmentally acceptable products, N_2 and CO_2

Surface reaction is rate-limiting

$$\begin{array}{ll} \left.\begin{array}{l} CO + S \rightleftarrows CO\cdot S \\ NO + S \rightleftarrows NO\cdot S \end{array}\right\} & \text{Rapid} \\ NO\cdot S + CO\cdot S \rightleftarrows CO_2 + N\cdot S + S \} & \text{Rate-limiting} \\ \left.\begin{array}{l} N\cdot S + N\cdot S \rightleftarrows N_2\cdot S \\ N_2\cdot S \longrightarrow N_2 + S \end{array}\right\} & \text{Rapid} \end{array}$$

Analysis of the rate law suggests that CO_2 and N_2 are weakly adsorbed, i.e., have infinitesimally small adsorption constants (see Problem P10-9_B).

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[9] From the literature cited in G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (New York: Wiley, 1994), p. 482.

10.3 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

$$C_6H_5CH(CH_3)_2 \longrightarrow C_6H_6 + C_3H_6$$

A conceptual model depicting the sequence of steps in this platinum-catalyzed reaction is shown in Figure 10-13. Figure 10-13 is only a schematic representation of the adsorption of cumene; a more realistic model is the formation of a complex of the π orbitals of benzene with the catalytic surface, as shown in Figure 10-14.

- Adsorption
- Surface reaction
- Desorption

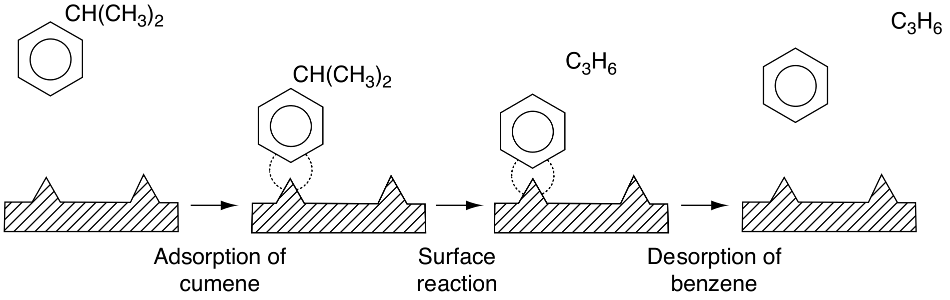


Figure 10-13 Sequence of steps in a reaction-limited catalytic reaction.

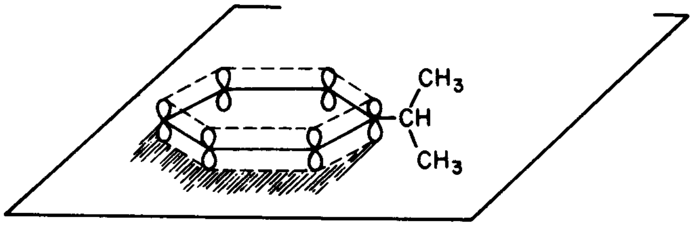


Figure 10-14 π-orbital complex on surface.

The nomenclature in Table 10-3 will be used to denote the various species in this reaction: C = cumene, B = benzene, and P = propylene. The reaction sequence for this decomposition is shown in Table 10-3.

Table 10-3 Steps in a Langmuir–Hinshelwood Kinetic Mechanism

These three steps represent the mechanism for cumene decomposition.

$C + S \underset{k_{-A}}{\overset{k_A}{\rightleftarrows}} C \cdot S$	Adsorption of cumene on the surface	(10-22)
$C \cdot S \underset{k_{-S}}{\overset{k_S}{\rightleftarrows}} B \cdot S + P$	Surface reaction to form adsorbed benzene and propylene in the gas phase	(10-23)
$B \cdot S \underset{k_{-D}}{\overset{k_D}{\rightleftarrows}} B + S$	Desorption of benzene from surface	(10-24)

Equations (10-22) through (10-24) represent the mechanism proposed for this reaction.

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

Ideal gas law $P_C = C_C RT$

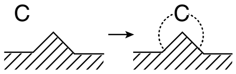
$$C_C \longrightarrow P_C$$

There is no theoretical reason for this replacement of the concentration, C_C, with the partial pressure, P_C; it is just the convention initiated in the 1930s and used ever since. Fortunately, P_C can be calculated easily and directly from C_C using the ideal gas law (i.e., $P_C = C_C RT$).

The rate expression for the adsorption of cumene as given in Equation (10-22) is

$C + S \underset{k_{-A}}{\overset{k_A}{\rightleftarrows}} C \cdot S$

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



$$\boxed{\text{Adsorption:} \qquad r_{AD} = k_A \left(P_C C_v - \frac{C_{C \cdot S}}{K_C} \right)} \tag{10-25}$$

If r_{AD} has units of (mol/g-cat·s) and $C_{C \cdot S}$ has units of (mol cumene adsorbed/g-cat), then typical units of k_A, k_{-A}, and K_C would be

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

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

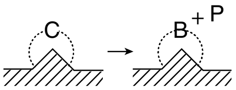
$$[K_C] \equiv \left[\frac{k_A}{k_{-A}} \right] \equiv \text{kPa}^{-1}$$

The rate law for the surface-reaction step producing adsorbed benzene and propylene in the gas phase

$$C \cdot S \underset{k_{-S}}{\overset{k_S}{\rightleftarrows}} B \cdot S + P(g) \tag{10-23}$$

is

$$r_S = k_S C_{C \cdot S} - k_{-S} P_P C_{B \cdot S}$$



$$\boxed{\text{Surface reaction:} \qquad r_{\mathrm{S}} = k_{\mathrm{S}}\left(C_{\mathrm{C\cdot S}} - \frac{P_{\mathrm{P}}C_{\mathrm{B\cdot S}}}{K_{\mathrm{S}}}\right)} \tag{10-26}$$

with the *surface reaction equilibrium constant* being

$$K_{\mathrm{S}} = \frac{k_{\mathrm{S}}}{k_{-\mathrm{S}}}$$

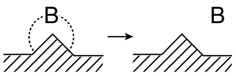
Typical units for k_{S} and K_{S} are s^{-1} and kPa, respectively.

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

$$C_{\mathrm{P\cdot S}} = 0$$

The rate of benzene desorption [see Equation (10-24)] is

$$r_{\mathrm{D}} = k_{\mathrm{D}}C_{\mathrm{B\cdot S}} - k_{-\mathrm{D}}P_{\mathrm{B}}C_v \tag{10-27}$$



$$\boxed{\text{Desorption:} \qquad r_{\mathrm{D}} = k_{\mathrm{D}}\left(C_{\mathrm{B\cdot S}} - \frac{P_{\mathrm{B}}C_v}{K_{\mathrm{DB}}}\right)} \tag{10-28}$$

Typical units of k_{D} and K_{DB} are s^{-1} and kPa, respectively. By viewing the desorption of benzene

$$\mathrm{B\cdot S} \rightleftarrows \mathrm{B + S}$$

from right to left, we see that desorption is just the reverse of the adsorption of benzene. Consequently, as mentioned earlier, it is easily shown that the benzene adsorption equilibrium constant K_{B} is just the reciprocal of the benzene desorption constant K_{DB}

$$K_{\mathrm{B}} = \frac{1}{K_{\mathrm{DB}}}$$

and Equation (10-28) can be written as

$$\boxed{\text{Desorption:} \qquad r_{\mathrm{D}} = k_{\mathrm{D}}(C_{\mathrm{B\cdot S}} - K_{\mathrm{B}}P_{\mathrm{B}}C_v)} \tag{10-29}$$

Because there is no accumulation of reacting species on the surface, the rates of each step in the sequence are all equal as discussed in Figure 10-12:

$$\boxed{-r'_{\mathrm{C}} = r_{\mathrm{AD}} = r_{\mathrm{S}} = r_{\mathrm{D}}} \tag{10-30}$$

For the mechanism postulated in the sequence given by Equations (10-22) through (10-24), 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 partial pressures and 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.

We will first start our development of the rate laws with the assumption that the adsorption step is rate-limiting and derive the rate law, and then proceed to assume that each of the other two steps' surface reaction and desorption limit the overall rate and then derive the rate law for each of these other two limiting cases.

10.3.1 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 postulating that this (or any other) step is rate-limiting, we are assuming 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).[10] The rate of adsorption is

Need to express C_v and $C_{C\cdot S}$ in terms of P_C, P_B, and P_P

$$\boxed{-r'_C = r_{AD} = k_A\left(P_C C_v - \frac{C_{C\cdot S}}{K_C}\right)} \tag{10-25}$$

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

For steady-state operation we have

$$-r'_C = r_{AD} = r_S = r_D \tag{10-30}$$

For adsorption-limited reactions, k_A is very small and k_S and k_D are very, very large by comparison. Consequently, the ratios r_S/k_S and r_D/k_D are very small (approximately zero), whereas the ratio r_{AD}/k_A is relatively large.

The surface reaction-rate law is

$$r_S = k_S\left(C_{C\cdot S} - \frac{C_{B\cdot S}P_P}{K_S}\right) \tag{10-31}$$

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

$$\frac{r_S}{k_S} \simeq 0 \tag{10-32}$$

and solve Equation (10-31) for $C_{C\cdot S}$

$$C_{C\cdot S} = \frac{C_{B\cdot S}P_P}{K_S} \tag{10-33}$$

---

[10] *Strictly speaking*, one should compare the product $k_A P_C$ with k_S and k_D.

$$r_{AD} = k_A P_C\left[C_v - \frac{C_{C\cdot S}}{K_C P_C}\right]$$

$$\frac{\text{mol}}{\text{s}\cdot\text{kg-cat}} = \left(\frac{1}{\text{s atm}}\right)\cdot(\text{atm})\cdot\left[\frac{\text{mol}}{\text{kg-cat}}\right] = \left[\frac{1}{\text{s}}\right]\frac{\text{mol}}{\text{kg-cat}}$$

Dividing r_{AD} by k_AP_C, we note $\frac{r_{AD}}{k_A P_C} = \frac{\text{mol}}{\text{kg-cat}}$. The reason we do this is that in order to compare terms, the ratios $\left(-\frac{r_{AD}}{k_A P_C}\right)$, $\left(\frac{r_S}{k_S}\right)$, and $\left(\frac{r_D}{k_D}\right)$ must all have the same units $\left[\frac{\text{mol}}{\text{kg-cat}}\right]$. Luckily for us, the end result is the same, however.

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

$$r_D = k_D\,(C_{B \cdot S} - K_B P_B C_v) \qquad (10\text{-}29)$$

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

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

$$\frac{r_D}{k_D} \simeq 0 \qquad (10\text{-}34)$$

and then solve Equation (10-29) for $C_{B \cdot S}$

$$C_{B \cdot S} = K_B P_B C_v \qquad (10\text{-}35)$$

After combining Equations (10-33) and (10-35), we have

$$C_{C \cdot S} = K_B \frac{P_B P_P}{K_S} C_v \qquad (10\text{-}36)$$

Replacing $C_{C \cdot S}$ in the rate equation by Equation (10-36) and then factoring C_v, we obtain

$$r_{AD} = k_A \left(P_C - \frac{K_B P_B P_P}{K_S K_C} \right) C_v = k_A \left(P_C - \frac{P_B P_P}{K_P} \right) C_v \qquad (10\text{-}37)$$

Let's look at how the thermodynamic constant pressure equilibrium constant, K_P, found its way into Equation (10-37) and how we can find its value for any reaction. First we observe that at equilibrium $r_{AD} = 0$, Equation (10-37) rearranges to

$$\frac{P_{Be} P_{Pe}}{P_{Ce}} = \frac{K_C K_S}{K_B}$$

We also know from thermodynamics (Appendix C) that for the reaction

$$C \rightleftarrows B + P$$

also at equilibrium $(-r'_C = 0)$, we have the following relationship for partial pressure equilibrium constant K_P

$$K_P = \frac{P_{Be} P_{Pe}}{P_{Ce}}$$

Consequently, the following relationship must hold

$$\boxed{\frac{K_S K_C}{K_B} = K_P} \qquad (10\text{-}38)$$

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

$$\boxed{RT \ln K = -\Delta G^\circ} \qquad (10\text{-}39)$$

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 (10-37) by utilizing the *site balance* to give the total concentration of sites, C_t, which is assumed constant[11]

$$\boxed{\text{Total sites} = \text{Vacant sites} + \text{Occupied sites}}$$

Because cumene and benzene are adsorbed on the surface, the concentration of occupied sites is ($C_{\text{C}\cdot\text{S}} + C_{\text{B}\cdot\text{S}}$), and the total concentration of sites is

Site balance

$$C_t = C_v + C_{\text{C}\cdot\text{S}} + C_{\text{B}\cdot\text{S}} \tag{10-40}$$

Substituting Equations (10-35) and (10-36) into Equation (10-40), we have

$$C_t = C_v + \frac{K_\text{B}}{K_\text{S}} P_\text{B} P_\text{P} C_v + K_\text{B} P_\text{B} C_v$$

Solving for C_v, we have

$$C_v = \frac{C_t}{1 + P_\text{B} P_\text{P} K_\text{B}/K_\text{S} + K_\text{B} P_\text{B}} \tag{10-41}$$

Combining Equations (10-41) and (10-37), we find that the rate law for the catalytic decomposition of cumene, assuming that the adsorption of cumene is the rate-limiting step, is

Cumene reaction rate law if adsorption were the limiting step

$$\boxed{-r'_\text{C} = r_\text{AD} = \frac{C_t k_\text{A} (P_\text{C} - P_\text{P} P_\text{B}/K_P)}{1 + K_\text{B} P_\text{P} P_\text{B}/K_\text{S} + K_\text{B} P_\text{B}}} \tag{10-42}$$

We now wish to sketch a plot of the initial rate of reaction as a function of the partial pressure of cumene, $P_{\text{C}0}$. Initially, no products are present; consequently, $P_\text{P} = P_\text{B} = 0$. The initial rate is given by

$$-r'_{\text{C}0} = C_t k_\text{A} P_{\text{C}0} = k P_{\text{C}0} \tag{10-43}$$

If the cumene decomposition is adsorption rate limited, then from Equation (10-43) we see that the initial rate will be linear with the initial partial pressure of cumene, as shown in Figure 10-15.

Before checking to see if Figure 10-15 is consistent with experimental observation, we shall derive the corresponding rate laws for the other possible rate-limiting steps and then develop corresponding initial rate plots for the case when the surface reaction is rate-limiting and then for the case when the desorption of benzene is rate-limiting.

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[11] Some (I won't mention any names) prefer to write the surface reaction rate in terms of the fraction of the surface of sites covered (i.e., f_A) rather than the number of sites $C_{\text{A}\cdot\text{S}}$ 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_S, and so on, are all lumped into the reaction-rate constant, k.

If adsorption were rate-limiting, the data should show $-r'_{CO}$ increasing linearly with P_{CO}.

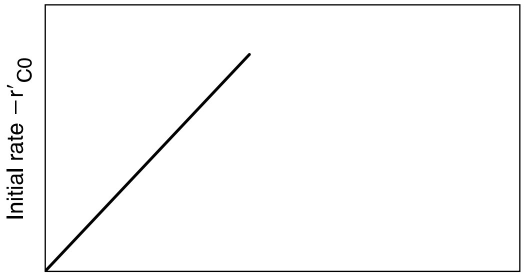


Figure 10-15 Adsorption-limited reaction.

10.3.2 Is the Surface Reaction Rate-Limiting?

The rate of surface reaction is

Single-site mechanism

$$\boxed{r_S = k_S\left(C_{C\cdot S} - \frac{P_P C_{B\cdot S}}{K_S}\right)} \tag{10-26}$$

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

From the adsorption rate expression in Equation (10-25) and the condition that k_A and k_D are very large by comparison with k_S when the surface reaction is limiting (i.e., $r_{AD}/k_A \simeq 0$),[12] we obtain a relationship for the surface concentration for adsorbed cumene

$$C_{C\cdot S} = K_C P_C C_v$$

Using $\frac{r_{AD}}{k_A} \cong 0 \cong \frac{r_D}{k_D}$ to find $C_{B\cdot S}$ and $C_{C\cdot S}$ in terms of partial pressures

In a similar manner, the surface concentration of adsorbed benzene can be evaluated from the desorption rate expression, Equation (10-29), together with the approximation

$$\text{when } \frac{r_D}{k_D} \cong 0$$

then we get the same result for $C_{B\bullet S}$ as before when we had adsorption limitation, i.e.,

$$C_{B\cdot S} = K_B P_B C_v$$

Substituting for $C_{B\cdot S}$ and $C_{C\cdot S}$ in Equation (10-26) gives us

$$r_S = k_S\left(P_C K_C - \frac{K_B P_B P_P}{K_S}\right) C_v = k_S K_C\left(P_C - \frac{P_B P_P}{K_P}\right) C_v \tag{10-26a}$$

where the thermodynamic equilibrium constant was used to replace the ratio of surface reaction and adsorption constants, i.e.,

$$K_P = \frac{K_C K_S}{K_B} \tag{10-26b}$$

---

[12] See footnote 10 on page 424.

The only variable left to eliminate is C_v and we use a site balance to accomplish this, i.e.,

Site balance

$$C_t = C_v + C_{B\cdot S} + C_{C\cdot S} \tag{10-40}$$

Substituting for concentrations of the adsorbed species, $C_{B\cdot S}$, and $C_{C\cdot S}$, factoring out C_V, and rearranging yields

$$C_v = \frac{C_t}{1+K_BP_B+K_CP_C}$$

Substituting for C_V in Equation (10-26a)

Cumene rate law for surface-reaction-limiting

$$\boxed{-r'_C = r_S = \frac{\overbrace{k_SC_tK_C}^{k}\,(P_C-P_PP_B/K_P)}{1+P_BK_B+K_CP_C}} \tag{10-44}$$

The initial rate of reaction is

$$-r'_{C0} = \frac{\overbrace{k_SC_tK_C}^{k}\;P_{C0}}{1+K_CP_{C0}} = \frac{kP_{C0}}{1+K_CP_{C0}} \tag{10-45}$$

Figure 10-16 shows the initial rate of reaction as a function of the initial partial pressure of cumene for the case of surface-reaction-limiting.

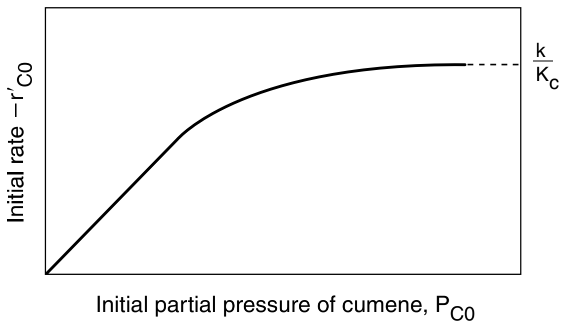


Figure 10-16 Surface-reaction-limited.

At low partial pressures of cumene

$$1 \gg K_CP_{C0}$$

and we observe that the initial rate will increase linearly with the initial partial pressure of cumene:

$$-r'_{C0} \approx kP_{C0}$$

At high partial pressures

$$K_CP_{C0} \gg 1$$

and Equation (10-45) becomes

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

$$-r'_{C0} \cong \frac{kP_{C0}}{K_CP_{C0}} = \frac{k}{K_C}$$

and the initial rate is independent of the initial partial pressure of cumene.

10.3.3 Is the Desorption of Benzene Rate-Limiting?

The rate expression for the desorption of benzene is

$$\boxed{r_D = k_D\,(C_{B\cdot S} - K_B P_B C_v)} \tag{10-29}$$

For desorption-limited reactions, both k_A and k_S are very large compared with k_D, which is small.

From the rate expression for surface reaction, Equation (10-26), we set

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

to obtain

$$C_{B\cdot S} = K_S\left(\frac{C_{C\cdot S}}{P_P}\right) \tag{10-46}$$

Similarly, for the adsorption step, Equation (10-25), we set

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

to obtain

$$C_{C\cdot S} = K_C P_C C_v$$

then substitute for $C_{C\cdot S}$ in Equation (10-46) to obtain

$$C_{B\cdot S} = \frac{K_C K_S P_C C_v}{P_P} \tag{10-47}$$

Combining Equations (10-26b), (10-29), and (10-47) gives us

$$r_D = k_D K_C K_S\left(\frac{P_C}{P_P} - \frac{P_B}{K_P}\right) C_v \tag{10-48}$$

where K_C is the cumene adsorption constant, K_S is the surface-reaction equilibrium constant, and K_P is the thermodynamic gas-phase equilibrium constant, Equation (10-38), for the reaction. The expression for C_v is obtained from a site balance:

$$\text{Site balance:} \qquad C_t = C_{C\cdot S} + C_{B\cdot S} + C_v \tag{10-40}$$

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

$$C_v = \frac{C_t}{1 + K_C K_S P_C/P_P + K_C P_C} \tag{10-49}$$

Replacing C_v in Equation (10-48) by Equation (10-49) and multiplying the numerator and denominator by P_P, we obtain the rate expression for desorption control

Cumene decomposition rate law *if* desorption were limiting

$$\boxed{-r'_C = r_D = \frac{\overbrace{k_D C_t K_S K_C}^{k}\,(P_C - P_B P_P/K_P)}{P_P + P_C K_C K_S + K_C P_P P_C}} \tag{10-50}$$

If desorption limits, the initial rate is independent of the initial partial pressure of cumene.

To determine the dependence of the initial rate of reaction on the initial partial pressure of cumene, we again set $P_P = P_B = 0$, and the rate law reduces to

$$-r'_{C0} = k_D C_t$$

with the corresponding plot of $-r'_{C0}$ shown in Figure 10-17. If desorption were rate limiting, we would see that the initial rate of reaction would be independent of the initial partial pressure of cumene.

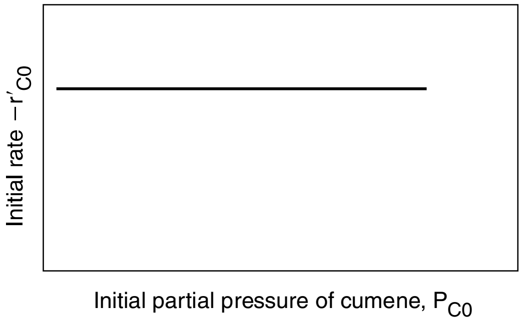


Figure 10-17 Desorption-limited reaction.

10.3.4 Summary of the Cumene Decomposition

Cumene decomposition is surface-reaction-limited

Surface-reaction-limited mechanism is consistent with experimental data.

The experimental observations of $-r'_{C0}$ as a function of P_{C0} are shown in Figure 10-18. From the plot in Figure 10-18, we can clearly see that neither adsorption nor desorption is rate-limiting. For the reaction and mechanism given by

$$C + S \rightleftarrows C\cdot S \tag{10-22}$$

$$C\cdot S \rightleftarrows B\cdot S + P \tag{10-23}$$

$$B\cdot S \rightleftarrows B + S \tag{10-24}$$

the rate law derived by assuming that the surface reaction is rate-limiting agrees with the data.

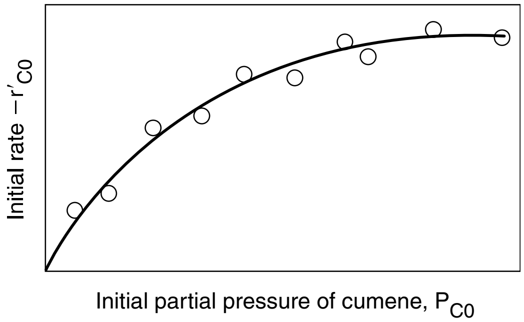


Figure 10-18 Actual initial rate as a function of partial pressure of cumene.

The rate law for the case of no inerts adsorbing on the surface is

$$\boxed{-r'_{\mathrm{C}}=\frac{k\,(P_{\mathrm{C}}-P_{\mathrm{B}}P_{\mathrm{P}}/K_{\mathrm{P}})}{1+K_{\mathrm{B}}P_{\mathrm{B}}+K_{\mathrm{C}}P_{\mathrm{C}}}} \tag{10-44}$$

The forward cumene decomposition reaction is a single-site mechanism involving only adsorbed cumene, while the reverse reaction of propylene in the gas phase reacting with adsorbed benzene is an Eley–Rideal mechanism.

If we were to have an adsorbing inert in the feed, the inert would not participate in the reaction but would occupy active sites on the catalyst surface:

$$\mathrm{I}+\mathrm{S} \rightleftarrows \mathrm{I}\cdot\mathrm{S}$$

Our site balance is now

$$C_t = C_v + C_{\mathrm{C\cdot S}} + C_{\mathrm{B\cdot S}} + C_{\mathrm{I\cdot S}} \tag{10-51}$$

Because the adsorption of the inert is at equilibrium, the concentration of sites occupied by the inert is

$$C_{\mathrm{I\cdot S}} = K_{\mathrm{I}}P_{\mathrm{I}}C_v \tag{10-52}$$

Substituting for the inert sites in the site balance, the rate law for surface reaction control when an adsorbing inert is present is

Adsorbing inerts

$$-r'_{\mathrm{C}}=\frac{k\,(P_{\mathrm{C}}-P_{\mathrm{B}}P_{\mathrm{P}}/K_{\mathrm{P}})}{1+K_{\mathrm{C}}P_{\mathrm{C}}+K_{\mathrm{B}}P_{\mathrm{B}}+K_{\mathrm{I}}P_{\mathrm{I}}} \tag{10-53}$$

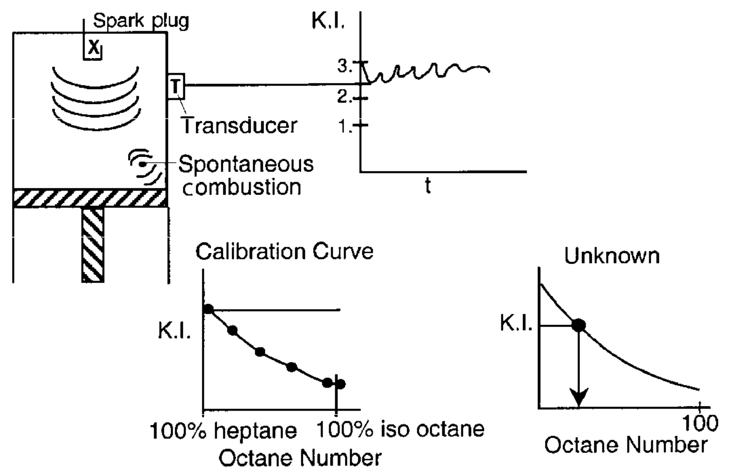
One observes that the rate decreases as the partial pressure of adsorbing inerts increases.

10.3.5 Reforming Catalysts

We now consider a dual-site mechanism, which is a reforming reaction found in petroleum refining to upgrade the octane number of gasoline.

Side Note: Octane Number. Fuels with low octane numbers can produce spontaneous combustion in the car cylinder before the air/fuel mixture is compressed to its desired volume and ignited by the spark plug. The following figure shows the desired combustion wave front moving down from the spark plug and the unwanted spontaneous combustion wave in the lower right-hand corner. This spontaneous combustion produces detonation waves, which constitute engine knock. The lower the octane number, the greater the chance of spontaneous combustion and engine knock.

The octane number of a gasoline is determined from a calibration curve relating knock intensity to the % iso-octane in a mixture of iso-octane and heptane. One way to calibrate the octane number is to place a transducer on the side of the cylinder to measure the knock intensity (K.I.) (pressure pulse) for various mixtures of heptane and iso-octane. The octane number is the percentage of iso-octane in this mixture. That is, pure iso-octane has an octane number of 100, 80% iso-octane/20% heptane has an octane number of 80, and so on. The knock intensity is measured for this



80/20 mixture and recorded. The relative percentages of iso-octane and heptane are changed (e.g., 90/10), and the test is repeated. After a series of experiments, a calibration curve is constructed. The gasoline to be calibrated is then used in the test engine, where the standard knock intensity is measured. Knowing the knock intensity, the octane rating of the fuel is read off the calibration curve. A gasoline with an octane rating of 92 means that it matches the performance of a mixture of 92% iso-octane and 8% heptane. Another way to calibrate the octane number is to set the knock intensity and increase the compression ratio. A fixed percentage of iso-octane and heptane is placed in a test engine and the compression ratio (CR) is increased continually until spontaneous combustion occurs, producing an engine knock. The compression ratio and the corresponding composition of the mixture are then recorded, and the test is repeated to obtain the calibration curve of compression ratio as a function of % iso-octane. After the calibration curve is obtained, the unknown is placed in the cylinder, and the compression ratio (CR) is increased until the set knock intensity is exceeded. The CR is then matched to the calibration curve to find the octane number.

The more compact the molecule, the greater the octane number.

The more compact the hydrocarbon molecule, the less likely it is to cause spontaneous combustion and engine knock. Consequently, it is desired to isomerize straight-chain hydrocarbon molecules into more compact molecules through a catalytic process called *reforming*.

In the U.S., the higher the octane number the greater the cost of a gallon (liter) of gasoline. However, because of government regulations, the cost of a gallon (liter) of gasoline in Jofostan is the same for all octane numbers.

Catalyst manufacture

One common reforming catalyst is platinum on alumina. Platinum on alumina (Al_2O_3) (see SEM photo in Figure 10-19) is a bifunctional catalyst that can be prepared by exposing alumina pellets to a chloroplatinic acid solution, drying, and then heating in air at 775 K to 875 K for several hours. Next, the material is exposed to hydrogen at temperatures around 725 K to 775 K to produce very small clusters of Pt on alumina. These clusters have sizes on the order of 10 Å, while the alumina pore sizes on which the Pt is deposited are on the order of 100 Å to 10,000 Å (i.e., 10 nm to 1000 nm).

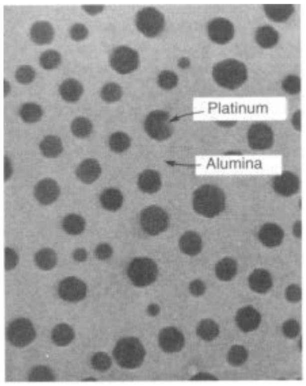


Figure 10-19 Platinum on alumina. (Masel, Richard. *Chemical Kinetics and Catalysis*, p. 700. © John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.)

As an example of catalytic reforming, we shall consider the isomerization of *n*-pentane to *i*-pentane

$$n\text{-pentane} \xrightleftharpoons[\mathrm{Al_2O_3}]{0.75\text{ wt\% Pt}} i\text{-pentane}$$

Gasoline	
C_5	10%
C_6	10%
C_7	20%
C_8	25%
C_9	20%
C_{10}	10%
$C_{11\text{-}12}$	5%

Normal pentane has an octane number of 62, while *iso*-pentane, which is more compact, has an octane number of 90! The *n*-pentane adsorbs onto the platinum, where it is dehydrogenated to form *n*-pentene. The *n*-pentene desorbs from the platinum and adsorbs onto the alumina, where it is isomerized to *i*-pentene, which then desorbs and subsequently adsorbs onto platinum, where it is hydrogenated to form *i*-pentane. That is

$$n\text{-pentane} \xrightleftharpoons[\mathrm{Pt}]{-\mathrm{H_2}} n\text{-pentene} \xrightleftharpoons{\mathrm{Al_2O_3}} i\text{-pentene} \xrightleftharpoons[\mathrm{Pt}]{+\mathrm{H_2}} i\text{-pentane}$$

We shall focus on the isomerization step to develop the mechanism and the rate law

$$n\text{-pentene} \xrightleftharpoons{\mathrm{Al_2O_3}} i\text{-pentene}$$

$$\mathrm{N} \rightleftarrows \mathrm{I}$$

The procedure for formulating a mechanism, rate-limiting step, and corresponding rate law is given in Table 10-4.

Table 10-4 Algorithm for Determining the Reaction Mechanism and Rate-Limiting Step

---

Isomerization of *n*-pentene (N) to *i*-pentene (I) over alumina

$$\mathrm{N} \underset{}{\overset{\mathrm{Al_2O_3}}{\rightleftarrows}} \mathrm{I}$$

Reforming reaction to increase octane number of gasoline

Step 1. *Select a mechanism.* (Let's choose a Dual Site Mechanism)

$$\begin{aligned}
&\text{Adsorption:} && \mathrm{N + S \rightleftarrows N\cdot S}\\
&\text{Surface reaction:} && \mathrm{N\cdot S + S \rightleftarrows I\cdot S + S}\\
&\text{Desorption:} && \mathrm{I\cdot S \rightleftarrows I + S}
\end{aligned}$$

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

Step 2. *Assume a rate-limiting step.* We choose the surface reaction first, because *more than 75% of all heterogeneous reactions that are not diffusion-limited are surface-reaction-limited.* We note that the PSSH must be used when more than one step is limiting (see Section 10.3.6). The rate law for the surface reaction step is

$$-r'_{\mathrm{N}} = r_{\mathrm{S}} = k_{\mathrm{S}}\left(C_v C_{\mathrm{N\cdot S}} - \frac{C_{\mathrm{I\cdot S}}C_v}{K_{\mathrm{S}}}\right)$$

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


Following the Algorithm

$$\text{From } \frac{r_{\mathrm{AD}}}{k_{\mathrm{A}}} \simeq 0: \qquad C_{\mathrm{N\cdot S}} = P_{\mathrm{N}} K_{\mathrm{N}} C_v$$

$$\text{From } \frac{r_{\mathrm{D}}}{k_{\mathrm{D}}} \simeq 0: \qquad C_{\mathrm{I\cdot S}} = \frac{P_{\mathrm{I}} C_v}{K_{\mathrm{D}}} = K_{\mathrm{I}} P_{\mathrm{I}} C_v$$

Step 4. *Write a site balance.*

$$C_t = C_v + C_{\mathrm{N\cdot S}} + C_{\mathrm{I\cdot S}}$$

Step 5. *Derive the rate law.* Combine Steps 2, 3, and 4 to arrive at the rate law

$$-r'_{\mathrm{N}} = r_{\mathrm{S}} = \frac{\overbrace{k_{\mathrm{S}} C_t^2 K_{\mathrm{N}}}^{k}\,(P_{\mathrm{N}} - P_{\mathrm{I}}/K_{\mathrm{P}})}{(1 + K_{\mathrm{N}} P_{\mathrm{N}} + K_{\mathrm{I}} P_{\mathrm{I}})^2}$$

Step 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:

a. Assume a different rate-limiting step and repeat Steps 2 through 6.

b. If, after assuming that each step is rate-limiting, none of the derived rate laws agrees with the experimental data, select a different mechanism (e.g., a single-site mechanism)

$$\begin{aligned}
\mathrm{N + S} &\rightleftarrows \mathrm{N\cdot S}\\
\mathrm{N\cdot S} &\rightleftarrows \mathrm{I\cdot S}\\
\mathrm{I\cdot S} &\rightleftarrows \mathrm{I + S}
\end{aligned}$$

and then proceed through Steps 2 through 6.

The single-site mechanism turns out to be the correct one. For this mechanism, the rate law is

$$-r'_{\mathrm{N}} = \frac{k(P_{\mathrm{N}} - P_{\mathrm{I}}/K_{\mathrm{P}})}{(1 + K_{\mathrm{N}} P_{\mathrm{N}} + K_{\mathrm{I}} P_{\mathrm{I}})}$$

c. If two or more models agree, the statistical tests discussed in Chapter 7 (e.g., comparison of residuals) should be used to discriminate between them (see the Supplementary Reading).

We note that in Table 10-4 for the dual-site mechanism, the denominator of the rate law for $-r'_{\mathrm{A}}$ is squared (i.e., in Step 5 [1/( )^2)]), while for a single-site mechanism, it is not squared (i.e., Step 6 [1/( )]). This fact is useful when analyzing catalyzed reactor data.

Table 10-5 gives rate laws for different reaction mechanisms that are irreversible and surface-reaction-limited.

TABLE 10-5 IRREVERSIBLE SURFACE-REACTION-LIMITED RATE LAWS

Single site	
$A\cdot S \longrightarrow B\cdot S$	$-r'_A = \dfrac{kP_A}{1+K_AP_A+K_BP_B}$
Dual site	
$A\cdot S + S \longrightarrow B\cdot S + S$	$-r'_A = \dfrac{kP_A}{(1+K_AP_A+K_BP_B)^2}$
$A\cdot S + B\cdot S \longrightarrow C\cdot S + S$	$-r'_A = \dfrac{kP_AP_B}{(1+K_AP_A+K_BP_B+K_CP_C)^2}$
Eley–Rideal	
$A\cdot S + B(g) \longrightarrow C\cdot S$	$-r'_A = \dfrac{kP_AP_B}{1+K_AP_A+K_CP_C}$

We need a word of caution at this point. Just because the mechanism and rate-limiting step may fit the rate data does not imply that the mechanism is correct.[13] Usually, spectroscopic measurements are needed to confirm a mechanism absolutely. However, the development of various mechanisms and rate-limiting steps can provide insight into the best way to correlate the data and develop a rate law.

10.3.6 Rate Laws Derived from the Pseudo-Steady-State Hypothesis (PSSH)

In Section 9.1 we discussed the PSSH, where the net rate of formation of *reactive intermediates* was assumed to be zero. An alternative way to derive a catalytic rate law rather than setting

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

is to assume that each species adsorbed on the surface is a *reactive intermediate*. Consequently, the net rate of formation of species *i* adsorbed on the surface will be zero

$$r^*_{i\cdot S} = 0 \tag{10-54}$$

The PSSH is primarly used when more than one step is rate-limiting. The isomerization example shown in Table 10-4 is reworked using the PSSH in the Chapter 10 Expanded Material on the CRE Web site.

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[13] R. I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces* (New York: Wiley, 1996), p. 506, *www.masel.com*. This is a terrific book.

10.3.7 Temperature Dependence of the Rate Law

Consider a surface-reaction-limited irreversible isomerization

$$A \longrightarrow B$$

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

$$-r'_A = \frac{kP_A}{1+K_AP_A+K_BP_B} \tag{10-55}$$

The specific reaction rate, k, will usually follow an Arrhenius temperature dependence and increase exponentially with temperature. However, the adsorption of all species on the surface is exothermic. Consequently, the higher the temperature, the smaller the adsorption equilibrium constant. That is, as the temperature increases, K_A and K_B decrease resulting in less coverage of the surface by A and B. Therefore, at high temperatures, the denominator of catalytic rate laws approaches 1. That is, at high temperatures (low coverage)

$$1 \gg (P_AK_A + P_BK_B)$$

Neglecting the adsorbed species at high temperatures

The rate law could then be approximated as

$$-r'_A \simeq kP_A \tag{10-56}$$

or for a reversible isomerization we would have

$$-r'_A \simeq k\left(P_A - \frac{P_B}{K_P}\right) \tag{10-57}$$

Algorithm
Deduce
Rate law
Find
Mechanism
Evaluate
Rate-law parameters
Design
PBR
CSTR

The algorithm we can use as a start in postulating a reaction mechanism and rate-limiting step is shown in Table 10-4. Again, we can never really prove a mechanism to be correct by comparing the derived rate law with experimental data. Independent spectroscopic experiments are 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 10-4. Rather than taking all the experimental data and then trying to build a model from the data, Box et al. describe techniques of sequential data collection and model building.[14]

10.4 Heterogeneous Data Analysis for Reactor Design

In this section we focus on four operations that chemical reaction engineers need to be able to accomplish:


Following the Algorithm

(1) Developing an algebraic rate law consistent with experimental observations,

(2) Analyzing the rate law in such a manner that the rate-law parameters (e.g., k, K_A) can readily be determined from the experimental data,

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

(3) Finding a mechanism and rate-limiting step consistent with the experimental data

(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 form methane and benzene[15]

$$C_6H_5CH_3 + H_2 \xrightarrow[\text{catalyst}]{} C_6H_6 + CH_4$$

We wish to design a packed-bed reactor and a fluidized CSTR to process a feed consisting of 30% toluene, 45% hydrogen, and 25% inerts. Toluene is fed at a rate of 50 mol/min at a temperature of 640°C and a pressure of 40 atm (4052 kPa). To design the PBR, we must first determine the rate law from the differential reactor data presented in Table 10-6. In this table, we are given the rate of reaction of toluene as a function of the partial pressures of hydrogen (H_2), 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, none of the products was present in the feedstream. Because the conversion was less than 1% in the differential reactor, the partial pressures of the products, methane and benzene, formed in these runs were essentially zero, and the reaction rates were equivalent to initial rates of reaction.

Unscramble the data to find the rate law

TABLE 10-6 DATA FROM A DIFFERENTIAL REACTOR

	$-r'_T \times 10^{10}$	*Partial Pressure* (atm)			
Run	$\left(\frac{\text{g mol toluene}}{\text{g-cat}\cdot\text{s}}\right)$	*Toluene* (T), P_T	*Hydrogen* (H_2), P_{H_2}	*Methane* (M), P_M	*Benzene* (B), 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

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[15] J. Papp, D. Kallo, and G. Schay, *J. Catal.*, 23, 168.

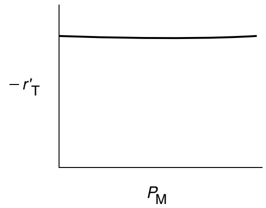
10.4.1 Deducing a Rate Law from the Experimental Data

Following the Algorithm

First, let's look at run 3. In run 3, there is no possibility of the reverse reaction taking place because the concentration of methane is zero, i.e., $P_M = 0$, whereas in run 5 the reverse reaction could take place because all products are present. Comparing runs 3 and 5, we see that the initial rate is essentially the same for both runs, and we can assume that the reaction is essentially irreversible.

$$T + H_2 \xrightarrow[\text{catalyst}]{} M + B$$

We now 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.



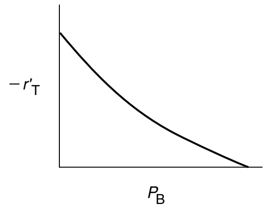
1. *Dependence on the product methane. If* methane were adsorbed on the surface, the partial pressure of methane would appear in the denominator of the rate expression and the rate would vary inversely with methane concentration

$$-r'_T \sim \frac{[\cdot]}{1 + K_M P_M + \cdots} \tag{10-67}$$

However, comparing runs 1 and 2 we observe that a fourfold increase in the pressure of methane has little effect on $-r'_T$. Consequently, we assume 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 previously discussed.

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

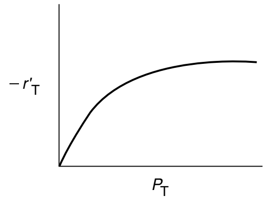
2. *Dependence on the product benzene.* In runs 3 and 4, we observe that, for fixed concentrations (partial pressures) of hydrogen and toluene, the rate decreases with increasing concentration of benzene. A rate expression in which the benzene partial pressure appears in the denominator could explain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



$$-r'_T \sim \frac{1}{1 + K_B P_B + \cdots} \tag{10-68}$$

The type of dependence of $-r'_T$ on P_B given by Equation (10-68) suggests that benzene is adsorbed on the clinoptilolite surface.

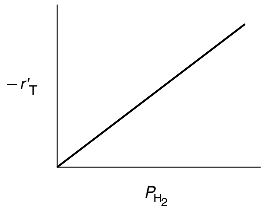
3. *Dependence on toluene.* At low concentrations of toluene (runs 10 and 11), the rate increases with increasing partial pressure of toluene, while at high toluene concentrations (runs 14 and 15), the rate is virtually independent of the toluene partial pressure. A form of the rate expression that would describe this behavior is



$$-r'_T \sim \frac{P_T}{1 + K_T P_T + \cdots} \tag{10-69}$$

A combination of Equations (10-68) and (10-69) suggests that the rate law may be of the form

$$-r'_T \sim \frac{P_T}{1 + K_T P_T + K_B P_B + \cdots} \tag{10-70}$$



4. *Dependence on hydrogen.* When we compare runs 7, 8, and 9 in Table 10-6, we see that the rate increases linearly with increasing hydrogen concentration, and we conclude that the reaction is first order in H_2. In light of this fact, hydrogen is either not adsorbed on the surface or its coverage of the surface is extremely low $(1 \gg K_{H_2}P_{H_2})$ for the pressures used. If H_2 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 (10-69)]. For first-order dependence on H_2,

$$-r'_T \sim P_{H_2} \tag{10-71}$$

Combining Equations (10-67) through (10-71), we find that the rate law

$$\boxed{-r'_T = \frac{kP_{H_2}P_T}{1+K_BP_B+K_TP_T}}$$

is in qualitative agreement with the data shown in Table 10-6.

10.4.2 Finding a Mechanism Consistent with Experimental Observations

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

We now propose a mechanism for the hydrodemethylation of toluene. We assume that the reaction follows an *Eley-Rideal mechanism* where 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. Because approximately 75% to 80% 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

Eley–Rideal mechanism

Proposed Mechanism

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

$$r_{AD} = k_A\left(C_vP_T - \frac{C_{T\cdot S}}{K_T}\right) \tag{10-72}$$

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

$$r_S = k_S\left(P_{H_2}C_{T\cdot S} - \frac{C_{B\cdot S}P_M}{K_S}\right) \tag{10-73}$$

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

$$r_D = k_D\,(C_{B\cdot S} - K_BP_BC_v) \tag{10-74}$$

For surface-reaction-limited mechanisms

$$r_S = k_S\left(P_{H_2}C_{T\cdot S} - \frac{C_{B\cdot S}P_M}{K_S}\right) \tag{10-73}$$

we see that we need to replace $C_{\mathrm{T\cdot S}}$ and $C_{\mathrm{B\cdot S}}$ in Equation (10-73) by quantities that we can measure.

For surface-reaction-limited mechanisms, we use the adsorption rate Equation (10-72) for toluene to obtain $C_{\mathrm{T\cdot S}}$[16], i.e.,

$$\frac{r_{\mathrm{AD}}}{k_{\mathrm{A}}} \approx 0$$

Then

$$\boxed{C_{\mathrm{T\cdot S}} = K_{\mathrm{T}} P_{\mathrm{T}} C_v} \tag{10-75}$$

and we use the desorption rate Equation (10-74) for benzene to obtain $C_{\mathrm{B\cdot S}}$:

$$\frac{r_{\mathrm{D}}}{k_{\mathrm{D}}} \approx 0$$

Then

$$\boxed{C_{\mathrm{B\cdot S}} = K_{\mathrm{B}} P_{\mathrm{B}} C_v} \tag{10-76}$$

The total concentration of sites is

Perform a site balance to obtain C_v.

$$\boxed{C_t = C_v + C_{\mathrm{T\cdot S}} + C_{\mathrm{B\cdot S}}} \tag{10-77}$$

Substituting Equations (10-75) and (10-76) into Equation (10-77) and rearranging, we obtain

$$C_v = \frac{C_t}{1 + K_{\mathrm{T}} P_{\mathrm{T}} + K_{\mathrm{B}} P_{\mathrm{B}}} \tag{10-78}$$

Next, substitute for $C_{\mathrm{T\cdot S}}$ and $C_{\mathrm{B\cdot S}}$, and then substitute for C_v in Equation (10-73) to obtain the rate law for the case when the reaction is surface-reaction-rate-limited

$$-r'_{\mathrm{T}} = \frac{\overbrace{C_t k_{\mathrm{S}} K_{\mathrm{T}}}^{k} \, (P_{\mathrm{H_2}} P_{\mathrm{T}} - P_{\mathrm{B}} P_{\mathrm{M}} / K_{\mathrm{P}})}{1 + K_{\mathrm{T}} P_{\mathrm{T}} + K_{\mathrm{B}} P_{\mathrm{B}}} \tag{10-79}$$

We have shown by comparing runs 3 and 5 that we can neglect the reverse reaction, i.e., the thermodynamic equilibrium constant K_{P} is very, very large. Consequently, we obtain

Rate law for Eley–Rideal surface-reaction-limited mechanism

$$\boxed{-r'_{\mathrm{T}} = \frac{k P_{\mathrm{H_2}} P_{\mathrm{T}}}{1 + K_{\mathrm{B}} P_{\mathrm{B}} + K_{\mathrm{T}} P_{\mathrm{T}}}} \tag{10-80}$$

Again we note that the adsorption equilibrium constant of a given species is exactly the reciprocal of the desorption equilibrium constant of that species.

10.4.3 Evaluation of the Rate-Law Parameters

In the original work on this reaction by Papp et al.,[17] over 25 models were tested against experimental data, and it was concluded that the preceding

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[16] See footnote 10 on page 424.

[17] Ibid.

mechanism and rate-limiting step (i.e., the surface reaction between adsorbed toluene and H_2 gas) is the correct one. Assuming that the reaction is essentially irreversible, the rate law for the reaction on clinoptilolite is

$$-r'_{T} = k\,\frac{P_{H_2}P_{T}}{1+K_{B}P_{B}+K_{T}P_{T}} \tag{10-80}$$

We now wish to determine how best to analyze the data to evaluate the rate-law parameters, k, K_T, and K_B. This analysis is referred to as *parameter estimation.*[18] We now rearrange our rate law to obtain a linear relationship between our measured variables. For the rate law given by Equation (10-80), we see that if both sides of Equation (10-80) are divided by $P_{H_2}P_T$ and the equation is then inverted

Linearize the rate equation to extract the rate-law parameters.

$$\boxed{\frac{P_{H_2}P_{T}}{-r'_{T}} = \frac{1}{k}+\frac{K_{B}P_{B}}{k}+\frac{K_{T}P_{T}}{k}} \tag{10-81}$$

A linear least-squares analysis of the data shown in Table 10-6 is presented on the CRE Web site.

The regression techniques described in Chapter 7 could be used to determine the rate-law parameters by using the equation

$$\boxed{Y_j = a_0+a_1X_{1j}+a_2X_{2j}}$$

One can use the linearized least-squares analysis (PRS 7.3) to obtain initial estimates of the parameters k, K_T, K_B, in order to obtain convergence in nonlinear regression. However, in many cases it is possible to use a nonlinear regression analysis directly, as described in Sections 7.5 and 7.6, and in Example 10-1.

Example 10–1 Nonlinear Regression Analysis to Determine the Model Parameters k, K_B, and K_T

(a) Use nonlinear regression, as discussed in Chapter 7, along with the data in Table 10-6, to find the best estimates of the rate-law parameters k, K_B, and K_T in Equation (10-80).

(b) Write the rate law solely as a function of the partial pressures.

(c) Find the ratio of the sites occupied by toluene, $C_{T\cdot S}$, to those occupied by benzene, $C_{B\cdot S}$, at 40% conversion of toluene.

Solution

The data from Table 10-6 were entered into the Polymath nonlinear least-squares program with the following modification. The rates of reaction in column 1 were multiplied by 10^{10}, so that each of the numbers in column 1 was entered directly (i.e., 71.0, 71.3, …). The model equation was

Living Example Problem

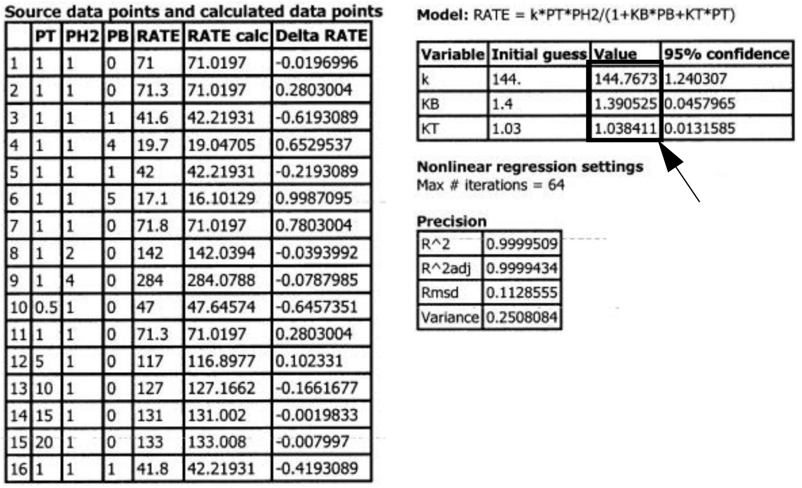
$$\text{Rate} = \frac{kP_{T}P_{H_2}}{1+K_{B}P_{B}+K_{T}P_{T}} \tag{E10-1.1}$$

---

[18] See the Supplementary Reading (page 492) for a variety of techniques for estimating the rate-law parameters.

Following the step-by-step regression procedure in Chapter 7 and on the CRE Web site *Summary Notes*, we arrive at the following parameter values shown in Table E10-1.1.

TABLE E10-1.1 PARAMETER VALUES



Source data points and calculated data points

	PT	PH2	PB	RATE	RATE calc	Delta RATE
1	1	1	0	71	71.0197	-0.0196996
2	1	1	0	71.3	71.0197	0.2803004
3	1	1	1	41.6	42.21931	-0.6193089
4	1	1	4	19.7	19.04705	0.6529537
5	1	1	1	42	42.21931	-0.2193089
6	1	1	5	17.1	16.10129	0.9987095
7	1	1	0	71.8	71.0197	0.7803004
8	1	2	0	142	142.0394	-0.0393992
9	1	4	0	284	284.0788	-0.0787985
10	0.5	1	0	47	47.64574	-0.6457351
11	1	1	0	71.3	71.0197	0.2803004
12	5	1	0	117	116.8977	0.102331
13	10	1	0	127	127.1662	-0.1661677
14	15	1	0	131	131.002	-0.0019833
15	20	1	0	133	133.008	-0.007997
16	1	1	1	41.8	42.21931	-0.4193089

Model: RATE = k*PT*PH2/(1+KB*PB+KT*PT)

Variable	Initial guess	Value	95% confidence
k	144.	144.7673	1.240307
KB	1.4	1.390525	0.0457965
KT	1.03	1.038411	0.0131585

Nonlinear regression settings
Max # iterations = 64

Precision

R^2	0.9999509
R^2adj	0.9999434
Rmsd	0.1128555
Variance	0.2508084

(a) The best estimates are shown in the upper-right-hand box of Table E10-1.1.

(b) Converting the rate law to kilograms of catalyst and minutes,

$$-r'_{\mathrm{T}} = \frac{1.45\times10^{-8} P_{\mathrm{T}} P_{\mathrm{H_2}}}{1+1.39 P_{\mathrm{B}}+1.038 P_{\mathrm{T}}} \frac{\text{mol T}}{\text{g-cat}\cdot\text{s}} \times \frac{1000\text{ g}}{1\text{ kg}} \times \frac{60\text{ s}}{\text{min}} \tag{E10-1.2}$$

we have

$$\boxed{-r'_{\mathrm{T}} = \frac{8.7\times10^{-4} P_{\mathrm{T}} P_{\mathrm{H_2}}}{1+1.39 P_{\mathrm{B}}+1.038 P_{\mathrm{T}}} \left(\frac{\text{g mol T}}{\text{kg-cat.}\cdot\text{min}}\right)} \tag{E10-1.3}$$

Ratio of sites occupied by toluene to those occupied by benzene

(c) After we have the adsorption constants, K_{T} and K_{B}, we can calculate the ratio of sites occupied by the various adsorbed species. For example, taking the ratio of Equation (10-75) to Equation (10-76), the ratio of toluene-occupied sites to benzene- occupied sites at 40% conversion is

$$\frac{C_{\mathrm{T \cdot S}}}{C_{\mathrm{B \cdot S}}} = \frac{C_v K_{\mathrm{T}} P_{\mathrm{T}}}{C_v K_{\mathrm{B}} P_{\mathrm{B}}} = \frac{K_{\mathrm{T}} P_{\mathrm{T}}}{K_{\mathrm{B}} P_{\mathrm{B}}} = \frac{K_{\mathrm{T}} P_{\mathrm{A0}}(1-X)}{K_{\mathrm{B}} P_{\mathrm{A0}} X}$$

$$= \frac{K_{\mathrm{T}}(1-X)}{K_{\mathrm{B}} X} = \frac{1.038\,(1-0.4)}{1.39\,(0.4)} = 1.12$$

We see that at 40% conversion there are approximately 12% more sites occupied by toluene than by benzene. This fact is *common knowledge* to every chemical engineering student at Jofostan University, Riça, Jofostan.

Analysis: This example shows once again how to determine the values of rate-law parameters from experimental data using Polymath regression. It also shows how to calculate the different fraction of sites, both vacant and occupied, as a function of conversion.

10.4.4 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, $-r'_A$, as a function of conversion, and carry out the integration of the packed-bed design equation

$$\frac{dX}{dW} = \frac{-r'_A}{F_{A0}} \tag{2-17}$$

Example 10–2 Catalytic Reactor Design

Living Example Problem

The hydrodemethylation of toluene is to be carried out in a PBR catalytic reactor.

$$C_6H_5CH_3 + H_2 \xrightarrow[\text{catalyst}]{} C_6H_6 + CH_4$$

The molar feed rate of toluene to the reactor is 50 mol/min, and the reactor inlet is at 40 atm and 640°C. The feed consists of 30% toluene, 45% hydrogen, and 25% inerts. Hydrogen is used in excess to help prevent coking. The pressure-drop parameter, α, is 9.8×10^{-5} kg^{-1}.

(a) Plot and analyze the conversion, the pressure ratio, p, and the partial pressures of toluene, hydrogen, and benzene as a function of PBR catalyst weight.

(b) Determine the catalyst weight in a fluidized CSTR with a bulk density of 400 kg/m^3 (0.4 g/cm^3) to achieve 65% conversion.

Solution

(a) PBR with pressure drop

1. Mole Balance:

Balance on toluene (T)

$$\frac{dF_T}{dW} = r'_T$$

$$\frac{dX}{dW} = \frac{-r'_T}{F_{T0}} \tag{E10-2.1}$$

2. **Rate Law:** From Equation (E10-1.1) we have

$$-r'_T = \frac{kP_{H_2}P_T}{1+K_BP_B+K_TP_T} \tag{E10-2.2}$$

with $k = 0.00087$ mol/atm^2/kg-cat/min, $K_B = 1.39$ atm^{-1}, and $K_T = 1.038$ atm^{-1}.

3. Stoichiometry:

$$P_T = C_TRT = C_{T0}RT_0\left(\frac{1-X}{1+\varepsilon X}\right)p = P_{T0}\left(\frac{1-X}{1+\varepsilon X}\right)p$$

$$\varepsilon = y_{T0}\delta = 0.3(0) = 0$$

$$p = \frac{P}{P_0}$$

Relating
Toluene (T)
Benzene (B)
Hydrogen (H_2)

$$P_T = P_{T0}(1 - X)p \tag{E10-2.3}$$

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

$$\Theta_{H_2} = \frac{0.45}{0.30} = 1.5$$

$$P_{H_2} = P_{T0}(1.5 - X)p \tag{E10-2.4}$$

$$P_B = P_{T0}Xp \tag{E10-2.5}$$

Because $\varepsilon = 0$, we can use the integrated form of the pressure-drop term.

P_0 = total pressure at the entrance

$$p = \frac{P}{P_0} = (1-\alpha W)^{1/2} \tag{5-33}$$

$$\alpha = 9.8 \times 10^{-5}\ \text{kg}^{-1}$$

Note that P_{T0} designates the inlet partial pressure of toluene. In this example, the inlet total pressure is designated P_0 to avoid any confusion. The inlet mole fraction of toluene is 0.3 (i.e., $y_{T0} = 0.3$), so that the inlet partial pressure of toluene is

Pressure drop in PBRs is discussed in Section 5.5.

$$P_{T0} = (0.3)(40) = 12\ \text{atm}$$

We now calculate the maximum catalyst weight we can have, such that the exiting pressure will not fall below atmospheric pressure (i.e., 1.0 atm) for the specified feed rate. This weight is calculated by substituting the entering pressure of 40 atm and the exiting pressure of 1 atm into Equation (5-33), i.e.,

$$p = \frac{P}{P_0} = (1-\alpha w)^{1/2}$$

$$\frac{1}{40} = (1 - 9.8 \times 10^{-5}W)^{1/2}$$

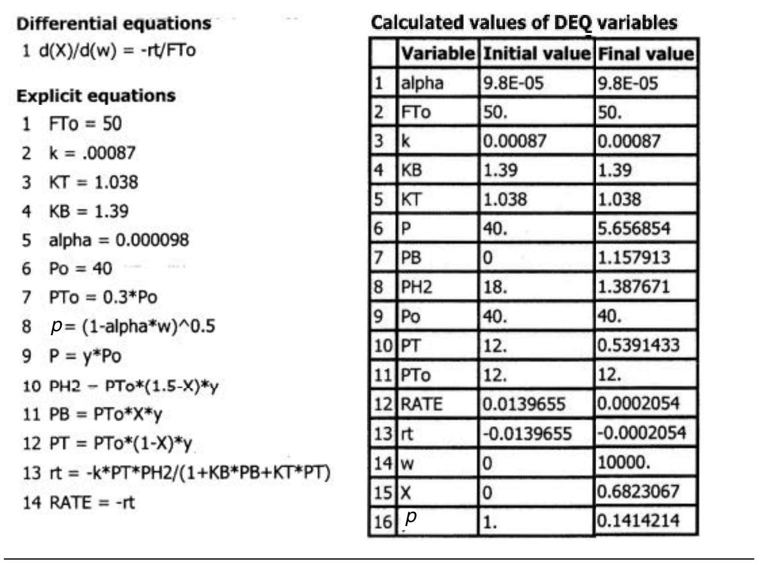
$$W = 10{,}197\ \text{kg}$$

4. Evaluate: Consequently, we will set our final weight at 10,000 kg and determine the conversion profile as a function of catalyst weight up to this value. Equations (E10-2.1) through (E10-2.5) are shown in the Polymath program in Table E10-2.1. The conversion is shown as a function of catalyst weight in Figure E10-2.1, and profiles of the partial pressures of toluene, hydrogen, and benzene are shown in Figure E10-2.2. We note that the pressure drop causes (cf. Equation E10-2.5) the partial pressure of benzene to go through a maximum as one traverses the reactor.

Living Example Problem

Conversion profile down the packed bed

TABLE E10-2.1 POLYMATH PROGRAM AND OUTPUT



```
Differential equations
d(X)/d(w) = -rt/FTo

Explicit equations
FTo = 50
k = .00087
KT = 1.038
KB = 1.39
alpha = 0.000098
Po = 40
PTo = 0.3*Po
p= (1-alpha*w)^0.5
P = y*Po
PH2 – PTo*(1.5-X)*y
PB = PTo*X*y
PT = PTo*(1-X)*y
rt = -k*PT*PH2/(1+KB*PB+KT*PT)
RATE = -rt
```

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	alpha	9.8E-05	9.8E-05
2	FTo	50.	50.
3	k	0.00087	0.00087
4	KB	1.39	1.39
5	KT	1.038	1.038
6	P	40.	5.656854
7	PB	0	1.157913
8	PH2	18.	1.387671
9	Po	40.	40.
10	PT	12.	0.5391433
11	PTo	12.	12.
12	RATE	0.0139655	0.0002054
13	rt	-0.0139655	-0.0002054
14	w	0	10000.
15	X	0	0.6823067
16	p	1.	0.1414214

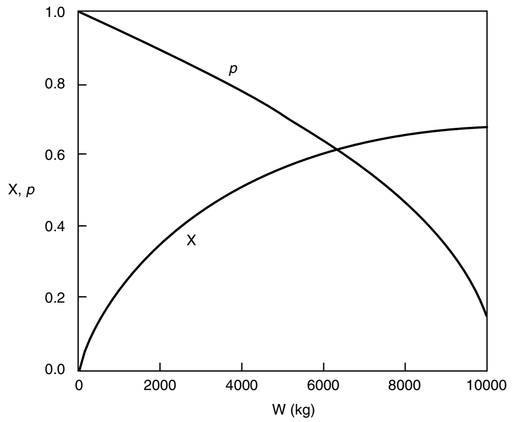


Figure E10-2.1 Conversion and pressure ratio profiles.

Note the partial pressure of benzene goes through a maximum. Why?

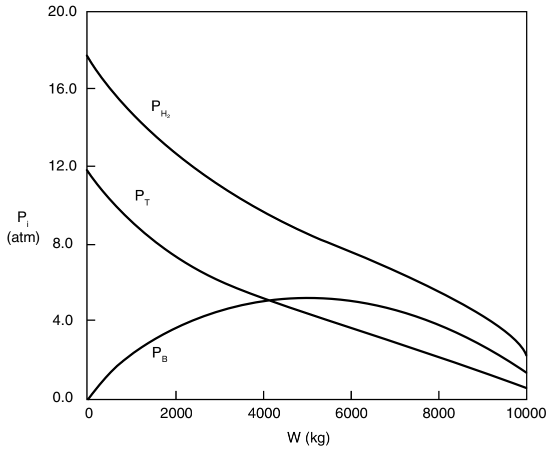


Figure E10-2.2 Partial pressure profiles.

If one had neglected ΔP it could have been very embarrassing.

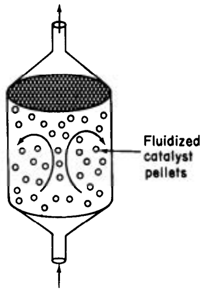
See YouTube video, "Reaction Engineering Gone Wrong," accessible from the CRE Web site home page.

PBR Analysis: For the case of no pressure drop, the conversion that would have been achieved with 10,000 kg of catalyst would have been 79%, compared with 68.2% when there is pressure drop in the reactor. To carry out this calculation, use the Living Example Program (**LEP**) on the CRE Web site and simply multiply the pressure-drop parameter by zero, i.e., line (5) would read α = 0.00098*0. *For the feed rate given, eliminating or minimizing pressure drop would increase the production of benzene by up to 61 million pounds per year!* Finally, we note in Figure E10-2.2 that the partial pressure of benzene (P_B) goes through a maximum. This maximum can be explained by recalling that P_B is just the product of the benzene mole fraction (y_B) times the total pressure (P) [i.e., $P_B = y_B P_T$]. Near the middle to end of the bed, benzene is no longer being formed so that y_B stops increasing. However, because of the pressure drop, the total pressure decreases and, as a result, so does P_B.

(b) Fluidized CSTR

We will now calculate the fluidized CSTR catalyst weight necessary to achieve the same (ca.) 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

Fluidized CSTR



1. Mole Balance:

$$\begin{array}{ccccccccc} \text{In} & - & \text{Out} & + & \text{Gen} & = & \text{Accum} \\ F_{T0} & - & F_T & + & r'_T W & = & 0 \end{array}$$

Rearranging

$$W = \frac{F_{T0} - F_T}{-r'_T} = \frac{F_{T0}X}{-r'_T} \qquad \text{(E10-2.6)}$$

2. Rate Law and **3. Stoichiometry** same as in part **(a)** PBR calculation

4. Combine and Evaluate: Writing Equation (E10-2.2) in terms of conversion (E10-2.3) and then substituting $X = 0.65$ and $P_{T0} = 12$ atm, we have

$$-r'_T = \frac{8.7\times10^{-4}P_T P_{H_2}}{1+1.39P_B+1.038P_T} = \frac{8.7\times10^{-4}P_{T0}^2(1-X)(1.5-X)}{1+1.39P_{T0}X+1.038P_{T0}(1-X)} = 2.3\times10^{-3}\frac{\text{mol}}{\text{kg-cat}\cdot\text{min}}$$

$$W = \frac{F_{T0}X}{-r'_T} = \frac{(50\text{ mol T/min})(0.65)}{2.3\times10^{-3}\text{ mol T/kg cat}\cdot\text{min}}$$

$$\boxed{W = 1.41\times10^4\text{ kg of catalyst}}$$

The corresponding reactor volume is

$$V = \frac{W}{\rho_b} = \frac{1.41\times10^4\text{ kg}}{400\text{ kg/m}^3} = 35.25\text{ m}^3$$

How can the weight of catalyst be reduced? Raise the temperature?

Analysis: This example used real data and the CRE algorithm to design a PBR and CSTR. An important point is that it showed how one could be embarrassed by not including pressure drop in the design of a packed-bed reactor. We also note that for both the PBR and fluidized CSTR, the values of the catalyst weight and reactor volume are quite high, especially for the low feed rates given. *Consequently, the temperature of the reacting mixture should be increased to reduce the catalyst weight, provided that side reactions and catalyst decay do not become a problem at higher temperatures.*

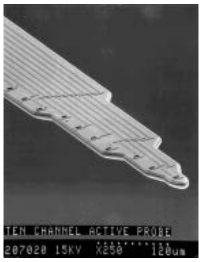
Example 10-2 illustrated the major activities pertinent to catalytic reactor design described earlier in Figure 10-6. In this example, the rate law was extracted directly from the data and then a mechanism was found that was consistent with experimental observation. Conversely, developing a feasible mechanism may guide one in the synthesis of the rate law.

10.5 Reaction Engineering in Microelectronic Fabrication

10.5.1 Overview

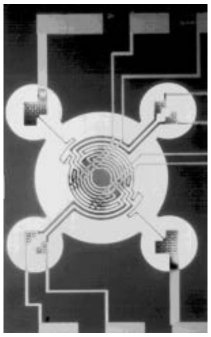
We now extend the principles of the preceding sections to one of the emerging technologies in chemical engineering. Chemical engineers are now playing an important role in the electronics industry. Specifically, they are becoming more involved in the manufacture of electronic and photonic devices, recording materials, and especially medical lab-on-a-chip devices.

Surface reactions play an important role in the manufacture of microelectronic devices. One of the single most important developments of the twentieth century was the invention of the integrated circuit. Advances in the development of integrated circuitry have led to the production of circuits that can be placed on a single semiconductor chip the size of a pinhead and perform a wide variety of tasks by controlling the electron flow through a vast network of channels. These channels, which are made from semiconductors such as silicon, gallium arsenide, indium phosphide, and germanium, have led to the development of a multitude of novel microelectronic devices. Examples of microelectronic sensing devices manufactured using chemical reaction engineering principles are shown in the left-hand margin.



The manufacture of an integrated circuit requires the fabrication of a network of pathways for electrons. The principal reaction engineering steps of the fabrication process include depositing material on the surface of a material called a *substrate* (e.g., by chemical vapor deposition, abbreviated as CVD), changing the conductivity of regions of the surface (e.g., by boron doping or ion inplantation), and removing unwanted material (e.g., by etching). By applying these steps systematically, miniature electronic circuits can be fabricated on very small semiconductor chips. The fabrication of microelectronic devices may include as few as 30 or as many as 200 individual steps to produce chips with up to 10^9 elements per chip.

An abbreviated schematic of the steps involved in producing a typical metal-oxide, semiconductor, field-effect transistor (MOSFET) device is shown in Figure 10-20. Starting from the upper left, we see that single-crystal silicon ingots are grown in a Czochralski crystallizer, sliced into wafers, and chemically and physically polished. These polished wafers serve as starting materials for a variety of microelectronic devices. A typical fabrication sequence is shown for processing the wafer, beginning with the formation of an SiO_2 layer on top of the silicon. The SiO_2 layer may be formed either by oxidizing a silicon layer or by laying down a SiO_2 layer by chemical vapor deposition (CVD). Next, the wafer is masked with a polymer photoresist, a template with the pattern to be etched onto the SiO_2 layer is placed over the photoresist, and the wafer is exposed to ultraviolet irradiation. If the mask is a positive photoresist, the light will cause the exposed areas of the polymer to dissolve when the wafer is placed in the developer. On the other hand, when a negative photoresist mask is exposed to ultraviolet irradiation, cross-linking of the polymer chains occurs, and the *unexposed* areas dissolve in the developer. The undeveloped portion of the photoresist (in either case) will protect the covered areas from etching.



Chemical engineering principles are involved in virtually every step!

After the exposed areas of SiO_2 are etched to form trenches (either by wet etching or by plasma etching), the remaining photoresist is removed. Next, the wafer is placed in a furnace containing gas molecules of the desired dopant, which then diffuse into the exposed silicon. After diffusion of dopant to the desired depth in the wafer, the wafer is removed and then SiO_2 is removed by etching. The sequence of masking, etching, CVD, and metallization continues until the desired device is formed. A schematic of a final chip is

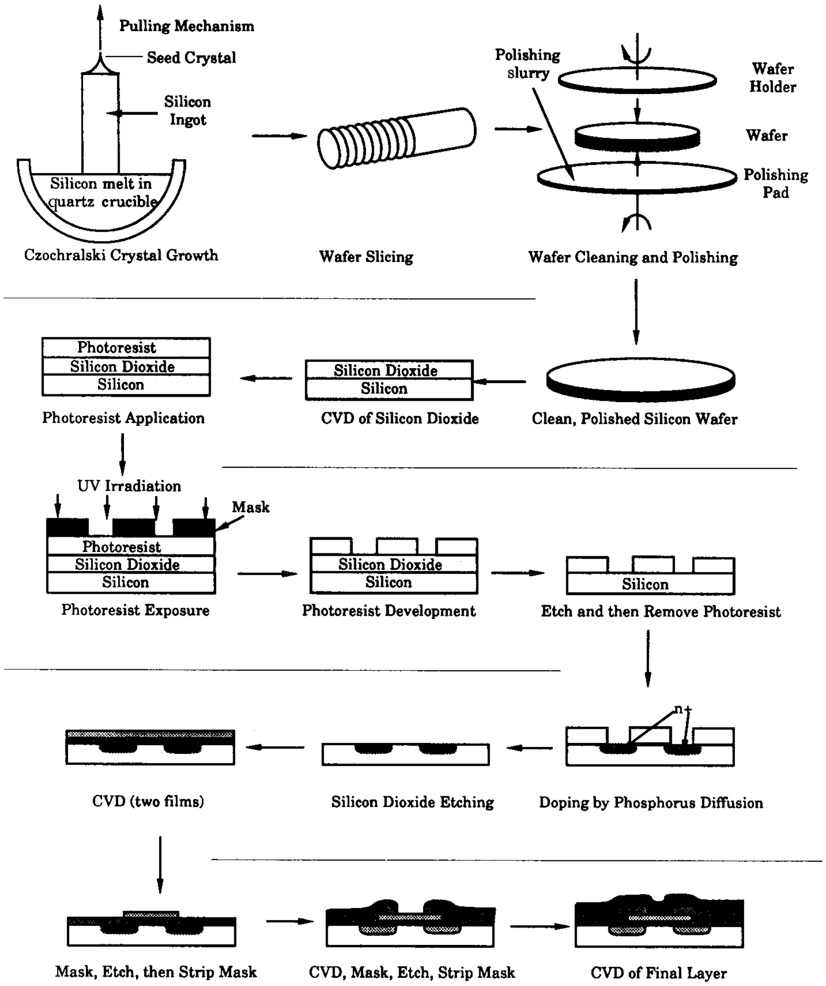


Figure 10-20 Microelectronic fabrication steps.

shown in the lower-right-hand corner of Figure 10-20. In Section 10.5.2, we discuss one of the key processing steps, CVD.

10.5.2 Chemical Vapor Deposition

The mechanisms by which CVD occurs are very similar to those of heterogeneous catalysis discussed earlier in this chapter. The reactant(s) adsorbs on the surface and then reacts on the surface to form a new surface. This process may be followed by a desorption step, depending on the particular reaction.

Ge used in solar cells

The growth of a germanium epitaxial film as an interlayer between a gallium arsenide layer and a silicon layer has received attention in the microelectronics industry.[19] 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

---

[19] H. Ishii and Y. Takahashi, *J. Electrochem. Soc.*, 135, p. 1539.

$$\text{Gas-phase dissociation:} \quad GeCl_4(g) \rightleftarrows GeCl_2(g) + Cl_2(g)$$

$$\text{Adsorption:} \quad GeCl_2(g) + S \overset{k_A}{\rightleftarrows} GeCl_2 \cdot S$$

Mechanism

$$\text{Adsorption:} \quad H_2 + 2S \overset{k_H}{\rightleftarrows} 2H \cdot S$$

$$\text{Surface reaction:} \quad GeCl_2 \cdot S + 2H \cdot S \xrightarrow{k_S} Ge(s) + 2HCl(g) + 2S$$

At first it may appear that a site has been lost when comparing the right- and left-hand sides of the surface reaction step. However, the newly formed germanium atom on the right-hand side is a site for the future adsorption of $H_2(g)$ or $GeCl_2(g)$, and there are three sites on both the right- and left-hand sides of the surface reaction step. These sites are shown schematically in Figure 10-21.

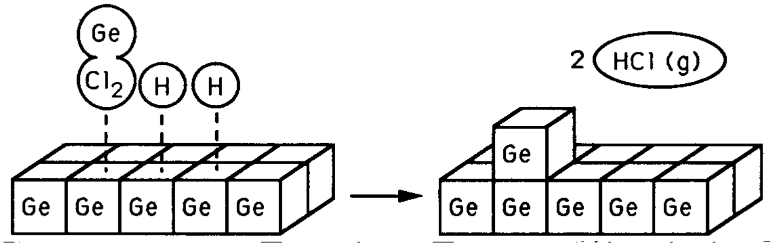


Figure 10-21 CVD surface reaction step for germanium.

The surface reaction between adsorbed molecular hydrogen and germanium dichloride is believed to be rate-limiting. The reaction follows an elementary rate law with the rate being proportional to the fraction of the surface covered by $GeCl_2$ times the square of the fraction of the surface covered by molecular hydrogen.

Rate law for rate-limiting step

$$\boxed{r''_{\text{Dep}} = k_S f_{\text{GeCl}_2} f_H^2} \tag{10-82}$$

where r''_{Dep} = deposition rate per unit surface area, nm/s
k_S = surface specific reaction rate, nm/s
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 nanometers per second and is easily converted to a molar rate ($\text{mol/m}^2 \cdot \text{s}$) by multiplying by the molar density of solid germanium (mol/m^3).

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., the fraction of the surface that is vacant, f_v). The total fraction of surface available for adsorption should, of course, add up to 1.0.

Area balance

$$\text{Fractional area balance:} \quad \boxed{f_v + f_{\text{GeCl}_2} + f_H = 1} \tag{10-83}$$

We will first focus our attention on the adsorption of $GeCl_2$. The rate of jumping on to the surface is proportional to the partial pressure of $GeCl_2$, P_{GeCl_2}, and the fraction of the surface that is vacant, f_v. The net rate of $GeCl_2$ adsorption is

$$r_{AD} = k_A \left(f_v P_{GeCl_2} - \frac{f_{GeCl_2}}{K_A} \right) \tag{10-84}$$

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

Adsorption of $GeCl_2$ not rate-limiting

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

Solving Equation (10-84) for the fractional surface coverage of $GeCl_2$ gives

$$\boxed{f_{GeCl_2} = f_v K_A P_{GeCl_2}} \tag{10-85}$$

For the dissociative adsorption of hydrogen on the Ge surface, the equation analogous to Equation (10-84) is

$$r_{ADH_2} = k_H \left(P_{H_2} f_v^2 - \frac{f_H^2}{K_H} \right) \tag{10-86}$$

Since the surface reaction is rate-limiting

Adsorption of H_2 is not rate-limiting

$$\frac{r_{ADH_2}}{k_H} \approx 0$$

Then

$$\boxed{f_H = f_v \sqrt{K_H P_{H_2}}} \tag{10-87}$$

Recalling the rate of deposition of germanium, we substitute for f_{GeCl_2} and f_H in Equation (10-82) to obtain

$$r''_{Dep} = f_v^3 k_S K_A P_{GeCl_2} K_H P_{H_2} \tag{10-88}$$

We solve for f_v in an identical manner to that for C_v in heterogeneous catalysis. Substituting Equations (10-85) and (10-87) into Equation (10-83) gives

$$f_v + f_v \sqrt{K_H P_{H_2}} + f_v K_A P_{GeCl_2} = 1$$

Rearranging yields

$$f_v = \frac{1}{1 + K_A P_{GeCl_2} + \sqrt{K_H P_{H_2}}} \tag{10-89}$$

Finally, substituting for f_v in Equation (10-88), we find that

$$r''_{\text{Dep}} = \frac{k_S K_H K_A P_{\text{GeCl}_2} P_{\text{H}_2}}{(1 + K_A P_{\text{GeCl}_2} + \sqrt{K_H P_{\text{H}_2}})^3}$$

and lumping K_A, K_H, and k_S into a specific reaction rate k' yields

Rate of deposition of Ge

$$\boxed{r''_{\text{Dep}} = \frac{k' P_{\text{GeCl}_2} P_{\text{H}_2}}{(1 + K_A P_{\text{GeCl}_2} + \sqrt{K_H P_{\text{H}_2}})^3}} \tag{10-90}$$

We now need to relate the partial pressure of $GeCl_2$ to the partial pressure of $GeCl_4$ in order to calculate the conversion of $GeCl_4$. If we assume that the gas-phase reaction

Equilibrium in gas phase

$$\text{GeCl}_4(g) \rightleftarrows \text{GeCl}_2(g) + \text{Cl}_2(g)$$

is in equilibrium, we have

$$K_P = \frac{P_{\text{GeCl}_2} P_{\text{Cl}_2}}{P_{\text{GeCl}_4}}$$

$$P_{\text{GeCl}_2} = \frac{P_{\text{GeCl}_4}}{P_{\text{Cl}_2}} \cdot K_P$$

and if hydrogen is weakly adsorbed $(\sqrt{K_H P_{H_2}} < 1)$, we obtain the rate of deposition as

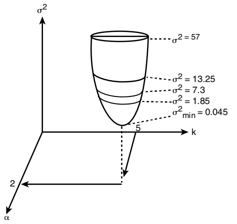
Rate of deposition of Ge when H_2 is weakly adsorbed

$$r''_{\text{Dep}} = \frac{k P_{\text{GeCl}_4} P_{\text{H}_2} P^2_{\text{Cl}_2}}{(P_{\text{Cl}_2} + K_P P_{\text{GeCl}_4})^3} \tag{10-91}$$

We now can use stoichiometry to express each of the species' partial pressures in terms of conversion and the entering partial pressure of $GeCl_4$, $P_{\text{GeCl}_{4,0}}$, and then proceed to calculate the conversion.

It should also be noted that it is possible that $GeCl_2$ may also be formed by the reaction of $GeCl_4$ and a Ge atom on the surface, in which case a different rate law would result.

10.6 Model Discrimination



Regression

We have seen that for each mechanism and each rate-limiting step we can derive a rate law. Consequently, if we had three possible mechanisms and three rate-limiting steps for each mechanism, we would have nine possible rate laws to compare with the experimental data. We will use the regression techniques discussed in Chapter 7 to identify which model equation best fits the data by choosing the one with the smaller sums of squares and/or carrying out an F-test. We could also compare the residual plots for each model, which not only show the error associated with each data point but also show if the error is randomly distributed or if there is a trend in the error. If the error is randomly distributed, this result is an additional indication that the correct rate law has been chosen.

CAUTION

We need to raise a caution here about choosing the model with the smallest sums of squares. The caution is that the model parameter values that give the smallest sum must be realistic. In the case of heterogeneous catalysis, *all values of the adsorption equilibrium constants* ***must*** *be positive*. In addition, if the temperature dependence is given, because adsorption is exothermic, the adsorption equilibrium constant must decrease with increasing temperature. To illustrate these principles, let's look at the following example.

Example 10–3 Hydrogenation of Ethylene to Ethane

The hydrogenation (H) of ethylene (E) of form ethane (EA),

$$H_2 + C_2H_4 \rightarrow C_2H_6$$

is carried out over a cobalt molybdenum catalyst [*Collect. Czech. Chem. Commun.,* 51, 2760 (1988)]. Carry out a nonlinear regression analysis on the data given in Table E10-3.1, and determine which rate law best describes the data.

Procedure
- Enter data
- Enter model
- Make initial estimates of parameters
- Run regression
- Examine parameters and variance
- Observe error distribution
- Choose model

TABLE E10-3.1 DIFFERENTIAL REACTOR DATA

Run Number	*Reaction Rate (mol/kg-cat. · s)*	P_E *(atm)*	P_{EA} *(atm)*	P_H *(atm)*
1	1.04	1	1	1
2	3.13	1	1	3
3	5.21	1	1	5
4	3.82	3	1	3
5	4.19	5	1	3
6	2.391	0.5	1	3
7	3.867	0.5	0.5	5
8	2.199	0.5	3	3
9	0.75	0.5	5	1

Determine which of the following rate laws best describes the data in Table E10-3.1.

(a) $$-r'_E = \frac{kP_EP_H}{1+K_{EA}P_{EA}+K_EP_E}$$

(c) $$-r'_E = \frac{kP_EP_H}{(1+K_EP_E)^2}$$

(b) $$-r'_E = \frac{kP_EP_H}{1+K_EP_E}$$

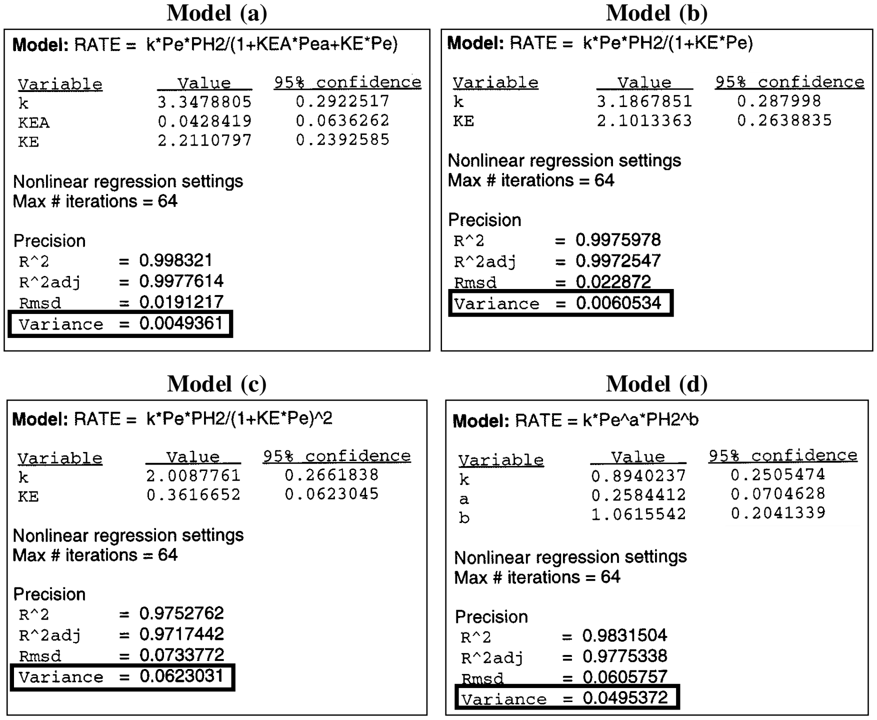
(d) $$-r'_E = kP_E^aP_H^b$$

Solution

Summary Notes

Polymath was chosen as the software package to solve this problem. The data in Table E10-3.1 were entered into the program. A screen-shot-by-screen-shot set of instructions on how to carry out the regression is given on the CRE Web site, at the end of the *Summary Notes* for Chapter 7. After entering the data and following the step-by-step procedures, the results shown in Table E10-3.2 were obtained.

TABLE E10-3.2 RESULTS OF THE POLYMATH NONLINEAR REGRESSION



Model (a)

```
Model: RATE = k*Pe*PH2/(1+KEA*Pea+KE*Pe)

Variable        Value       95% confidence
k               3.3478805     0.2922517
KEA             0.0428419     0.0636262
KE              2.2110797     0.2392585

Nonlinear regression settings
Max # iterations = 64

Precision
R^2          = 0.998321
R^2adj       = 0.9977614
Rmsd         = 0.0191217
Variance     = 0.0049361
```

Model (b)

```
Model: RATE = k*Pe*PH2/(1+KE*Pe)

Variable        Value       95% confidence
k               3.1867851     0.287998
KE              2.1013363     0.2638835

Nonlinear regression settings
Max # iterations = 64

Precision
R^2          = 0.9975978
R^2adj       = 0.9972547
Rmsd         = 0.022872
Variance     = 0.0060534
```

Model (c)

```
Model: RATE = k*Pe*PH2/(1+KE*Pe)^2

Variable        Value       95% confidence
k               2.0087761     0.2661838
KE              0.3616652     0.0623045

Nonlinear regression settings
Max # iterations = 64

Precision
R^2          = 0.9752762
R^2adj       = 0.9717442
Rmsd         = 0.0733772
Variance     = 0.0623031
```

Model (d)

```
Model: RATE = k*Pe^a*PH2^b

Variable        Value       95% confidence
k               0.8940237     0.2505474
a               0.2584412     0.0704628
b               1.0615542     0.2041339

Nonlinear regression settings
Max # iterations = 64

Precision
R^2          = 0.9831504
R^2adj       = 0.9775338
Rmsd         = 0.0605757
Variance     = 0.0495372
```

Living Example Problem

Model (a) Single site, surface-reaction, rate-limited with hydrogen weakly adsorbed

From Table E10-3.2 data, we can obtain

$$-r'_E = \frac{3.348\ P_E P_H}{1+0.043 P_{EA}+2.21\ P_E} \tag{E10-3.1}$$

We now examine the sums of squares (variance) and range of variables themselves. The sums of squares is reasonable and, in fact, the smallest of all the models at 0.0049. *However*, let's look at K_{EA}. We note that the value for the 95% confidence limit of ±0.0636 is greater than the nominal value of $K_{EA} = 0.043$ atm^{-1} itself (i.e., $K_{EA} = 0.043 \pm 0.0636$). The 95% confidence limit means that if the experiment were run 100 times and then 95 times it would fall within the range
$(-0.021) < K_{EA} < (0.1066)$. Because K_{EA} can never be negative, we are going to reject this model. Consequently, we set $K_{EA} = 0$ and proceed to Model (b).

Model (b) Single site, surface-reaction, rate-limited with ethane and hydrogen weakly adsorbed

From Table E10-3.2 we can obtain

$$-r'_E = \frac{3.187\ P_E P_H}{1+2.1\ P_E} \tag{E10-3.2}$$

The value of the adsorption constant $K_E = 2.1$ atm^{-1} is reasonable and is not negative within the 95% confidence limit. Also, the variance is small at $\sigma_B^2 = 0.0061$.

Model (c) Dual site, surface-reaction, rate-limited with hydrogen and ethane weakly adsorbed

From Table E10-3.2 we can obtain

$$-r'_E = \frac{2.0\ P_E P_{H_2}}{(1+0.036\ P_E)^2} \tag{E10-3.3}$$

While K_E is small, it never goes negative within the 95% confidence interval. The variance of this model at $\sigma_C^2 = 0.0623$ is much larger than the other models. Comparing the variance of model **(c)** with model **(b)**

$$\frac{\sigma_C^2}{\sigma_B^2} = \frac{0.0623}{0.0061} = 10.2$$

We see that the σ_C^2 is an order of magnitude greater than σ_B^2, and therefore we eliminate model **(c)**.[20]

Model (d) Empirical

Similarly for the power law model, we obtain from Table E10-3.2

$$-r'_E = 0.894\ P_E^{0.26} P_{H_2}^{1.06} \tag{E10-3.4}$$

As with model **(c)**, the variance is quite large compared to model **(b)**

$$\frac{\sigma_D^2}{\sigma_B^2} = \frac{0.049}{0.0061} = 8.03$$

So we also eliminate model (**d**). For heterogeneous reactions, Langmuir-Hinshelwood rate laws are preferred over power-law models.

Analysis: *Choose the Best Model.* In this example, we were presented with four rate laws and were asked which law best fits the data. Because all the parameter values are realistic for **model (b)** and the sums of squares are significantly smaller for **model (b)** than for the other models, we choose **model (b)**. We note again that there is a caution we need to point out regarding the use of regression! One cannot simply carry out a regression and then choose the model with the lowest value of the sums of squares. If this were the case, we would have chosen **model (a)**, which had the smallest sums of squares of all the models with $\sigma^2 = 0.0049$. However, one must consider the physical realism of the parameters in the model. In **model (a)** the 95% confidence interval was greater than the parameter itself, thereby yielding negative values of the parameter, K_{AE}, which is physically impossible.

10.7 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

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[20] See G. F. Froment and K. B. Bishoff, *Chemical Reaction Analysis and Design*, 2nd ed. (New York: Wiley, 1990), p. 96.

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, to explain and model catalyst deactivation.[21]

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. *However, please don't worry,* 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 *nonseparable kinetics*. In separable kinetics, we separate the rate law and activity

$$\text{Separable kinetics: } -r'_A = a(\text{Past history}) \times -r'_A \text{ (Fresh catalyst)}$$

When the kinetics and activity are separable, it is possible to study catalyst decay and reaction kinetics independently. However, nonseparability

$$\text{Nonseparable kinetics: } -r'_A = -r'_A \text{ (Past history, fresh catalyst)}$$

must be accounted for by assuming the existence of a nonideal surface or by describing deactivation by a mechanism composed of several elementary steps.[22]

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 ($t = 0$):

$a(t)$: catalyst activity

$$\boxed{a(t) = \frac{-r'_A(t)}{-r'_A(t=0)}} \tag{10-92}$$

Because of the catalyst decay, the activity decreases with time and a typical curve of the activity as a function of time is shown in Figure 10-22.

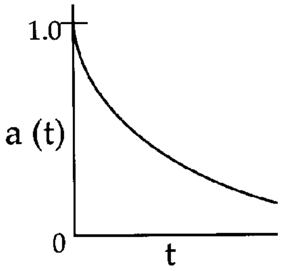

Figure 10-22 Activity as a function of time.

Combining Equations (10-92) and (3-2), the rate of disappearance of reactant A on a catalyst that has been utilized for a time t is

Reaction rate law accounting for catalyst activity

$$\boxed{-r'_A = a(t)k(T)\,\text{fn}(C_A, C_B, \ldots, C_P)} \tag{10-93}$$

---

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

[22] D. T. Lynch and G. Emig, *Chem. Eng. Sci.*, 44(6), 1275–1280 (1989).

where $a(t)$ = catalytic activity, time-dependent
$k(T)$ = specific reaction rate, temperature-dependent
C_i = gas-phase concentration of reactants, products, or contaminant

The rate of catalyst decay, r_d, can be expressed in a rate law analogous to Equation (10-93)

Catalyst decay rate law

$$r_d = -\frac{da}{dt} = p[a(t)]k_d(T)h(C_A, C_B, \ldots, C_P) \tag{10-94}$$

e.g., $p[a(t)] = [a(t)]^2$

where $p[a(t)]$ is some function of the catalyst activity, k_d is the specific decay constant, and $h(C_i)$ is the functionality of rate of decay, r_d, on the reacting species concentrations. For the cases presented in this chapter, this functionality either will be independent of concentration (i.e., $h = 1$) or will be a linear function of species concentration (i.e., $h = C_i$).

The functionality of the activity term, $p[a(t)]$, in the decay law can take a variety of forms. For example, for a first-order decay

$$p(a) = a \tag{10-95}$$

and for a second-order decay

$$p(a) = a^2 \tag{10-96}$$

The particular function, $p(a)$, will vary with the gas catalytic system being used and the reason or mechanism for catalytic decay.

10.7.1 Types of Catalyst Deactivation

- Sintering
- Fouling
- Poisoning

There are three categories into which the loss of catalytic activity can traditionally be divided: sintering or aging, fouling or coking, and poisoning.

Deactivation by Sintering (Aging).[23] Sintering, also referred to as aging, is the loss of catalytic activity due to a loss of active surface area resulting from the prolonged exposure to high gas-phase temperatures. The active surface area may be lost either by crystal agglomeration and growth of the metals deposited on the support or by narrowing or closing of the pores inside the catalyst pellet. A change in the surface structure may also result from either surface recrystallization or the formation or elimination of surface defects (active sites). The reforming of heptane over platinum on alumina is an example of catalyst deactivation as a result of sintering.

Figure 10-23 shows the loss of surface area resulting from the flow of the solid porous catalyst support at high temperatures to cause pore closure. Figure 10-24 shows the loss of surface area by atomic migration and agglomeration of small metal sites deposited on the surface into a larger site where the interior

The catalyst support becomes soft and flows, resulting in pore closure.

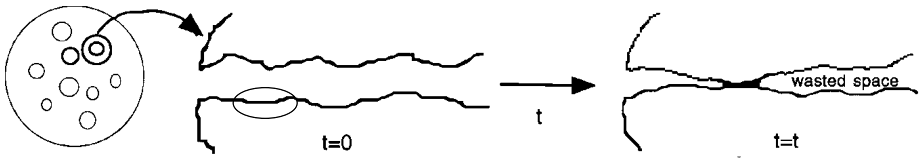

Figure 10-23 Decay by sintering: pore closure; loss of reactive surface area.

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[23] See G. C. Kuczynski, ed., *Sintering and Catalysis*, vol. 10 of *Materials Science Research* (New York: Plenum Press, 1975).

The atoms move along the surface and agglomerate.

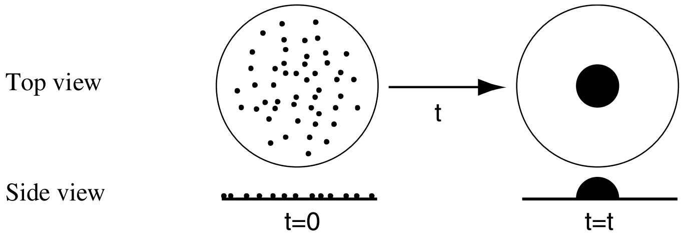


Figure 10-24 Decay by sintering: agglomeration of deposited metal sites; loss of reactive surface area.

atoms are not accessible to the reaction. Sintering is usually negligible at temperatures below 40% of the melting temperature of the solid.[24]

Deactivation by sintering may in some cases be a function of the mainstream gas concentration. Although other forms of the sintering decay rate laws exist, one of the most commonly used decay laws is second order with respect to the present activity

$$r_d = k_d a^2 = -\frac{da}{dt} \tag{10-97}$$

Integrating, with $a = 1$ at time $t = 0$, yields

Sintering: second-order decay

$$\boxed{a(t) = \frac{1}{1 + k_d t}} \tag{10-98}$$

The amount of sintering is usually measured in terms of the active surface area of the catalyst S_a

$$S_a = \frac{S_{a0}}{1 + k_d t} \tag{10-99}$$

The sintering decay constant, k_d, follows the Arrhenius equation

$$\boxed{k_d = k_d(T_0)\exp\left[\frac{E_d}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]} \tag{10-100}$$

Minimizing sintering

The decay activation energy, E_d, for the reforming of heptane on Pt/Al_2O_3 is on the order of 70 kcal/mol, which is rather high. As mentioned earlier, sintering can be reduced by keeping the temperature below 0.3 to 0.4 times the metal's melting point.

We will now stop and consider reactor design for a fluid–solid system with decaying catalyst. To analyze these reactors, we only add one step to our algorithm; that is, determine the catalyst decay law. The sequence is shown here.

The algorithm

Mole balance ⟶ Reaction rate law ⟶ *Decay rate law* ⟶
Stoichiometry ⟶ Combine and solve ⟶ Numerical techniques

---

[24] R. Hughes, *Deactivation of Catalysts* (San Diego: Academic Press, 1984).

Example 10–4 Calculating Conversion with Catalyst Decay in Batch Reactors

The first-order isomerization

$$A \longrightarrow B$$

is being carried out isothermally in a batch reactor on a catalyst that is decaying as a result of aging. Derive an equation for conversion as a function of time.

Solution

1. **Mol Balance:**

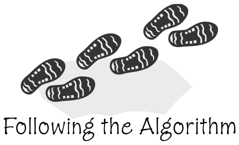
$$N_{A0} = \frac{dX_d}{dt} = -r'_A W \qquad \text{(E10-4.1)}$$

where X_d is the conversion of A when the catalyst is decaying.

2. **Reaction-Rate Law:**

$$-r'_A = k'a(t)\,C_A \qquad \text{(E10-4.2)}$$

One extra step (number 3) is added to the algorithm.



3. **Decay Law:** For second-order decay by sintering:

$$\boxed{a(t) = \frac{1}{1+k_d t}} \qquad \text{(10-98)}$$

4. **Stoichiometry:**

$$C_A = C_{A0}(1 - X_d) = \frac{N_{A0}}{V}(1 - X_d) \qquad \text{(E10-4.3)}$$

5. **Combining** gives us

$$\frac{dX_d}{dt} = k'(1-X_d)a\frac{W}{V} \qquad \text{(E10-4.4)}$$

Let $k = k'W/V$. Substituting for catalyst activity a, we have

$$\boxed{\frac{dX_d}{dt} = k(1-X_d)a = k\frac{(1-X_d)}{(1+k_d t)}} \qquad \text{(E10-4.5)}$$

where X_d is the conversion when there is decay. We want to compare the conversion with and without catalyst decay.

For no decay $k_d = 0$

$$\frac{dX}{dt} = k(1-X)$$

The Polymath program and a comparison of the conversion with decay X_d and without decay X are shown below.

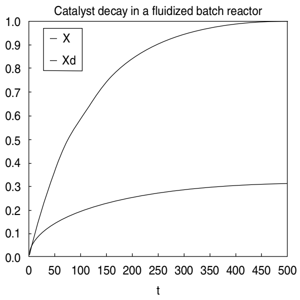
POLYMATH Report
Ordinary Differential Equations

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	k	0.01	0.01
2	kd	0.1	0.1
3	t	0	500.
4	X	0	0.9932621
5	Xd	0	0.2013514

Differential equations
1 d(x)/d(t) = k*(1-X)
2 d(Xd)/d(t) = k*(1-X)/(1+kd*t)

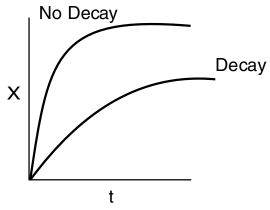
Explicit equations
1 k = .01
2 kd = .1



One can also obtain an analytical solution for this reaction order and low decay. Separating variables and integrating yields

$$\int_0^X \frac{dX_d}{1-X_d} = k\int_0^t \frac{dt}{1+k_d t} \tag{E10-4.6}$$

$$\boxed{\ln\frac{1}{1-X_d} = \frac{k}{k_d}\ln(1+k_d t)} \tag{E10-4.7}$$



6. **Solving** for the conversion X_d at any time t, we find that

$$X_d = 1 - \frac{1}{(1+k_d t)^{k/k_d}} \tag{E10-4.8}$$

the analytical solution **without decay**

$$\boxed{\ln\frac{1}{1-X} = kt} \tag{E10-4.9}$$

Analysis: One observes that for long times the conversion with decay approaches a rather flat plateau and reaches conversion of about 30%. This is the conversion that will be achieved in a batch reactor for a first-order reaction when the catalyst decay law is second order. By comparison, we obtain virtually complete conversion in 500 minutes when there is no decay. The purpose of this example was to demonstrate the algorithm for isothermal catalytic reactor design for a decaying catalyst. In problem P10-1$_B$(d) you are asked to sketch the temperature–time trajectories for various values of k and k_d.

Deactivation by Coking or Fouling. This mechanism of decay (see Figures 10-25 and 10-26) is common to reactions involving hydrocarbons. It results from a carbonaceous (coke) material being deposited on the surface of a catalyst.

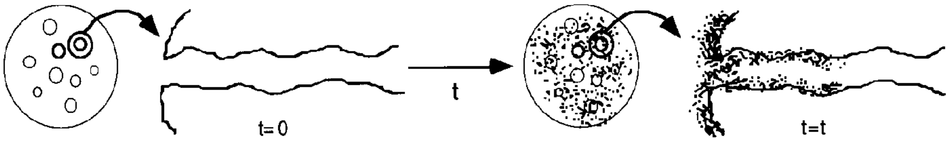
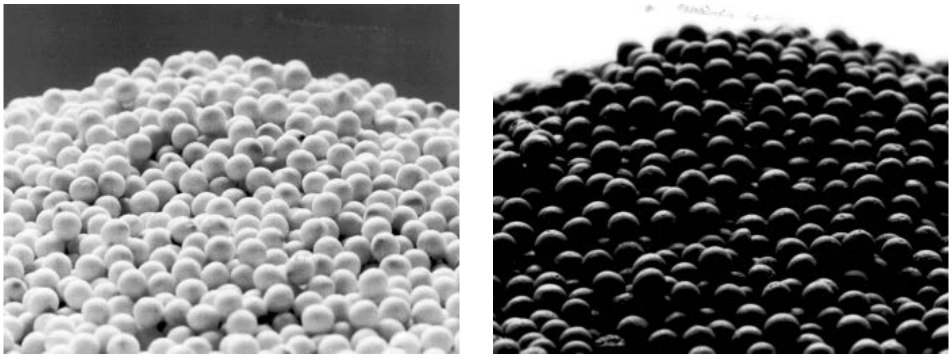


Figure 10-25 Schematic of decay by coking; loss of reactive surface area.



(a) Fresh catalyst (b) Spent catalyst

Figure 10-26 Decay by coking. (Photos courtesy of Engelhard catalyst, copyright by Michael Gaffney Photographer, Mendham, NJ.)

The amount of coke on the surface after a time t has been found to obey the following empirical relationship

$$\boxed{C_C = At^n} \qquad (10\text{-}101)$$

where C_C is the concentration of carbon on the surface (g/m^2) and n and A are fouling parameters, which can be functions of the feed rate. This expression was originally developed by Voorhies and has been found to hold for a wide variety of catalysts and feed streams.[25] Representative values of A and n for the cracking of East Texas light gas oil yield[26]

$$\%\ \text{coke} = 0.47\sqrt{t(\text{min})}$$

Different functionalities between the activity and amount of coke on the surface have been observed. One commonly used form is

$$a = \frac{1}{k_{Ck}C_C^p + 1} \qquad (10\text{-}102)$$

or, in terms of time, we combine Equations (10-101) and (10-102)

$$a = \frac{1}{k_{Ck}A^p t^{np} + 1} = \frac{1}{1 + k' t^m} \qquad (10\text{-}103)$$

For light Texas gas oil being cracked at 750°F over a synthetic catalyst for short times, the decay law is

$$\boxed{a = \frac{1}{1 + 7.6\,t^{1/2}}} \qquad (10\text{-}104)$$

where t is in seconds.

Activity for deactivation by coking

Other commonly used forms are

$$a = e^{-\alpha_1 C_C} \qquad (10\text{-}105)$$

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[25] A. Voorhies, *Ind. Eng. Chem.*, 37, 318 (1945).

[26] C. O. Prater and R. M. Lago, *Adv. Catal.*, 8, 293 (1956).

and

$$\boxed{a = \frac{1}{1+\alpha_2 C_C}} \qquad (10\text{-}106)$$

A dimensionless fouling correlation has been developed by Pacheco and Petersen.[27]

Minimizing coking

When possible, coking can be reduced by running at elevated pressures (2000 to 3000 kPa) and hydrogen-rich streams. A number of other techniques for minimizing fouling are discussed by Bartholomew.[28] Catalysts deactivated by coking can usually be regenerated by burning off the carbon.

Deactivation by Poisoning. Deactivation by this mechanism occurs when the poisoning molecules become irreversibly chemisorbed to active sites, thereby reducing the number of sites available for the main reaction. The poisoning molecule, P, may be a reactant and/or a product in the main reaction, or it may be an impurity in the feed stream.

It's going to cost you.

Side Note. One of the most significant examples of catalyst poisoning occurred at the gasoline pump. Oil companies found that adding lead to the gasoline increased the octane number. The television commercials said "We are going to enhance your gasoline, *but it's going to cost you* for the added tetra-ethyl lead." So for many years they used lead as an antiknock component. As awareness grew about NO, HC, and CO emission from the engine, it was decided to add a catalytic afterburner in the exhaust system to reduce these emissions. Unfortunately, it was found that the lead in the gasoline poisoned the reactive catalytic sites. So, the television commercials now said "We are going to take the lead out of gasoline but to receive the same level of performance as without lead, *but it's going to cost you* because of the added refining costs to raise the octane number." Do you think that, financially, consumers would have been better off if they never put the lead in the gasoline in the first place?

Poison in the Feed. Many petroleum feed stocks contain trace impurities such as sulfur, lead, and other components that are too costly to remove, yet poison the catalyst slowly over time. For the case of an impurity, P, in the feed stream, such as sulfur, for example, in the reaction sequence

$$\text{Main reaction:}\quad \left\{\begin{array}{lcl} A+S & \rightleftarrows & (A\cdot S) \\ A\cdot S & \rightleftarrows & (B\cdot S + C(g)) \\ B\cdot S & \rightleftarrows & (B+S) \end{array}\right\} -r'_A = a(t)\,\frac{kC_A}{1+K_AC_A+K_BC_B}$$

$$\text{Poisoning reaction:}\quad P+S \longrightarrow P\cdot S \qquad r_d = -\frac{da}{dt} = k'_d C_p^m a^q \qquad (10\text{-}107)$$

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[27] M. A. Pacheco and E. E. Petersen, *J. Catal.*, 86, 75 (1984).

[28] R. J. Farrauto and C. H. Bartholomew, *Fundamentals of Industrial Catalytic Processes, 2nd edition* (New York: Blackie Academic and Professional, 2006). This book is one of the most definitive resources on catalyst decay.

the surface sites would change with time as shown in Figure 10-27.

Progression of sites being poisoned

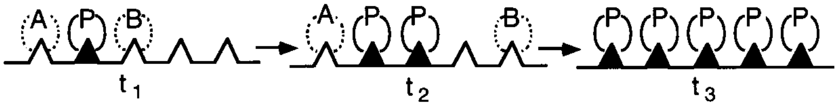

Figure 10-27 Decay by poisoning.

If we assume the rate of removal of the poison, $r_{\text{P}\cdot\text{S}}$, from the reactant gas stream onto the catalyst sites is proportional to the number of sites that are unpoisoned $(C_{t0} - C_{\text{P}\cdot\text{S}})$ and the concentration of poison in the gas phase is C_{P} then

$$r_{\text{P}\cdot\text{S}} = k_d(C_{t0} - C_{\text{P}\cdot\text{S}})C_{\text{P}}$$

where $C_{\text{P}\cdot\text{S}}$ is the concentration of poisoned sites and C_{t0} is the total number of sites initially available. Because every molecule that is adsorbed from the gas phase onto a site is assumed to poison the site, this rate is also equal to the rate of removal of total active sites (C_t) from the surface

$$-\frac{dC_t}{dt} = \frac{dC_{\text{P}\cdot\text{S}}}{dt} = r_{\text{P}\cdot\text{S}} = k_d(C_{t0} - C_{\text{P}\cdot\text{S}})C_{\text{P}}$$

Dividing through by C_{t0} and letting f be the fraction of the total number of sites that have been poisoned yields

$$\frac{df}{dt} = k_d(1 - f)C_{\text{P}} \tag{10-108}$$

The fraction of sites available for adsorption $(1 - f)$ is essentially the activity $a(t)$. Consequently, Equation (10-108) becomes

$$\boxed{-\frac{da}{dt} = a(t)k_dC_{\text{P}}} \tag{10-109}$$

A number of examples of catalysts with their corresponding catalyst poisons are given by Farrauto and Bartholomew.[29]

Packed-Bed Reactors. In packed-bed reactors where the poison is removed from the gas phase by being adsorbed on the specific catalytic sites, the deactivation process can move through the packed bed as a wave front. Here, at the start of the operation, only those sites near the entrance to the reactor will be deactivated because the poison (which is usually present in trace amounts) is removed from the gas phase by the adsorption; consequently, the catalyst sites farther down the reactor will not be affected. However, as time continues, the sites near the entrance of the reactor become saturated, and the poison must travel farther downstream before being adsorbed (removed) from the gas phase and attaching to a site to deactivate it. Figure 10-28 shows the corresponding activity profile for this type of poisoning process. We see in Figure 10-28 that by time t_4 the entire bed has become deactivated. The corresponding overall conversion at the exit of the reactor might vary with time as shown in Figure 10-29.

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[29] Ibid.

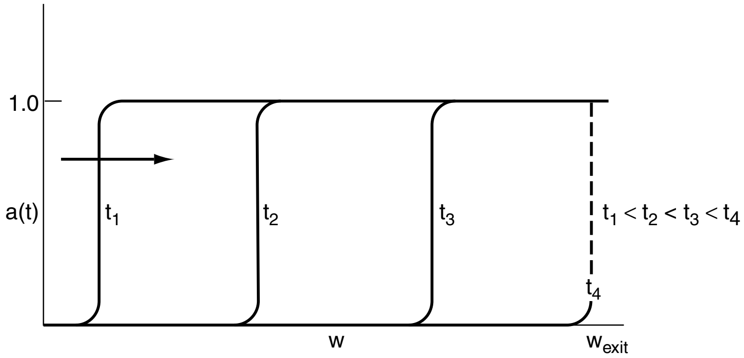


Figure 10-28 Movement of activity front in a packed bed.

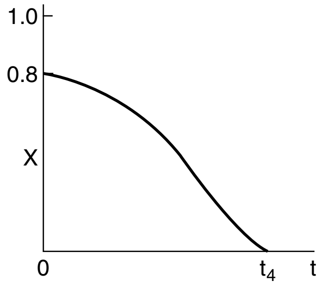


Figure 10-29 Exit conversion as a function of time.

Summary Notes

The partial differential equations that describe the movement of the reaction front shown in Figure 10-28 are derived and solved in an example on the CRE Web site, at the very end of the *Summary Notes* for Chapter 10.

Poisoning by Either Reactants or Products. For the case where the main reactant also acts as a poison, the rate laws are

Main reaction: $A+S \longrightarrow B+S \qquad -r'_A = k_A C_A^n$

Poisoning reaction: $A+S \longrightarrow A \cdot S \qquad r_d = k'_d C_A^m a^q$

An example where one of the reactants acts as a poison is in the reaction of CO and H_2 over ruthenium to form methane, with

$$-r_{CO} = ka(t)C_{CO}$$

$$-\frac{da}{dt} = r_d = k'_d a(t)\, C_{CO}$$

Similar rate laws can be written for the case when the product B acts as a poison.

For *separable deactivation kinetics* resulting from contacting a poison at a constant concentration C_{P_0} and no spatial variation

Separable deactivation kinetics

$$\boxed{-\frac{da}{dt} = r_d = k'_d C_{P_0}^n a^n(t) = k_d a^n} \qquad (10\text{-}110)$$

The solution to this equation for the case of first-order decay, n = 1

$$-\frac{da}{dt} = k_d a \tag{10-111}$$

is

$$a = e^{-k_d t} \tag{10-112}$$

Empirical Decay Laws. Table 10-7 gives a number of empirical decay laws along with the reaction systems to which they apply.

Examples of reactions with decaying catalysts and their decay laws

TABLE 10-7 DECAY RATE LAWS

Functional Form of Activity	*Decay Reaction Order*	*Differential Form*	*Integral Form*	*Examples*
Linear	0	$-\frac{da}{dt} = \beta_0$	$a = 1 - \beta_0 t$	Conversion of *para*-hydrogen on tungsten when poisoned with oxygen[a*]
Exponential	1	$-\frac{da}{dt} = \beta_1 a$	$a = e^{-\beta_1 t}$	Ethylene hydrogenation on Cu poisoned with CO[b] Paraffin dehydrogenation on $Cr \cdot Al_2O_3$[c] Cracking of gas oil[d] Vinyl chloride monomer formation[e]
Hyperbolic	2	$-\frac{da}{dt} = \beta_2 a^2$	$\frac{1}{a} = 1 + \beta_2 t$	Vinyl chloride monomer formation[f] Cyclohexane dehydrogenation on Pt/Al_2O_3[g] Isobutylene hydrogenation on Ni[h]
Reciprocal power	$\frac{\beta_3 + 1}{\beta_3} = \gamma$	$-\frac{da}{dt} = \beta_3 a^n A_0^{1/5}$	$a = A_0 t^{-\beta_3}$	Cracking of gas oil and gasoline on clay[i]
	$\frac{\beta_4 + 1}{\beta_4} = n$	$-\frac{da}{dt} = \beta_4 a^n A_0^{1/5}$	$a = A_0 t^{-\beta_4}$	Cyclohexane aromatization on NiAl[j]

[*a] D. D. Eley and E. J. Rideal, *Proc. R. Soc. London*, A178, 429 (1941).
[b] R. N. Pease and L. Y. Steward, *J. Am. Chem. Soc.*, 47, 1235 (1925).
[c] E. F. K. Herington and E. J. Rideal, *Proc. R. Soc. London*, A184, 434 (1945).
[d] V. W. Weekman, *Ind. Eng. Chem. Process Des. Dev.*, 7, 90 (1968).
[e] A. F. Ogunye and W. H. Ray, *Ind. Eng. Chem. Process Des. Dev.*, 9, 619 (1970).
[f] A. F. Ogunye and W. H. Ray, *Ind. Eng. Chem. Process Des. Dev.*, 10, 410 (1971).
[g] H. V. Maat and L. Moscou, *Proc. 3rd lnt. Congr. Catal.* (Amsterdam: North-Holland, 1965), p. 1277.
[h] A. L. Pozzi and H. F. Rase, *Ind. Eng. Chem.*, 50, 1075 (1958).
[i] A. Voorhies, Jr., *Ind. Eng. Chem.*, 37, 318 (1945); E. B. Maxted, *Adv. Catal.*, 3, 129 (1951).
[j] C. G. Ruderhausen and C. C. Watson, *Chem. Eng. Sci.*, 3, 110 (1954).
Source: J. B. Butt, Chemical Reactor Engineering–Washington, *Advances in Chemistry Series* 109 (Washington, D.C.: American Chemical Society, 1972), p. 259. Also see CES 23, 881(1968).

Key resource for catalyst deactivation

One should also see *Fundamentals of Industrial Catalytic Processes,* by Farrauto and Bartholomew, which contains rate laws similar to those in Table 10-7, and also gives a comprehensive treatment of catalyst deactivation.[30]

10.7.2 Reactors That Can Be Used to Help Offset Catalyst Decay

We will now consider three reaction systems that can be used to handle systems with decaying catalyst. We will classify these systems as those having slow, moderate, and rapid losses of catalytic activity. To offset the decline in chemical reactivity of decaying catalysts in continuous-flow reactors, the following three methods are commonly used:

Matching the reactor type with speed of catalyst decay

- Slow decay – *Temperature–Time Trajectories* (10.7.3)
- Moderate decay – *Moving-Bed Reactors* (10.7.4)
- Rapid decay – *Straight-Through Transport Reactors* (10.7.5)

10.7.3 Temperature–Time Trajectories

In many large-scale reactors, such as those used for hydrotreating, and reaction systems where deactivation by poisoning occurs, the catalyst decay is relatively slow. In these continuous flow systems, constant conversion is usually necessary in order that subsequent processing steps (e.g., separation) are not upset. One way to maintain a constant conversion with a decaying catalyst in a packed or fluidized bed is to increase the reaction rate by steadily increasing the feed temperature to the reactor. Operation of a "fluidized" bed in this manner is shown in Figure 10-30.

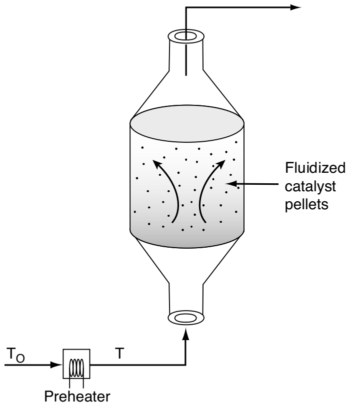


Figure 10-30 Reactor with preheater to continually increase feed temperature.

We are going to increase the feed temperature in such a manner that the reaction rate remains constant with time:

$$-r'_A(t = 0, T_0) = -r'_A(t, T) = a(t, T)[-r'_A(t = 0, T)]$$

For a first-order reaction we have

$$k(T_0)C_A = a(t, T)k(T)C_A$$

---

[30] Ibid.

Slow rate of catalyst decay

We will neglect any variations in concentration so that the product of the activity (a) and specific reaction rate (k) is constant and equal to the specific reaction rate, k_0 at time $t = 0$ and temperature T_0; that is

$$k(T)a(t, T) = k_0 \tag{10-113}$$

The goal is to find *how* the temperature should be increased with time (i.e., the temperature–time trajectory) to maintain constant conversion. Using the Arrhenius equation to substitute for k in terms of the activation energy, E_A, gives

$$k_0 e^{(E_A/R)(1/T_0 - 1/T)}\, a = k_0 \tag{10-114}$$

Gradually raising the temperature can help offset effects of catalyst decay.

Solving for $1/T$ yields

$$\boxed{\frac{1}{T} = \frac{R}{E_A}\ln a + \frac{1}{T_0}} \tag{10-115}$$

The decay law also follows an Arrhenius-type temperature dependence

$$-\frac{da}{dt} = k_{d0} e^{(E_d/R)(1/T_0 - 1/T)}\, a^n \tag{10-116}$$

where k_{d0} =decay constant at temperature T_0, s^{-1}
E_A = activation energy for the main reaction (e.g., A → B), kJ/mol
E_d = activation energy for catalyst decay, kJ/mol

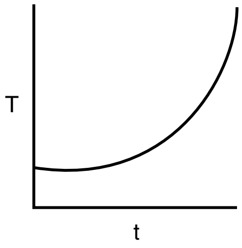
Substituting Equation (10-115) into (10-116) and rearranging yields

$$-\frac{da}{dt} = k_{d0}\exp\left(-\frac{E_d}{E_A}\ln a\right)a^n = k_{d0}a^{(n - E_d/E_A)} \tag{10-117}$$

Integrating with $a = 1$ at $t = 0$ for the case $n \neq (1 + E_d/E_A)$, we obtain

$$t = \frac{1 - a^{1-n+E_d/E_A}}{k_{d0}(1 - n + E_d/E_A)} \tag{10-118}$$

Solving Equation (10-114) for a and substituting in (10-118) gives

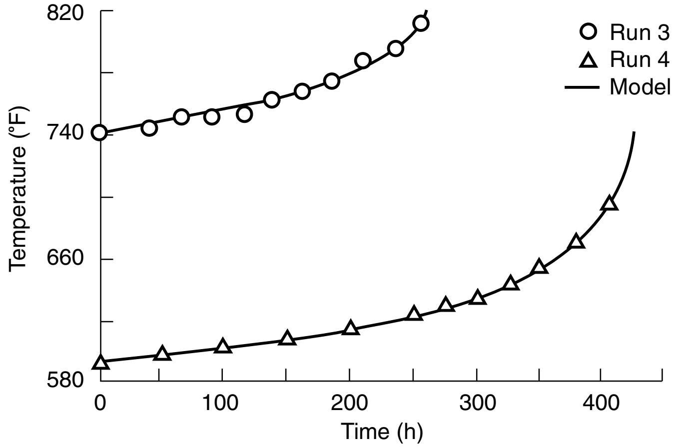


$$\boxed{t = \frac{1 - \exp\left[\frac{E_A - nE_A + E_d}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]}{k_{d0}(1 - n + E_d/E_A)}} \tag{10-119}$$

Equation (10-119) tells us how the temperature of the catalytic reactor should be increased with time in order for the reaction rate to remain constant.

In many industrial reactions, the decay rate law changes as temperature increases. In hydrocracking, the temperature–time trajectories are divided into three regimes. Initially, there is fouling of the acidic sites of the catalyst followed by a linear regime due to slow coking and, finally, accelerated coking characterized by an exponential increase in temperature. The temperature–time trajectory for a deactivating hydrocracking catalyst is shown in Figure 10-31.

Comparing theory and experiment



Run	E_A (cal/mol)	A (h^{-1})	E_d (cal/mol)	A_d (h^{-1})
3	30.0	0.52×10^{12}	42.145	1.54×10^{11}
4	30.0	0.52×10^{12}	37.581	2.08×10^{11}

Figure 10-31 Temperature–time trajectories for deactivating hydrocracking catalyst, runs 3 and 4. (Krishnaswamy, S., and J. R. Kittrell. Analysis of Temperature–Time Data for Deactivating Catalysts. *Industry and Engineering Chemistry Process Design and Development*, 1979, 18(3), 399–403. Copyright © 1979, American Chemical Society. Reprinted by permission.)

For a first-order decay, Krishnaswamy and Kittrell's expression, Equation (10-119), for the temperature–time trajectory reduces to

$$t = \frac{E_A}{k_{d0}E_d}\left[1 - e^{(E_d/R)(1/T - 1/T_0)}\right] \tag{10-120}$$

10.7.4 Moving-Bed Reactors

Reaction systems with significant catalyst decay require the continual regeneration and/or replacement of the catalyst. Two types of reactors currently in commercial use that accommodate production with decaying catalysts are the moving-bed and straight-through transport reactor. A schematic diagram of a moving-bed reactor (used for catalytic cracking) is shown in Figure 10-32.

The freshly regenerated catalyst enters the top of the reactor and then moves through the reactor as a compact packed bed. The catalyst is coked continually as it moves through the reactor until it exits the reactor into the kiln, where air is used to burn off the carbon. The regenerated catalyst is lifted from the kiln by an airstream and then fed into a separator before it is returned to the reactor. The catalyst pellets are typically between one-quarter and one-eighth in. in diameter.

The reactant feed stream enters at the top of the reactor and flows rapidly through the reactor relative to the flow of the catalyst through the reactor (Figure 10-33). If the feed rates of the catalyst and the reactants do not vary

Moving bed reactor, used for reactions with moderate rate of catalyst decay

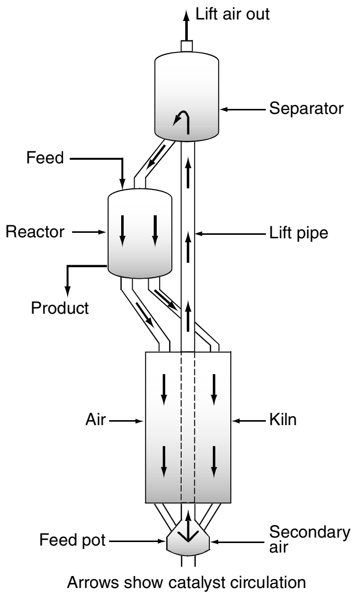


Figure 10-32 Thermofor catalytic cracking (TCC) unit. (Weekman, V. *AIChE Monogr. Ser.*, 75(11), 4 (1979). With permission of the American Institute of Chemical Engineers. Copyright © 1979 AIChE. All rights reserved.)

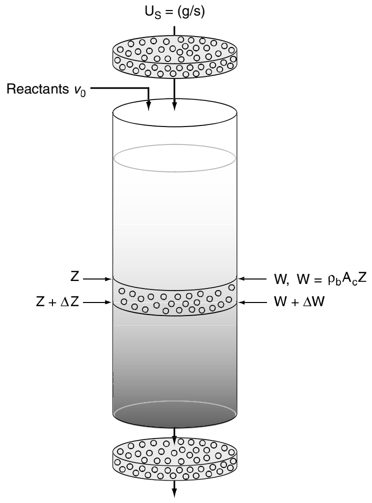


Figure 10-33 Moving-bed reactor schematic. The value of the catalyst contained in a reactor of this type is approximately $1 million.

with time, the reactor operates at steady state; that is, conditions at any point in the reactor do not change with time. The mole balance on reactant A over ΔW is

$$\begin{array}{ccccccc} \begin{bmatrix} \text{Molar} \\ \text{flow} \\ \text{rate of A in} \end{bmatrix} & - & \begin{bmatrix} \text{Molar} \\ \text{flow} \\ \text{rate of A out} \end{bmatrix} & + & \begin{bmatrix} \text{Molar} \\ \text{rate of} \\ \text{generation of A} \end{bmatrix} & = & \begin{bmatrix} \text{Molar} \\ \text{rate of} \\ \text{accumulation of A} \end{bmatrix} \\ F_A(W) & - & F_A(W+\Delta W) & + & r'_A \Delta W & = & 0 \end{array} \tag{10-121}$$

Dividing by ΔW, letting ΔW approach zero, and expressing the flow rate in terms of conversion gives

Mole Balance

$$F_{A0}\frac{dX}{dW} = -r'_A \tag{2-17}$$

The rate of reaction at any time t is

$$-r'_A = a(t)[-r'_A(t=0)] = a(t)[k\,\text{fn}(C_A, C_B, \ldots, C_P)] \tag{10-93}$$

The activity, as before, is a function of the time the catalyst has been in contact with the reacting gas stream. The decay rate law is

Decay Law

$$-\frac{da}{dt} = k_d a^n \tag{10-110}$$

We now need to relate the contact time to the weight of the catalyst. Consider a point z in the reactor, where the reactant gas has passed cocurrently through a catalyst weight W. Because the solid catalyst is moving through the bed at a rate U_s (mass per unit time), the time t that the catalyst has been in contact with the gas when the catalyst reaches a point z is

$$t = \frac{W}{U_s} \tag{10-122}$$

If we now differentiate Equation (10-122)

$$dt = \frac{dW}{U_s} \tag{10-123}$$

and combine it with the decay rate law, we obtain

$$\boxed{-\frac{da}{dW} = \frac{k_d}{U_s} a^n} \tag{10-124}$$

The activity equation is combined with the mole balance

The design equation for moving-bed reactors

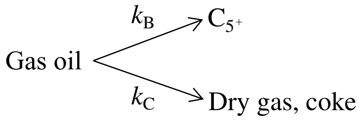
$$\boxed{\frac{dX}{dW} = \frac{a[-r'_A(t=0)]}{F_{A0}}} \tag{10-125}$$

these two coupled differential equations (i.e., Equations (10-124) and (10-125)) are numerically solved simultaneously with an ODE solver, e.g., Polymath.

Living Example Problem

Example 10–5 Catalytic Cracking in a Moving-Bed Reactor

The catalytic cracking of a gas-oil charge, A, to form C_5+ (B) and to form coke and dry gas (C) is to be carried out in a screw-type conveyor, moving-bed reactor at 900°F:



This cracking of gas oil can also be written as

$$\text{A} \xrightarrow{k_1} \text{Products}$$

While pure hydrocarbons are known to crack according to a first-order rate law, the fact that the gas-oil exhibits a wide spectrum of cracking rates gives rise to the fact that the lumped cracking rate is well represented by a second-order rate law (see Web Problem CDP5-H_B) with the following specific reaction rate:[31]

$$-r'_A = 600 \, \frac{(\text{dm})^6}{(\text{kg cat})(\text{mol})(\text{min})} \, C_A^2$$

The catalytic deactivation is independent of gas-phase concentration and follows a first-order decay rate law, with a decay constant, k_d of 0.72 reciprocal minutes. The feed stream is diluted with nitrogen so that as a first approximation,

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[31] Estimated from V. W. Weekman and D. M. Nace, *AIChE J.*, *16*, 397 (1970).

volume changes can be neglected with reaction. The reactor contains 22 kg of catalyst that moves through the reactor at a rate of 10 kg/min. The gas-oil is fed at a rate of 30 mol/min at a concentration of 0.075 mol/dm^3. Determine the conversion that can be achieved in this reactor.

Solution

1. **Mole Balance:**

$$F_{A0}\frac{dX}{dW} = a(-r'_A) \tag{E10-5.1}$$

2. **Rate Law:**

$$-r'_A = kC_A^2 \tag{E10-5.2}$$

3. **Decay Law.** First-order decay

$$-\frac{da}{dt} = k_d a$$

Moving beds: moderate rate of catalyst decay

Using Equation (10-124), we obtain

$$-\frac{da}{dW} = \frac{k_d}{U_s}a \tag{E10-5.3}$$

Integrating

$$a = e^{-(k_d/U_s)W} \tag{E10-5.4}$$

4. **Stoichiometry.** If $v \approx v_0$, then

$$C_A = C_{A0}(1-X) \tag{E10-5.5}$$

5. **Combining** we have

$$\frac{dX}{dt} = a\frac{kC_{A0}^2(1-X)^2}{F_{A0}} \tag{E10-5.6}$$

$$a = e^{-(k_d/U_s)W}$$

The polymath program is shown below along with a conversion profile.

POLYMATH Report

Ordinary Differential Equations

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	a	1.	0.2051528
2	Ca	0.075	0.033453
3	Cao	0.075	0.075
4	Fao	30.	30.
5	k	600.	600.
6	kd	0.72	0.72
7	raprime	-3.375	-0.6714636
8	Us	10.	10.
9	W	0	22.
10	X	0	0.5539595

Differential equations

1 d(a)/d(W) = -kd*a/Us

2 d(X)/d(W) = a*(-raprime)/Fao

Explicit equations

1 Us = 10

2 kd = 0.72

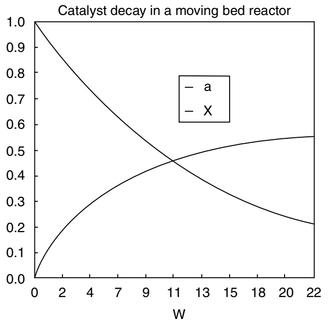
3 Fao = 30

4 Cao = 0.075

5 Ca = Cao*(1-X)

6 k = 600

7 raprime = -k*Ca^2



For the simple rate law and activity law given here, we also could have solved this problem analytically.

6. **Separating and integrating** yields

$$F_{A0}\frac{dX}{dW} = e^{-(k_d/U_s)W}\,kC_{A0}^2(1-X)^2$$

$$\frac{F_{A0}}{kC_{A0}^2}\int_0^X \frac{dX}{(1-X)^2} = \int_0^W e^{-(k_d/U_s)W}\,dW \tag{E10-5.7}$$

$$\frac{X}{1-X} = \frac{kC_{A0}^2 U_s}{F_{A0}k_d}\left(1-e^{-k_dW/U_s}\right) \tag{E10-5.8}$$

7. **Numerical evaluation:**

$$\frac{X}{1-X} = \frac{0.6\ \text{dm}^6}{\text{mol}\cdot\text{g cat.}\cdot\text{min}}\times\frac{(0.075\ \text{mol/dm}^3)^2}{30\ \text{mol/min}}\,\frac{10{,}000\ \text{g cat/min}}{0.72\ \text{min}^{-1}}$$

$$\times\left(1-\exp\left[\frac{(-0.72\ \text{min}^{-1})(22\ \text{kg})}{10\ \text{kg/min}}\right]\right)$$

$$\frac{X}{1-X} = 1.24$$

$$X = 55\%$$

If there were no catalyst decay, the conversion would be

$$\frac{X}{1-X} = \frac{kC_{A0}^2}{F_{A0}}W$$

$$= 600\left(\frac{\text{dm}^6}{(\text{kg cat})(\text{mol})(\text{min})}\times\frac{(0.075\ \text{mol/dm}^3)^2}{(30\ \text{mol/min})}\,(22\ \text{ckg cat})\right)$$

$$= 7.48$$

$$X = 0.71$$

Analysis: The purpose of this example was to show step-by-step how to apply the algorithm to a moving-bed reactor that has been used to reduce the effects of catalyst decay that would occur in a PBR.

We will now rearrange Equation (E10-5.8) to a form more commonly found in the literature. Let λ be a dimensionless decay time

$$\lambda = k_d t = \frac{k_d W}{U_s} \tag{10-126}$$

and Da_2 be the Damköhler number for a second-order reaction (*a reaction rate divided by a transport rate*) for a packed-bed reactor

$$Da_2 = \frac{(kC_{A0}^2)(W)}{F_{A0}} = \frac{kC_{A0}W}{v_0} \tag{10-127}$$

Through a series of manipulations we arrive at the equation for the conversion in a *moving bed* where a second-order reaction is taking place[32]

Second-order reaction in a moving-bed reactor

$$\boxed{X = \frac{\mathrm{Da}_2(1-e^{-\lambda})}{\lambda+\mathrm{Da}_2(1-e^{-\lambda})}} \tag{10-128}$$

Similar equations are given or can easily be obtained for other reaction orders or decay laws.

10.7.5 Straight-Through Transport Reactors (STTR)

This reactor is used for reaction systems in which the catalyst deactivates very rapidly. Commercially, the STTR is used in the production of gasoline from the cracking of heavier petroleum fractions where coking of the catalyst pellets occurs very rapidly. In the STTR, the catalyst pellets and the reactant feed enter together and are transported very rapidly through the reactor. The bulk density of the catalyst particle in the STTR is significantly smaller than in moving-bed reactors, and often the particles are carried through at the same velocity as the gas velocity. In some places the STTR is also referred to as a circulating fluidized bed (CFB). A schematic diagram is shown in Figure 10-34.

A mole balance on the reactant A over the differential reactor volume

$$\Delta V = A_C\,\Delta z$$

is

$$F_A\big|_z - F_A\big|_{z+\Delta z} + r_A A_C\,\Delta z = 0$$

STTR: Used when catalyst decay (usually coking) is very rapid

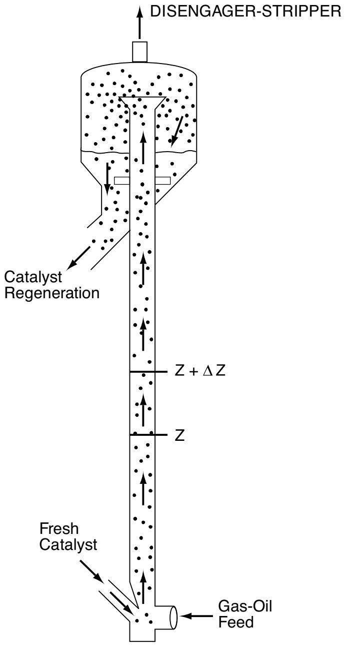


Figure 10-34 Straight-through transport reactor.

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[32] Ibid.

Dividing by Δz and taking the limit as $\Delta z \to 0$ and recalling that $r_A = \rho_B r'_A$, we obtain

$$\frac{dF_A}{dz} = r_A A_C = r'_A \rho_B A_C \tag{10-129}$$

In terms of conversion and catalyst activity

$$\frac{dX}{dz} = \left(\frac{\rho_B A_C}{F_{A0}}\right)[-r'_A(t=0)]\,a(t) \tag{10-130}$$

For a catalyst particle traveling through the reactor with a particle velocity U_P, the time the catalyst pellet has been in the reactor when it reaches a height z is just

$$t = \frac{z}{U_P} \tag{10-131}$$

Substituting for time t in terms of distance z [i.e., $a(t) = a(z/U_P)$], the mole balance now becomes

$$\frac{dX}{dz} = \frac{\rho_B A_C[-r'_A(t=0)]\,a(z/U_P)}{F_{A0}}$$

The entering molar flow rate, F_{A0}, can be expressed in terms of the gas velocity U_g, C_{A0}, and A_C

$$F_{A0} = U_o A_C C_{A0}$$

Substituting for F_{A0}, we have

$$\boxed{\frac{dX}{dz} = \frac{\rho_B\, a\,(z/U_P)\,[-r'_A(t=0)]}{C_{A0}U_o}} \tag{10-132}$$

Living Example Problem

Example 10–6 Decay in a Straight-Through Transport Reactor

The vapor-phase cracking of a gas-oil is to be carried out in a straight-through transport reactor (STTR) that is 10-m high and 1.5 m in diameter. Gas-oil is a mixture of normal and branched paraffins (C_{12}–C_{40}), naphthenes, and aromatics, all of which will be lumped as a single species, A. We shall lump the primary hydrocarbon products according to distillate temperature into two respective groups, dry gas (C–C_4) B and gasoline (C_5–C_{14}) C. The reaction

A typical cost of the catalyst in the reactor system is \$1 million.

$$\text{Gas-oil (g)} \longrightarrow \text{Products (g)} + \text{Coke}$$

can be written symbolically as

$$A \longrightarrow B + C + \text{Coke}$$

Both B and C are adsorbed on the surface. The rate law for a gas-oil cracking reaction on fresh catalyst can be approximated by

$$-r'_A = \frac{k'P_A}{1 + K_AP_A + K_BP_B + K_CP_C}$$

with $k' = 0.0014$ kmol/kg-cat·s·atm, $K_A = 0.05$ atm^{-1}, $K_B = 0.15$ atm^{-1}, and $K_C = 0.1$ atm^{-1}. The catalyst decays by the deposition of coke, which is produced in most cracking reactions along with the reaction products. The decay law is

$$a = \frac{1}{1 + At^{1/2}} \qquad \text{with } A = 7.6\ \text{s}^{-1/2}$$

Pure gas-oil enters at a pressure of 12 atm and a temperature of 400°C. The bulk density of catalyst in the STTR is 80 kg-cat/m^3. Plot the activity and conversion of gas-oil up the reactor for entering gas velocity $U_0 = 2.5$ m/s.

Solution

Mole Balance:

$$F_{A0}\frac{dX}{dz} = -r_A A_C$$

$$\boxed{\frac{dX}{dz} = \frac{-r_A}{U_o C_{A0}}} \tag{E10-6.1}$$

Following the Algorithm

The height of the catalyst particle at time "t" after entering the STTR is

$$z = \int_0^t U dt$$

Differentiating, we can find a relation between the time the catalyst particle has been in the STTR and reached a height z, which we can use to find the activity a.

$$\frac{dt}{dz} = \frac{1}{U}$$

Rate Law:

$$-r_A = \rho_B(-r'_A) \tag{E10-6.2}$$

$$-r'_A = a[-r'_A(t=0)] \tag{E10-6.3}$$

On fresh catalyst

$$-r'_A(t=0) = k'\frac{P_A}{1 + K_AP_A + K_BP_B + K_CP_C} \tag{E10-6.4}$$

Combining Equations (E10-6.2) through (E10-6.4) gives

$$\boxed{-r_A = a\left(\rho_B k'\frac{P_A}{1 + K_AP_A + K_BP_B + K_CP_C}\right)} \tag{E10-6.5}$$

Decay Law. Assuming that the catalyst particle and gas travel up the reactor at the velocity $U_P = U_g = U$, we obtain

$$t = \frac{z}{U} \tag{E10-6.6}$$

$$\boxed{a = \frac{1}{1 + A\,(z/U)^{1/2}}} \tag{E10-6.7}$$

where $U = v/A_C = v_0(1+\varepsilon X)/A_C$ and $A_C = \pi D^2/4$.

Stoichiometry (gas-phase isothermal and no pressure drop):

$$P_A = P_{A0}\frac{1-X}{1+\varepsilon X} \tag{E10-6.8}$$

$$P_B = \frac{P_{A0}X}{1+\varepsilon X} \tag{E10-6.9}$$

$$P_C = P_B \tag{E10-6.10}$$

Parameter Evaluation:

$$\varepsilon = y_{A0}\delta = (1+1-1) = 1$$

$$U = U_0(1+\varepsilon X)$$

$$C_{A0} = \frac{P_{A0}}{RT_0} = \frac{12\text{ atm}}{(0.082\text{ m}^3\cdot\text{atm/kmol}\cdot\text{K})(673\text{ K})} = 0.22\,\frac{\text{kmol}}{\text{m}^3}$$

Equations (E10-6.1), (E10-6.5), (E10-6.7), and (E10-6.8) through (E10-6.10) are now combined and solved using an ODE solver. The Polymath program is shown in Table E10-6.1, and the computer output is shown in Figure E10-6.1.

TABLE E10-6.1 EQUATIONS FOR THE STTR: LANGMUIR–HINSHELWOOD KINETICS

POLYMATH Report
Ordinary Differential Equations

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	A	7.6	7.6
2	a	1.	0.0760585
3	Cao	0.2174465	0.2174465
4	D	1.5	1.5
5	eps	1.	1.
6	Ka	0.05	0.05
7	Kb	0.15	0.15
8	Kc	0.1	0.1
9	Kca	2.7593	2.7593
10	kprime	0.0014	0.0014
11	Pa	12.	3.329127
12	Pao	12.	12.
13	Pb	0	4.335437
14	Pc	0	4.335437
15	R	0.082	0.082
16	ra	-0.84	-0.0126024
17	raprime	-0.0105	-0.0001575
18	rho	80.	80.
19	T	673.	673.
20	U	2.5	3.914117
21	Uo	2.5	2.5
22	vo	4.417875	4.417875
23	X	0	0.5656469
24	x	0	10.

Differential equations

```
1 d(X)/d(z) = -ra/U/Cao
```

Explicit equations

```
1  Ka = 0.05
2  kb = .15
3  Pao = 12
4  eps = 1
5  A = 7.6
6  R = 0.082
7  T = 400+273
8  rho = 80
9  kprime = 0.0014
10 D = 1.5
11 Uo = 2.5
12 Kc = 0.1
13 U = Uo*(1+eps*X)
14 Pa = Pao*(1-X)/(1+eps*X)
15 Pb = Pao*X/(1+eps*X)
16 vo = Uo*3.1416*D*D/4
17 Cao = Pao/R/T
18 Kca = Ka*R*T
19 Pc = Pb
20 a = 1/(1+A*(z/U)^0.5)
21 raprime = a*(-kprime*Pa/(1+Ka*Pa+Kb*Pb+Kc*Pc))
22 ra = rho*raprime
```

Living Example Problem

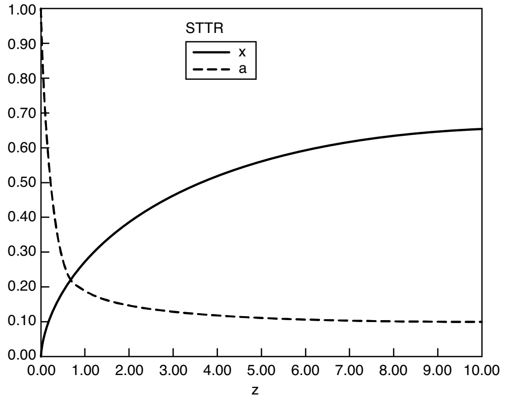


Figure E10-6.1 Activity and conversion profiles.

Analysis: In this example we applied the algorithm to a STTR in which the gas velocity and, hence, particle velocity increases as we move through the reactor. The decay is quite rapid and the activity is only 15% of its initial value at $z = 3$ m into the reactor and the conversion begins to plateau at $z = 6$ m at 60% conversion. If there were no catalyst decay (a = 0) the conversion would have been 97%.

Closure. After reading this chapter, the reader should be able to discuss the steps in a heterogeneous reaction (adsorption, surface reaction, and desorption) and describe what is meant by a rate-limiting step. The differences between molecular adsorption and dissociated adsorption should be explained by the reader, as should the different types of surface reactions (single site, dual site, and Eley–Rideal). Given heterogeneous reaction-rate data, the reader should be able to analyze the data and develop a rate law for Langmuir–Hinshelwood kinetics. The reader should also be able to discriminate between rate laws to find which rate law best fits the data. After evaluating the rate-law parameters, the reader can proceed to the design of PBRs and fluidized CSTRs.

Applications of CRE in the electronics industry were discussed and readers should be able to describe the analogy between Langmuir–Hinshelwood kinetics and chemical vapor deposition (CVD), and to derive a rate law for CVD mechanisms.

Because of the high temperatures and harsh environment, catalysts do not maintain their original activity and the catalysts decay during the course of the reaction. The reader should be able to discuss the three basic types of catalyst decay (sintering, coking or fouling, and poisoning). In addition, the reader should be able to suggest reactors (e.g., moving bed) to use to offset catalyst decay and should be able to carry out calculations to predict the conversion.

SUMMARY

1. Types of adsorption:
   a. Chemisorption
   b. Physical adsorption
2. The **Langmuir isotherm** relating the concentration of species A on the surface to the partial pressure of A in the gas phase is

$$C_{A\cdot S} = \frac{K_A C_t P_A}{1 + K_A P_A} \qquad \text{(S10-1)}$$

3. The sequence of steps for the solid-catalyzed isomerization

$$\mathbf{A} \longrightarrow \mathbf{B} \qquad \text{(S10-2)}$$

   is:

   a. **Mass transfer of A** from the bulk fluid to the external surface of the pellet
   b. **Diffusion of A** into the interior of the pellet
   c. **Adsorption of A** onto the catalytic surface
   d. **Surface reaction of A** to form **B**
   e. **Desorption of B** from the surface
   f. **Diffusion of B** from the pellet interior to the external surface
   g. **Mass transfer of B** away from the solid surface to the bulk fluid

4. Assuming that mass transfer is not rate-limiting, the rate of adsorption is

$$r_{AD} = k_A \left(C_v P_A - \frac{C_{A\cdot S}}{K_A} \right) \qquad \text{(S10-3)}$$

   The rate of surface reaction is

$$r_S = k_S \left(C_{A\cdot S} - \frac{C_{B\cdot S}}{K_S} \right) \qquad \text{(S10-4)}$$

   The rate of desorption is

$$r_D = k_D \left(C_{B\cdot S} - K_B P_B C_v \right) \qquad \text{(S10-5)}$$

   At steady state

$$-r'_A = r_{AD} = r_S = r_D \qquad \text{(S10-6)}$$

   If there are no inhibitors present, the total concentration of sites is

$$C_t = C_v + C_{A\cdot S} + C_{B\cdot S} \qquad \text{(S10-7)}$$

5. If we assume that the surface reaction is rate-limiting, we set

$$\frac{r_{AD}}{k_A} \simeq 0 \qquad \frac{r_D}{k_D} \simeq 0$$

and solve for $C_{A \cdot S}$ and $C_{B \cdot S}$ in terms of P_A and P_B. After substitution of these quantities in Equation (S10-4), the concentration of vacant sites is eliminated with the aid of Equation (S10-7)

$$-r'_A = r_S = \frac{\overbrace{C_t k_S K_A}^{k}\left(P_A - P_B / K_P\right)}{1 + K_A P_A + K_B P_B} \tag{S10-8}$$

Recall that the equilibrium constant for desorption of species B is the reciprocal of the equilibrium constant for the adsorption of species B

$$K_B = \frac{1}{K_{DB}} \tag{S10-9}$$

and the thermodynamic equilibrium constant, K_P, is

$$K_P = K_A K_S / K_B \tag{S10-10}$$

6. Chemical vapor deposition

$$\text{SiH}_4(\text{g}) \rightleftarrows \text{SiH}_2(\text{g}) + \text{H}_2(\text{g}) \tag{S10-11}$$

$$\text{SiH}_2(\text{g}) + \text{S} \longrightarrow \text{SiH}_2 \cdot \text{S} \tag{S10-12}$$

$$\text{SiH}_2 \cdot \text{S} \longrightarrow \text{Si(s)} + \text{H}_2(\text{g}) \tag{S10-13}$$

$$r_{\text{Dep}} = \frac{kP_{\text{SiH}_4}}{P_{\text{H}_2} + KP_{\text{SiH}_4}} \tag{S10-14}$$

7. **Catalyst deactivation.** The catalyst activity is defined as

$$a(t) = \frac{-r'_A(t)}{-r'_A(t=0)} \tag{S10-15}$$

The rate of reaction at any time t is

$$-r'_A = a(t)k(T)\,\text{fn}(C_A, C_B, \ldots, C_P) \tag{S10-16}$$

The rate of catalyst decay is

$$r_d = -\frac{da}{dt} = p\,[a(t)]\,k_d(T)g(C_A, C_B, \ldots, C_P) \tag{S10-17}$$

For first-order decay

$$p(a) = a \tag{S10-18}$$

For second-order decay

$$p(a) = a^2 \tag{S10-19}$$

8. For slow catalyst decay, the idea of a **temperature–time trajectory** is to increase the temperature in such a way that the rate of reaction remains constant.
9. The coupled differential equations to be solved for a **moving-bed reactor** are

$$F_{A0}\frac{dX}{dW} = a(-r'_A) \tag{S10-20}$$

For *n*th-order activity decay and *m* order in a gas-phase concentration of species *i*

$$-\frac{da}{dW}=\frac{k_d a^n C_i^m}{U_s} \tag{S10-21}$$

$$t=\frac{W}{U_s} \tag{S10-22}$$

10. The coupled differential equations to be solved in a **straight-through transport reactor** for the case when the particle and gas velocities, *U*, are identical are

$$\frac{dX}{dz}=\frac{a(t)[-r'_A(t=0)]}{U_g}\left(\frac{\rho_b A_c}{C_{A0}}\right) \tag{S10-23}$$

$$t=\frac{z}{U_g} \tag{S10-24}$$

For coking

$$a(t)=\frac{1}{1+At^{1/2}} \tag{S10-25}$$

ODE SOLVER ALGORITHM

The isomerization A → B is carried out over a decaying catalyst in a *moving-bed reactor*. Pure A enters the reactor and the catalyst flows through the reactor at a rate of 2.0 kg/s.

$$\frac{dX}{dW}=\frac{-r'_A}{F_{A0}} \qquad k = 0.1\ \text{mol/(kg-cat}\cdot\text{s}\cdot\text{atm)}$$

$$r'_A=\frac{-akP_A}{1+K_AP_A} \qquad K_A = 1.5\ \text{atm}^{-1}$$

$$\frac{da}{dW}=\frac{-k_d a^2 P_B}{U_s} \qquad k_d=\frac{0.75}{\text{s}\cdot\text{atm}}$$

$$P_A = P_{A0}(1-X)p \qquad F_{A0} = 10\ \text{mol/s}$$

$$P_B = P_{A0}Xp \qquad P_{A0} = 20\ \text{atm}$$

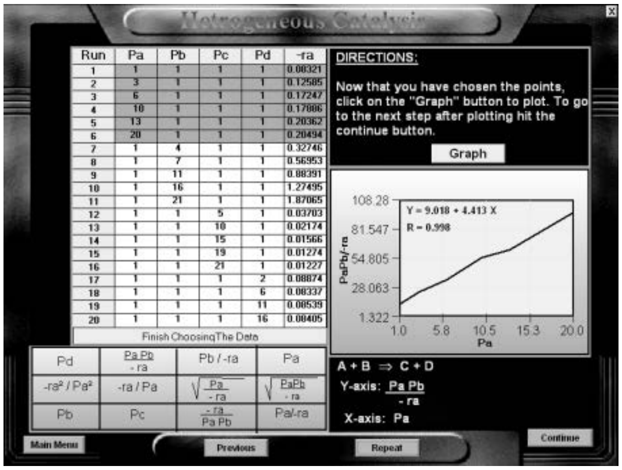
$$\frac{dp}{dW}=-\frac{\alpha}{2p} \qquad U_s = 2.0\ \text{kg-cat/s}$$

$$\alpha = 0.0019\ \text{kg}^{-1} \qquad W_f = 500\ \text{kg-cat}$$

CRE WEB SITE MATERIALS

- **Expanded Material**
    1. *Puzzle Problem "What's Wrong with this Solution?"*
    2. *Turn Over Frequency (TOF)*
    3. *Algorithm When More than One of the Three Steps in a Catalytic Reaction Mechanism (Adsorption, Surface Reaction, Desorption) Is Rate Limiting*
    4. *Additional Homework Problems*
- **Learning Resources**
    1. *Summary Notes for Chapter 10*
    2. *Interactive Computer Modules*
        A. Heterogeneous Catalysis

Summary Notes



Run	Pa	Pb	Pc	Pd	-ra
1	1	1	1	1	0.08321
2	3	1	1	1	0.12585
3	6	1	1	1	0.17247
4	10	1	1	1	0.17886
5	13	1	1	1	0.20362
6	20	1	1	1	0.20494
7	1	4	1	1	0.32746
8	1	7	1	1	0.56953
9	1	11	1	1	0.88391
10	1	16	1	1	1.27495
11	1	21	1	1	1.87065
12	1	1	5	1	0.03703
13	1	1	10	1	0.02174
14	1	1	15	1	0.01566
15	1	1	19	1	0.01274
16	1	1	21	1	0.01227
17	1	1	1	2	0.08874
18	1	1	1	6	0.08337
19	1	1	1	11	0.08539
20	1	1	1	16	0.08405

Finish ChoosingThe Data

Pd	$\frac{Pa\,Pb}{-ra}$	Pb / -ra	Pa
$-ra^2 / Pa^2$	-ra / Pa	$\sqrt{\frac{Pa}{-ra}}$	$\sqrt{\frac{PaPb}{-ra}}$
Pb	Pc	$\frac{-ra}{Pa\,Pb}$	Pa/-ra

DIRECTIONS:

Now that you have chosen the points, click on the "Graph" button to plot. To go to the next step after plotting hit the continue button.

$A + B \Rightarrow C + D$

Y-axis: $\frac{Pa\,Pb}{-ra}$

X-axis: Pa

3. *Solved Problems*
    Example Chapter 10 CRE Web Site: 10-1 Analysis of a Heterogeneous Reaction [Class Problem University of Michigan]
    Example Chapter 10 CRE Web Site: 10-2 Least Squares Analysis to Determine the Rate Law Parameters k, k_T, and k_B
    Example Chapter 10 CRE Web Site: 10-3 Decay in a Straight-Through Reactor
    Example Chapter 10 CRE Web Site: 10-4 Catalyst Poisoning in a Batch Reactor

Solved Problems

- **Living Example Problems**
    1. *Example 10-2 Regression Analysis to Determine Model Parameters*
    2. *Example 10-3 Fixed-Bed Reactor Design*
    3. *Example 10-4 Model Discrimination*
    4. *Example 10-5 Catalyst Decay in a Batch Reactor*
    5. *Example 10-6 Catalyst Decay in a Fluidized Bed Modeled as a CSTR*
    6. *Example 10-8 Decay in a Straight-Through Transport Reactor*

Living Example Problem

- **Professional Reference Shelf**
    R10.1. *Classification of Catalysts*
    R10.2. *Hydrogen Adsorption*
        A. Molecular Adsorption
        B. Dissociative Adsorption
    R10.2. *Analysis of Catalyst Decay Laws*
        A. Integral Method
        B. Differential Method
    R10.3. *Etching of Semiconductors*
        A. Dry Etching
        B. Wet Etching
        C. Dissolution Catalysis

Reference Shelf

R10.4. *Catalyst Deactivation*
- A. Type of Catalyst Deactivation
- B. Temperature–Time Trajectories
- C. Moving-Bed Reactors
- D. Straight-Through Transport Reactors

After Reading Each Page in This Book, Ask Yourself a Question About What You Read

QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

A = ● B = ■ C = ◆ D = ◆◆

Questions

Q10-1$_A$ Read over the problems at the end of this chapter. Make up an original problem that uses the concepts presented in this chapter. See Problem P5-1$_A$ for guidelines. To obtain a solution:

(a) Create your data and reaction.
(b) Use a real reaction and real data.
The journals listed at the end of Chapter 1 may be useful for part **(b)**.
(c) Choose an FAQ from Chapter 10 and explain why it was most helpful.
(d) Listen to the audios on the *Summary Notes*, pick one, and explain why it was most helpful.

Problems

P10-1$_B$ **(a)** **Example 10-1**. Plot and analyze (1) the ratio of toluene-occupied sites to benzene-occupied sites, (2) the fraction of vacant sites, and (3) the fraction of benzene-occupied sites as a function of conversion at 1 atm.

(b) **Example 10-2**. (1) What if the entering pressure were increased to 80 atm or reduced 1 atm, how would your answers change? (2) What if the molar flow rate were reduced by 50%, how would X and y change? (3) What catalyst weight would be required for 60% conversion?

(c) **Example 10-3**. (1) How would your answers change if the following data for run 10 were incorporated in your regression table?

$$-r'_E = 0.8 \text{ mol/kg-cat} \cdot \text{s},\ P_E = 0.5 \text{ atm},\ P_{EA} = 15 \text{ atm},\ P_H = 2 \text{ atm}.$$

(2) How do the rate laws **(e)** and **(f)**

$$\textbf{(e)}\ -r'_E = \frac{kP_EP_H}{(1+K_AP_{EA}+K_EP_E)^2} \qquad \textbf{(f)}\ -r'_E = \frac{kP_HP_E}{1+K_AP_{EA}}$$

compare with the other rate laws used to model the data?

(3) Write a question for this problem that involves critical thinking and explain why it involves critical thinking.

(d) **Example 10-4**. Vary k and k_d, and describe what you find.

(e) **Example 10-5**. (1) Sketch X vs. t for various values of k_d and k. Pay particular attention to the ratio k/k_d. (2) Repeat (1) for this example (i.e., the plotting of X vs. t) for a second-order reaction with (C_{A0} = 1 mol/dm^3) and first-order decay. (3) Repeat (2) for this example for a first-order reaction and first-order decay. (4) Repeat (1) for this example for a second-order reaction (C_{A0} = 1 mol/dm^3) and a second-order decay.

(f) **Example 10-7**. (1) What if the solids and reactants entered from opposite ends of the reactor? How would your answers change? (2) What if the decay in the moving bed were second order? By how much must the catalyst charge, U_s, be increased to obtain the same conversion? (3) What if $\varepsilon = 2$ (e.g., $A \to 3B$) instead of zero, how would the results be affected?

(g) **Example 10-8**. (1) What if you varied the parameters P_{A0}, U_g, A, and k' in the STTR? What parameter has the greatest effect on either increasing or decreasing the conversion? Ask questions such as: What is the effect of varying the ratio of k to U_g or of k to A on the conversion? Make a plot of conversion versus distance as U_g is varied between 0.5 and 50 m/s. Sketch the activity and conversion profiles for U_g = 0.025, 0.25, 2.5, and 25 m/s. What generalizations can you make? Plot the exit conversion and activity as a function of gas velocity between velocities of 0.02 and 50 m/s. What gas velocity do you suggest operating at? What is the corresponding entering volumetric flow rate? What concerns do you have operating at the velocity you selected? Would you like to choose another velocity? If so, what is it?

(h) What if you were asked to sketch the temperature–time trajectories and to find the catalyst lifetimes for first- and for second-order decay when E_A = 35 kcal/mol, E_d = 10 kcal/mol, k_{d0} = 0.01 day^{-1}, and T_0 = 400 K? How would the trajectory of the catalyst lifetime change if E_A = 10 kcal/mol and E_d = 35 kcal/mol? At what values of k_{d0} and ratios of E_d to E_A would temperature–time trajectories not be effective? What would your temperature–time trajectory look like if $n = 1 + E_d/E_A$?

(i) Write a question for this problem that involves critical thinking and explain why it involves critical thinking.

P10-2$_A$ Download the Interactive Computer Games (**ICG**) from the CRE Web site. Play the game and then record your performance number for the game, which indicates your mastery of the material. Your professor has the key to decode your performance number. (This ICG is a little longer than the other ICGs.)
ICG Heterogeneous Catalysis Performance # _____________.

P10-3$_A$ t-Butyl alcohol (TBA) is an important octane enhancer that is used to replace lead additives in gasoline [*Ind. Eng. Chem. Res.*, 27, 2224 (1988)]. TBA was produced by the liquid-phase hydration (W) of isobutene (I) over an Amberlyst-15 catalyst. The system is normally a multiphase mixture of hydrocarbon, water, and solid catalysts. However, the use of cosolvents or excess TBA can achieve reasonable miscibility.

The reaction mechanism is believed to be

$$\mathrm{I + S \rightleftarrows I \cdot S} \tag{P10-3.1}$$

$$\mathrm{W + S \rightleftarrows W \cdot S} \tag{P10-3.2}$$

$$\mathrm{W \cdot S + I \cdot S \rightleftarrows TBA \cdot S + S} \tag{P10-3.3}$$

$$\mathrm{TBA \cdot S \rightleftarrows TBA + S} \tag{P10-3.4}$$

Derive a rate law assuming:

(a) The surface reaction is rate-limiting.

(b) The adsorption of isobutene is limiting.

(c) The reaction follows Eley–Rideal kinetics

$$\mathrm{I \cdot S + W \longrightarrow TBA \cdot S} \tag{P10-3.5}$$

and the surface reaction is limiting.

(d) Isobutene (I) and water (W) are adsorbed on different sites.

$$\mathrm{I + S_1 \rightleftarrows I \cdot S_1} \tag{P10-3.6}$$

$$\mathrm{W + S_2 \rightleftarrows W \cdot S_2} \tag{P10-3.7}$$

TBA is *not* on the surface, and the surface reaction is rate-limiting.

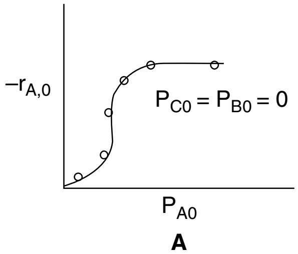
$$\left[\textit{\textbf{Ans.:}}\ r'_{TBA} = -r'_I = \frac{k[C_I C_W - C_{TBA}/K_c]}{(1+K_W C_W)(1+K_I C_I)}\right]$$

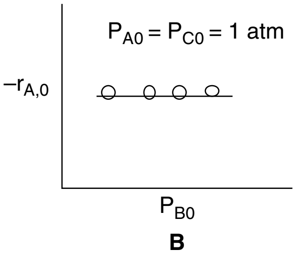
(e) What generalization can you make by comparing the rate laws derived in parts **(a)** through **(d)**?

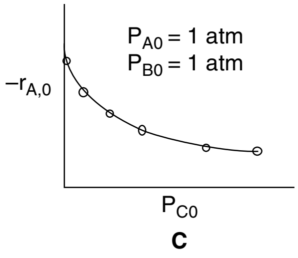
P10-4$_B$ Consider the catalytic reaction as a function of the initial partial pressures

$$2A \rightleftarrows B + C$$

The rate of disappearance of species A was obtained in a differential reactor and is shown below.







(a) What species are on the surface?
(b) What does Figure B tell you about the reversibility and what's adsorbed on the surface?
(c) Derive the rate law and suggest a rate-liming step consistent with the above figures.
(d) How would you plot your data to linearize the initial rate data in Figure A?
(e) Assuming pure A is fed, and the adsorption constants for A and C are $K_A = 0.5$ atm^{-1} and $K_C = 0.25$ atm^{-1} respectively, at what conversion are the number of sites with A adsorbed on the surface and C adsorbed on the surface equal? (***Ans.:*** $X = 0.66$)

P10-5$_A$ The rate law for the hydrogenation (H) of ethylene (E) to form ethane (A) over a cobalt-molybdenum catalyst [*Collection Czech. Chem. Commun.*, 51, 2760 (1988)] is

$$-r'_E = \frac{kP_E P_H}{1 + K_E P_E}$$

(a) Suggest a mechanism and rate-limiting step consistent with the above rate law.
(b) What was the most difficult part in finding the mechanism?

P10-6$_B$ The formation of propanol on a catalytic surface is believed to proceed by the following mechanism

$$O_2 + 2S \overset{\text{cat}}{\rightleftarrows} 2O \cdot S$$

$$C_3H_6 + O \cdot S \rightarrow C_3H_5OH \cdot S$$

$$C_3H_5OH \cdot S \rightleftarrows C_3H_5OH + S$$

Suggest a rate-limiting step and derive a rate law.

P10-7$_B$ The dehydration of *n*-butyl alcohol (butanol) over an alumina-silica catalyst was investigated by J. F. Maurer (Ph.D. thesis, University of Michigan). The data in Figure P10-7$_B$ were obtained at 750°F in a modified differential reactor. The feed consisted of pure butanol.

(a) Suggest a mechanism and rate-limiting step that are consistent with the experimental data.
(b) Evaluate the rate-law parameters.
(c) At the point where the initial rate is a maximum, what is the fraction of vacant sites? What is the fraction of occupied sites by both A and B? % vacant = 0.41
(d) What generalizations can you make from studying this problem?
(e) Write a question that requires critical thinking and then explain why your question requires critical thinking. *Hint:* See Preface Section I.
(f) Apply one or more of the six ideas in Preface Table P-4, page xxviii, to this problem.

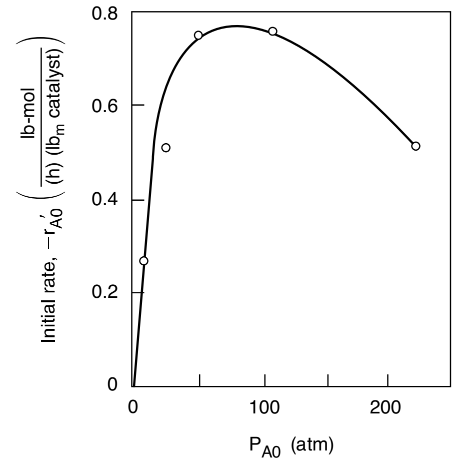
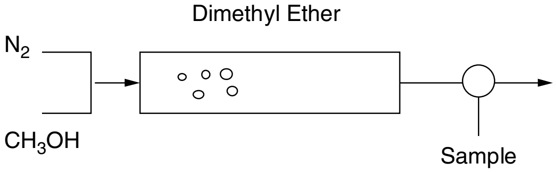


Figure P10-7$_B$ Initial reaction rate as function of initial partial pressure of butanol.

P10-8$_B$ The catalytic dehydration of methanol (ME) to form dimethyl ether (DME) and water was carried out over an ion exchange catalyst [K. Klusacek, *Collection Czech. Chem. Commun.*, 49, 170 (1984)]. The packed bed was initially filled with nitrogen, and at $t = 0$. The N_2 feed is switched to pure methanol vapor entering the reactor at 413 K, 100 kPa, and 0.2 cm^3/s. The following partial pressures were recorded at the exit to the differential reactor containing 1.0 g of catalyst in 4.5 cm^3 of reactor volume.

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

$$2ME \longrightarrow DME + H_2O$$



	t(s)						
	0	10	50	100	150	200	300
P_{N_2} (kPa)	100	50	10	2	0	0	0
P_{ME} (kPa)	0	2	15	23	25	26	26
P_{H_2O} (kPa)	0	10	15	30	35	37	37
P_{DME} (kPa)	0	38	60	45	40	37	37

Use parts **(a)** through **(f)** to lead you to suggest a mechanism, rate-limiting step, and rate law consistent with this data.

(a) Using the data above, sketch the exit concentrations as a function of time.

(b) Which species took longer than others to exit the reactor in the gas phase? What could have caused this difference in exit times?

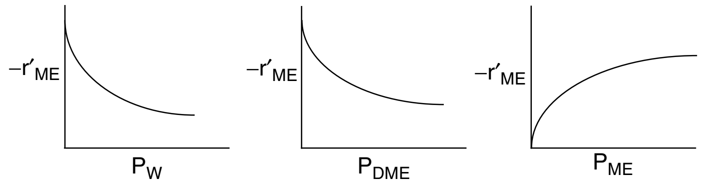
(c) What species are adsorbed on the surface?

(d) Are any species not adsorbed on the surface? If so, which ones?

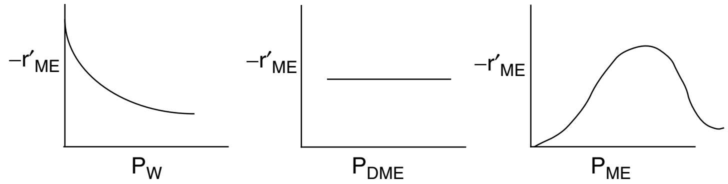
(e) Which set of figures, (1)-(4) below, correctly describes the functionality of the chemical reaction rate with the partial pressures P_W, P_{DME}, and P_{ME}?

(f) Derive a rate law for the catalytic dehydration of methanol. Dimethyl Either 2ME → DME + W.

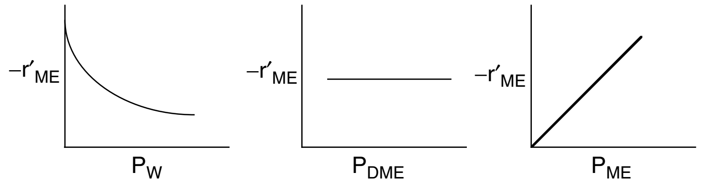
(1)



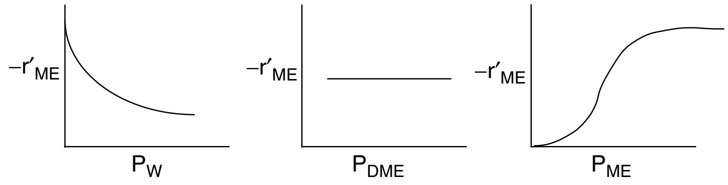
(2)



(3)



(4)



P10-9$_B$ In 1981, the U.S. government put forth the following plan for automobile manufacturers to reduce emissions from automobiles over the next few years.

	Year		
	1981	1993	2010
Hydrocarbons	0.41	0.25	0.125
CO	3.4	3.4	1.7
NO	1.0	0.4	0.2

All values are in grams per mile. An automobile emitting 3.74 lb_m of CO and 0.37 lb_m of NO on a journey of 1000 miles would meet the current government requirements.

To remove oxides of nitrogen (assumed to be NO) from automobile exhaust, a scheme has been proposed that uses unburned carbon monoxide (CO) in the exhaust to reduce the NO over a solid catalyst, according to the reaction

$$\text{CO} + \text{NO} \xrightarrow[\text{catalyst}]{} \text{Products } (\text{N}_2, \text{CO}_2)$$

Experimental data for a particular solid catalyst indicate that the reaction rate can be well represented over a large range of temperatures by

$$-r'_N = \frac{kP_N P_C}{(1+K_1P_N+K_2P_C)^2} \tag{P10-9.1}$$

where
P_N = gas-phase partial pressure of NO
P_C = gas-phase partial pressure of CO
k, K_1, K_2 = coefficients depending only on temperature

(a) Propose an adsorption–surface reaction–desorption mechanism and rate-limiting step that are consistent with the experimentally observed rate law. Do you need to assume any species are weakly adsorbed to get agreement with Equation (P10-9.1)?

(b) A certain engineer thinks that it would be desirable to operate with a very large stoichiometric excess of CO to minimize catalytic reactor volume. Do you agree or disagree? Explain.

(c) What would be the relevance of the problem if everyone were driving a hybrid by 2018? A driverless car by 2020?

P10-10$_B$ Methyl ethyl ketone (MEK) is an important industrial solvent that can be produced from the dehydrogenation of butan-2-ol (Bu) over a zinc oxide catalyst [*Ind. Eng. Chem. Res.*, 27, 2050 (1988)]:

$$\text{Bu} \xrightarrow[\text{catalyst}]{} \text{MEK} + \text{H}_2$$

The following data giving the reaction rate for MEK were obtained in a differential reactor at 490°C.

P_{Bu} (atm)	2	0.1	0.5	1	2	1
P_{MEK} (atm)	5	0	2	1	0	0
P_{H_2} (atm)	0	0	1	1	0	10
r'_{MEK} (mol/h·g-cat.)	0.044	0.040	0.069	0.060	0.043	0.059

(a) Suggest a rate law consistent with the experimental data.

(b) Suggest a reaction mechanism and rate-limiting step consistent with the rate law. *Hint*: Some species might be weakly adsorbed.

(c) Apply one or more of the six ideas in Preface Table P-4, page xxviii, to this problem.

(d) Plot conversion (up to 90%) and reaction rate as a function of catalyst weight for an entering molar flow rate of pure butan-2-ol of 10 mol/min at an entering pressure $P_0 = 10$ atm up to a catalyst weight $W_{\max} = 23$ kg.

(e) Write a question that requires critical thinking and then explain why your question requires critical thinking. *Hint:* See Preface Section I.

(f) Repeat part **(d)**, accounting for pressure drop and $\alpha = 0.03\ \text{kg}^{-1}$. Plot p and X as a function of catalyst weight down the reactor.

P10-11$_B$ Cyclohexanol was passed over a catalyst to form water and cyclohexene:

$$\text{Cyclohexanol} \xrightarrow[\text{catalyst}]{} \text{Water} + \text{Cyclohexene}$$

It is suspected that the reaction may involve a dual-site mechanism, but it is not known for certain. It is believed that the adsorption equilibrium constant for cyclohexanol is around 1.0 and is roughly one or two orders of magnitude greater than the adsorption equilibrium constants for the other compounds. Using these data:

TABLE P10-11$_B$ DATA FOR CATALYTIC FORMATION OF CYCLOHEXENE

Run	*Reaction Rate* (mol/dm^3·s) × 10^5	*Partial Pressure of Cyclohexanol (atm)*	*Partial Pressure of Cyclohexene (atm)*	*Partial Pressure of Steam (H_2O) (atm)*
1	3.3	1	1	1
2	1.05	5	1	1
3	0.565	10	1	1
4	1.826	2	5	1
5	1.49	2	10	1
6	1.36	3	0	5
7	1.08	3	0	10
8	0.862	1	10	10
9	0	0	5	8
10	1.37	3	3	3

(a) Suggest a rate law and mechanism consistent with the data given here.
(b) Determine the values of the rate-law parameters. (*Ind. Eng. Chem. Res.*, 32, 2626–2632.)
(c) Why do you think estimates of the rate-law parameters were given?
(d) For an entering molar flow rate of cychlohexanol of 10 mol/s at a partial pressure of 15 atm, what catalyst weight is necessary to achieve 85% conversion when the bulk density is 1500 gm/dm^3?

P10-12$_B$ Experimental data for the gas-phase catalytic reaction

$$A + B \rightarrow C$$

is shown below. The limiting step in the reaction is known to be irreversible, so that the overall reaction is irreversible. The reaction was carried out in a differential reactor to which A, B, and C were all fed.

Run Number	P_A (atm)	P_B (atm)	P_C (atm)	Reaction rate (mol)/(g-cat • s)
1	1	1	2	0.114
2	1	10	2	1.140
3	10	1	2	0.180
4	1	20	2	2.273
5	1	20	10	0.926
6	20	1	2	0.186
7	0.1	1	2	0.0243

(a) Suggest a rate law consistent with the experimental data. *Hint:* Sketch $(-r'_A)$ as a function of P_A, as a function of P_B, and as a function of P_C.
(b) From your rate expression, which species can you conclude are adsorbed on the surface?
(c) Suggest a rate law and then show that your mechanism is constant with the rate law in part (a).
(d) For an entering partial pressure of A of 2 atm in a PBR, what is the ratio of A to C sites at 80% conversion of A?
(e) At what conversion are the number of A and C sites equal? (***Ans.:*** $X = 0.235$)
(f) What catalyst weight is necessary to achieve 90% conversion of A for a stoichiometric feed and flow of A 2 mol/s? (***Ans.:*** $W = 8.9$ g-cat)

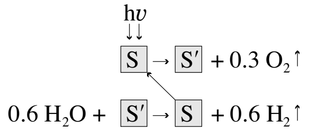
If necessary, feel free to use none, any, or all of the following parameter values:

$$k = 2.5 \frac{\text{mol}}{\text{atm}^2\text{g-cat}\bullet\text{s}}, \ K_A = 4 \text{ atm}^{-1}, K_C = 13 \text{ atm}^{-1}, K_I = 10 \text{ atm}^{-1}$$

P10-13$_B$ **Solar Energy Capture: Water Splitting.** Hydrogen and O_2 can be combined in fuel cells to generate electricity. Solar energy can be used to split water to generate the raw reactants H_2 and O_2 for fuel cells. One method of solar thermal reduction is with $NiFe_2O_4$ in the sequence

$$\text{Step (1) Solar Energy} + \overbrace{NiFe_2O_4}^{\text{Surface }(S)} \rightarrow \overbrace{1.2FeO + 0.4Fe_2O_3 + NiO}^{\text{Solid Solution}(S')} + 0.3O_2 \uparrow$$

$$\text{Step (2)} \ \overbrace{1.2FeO + 0.4Fe_2O_3 + NiO}^{\text{Solid Solution}(S')} + 0.6H_2O \rightarrow \overbrace{NiFe_2O_4}^{\text{Surface }(S)} + 0.6H_2 \uparrow$$



We note $NiFe_2O_4$ is regenerated in this process.[33]

(a) Derive a rate law for Step (2), assuming that water adsorbs on the solid solution as a single-site mechanism and that the reaction is irreversible.

(b) Repeat **(a)** when the reaction is reversible and the solid solution adsorption site for water (S') is different than the $NiFe_2O_4$ site for the adsorption of H_2, (S).

$$H_2O + S' \rightleftarrows S' \cdot H_2O$$

$$S' \cdot H_2O \rightleftarrows S \cdot H_2 + \frac{1}{2}O_2$$

$$H_2 \cdot S \rightleftarrows S + H_2$$

(c) How would your rate law change if we included Step 1?

$$S + hv \rightleftarrows S' \cdot O_2$$

$$S' \cdot O_2 \rightleftarrows S' + O_2$$

P10-14$_A$ Vanadium oxides are of interest for various sensor applications, owing to the sharp metal–insulator transitions they undergo as a function of temperature, pressure, or stress. Vanadium triisopropoxide (VTIPO) was used to grow vanadium oxide films by *chemical vapor deposition* [*J. Electrochem. Soc.*, 136, 897 (1989)]. The deposition rate as a function of VTIPO pressure for two different temperatures follows.

$\underline{T = 120°C:}$

Growth Rate (μm/h)	0.004	0.015	0.025	0.04	0.068	0.08	0.095	0.1
VTIPO Pressure (torr)	0.1	0.2	0.3	0.5	0.8	1.0	1.5	2.0

$\underline{T = 200°C:}$

Growth Rate (μm/h)	0.028	0.45	1.8	2.8	7.2
VTIPO Pressure (torr)	0.05	0.2	0.4	0.5	0.8

In light of the material presented in this chapter, analyze the data and describe your results. Specify where additional data should be taken.

P10-15$_A$ Titanium dioxide is a wide-bandgap semiconductor that is showing promise as an insulating dielectric in VLSI capacitors and for use in solar cells. Thin films of TiO_2 are to be prepared by *chemical vapor deposition* from gaseous titanium tetraisopropoxide (TTIP). The overall reaction is

$$Ti(OC_3H_7)_4 \longrightarrow TiO_2 + 4C_3H_6 + 2H_2O$$

The reaction mechanism in a CVD reactor is believed to be [K. L. Siefering and G. L. Griffin, *J. Electrochem. Soc.*, 137, 814 (1990)]

$$TTIP(g) + TTIP(g) \rightleftarrows I + P_1$$

$$I + S \rightleftarrows I \cdot S$$

$$I \cdot S \longrightarrow TiO_2 + P_2$$

---

[33] Scheffe, J.R., J. Li, and A. W. Weimer, "A Spinel Ferrite/Hercynite Water-Splitting Redox Cycle," *International Journal of Hydrogen Energy,* 35, 3333–3340 (2010).

where I is an active intermediate and P_1 is one set of reaction products (e.g., H_2O, C_3H_6), and P_2 is another set. Assuming the homogeneous gas-phase reaction for TTIP is in equilibrium, derive a rate law for the deposition of TiO_2. The experimental results show that at 200°C the reaction is second order at low partial pressures of TTIP and zero order at high partial pressures, while at 300°C the reaction is second order in TTIP over the entire pressure range. Discuss these results in light of the rate law you derived.

P10-16$_B$ The dehydrogenation of methylcyclohexane (M) to produce toluene (T) was carried out over a 0.3% Pt/Al_2O_3 catalyst in a differential catalytic reactor. The reaction is carried out in the presence of hydrogen (H_2) to avoid coking [*J. Phys. Chem.,* 64, 1559 (1960)].

(a) Determine the model parameters for each of the following rate laws.

$$(1)\ -r'_{M} = kP_{M}^{\alpha}P_{H_2}^{\beta} \qquad (3)\ -r'_{M} = \frac{kP_{M}P_{H_2}}{(1+K_{M}P_{M})^2}$$

$$(2)\ -r'_{M} = \frac{kP_{M}}{1+K_{M}P_{M}} \qquad (4)\ -r'_{M} = \frac{kP_{M}P_{H_2}}{1+K_{M}P_{M}+K_{H_2}P_{H_2}}$$

Use the data in Table P10-16$_B$ below.

(b) Which rate law best describes the data? *Hint*: Neither K_{H_2} or K_M can take on negative values.

(c) Where would you place additional data points?

(d) Suggest a mechanism and rate-limiting step consistent with the rate law you have chosen.

TABLE P10-16$_B$ DEHYDROGENATION OF METHYLCYCLOHEXANE

P_{H_2} (atm)	P_M (atm)	$r'_T \left(\frac{\text{mol toluene}}{\text{s}\cdot\text{kg-cat}}\right)$
1	1	1.2
1.5	1	1.25
0.5	1	1.30
0.5	0.5	1.1
1	0.25	0.92
0.5	0.1	0.64
3	3	1.27
1	4	1.28
3	2	1.25
4	1	1.30
0.5	0.25	0.94
2	0.05	0.41

P10-17$_A$ Sketch *qualitatively* the reactant, product, and activity profiles as a function of length at various times for a *packed-bed reactor* for each of the following cases. In addition, sketch the effluent concentration of A as a function of time. The reaction is a simple isomerization:

$$A \longrightarrow B$$

(a) Rate law: $-r'_A = kaC_A$

Decay law: $r_d = k_d a C_A$

Case I: $k_d \ll k$, Case II: $k_d = k$, Case III: $k_d \gg k$

(b) $-r'_A = kaC_A$ and $r_d = k_d a^2$

(c) $-r'_A = kaC_A$ and $r_d = k_d a C_B$

(d) Sketch similar profiles for the rate laws in parts (a) and (c) in a *moving-bed reactor* with the solids entering at the same end of the reactor as the reactant.

(e) Repeat part (d) for the case where the solids and the reactant enter at opposite ends.

P10-18$_\text{B}$ The elementary irreversible gas-phase catalytic reaction

$$\mathrm{A + B} \xrightarrow{k} \mathrm{C + D}$$

is to be carried out in a moving-bed reactor at constant temperature. The reactor contains 5 kg of catalyst. The feed is stoichiometric in A and B. The entering concentration of A is 0.2 mol/dm^3. The catalyst decay law is zero order with $k_D = 0.2\ \text{s}^{-1}$ and $k = 1.0\ \text{dm}^6/(\text{mol} \cdot \text{kg-cat} \cdot \text{s})$ and the volumetric flow rate is $v_0 = 1\ \text{dm}^3/\text{s}$.

(a) What conversion will be achieved for a catalyst feed rate of 0.5 kg/s? (***Ans.:*** $X = 0.2$)

(b) Sketch the catalyst activity as a function of catalyst weight (i.e., distance) down the reactor length for a catalyst feed rate of 0.5 kg/s.

(c) What is the maximum conversion that could be achieved (i.e., at an infinite catalyst loading rate)?

(d) What catalyst loading rate is necessary to achieve 40% conversion? (***Ans.:*** $U_S = 1.5$ kg/s)

(e) At what catalyst loading rate (kg/s) will the catalyst activity be exactly zero at the exit of the reactor?

(f) What does an activity of zero mean? Can catalyst activity be less than zero?

(g) How would your answer in part (a) change if the catalyst and reactant were fed at opposite ends? Compare with part (a).

(h) Now consider the reaction to be zero order with
$k = 0.2$ mol/kg-cat · min.
The economics:

- The product sells for $160 per gram mole.
- The cost of operating the bed is $10 per kilogram of catalyst exiting the bed.

What is the feed rate of solids (kg/min) that will give the maximum profit? (***Ans.:*** $U_s = 4$ kg/min.) (*Note:* For the purpose of this calculation, ignore all other costs, such as the cost of the reactant, the cost to the company of providing free lunches to workers, etc.)

P10-19$_\text{B}$ With the increasing demand for xylene in the petrochemical industry, the production of xylene from toluene disproportionation has gained attention in recent years [*Ind. Eng. Chem. Res.*, 26, 1854 (1987)]. This reaction,

$$2\ \text{Toluene} \longrightarrow \text{Benzene} + \text{Xylene}$$

$$2\mathrm{T} \xrightarrow{\text{catalyst}} \mathrm{B + X}$$

was studied over a hydrogen mordenite catalyst that decays with time. As a first approximation, assume that the catalyst follows second-order decay

$$r_d = k_d a^2$$

and the rate law for low conversions is

$$-r'_\mathrm{T} = k_\mathrm{T} P_\mathrm{T} a$$

with $k_\mathrm{T} = 20$ g mol/h·kg-cat·atm and $k_d = 1.6\ \text{h}^{-1}$ at 735 K.

(a) Compare the conversion-time curves in a batch reactor containing 5 kg-cat at different initial partial pressures (1 atm, 10 atm, etc.). The reaction volume containing pure toluene initially is 1 dm^3 and the temperature is 735 K.

(b) What conversion can be achieved in a *moving-bed reactor* containing 50 kg of catalyst with a catalyst feed rate of 2 kg/h? Toluene is fed at a pressure of 2 atm and a rate of 10 mol/min.

(c) Explore the effect of catalyst feed rate on conversion.

(d) Suppose that $E_\mathrm{T} = 25$ kcal/mol and $E_d = 10$ kcal/mol. What would the temperature–time trajectory look like for a CSTR? What if $E_\mathrm{T} = 10$ kcal/mol and $E_d = 25$ kcal/mol?

(e) The decay law more closely follows the equation

$$r_d = k_d P_T^2 a^2$$

with $k_d = 0.2 \text{ atm}^{-2} \text{ h}^{-1}$. Redo parts (b) and (c) for these conditions.

P10-20$_A$ The vapor-phase cracking of gas-oil in Example 10-6 is carried out over a different catalyst, for which the rate law is

$$-r_A' = k' P_A^2 \qquad \text{with } k' = 5 \times 10^{-5} \frac{\text{kmol}}{\text{kg-cat} \cdot \text{s} \cdot \text{atm}^2}$$

(a) Assuming that you can vary the entering pressure and gas velocity, what operating conditions would you recommend?

(b) What could go wrong with the conditions you chose?
Now assume the decay law is

$$-\frac{da}{dt} = k_D a C_{\text{coke}} \qquad \text{with } k_D = 100 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 400°\text{C}$$

where the concentration, C_{coke}, in mol/dm^3, can be determined from a stoichiometric table.

(c) For a temperature of 400°C and a reactor height of 15 m, what gas velocity do you recommend? Explain. What is the corresponding conversion?

(d) The reaction is now to be carried in an STTR 15 m high and 1.5 m in diameter. The gas velocity is 2.5 m/s. You can operate in the temperature range between 100 and 500°C. What temperature do you choose, and what is the corresponding conversion?

(e) What would the temperature–time trajectory look like for a CSTR?

Additional information:

$E_R = 3000$ cal/mol
$E_D = 15{,}000$ cal/mol

P10-21$_C$ When the impurity cumene hydroperoxide is present in trace amounts in a cumene feed stream, it can deactivate the silica-alumina catalyst over which cumene is being cracked to form benzene and propylene. The following data were taken at 1 atm and 420°C in a differential reactor. The feed consists of cumene and a trace (0.08 mol %) of cumene hydroperoxide (CHP).

Benzene in Exit Stream (mol %)	2	1.62	1.31	1.06	0.85	0.56	0.37	0.24
t (s)	0	50	100	150	200	300	400	500

(a) Determine the order of decay and the decay constant. (***Ans.:*** $k_d = 4.27 \times 10^{-3} \text{ s}^{-1}$.)

(b) As a first approximation (actually a rather good one), we shall neglect the denominator of the catalytic rate law and consider the reaction to be first order in cumene. Given that the specific reaction rate with respect to cumene is $k = 3.8 \times 10^3$ mol/kg fresh cat · s · atm, the molar flow rate of cumene (99.92% cumene, 0.08% CHP) is 200 mol/min, the entering concentration is 0.06 kmol/m^3, the catalyst weight is 100 kg, and the velocity of solids is 1.0 kg/min, what conversion of cumene will be achieved in a *moving-bed reactor*?

P10-22$_C$ The decomposition of spartanol to wulfrene and CO_2 is often carried out at high temperatures [*J. Theor. Exp.*, 15, 15 (2014)]. Consequently, the denominator of the catalytic rate law is easily approximated as unity, and the reaction is first order with an activation energy of 150 kJ/mol.

Fortunately, the reaction is irreversible. Unfortunately, the catalyst over which the reaction occurs decays with time on stream. The following conversion-time data were obtained in a differential reactor:

For $T = 500$ K:

t (days)	0	20	40	60	80	120
X (%)	1	0.7	0.56	0.45	0.38	0.29

For $T = 550$ K:

t (days)	0	5	10	15	20	30	40
X (%)	2	1.2	0.89	0.69	0.57	0.42	0.33

(a) If the initial temperature of the catalyst is 480 K, determine the *temperature–time trajectory* to maintain a constant conversion.

(b) What is the catalyst lifetime?

P10-23$_B$ The hydrogenation of ethylbenzene to ethylcyclohexane over a nickel-mordenite catalyst is zero order in both reactants up to an ethylbenzene conversion of 75% [*Ind. Eng. Chem. Res.*, 28 (3), 260 (1989)]. At 553 K, $k = 5.8$ mol ethylbenzene/(dm^3 of catalyst·h). When a 100-ppm thiophene concentration entered the system, the ethylbenzene conversion began to drop.

Time (h)	0	1	2	4	6	8	12
Conversion	0.92	0.82	0.75	0.50	0.30	0.21	0.10

The reaction was carried out at 3 MPa and a molar ratio of H_2/ETB = 10. Discuss the catalyst decay. Be quantitative where possible.

SUPPLEMENTARY READING

1. A terrific discussion of heterogeneous catalytic mechanisms and rate-controlling steps may or may not be found in

BURGESS, THORNTON W., *The Adventures of Grandfather Frog*. New York: Dover Publications, Inc., 1915.

MASEL, R. I., *Principles of Adsorption and Reaction on Solid Surfaces.* New York: Wiley, 1996. A great reference.

SOMORJAI, G. A., *Introduction to Surface Chemistry and Catalysis.* New York: Wiley, 1994.

2. A truly excellent discussion of the types and rates of adsorption together with techniques used in measuring catalytic surface areas is presented in

MASEL, R. I., *Principles of Adsorption and Reaction on Solid Surfaces.* New York: Wiley, 1996.

3. Techniques for discriminating between mechanisms and models can be found in

BOX, G. E. P., W. G. HUNTER, and J. S. HUNTER, *Statistics for Experimenters*. New York: Wiley, 1978.

4. Examples of applications of catalytic principles to microelectronic manufacturing can be found in

BUTT, JOHN B, *Reaction Kinetics and Reactor Design. Second Edition, Revised and Expanded.* New York: Marcel Dekker, Inc., 1999.

DOBKIN, D. M., and M. K. ZURAW. *Principles of Chemical Vapor Deposition.* The Netherlands: Kluwer Academic Publishers, 2003.