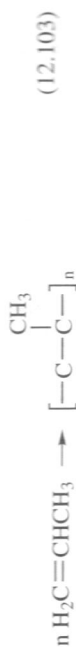


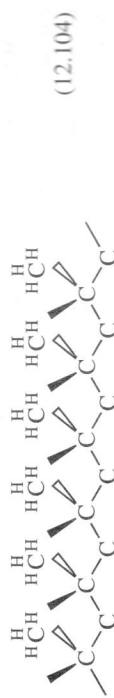
only when the reactants are in the correct configuration to react via the desired pathway. The result is that you get desired reaction and not an undesired one.

One specific example where this effect is very important is in the polymerization of propylene:

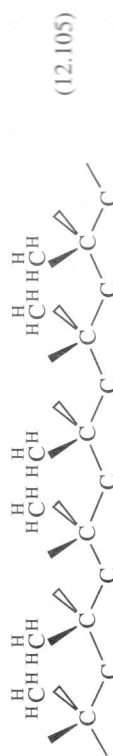


Polypropylene undergoes free-radical or cationic polymerization as discussed in Chapter 5. When the free-radical reaction occurs, the methyl group can go on the top or the bottom of the molecule. If the methyl groups are distributed randomly, the polymer has poor mechanical properties. As a result, the polymer cannot be used in many applications. In contrast, if one can control the positions of the methyl groups, one can produce polymers with much better mechanical properties. Such polymers are very valuable.

There are two key forms of oriented polypropylene: isotactic polypropylene, where all of the methyl groups are on one side



and syndiotactic polypropylene, where the methyl groups alternate from side to side:



Consider making isotactic polyethylene. Figure 12.24 shows a diagram of a step during the production of isotactic polypropylene where a single propylene unit is added to a growing polymer chain. Notice that one can add the propylene, with a methyl group facing in the correct direction or in the wrong direction. If one would add the propylene with the methyl group facing the wrong way, polymerization would still occur, but one would not end up with isotactic polypropylene.

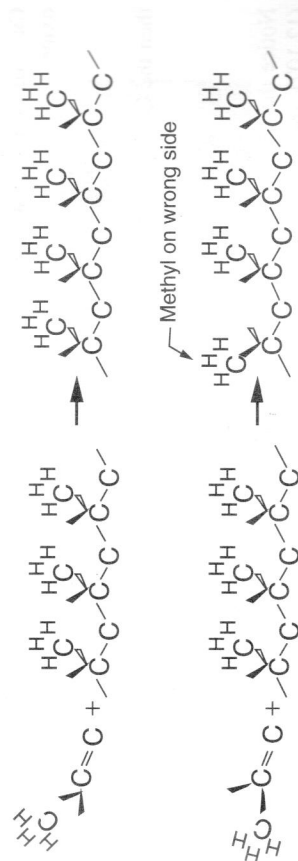


Figure 12.24 A rough diagram of one step during the production of isotactic polypropylene.

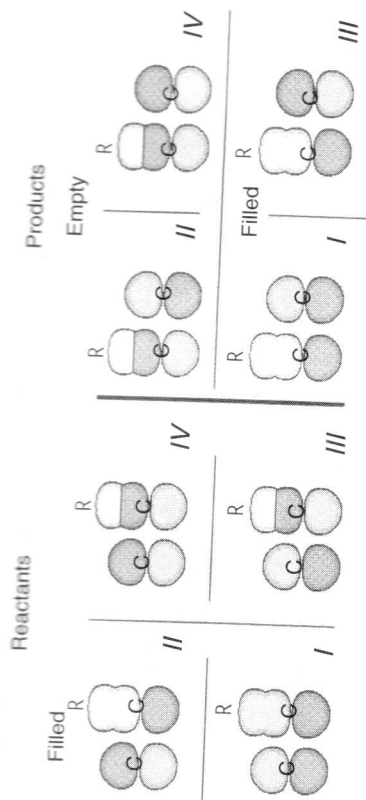


Figure 12.23 A rough diagram of the key MOs during reaction (12.101).

During reaction (12.101) the system starts out with the orbitals in the left of Figure 12.23. There are four MOs labeled I, II, III, and IV. In the diagram, we have arbitrarily assigned the lobe on the *R* group to have a positive sign, and then considered all possible signs on the *p* hybrids on the carbon. In MO I, both the *p*'s are positive; in MO II, the left *p* is negative, while the right *p* is positive. In the MO III the right *p* is negative and the left *p* is positive, while in MO IV, both *p*'s are negative. In MOs I and II, the π group has a bonding interaction with the carbon, while in III and IV, there is a sign change in moving from *R* to *C* and so the interaction is antibonding. As a result, orbitals I and II are bonding orbitals while orbitals III and IV are antibonding orbitals. In contrast, at the end of the reaction, the *R* group migrates from the right to the left of the molecule. In this case, orbitals I and III are bonding while orbitals II and IV are antibonding.

Now consider moving the *R* group. Notice that the *R* group needs to move across the molecule for reaction to occur. However, in order to move the positive orbital on the *R* group in orbital II, it will need to displace the negative nonbonding orbital on the carbon. In Chapter 10 we found that such orbital displacements have large barriers. The net effect is that 1,2 displacements have large barriers with neutral radicals.

Notice that the repulsion occurs only because the electrons in the *R* group are pushing up against the nonbonding orbital in the molecule. If one modifies the charges on the molecule, one can remove the electrons from the nonbonding orbital. If one puts a +1 charge on the molecule, there will be no repulsions.

Well, again on **superacid catalysts** the charge is nearly +1. That promotes easy isomerization. The net result is that the superacid catalyst is able to promote reaction (12.101). These results show that catalysts can modify the intrinsic barriers to reaction. These modifications allow very selective reactions to occur.

These results show that catalysts can be designed to modify the changes on the reactants in a way that facilitates reaction.

12.12 CATALYSTS CAN BE DESIGNED TO BLOCK SIDE REACTIONS

Another thing that catalysts can do is to block side reactions. The idea is simple. You design the catalyst so that it is shaped in such a way that the reactants can get together

There are several examples where the electron transfer process is more direct. For example, the electron transfer reaction

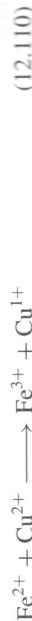


is slow because the +2 charge on the iron repels the +3 charge on the vanadium. Further, the solvation shells on the iron and vanadium get in the way of each other. The repulsion is less with Cu^{1+} because Cu^{1+} has only a +1 charge. Further copper has a much smaller solvation shell than either iron or nickel. As a result, copper ions can facilitate reaction (12.108).

The main mechanism of the reaction is electron exchange. First Cu^{1+} reacts with V^{4+} donating an electron:



Then the Cu^{1+} is regenerated by reaction with Fe^{2+} :



Notice that the copper is donating electrons in reaction (12.109) and accepting the electron back again in reaction (12.110). This is another example where the catalyst works by donating and accepting charge.

Another application of this technique is in fuel cells. Fuel cells are commonly used to generate electricity. Figure 12.26 shows a diagram of a simple hydrogen fuel cell. Generally, hydrogen reacts on a platinum catalyst on the anode of the fuel cell to produce protons and electrons:



where e^- is an electron. The protons are then transmitted through a polymer membrane in the fuel cell, where they react on the cathode:



Fuel cells can produce enough power to run an automobile. Notice that the catalyst on the anode is accepting electrons, while the catalyst on the cathode is giving up electrons. This is a further example showing that catalysts can work by accepting and donating electrons,

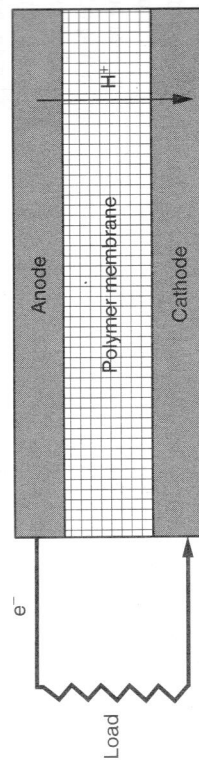


Figure 12.26 A diagram of a polymer fuel cell.

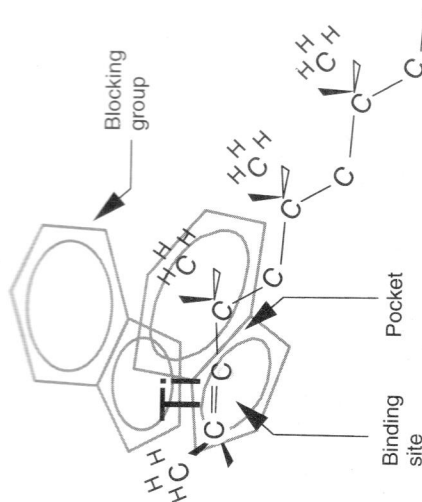


Figure 12.25 A diagram of propylene polymerization in a Ziegler-Natta catalyst.

When one runs these reactions industrially, one makes these polymers with what is called a *Ziegler-Natta catalyst*. The Ziegler-Natta catalyst is designed to produce only isotactic propylene. Figure 12.25 shows a diagram of the active site in a Ziegler-Natta catalyst. The titanium atom actually catalyzes the reaction. However, the titanium atom is surrounded by ligands that enclose the site. There are two pockets in the ligands. During the reaction, propylene squeezes into the pockets and reacts. The ligands prevent the propylene from twisting. That prevents the side reaction. The net result is that all of the methyl groups line up on the same side.

This example shows that there can be an advantage to designing a catalyst with blocking groups to prevent side reactions.

12.13 CATALYSTS CAN BE DESIGNED TO DONATE AND ACCEPT ELECTRONS

Another mode of catalytic action is for the catalyst to donate or accept electrons. Recall that in Section 2.3.2 we found that certain metal oxides are effective oxidation catalysts because they can store and give up lattice oxygen. Well, these catalysts work by a redox process where the metal is oxidized and reduced. For example, consider CO oxidation over a copper substrate. There are two stable copper oxides: Cu^{1+} oxide (i.e., Cu_2O) and Cu^{2+} oxide (i.e., CuO). During the reaction, the Cu^{1+} oxide is first oxidized to a Cu^{2+} oxide:



then the Cu^{2+} oxide reacts with CO to yield a Cu^{1+} oxide:



Notice that in step (12.106) the copper donates an electron to the oxygen, while in step (12.107), the oxygen donates electrons back to the copper. The donation and release of electrons makes copper a good catalyst for CO oxidation.

12.14 CATALYSTS CAN ACT AS AN EFFICIENT MEANS FOR ENERGY TRANSFER

There is one other mode of catalytic action that people do not talk about much in the literature. Catalysts can be designed to act as an efficient means for energy transfer. Recall from Chapter 9 that the rate of most unimolecular reactions and bimolecular recombination reactions is limited by the rate at which energy enters or leaves the molecule. For example, the reaction



has a zero rate in the absence of a collision partner even though the reaction is 98 kcal/mol exothermic. If you add a collision partner, the reaction goes very quickly. In a sense, the collision partner is acting like a catalyst to carry heat away from the reactants.

It happens that solid catalysts are often much better collision partners than are gaseous species. For example, when Polanyi (1932) first examined reaction (12.113), he found that most of the reaction occurred on the walls of his vessel. The walls were acting as an efficient means of heat transfer, and thereby allowed reaction to occur. All solid catalysts or solvents have similar effects. The catalysts provide very efficient means for heat transfer. That allows reaction to occur. In practice, most unimolecular and bimolecular reactants occur much more rapidly in the presence of a liquid or a solid. Therefore, the reaction is being catalyzed even though the catalyst never binds strongly to the reactants.

12.15 MASS TRANSFER EFFECTS ARE MORE IMPORTANT WHEN A CATALYST IS PRESENT

Finally, it is important to point out that mass transfer effects become more important when catalysts are present. Recall that, according to collision theory, the rate of reaction is determined by the rate that molecules collide, according to collision theory, the rate of reaction for the fact that not all molecules that collide react. In a solution, the collision rate is determined by mass transfer effects, while the fraction that reacts is determined by what happens after the reactants collide. A catalyst can modify the fraction of the molecules that react once the molecules collide. However, the catalyst cannot make the reactants collide more quickly. As a result, as you speed up a reaction with a catalyst, the rate of reaction will eventually be limited by the rate of collisions.

The rate of collisions is determined by the rate at which the reactants diffuse together. The diffusion rate is, in turn, determined by the mass transfer rate. The net effect is that mass transfer became more important as you improve catalysts, so mass transfer controls the rate of reaction on the very best catalysts.

When students first hear that mass transfer is controlling the rate, they think that the catalyst is not doing its job. However, catalysts are supposed to speed up rates of reactions, and if one speeds up a reaction enough, one always finds that diffusion starts to play a role. The best catalysts speed up a reaction so much that the reaction rate is instantaneous once the reactants collide. The result is that the mass transfer effects control the rate of reaction.

People usually quantify the role of mass transfer on the basis of two parameters: the Thiele parameter, Φ_p ; and what I call a mass transfer factor, η . The Thiele parameter is defined by

$$\Phi_p = \frac{\text{reaction rate}}{\text{diffusion rate}} \tag{12.114}$$

The mass transfer factor is defined by

$$\eta_e = \frac{\text{actual reaction rate}}{\text{reaction rate if mass transfer were instantaneous}} \tag{12.115}$$

In the literature people call the mass transfer factor an **effectiveness factor**. We derive equations for Φ_p and η_e in the supplemental material. The result for a first-order reaction occurring in a spherical catalyst pellet is

$$\eta_e = \frac{1}{\Phi_p} \left[\frac{1}{\tanh(3\Phi_p)} - \frac{1}{3\Phi_p} \right] \tag{12.116}$$

$$\Phi_p = y_p \sqrt{\frac{k_1}{D_e}} \tag{12.117}$$

where y_p is the radius of the pellet, k_1 is the rate constant for the reaction, and D_e is the diffusivity of the reactant in the pellet.

Figure 12.27 shows a plot of the mass transfer factor versus the Thiele parameter for diffusion into a solid catalyst pellet. Basically, the mass transfer factor is unity when the Thiele parameter is much less than one, and then tails off linearly when the Thiele parameter is greater than one. One can show that when $\Phi_p > 10$, the term in brackets in equation (12.116) is between 0.9 and 1, under these circumstances:

$$\eta_e \approx \frac{0.95}{\Phi_p} \tag{12.118}$$

To keep Figure 12.27 in perspective, there is some confusion created by calling η_e an effectiveness factor. The mass transfer factor does not measure the effectiveness of a catalyst. *Good catalysts can have low mass transfer factors, while bad catalysts can have high mass transfer factors.* Generally, if a catalyst is not speeding up the reaction very much, the Thiele parameter will be small, which means that, according to Figure 12.27, the mass transfer factor will be close to unity. Thus, a bad catalyst can have a large mass transfer factor.

In contrast, if the catalyst speeds up a reaction by a considerable amount Φ_p will be large. Figure 12.27 shows that the mass transfer factor is reduced under such circumstances.

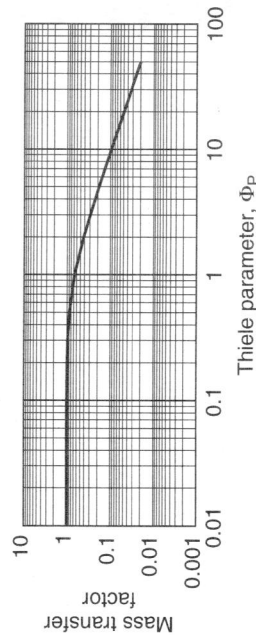


Figure 12.27 A plot of the mass transfer factor versus the Thiele parameter for diffusion in a porous catalyst pellet.

All of this is a balance because you can also get a large Φ_p if you have designed the catalyst pellet wrong so that D_e is too small. However, that is rarely an issue with modern support materials. Usually, a small mass transfer factor is associated with a very active catalyst. Consequently, *the mass transfer factor does not measure the effectiveness of a catalyst even though the mass transfer factor is often called an effectiveness factor in the literature.*

I believe it is important to think of η_e as a **mass transfer** factor, not an effectiveness factor. Generally, when η_e is small, you are near the mass transfer limit, so there is little that you can do to improve the catalyst except speedup the mass transfer rate. On the other hand, when η_e is large, the reaction rate is slow compared to the diffusion rate so that you can do to speed up the reaction. When I teach this material, I call η_e a mass transfer factor. However, η_e is still called an “effectiveness factor” in the literature.

12.15.1 Shape-Selective Catalysis

The other thing to recognize is that mass transfer limitations are not necessarily bad. In industrial practice, mass transfer limitations are used as design variables to improve the efficiency of catalysts.

One of the problems in designing a catalyst is that most catalytic materials speed up a wide variety of reactions. The rate of the desired reaction is enhanced. However, often the rates of some undesirable reactions are also enhanced. Fortunately, there is a design strategy to get around this difficulty:

- Use a solid catalyst.
- Design the solid in such a way that only the desired product can get out of the catalyst.
- Add enough catalytic components so that even if a side product is formed, the side product will be converted into the desired product.

An example of this strategy comes in the production of *para*-xylene. Xylene can be made via the alkylation of toluene over an acid catalyst



The alkylation reaction produces *meta*- and *ortho*-xylene in addition to *para*-xylene. People run the reaction in a catalyst that has acid sites in an interconnecting pore structure like that in Figure 12.28. The *o*-, *m*-, and *p*-xylene are formed at the acid sites, and then need to diffuse out of the pores before the xylene can leave the reactor.

Note that if you align *m*- and *o*-xylene standing with the methyl facing up, the *m*- and *o*-xylene are wider than the *para*-xylene. As a result, if one designs a structure like that in Figure 12.28 with pores that just fit *para*-xylene, *o*- and *m*-xylene will not be able to diffuse down the pores, so the *o*- and *m*-xylene get trapped in the catalyst. One then adds an occasional isomerization site to the catalyst. The isomerization site converts the *o*- and *m*-xylene to *p*-xylene. The net result is that the catalyst produces mainly *p*-xylene, even though the alkylation reaction, reaction (12.119), produces similar amounts of *o*-, *m*-, and *p*-xylene.

People call this type of catalyst a **shape-selective catalyst**, because you are able to select molecules according to their shape and how easily they diffuse. Shape-selective catalysis is very important, because one can design very selective catalysts. Still, it is not

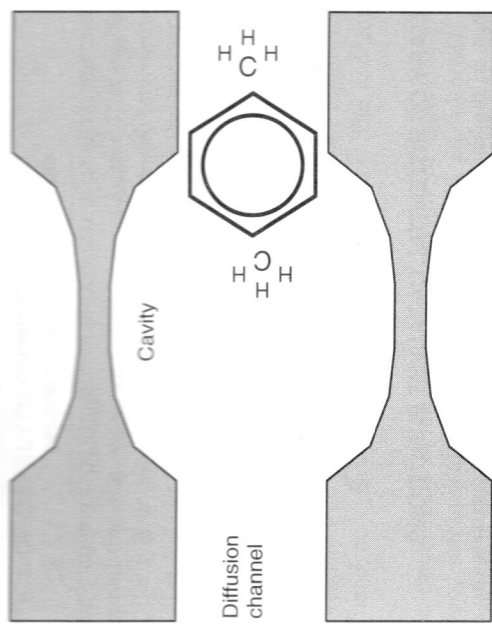


Figure 12.28 An interconnecting pore structure that is selective for the formation of *para*-xylene.

so easy to make a catalyst with just the right size pores, so this is an area where there is more art than science.

Table 12.12 lists several different materials that are used as shape-selective catalysts. Generally, shape-selective catalysts are made out of materials called **zeolites**. Zeolites are silica aluminas, with very uniform pores. Figure 12.5 shows a single unit cell in a zeolite. Generally, zeolites consist of small cages stacked on top of each other. There are small interconnecting pores between the cages. Table 12.12 shows the pore sizes in some zeolites, while Table 12.13 shows the dimensions of some typical molecules. Notice that you can choose the pore sizes so that only certain molecules can squeeze through the pores. Thus zeolite can be used to selectively produce a designed product, while not producing a larger side product.

Zeolites can be used with a wide variety of catalyst materials, and can be used to promote selectivity in a wide number of reactions. Therefore, they are very useful for catalyst design.

Table 12.12 Pore sizes in some zeolites

Zeolite	Size of	
	Diffusion Channel, Å	Size of Cavity, Å
Chabazite	3.6 × 3.7	5
Zeolite A	4.1 × 4.1	6.5
Erondite	3.6 × 5.2	11.6
Ferrierite	4.3 × 5.5	6.5
ZSM-5	5.5 × 5.6	10.5
Offretite	6.4 × 6.4	6.5
Mordenite	6.7 × 7.0	10.5
Faujasite	7.4 × 7.4	11.9
VFI	13 × 13	—

Table 12.13 Minimum diameters of some molecules

Molecule	Minimum Diameter, Å
Linear alkane	4
Isoalkane	5.5
Benzene	5.1
Paraxylene	5.1
Orthoxylene	5.7
2-Methyl alkenes	5.1
Naphthalene	7.3

12.16 SUMMARY OF POTENTIAL CATALYST FUNCTIONS

In summary, then, in the last few sections, we showed that catalysts *can* change rates in eight key ways:

- Catalysts can be designed to help initiate reactions.
- Catalysts can be designed to stabilize the intermediates of a reaction.
- Catalysts can be designed to hold the reactants in close proximity.
- Catalysts can be designed to hold the reactants in the right configuration to react.
- Catalysts can be designed to block side reactions.
- Catalysts can be designed to sequentially stretch bonds and otherwise make bonds easier to break.
- Catalysts can be designed to donate and accept electrons.
- Catalysts can be designed to act as an efficient means for energy transfer.

It is also important to realize that

- One needs a catalytic cycle to get reactions to happen.
- Mass transfer limitations are more important when a catalyst is present.

One of the questions I get when I teach this material is “Here are all of these effects, how do I know which effect will be the most important in a given catalyst system?” Unfortunately, at present we rarely know the answer to that question. As noted in Section 12.1, one would like the catalyst to do all of these things. For example, platinum is a wonderful catalyst for olefin hydrogenation. The platinum speeds up the initiation step during the hydrogenation process. The platinum stabilizes the intermediates of the reaction. The platinum holds the reactants in close proximity. The platinum also lowers the intrinsic barrier to hydrogenation.

Platinum does everything so it is a great catalyst. It is not clear how to know that *a priori*. Generally, the most important effect of a catalyst is to stabilize intermediates and initiate reactions. However, all of the other effects also occur to some extent with any catalyst. Consequently, catalytic reactions are less well understood than, for example, gas-phase reactions.

12.17 KINETICS OF CATALYTIC REACTIONS

Next, we will be changing topics to discuss the kinetics of catalytic reactions. So far in this chapter, we learned that most catalytic reactions are the same. The reactants bind to the catalyst. Then, the system goes through a catalytic cycle where intermediates are formed and destroyed. Finally, the products leave the catalyst and the catalyst is regenerated. In the next two sections, we will derive equations for the rates of catalytic reactions. We discussed many of the details in Section 5.10, but it is useful to repeat some of the findings here:

- First, all reactions go by a catalytic cycle. For example, Figure 12.29 shows two different catalytic cycles for the production of water. The reactants adsorb, then react.
- There are three kinds of mechanisms as shown in Figure 12.30: a Langmuir-Hinshelwood mechanism where all of the reactants are adsorbed; a Rideal-Eley mechanism, where a gas-phase species collides with an adsorbed species and reacts; and a precursor mechanism, where there is one strongly bound reactant bound and a precursor reactant in a weakly bound precursor state.

There are several examples of these mechanisms in Section 5.10. The reader should review Section 5.10 before proceeding.

Next, we note that it is important to think about the rate of a catalytic reaction in terms of a **turnover number**, T_N . The turnover number is also called the **turnover frequency**.

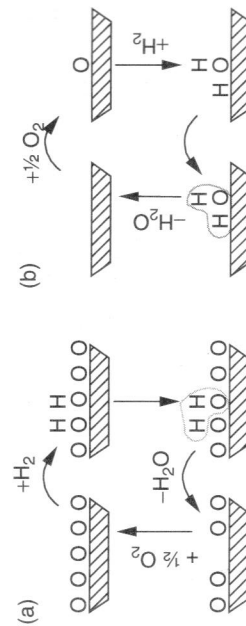


Figure 12.29 Catalytic cycles for the production of water via (a) disproportionation of OH groups, and (b) the reaction $\text{OH}_{(\text{ad})} + \text{H}_{(\text{ad})} \rightarrow \text{H}_2\text{O}$.

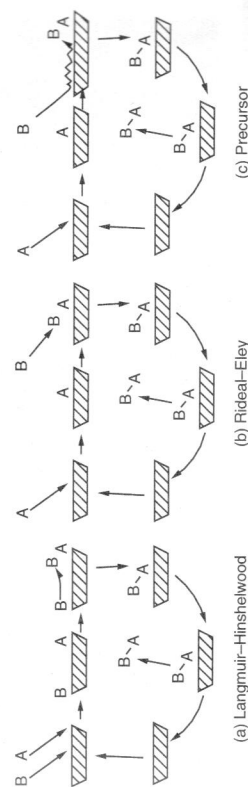


Figure 12.30 Schematic of (a) Langmuir-Hinshelwood, (b) Rideal-Eley, (c) precursor mechanism for the reaction $\text{A} + \text{B} \Rightarrow \text{AB}$ and $\text{AB} \Rightarrow \text{A} + \text{B}$.

In Chapter 2 we defined the turnover number as

$$T_N = \frac{R_A}{N_S} \quad (12.120)$$

where R_A is the rate of reaction per unit area and N_S is the number of metal atoms per unit area. Physically, the turnover number is the rate that the catalytic cycle occurs on each metal atom, measured in number of catalytic cycles per second.

Figure 12.31 shows some typical turnover numbers for catalytic reactions. The fastest reactions occur at rates of 100/second, while the slowest occur at 10^{-4} /second. There are a few examples of enzyme-catalyzed reactions that occur at 10^6 /second. In my experience, in industrial reactions, turnover numbers are most commonly between 0.1 and 10/second. Faster reactions are usually mass-transfer-limited. Slower reactions are usually indicative of a catalyst needing improvement.

12.17.1 Langmuir Rate Laws

As mentioned at the beginning of this section, next we want to discuss the kinetics of catalytic reactions. We briefly reviewed the kinetics of catalytic reactions in Section 2.7. Recall that we found that catalytic reactions show complex kinetics. Rates do not vary linearly with concentration. Arrhenius plots are curved. For example, Figures 12.32 and 12.33 show data for the reaction $\text{CO} + \frac{1}{2}\text{O}_2 \Rightarrow \text{CO}_2$. Notice that as we increase the CO partial pressure, the rate goes up, reaches a maximum, and then declines. In the remainder of this section we will derive an equation for the rate of a catalytic reaction to try to understand why the rates show such complex behavior.

The derivation will be based on Langmuir's model of adsorption. Langmuir proposed that gases bind to fixed sites on a catalyst's surface. During reaction, reactants bind to the surface sites as illustrated in Figure 12.34. Some sites will be empty, and some sites will be covered by reactants A or B. Langmuir proposed that adsorption will occur only when a gas-phase A molecule reacts with an empty site. Consequently, the rate of adsorption will be proportional to S , the number of empty sites on the catalyst surface.

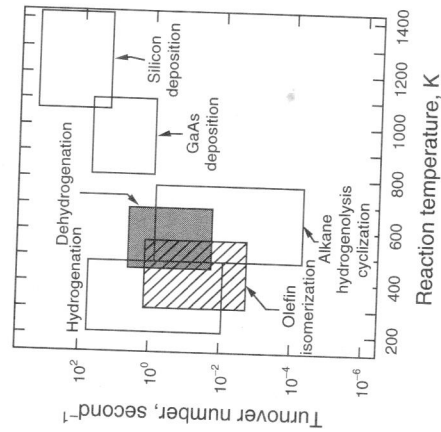


Figure 12.31 Turnover numbers for some typical processes.

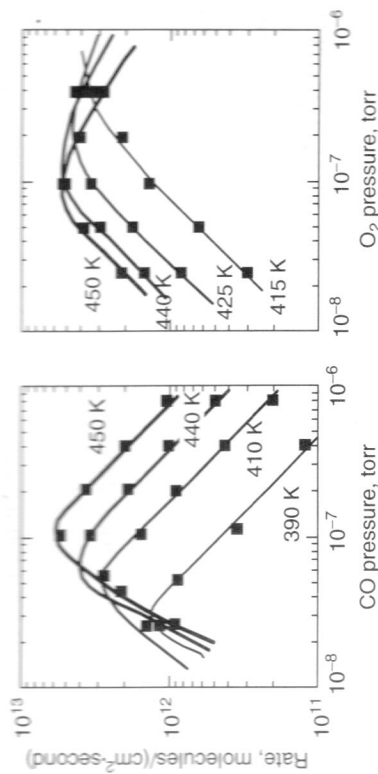


Figure 12.32 The influence of the CO pressure on the rate of CO oxidation on Rh(111). [Data of Schwartz et al. (1986).]

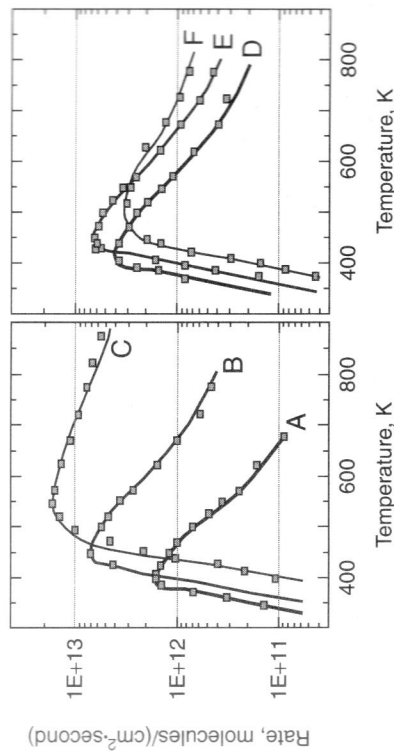


Figure 12.33 The rate of the reaction $\text{CO} + \frac{1}{2}\text{O}_2 \Rightarrow \text{CO}_2$ on Rh(111). (a) $P_{\text{CO}} = 2.5 \times 10^{-8}$ torr, $P_{\text{O}_2} = 2.5 \times 10^{-8}$ torr; (b) $P_{\text{CO}} = 1 \times 10^{-7}$ torr, $P_{\text{O}_2} = 2.5 \times 10^{-8}$ torr; (c) $P_{\text{CO}} = 8 \times 10^{-7}$ torr, $P_{\text{O}_2} = 2.5 \times 10^{-8}$ torr; (d) $P_{\text{CO}} = 2 \times 10^{-7}$ torr, $P_{\text{O}_2} = 4 \times 10^{-7}$ torr; (e) $P_{\text{CO}} = 2 \times 10^{-7}$ torr, $P_{\text{O}_2} = 2.5 \times 10^{-8}$ torr; (f) $P_{\text{CO}} = 2.5 \times 10^{-8}$ torr, $P_{\text{O}_2} = 2.5 \times 10^{-8}$ torr. [Data of Schwartz et al. (1986).]

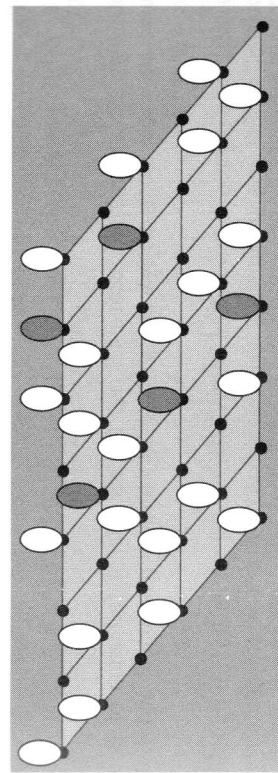
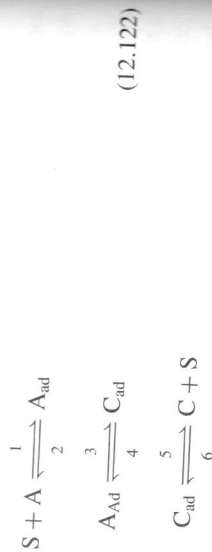


Figure 12.34 Langmuir's model for the adsorption of gas on a solid catalyst. The light gray area represents the surface of the catalyst. The black dots are the sites on the catalyst that are available to adsorb gas. The white ovals are the adsorbed A molecules. The dark ovals are adsorbed B molecules.

Consider the reaction



and assume that the reaction occurs via the following mechanism:



In reaction (12.121), A is a gas-phase molecule, S is an *empty* site, A_{ad} is an adsorbed A molecule, C_{ad} is an adsorbed C molecule, and C is a gas-phase C molecule.

We will assume that the reaction is being run in the presence of a species B, which adsorbs on the catalyst:



but does not participate in the reaction.

During reaction (12.122), A reacts with a bare site on the catalyst, S, to yield an adsorbed complex. Then the adsorbed complex rearranges to form a new species, C, and then the C desorbs, regenerating a bare site.

For purposes of derivation, it is useful to define

S_0 = the total concentration of sites available to adsorb gas (i.e., the total number of black dots in Figure 12.33), N/cm²

$[S]$ = the concentration of empty sites, N/cm² (i.e., the number of black dots that do not contain A or B)

$[A_{ad}]$ = the concentration of adsorbed A molecules, N/cm²

$[B_{ad}]$ = the concentration of adsorbed B molecules, N/cm²

$[C_{ad}]$ = the concentration of adsorbed C molecules, N/cm²

P_A = the partial pressure of A

P_B = the partial pressure of B

P_C = the partial pressure of C

Following the analysis in Section 4.3, r_B , the net rate of formation of B, can be measured anywhere along the reaction path. If we consider reactions 3 and 4, we find that r_C is given by:

$$r_C = k_3[A_{ad}] - k_4[C_{ad}] \quad (12.124)$$

where k_3 and k_4 are the rate constants for reactions 3 and 4, and $[A_{ad}]$ and $[C_{ad}]$ are the concentrations of adsorbed A and C. $[A_{ad}]$ and $[C_{ad}]$ have units of molecules/cm² (or mol/cm²) for a solid catalyst, molecules/cluster for a metal cluster catalyst, or molecules/enzyme for an enzyme catalyst.

One can calculate $[A_{ad}]$ and $[C_{ad}]$ from the steady-state approximation:

$$0 = r_{A_{ad}} = k_1 P_A [S] - k_2 [A_{ad}] - k_3 [A_{ad}] + k_4 [C_{ad}] \quad (12.125)$$

$$0 = r_{C_{ad}} = k_6 P_C [S] - k_5 [C_{ad}] - k_4 [C_{ad}] + k_3 [A_{ad}] \quad (12.126)$$

where $r_{A_{ad}}$ and $r_{C_{ad}}$ are the rates of formation of adsorbed A and B, P_A and P_C are the partial pressures of A and C over the reactive surface, and $[S]$ is the concentration of empty surface sites.

In the literature, it is common to assume that reactions 3 and 4 are rate-determining. Under such circumstances, k_3 will be much smaller than k_2 and k_6 , while k_4 will be much smaller than k_5 and k_1 . Therefore the last two terms in equations (12.125) and (12.126) will be negligible. Under such circumstances

$$[A_{ad}] = \left(\frac{k_1}{k_2} \right) P_A [S] \quad (12.127)$$

$$[C_{ad}] = \left(\frac{k_6}{k_5} \right) P_C [S] \quad (12.128)$$

Similarly for B

$$[B_{ad}] = \frac{k_8}{k_7} P_B [S] \quad (12.129)$$

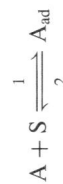
Rearranging equations (12.127)–(12.129) yields

$$\frac{[A_{ad}]}{P_A [S]} = \left(\frac{k_1}{k_2} \right) \quad (12.130)$$

$$\frac{[B_{ad}]}{P_B [S]} = \left(\frac{k_8}{k_7} \right) \quad (12.131)$$

$$\frac{[C_{ad}]}{P_C [S]} = \left(\frac{k_6}{k_5} \right) \quad (12.132)$$

Equations (12.130) and (12.131) imply that there is an equilibrium in the following reactions:



One needs an expression for $[S]$ to complete the analysis. One can get an expression for $[S]$ by assuming that on any catalyst, there are a finite number of sites to hold the reactants. Each site can be bare, or it can be covered by A, B or C as indicated in Figure 12.33. If we define S_0 as the total number of sites in the catalyst, we can show

$$S_0 = [S] + [A_{ad}] + [B_{ad}] + [C_{ad}] \quad (12.134)$$

Substituting equations (12.127)–(12.129) into equation (12.134) and then solving for $[S]$ yields

$$[S] = \frac{S_0}{1 + \frac{k_1 P_A}{k_2} + \frac{k_8 P_B}{k_7} + \frac{k_6 P_C}{k_5}} \quad (12.135)$$

Substituting equation (12.135) into equations (12.127) and (12.128) yields

$$[A_{\text{ad}}] = \frac{\left(\frac{k_1}{k_2}\right) P_A S_0}{1 + \frac{k_1 P_A}{k_2} + \frac{k_8 P_B}{k_7} + \frac{k_6 P_C}{k_5}} \quad (12.136)$$

$$[C_{\text{ad}}] = \frac{\left(\frac{k_6}{k_5}\right) P_C S_0}{1 + \frac{k_1 P_A}{k_2} + \frac{k_8 P_B}{k_7} + \frac{k_6 P_C}{k_5}} \quad (12.137)$$

According to the analysis in Section 4.3, the equilibrium constant for the adsorption of A is given by

$$K_A = \frac{k_1}{k_2} \quad (12.138)$$

Similarly, the equilibrium constants for the adsorption of B, and C are given by

$$K_B = \frac{k_8}{k_7} \quad (12.139)$$

$$K_C = \frac{k_6}{k_5} \quad (12.140)$$

Substituting equations (12.138)–(12.140) into equations (12.136) and (12.137) yields

$$[A_{\text{ad}}] = \frac{K_A P_A S_0}{1 + K_A P_A + K_B P_B + K_C P_C} \quad (12.141)$$

$$[C_{\text{ad}}] = \frac{K_C P_C S_0}{1 + K_A P_A + K_B P_B + K_C P_C} \quad (12.142)$$

Substituting equations (12.141) and (12.142) into equation (12.124) yields

$$r = \frac{k_3 K_A P_A S_0 - k_4 K_C P_C S_0}{1 + K_A P_A + K_B P_B + K_C P_C} \quad (12.143)$$

In the catalysis literature, equation (12.143) is called the **Langmuir–Hinshelwood** expression for the rate of the reaction $A \Rightarrow C$, since we assumed that the reaction obeyed a Langmuir–Hinshelwood mechanism and the equation was first derived for surface reaction by Langmuir (1915). The same equation is called the *Michaelis–Menten equation* in the enzyme literature since it was also derived by Michaelis and Menten (1913).

12.17.2 Langmuir–Hinshelwood–Hougan–Watson Rate Laws

Next, I want to talk about a trick. In the homework set, we ask the reader to derive several Langmuir–Hinshelwood–Michaelis–Menten rate equations. One could follow the derivation in Section 12.17. However, Hougan and Watson (1943) found a trick that makes it easier to do the derivation. In this section, we will discuss the trick.

Let's go back to the example in Section 12.17. Notice that k_3 is much smaller than k_4 while k_4 is much smaller than k_5 in equations (12.125) and (12.126). Consequently, the last two terms in equations (12.125) and (12.126) are negligible. Consider equation (12.125). If the last two terms in equation (12.125) are negligible, then

$$k_1 P_A [S] \cong k_2 [A_{\text{ad}}] \quad (12.144)$$

Notice that the left side of equation (12.144) is the rate of reaction 1, while the right side of equation (12.144) is the rate of reaction 2. Therefore, the implication of equation (12.144) is that when steps 3 and 4 are rate-determining, the rate of reaction 1 will almost equal the rate of reaction 2. A similar analysis shows that when reactions 3 and 4 are rate-determining, the rate of reaction 5 must almost equal the rate of reaction 6.

Note, however, that this is only an approximation. The rate of reaction 5 cannot be exactly equal to the rate of reaction 6, because then there would be no net production of products. Similarly, if the rate of reaction 1 were exactly equal to the rate of reaction 2, there would be no net consumption of reactants. However, the implication of the preceding derivation is that one can calculate an accurate value of the surface concentration of each of the species attached to the catalyst by assuming that the rate of reaction 1 approximately equals the rate of reaction 2 and the rate of reaction 5 approximately equals the rate of reaction 6, even though in reality, the rates are not exactly equal.

One can extend these ideas to other situations. Consider, for the moment, how the arguments would change if reactions 5 and 6 were rate-determining in reaction (12.122). If 5 and 6 were rate-determining, then a steady-state approximation on C_{ad} would give

$$0 = r_{B,\text{ad}} = k_3 [A_{\text{ad}}] - k_4 [C_{\text{ad}}] - k_5 [C_{\text{ad}}] \quad (12.145)$$

As before, the last term in equation (12.145) is negligible:

$$k_3 [A_{\text{ad}}] \cong k_4 [C_{\text{ad}}] \quad (12.146)$$

The left side of equation (12.146) is the rate of reaction 3, while the right side is the rate of reaction 4. Therefore, the implication of equation (12.146) is that one can calculate the concentrations of adsorbed A and C by assuming that the rate of reaction 3 is equal to the rate of reaction 4. Now consider reactions 1 and 2. The steady-state approximation for A_{ad} implies

$$0 = r_{A,\text{ad}} = k_1 P_A [S] - k_2 [A_{\text{ad}}] + k_4 [C_{\text{ad}}] - k_3 [A_{\text{ad}}] \quad (12.147)$$

Note, however, that according to equation (12.146), the last two terms in equation (12.147) are approximately equal when reactions 5 and 6 are rate-determining. Therefore, when reactions 5 and 6 are rate-determining, one obtains

$$k_1 P_A [S] \cong k_2 [A_{\text{ad}}] \quad (12.148)$$

The left side of equation (12.148) is the rate of reaction 1 and the right side is the rate of reaction 2. Therefore, the implication of equation (12.148) is that when reactions 5 and 6 are rate determining, the rate of reaction 1 is approximately equal to the rate of reaction 2. We note again that the rates are not exactly equal. However, the key result is that one can calculate accurate surface concentrations by assuming that the rates are almost equal even though the rates are not exactly equal.

One can generalize these results to say that when there is a simple rate-determining step in a reaction, one can calculate an accurate rate equation by assuming that

- All the steps before the rate-determining step are in equilibrium with the reactants. Consequently, the concentration of all of the species before the rate-determining step can be calculated via an equilibrium expression with the reactants.
- All the steps after the rate-determining step are in equilibrium with the products. Consequently, the concentration of all of the species after the rate-determining step can be calculated via an equilibrium expression with the products.
- Sites are conserved, so one can calculate the concentration of bare sites via a site balance.

For example, if we have the reaction $A + B \rightleftharpoons C$ following the mechanisms



then the rate of production of C is given by

$$r_c = k_{151}[A_{ad}][B_{ad}] \tag{12.152}$$

If step (12.151) is rate-determining, then it is okay to assume that steps (12.149) and (12.150) are in equilibrium:

$$\frac{[A_{ad}]}{P_A[S]} = K_A \tag{12.153}$$

$$\frac{[B_{ad}]^2}{P_B[S]^2} = K_B \tag{12.154}$$

In equations (12.152), (12.153), and (12.154), [S] is concentration of empty sites, P_A and P_B are the partial pressures of A and B_2 , $[A_{ad}]$ and $[B_{ad}]$ are the concentrations of adsorbed A and B, K_A and K_B are the equilibrium constants for the adsorption of A and B, and k_{151} is the rate constant for reaction (12.151). Some of the terms in equation (12.154) are squared because, according to (12.150), when B_2 adsorbs, it produces two adsorbed B atoms.

Solving equations (12.153) and (12.154) for $[A_{ad}]$ and $[B_{ad}]$ and substituting that result into equation (12.152) yields

$$r_c = k_{151}K_A(K_B)^{0.5}P_A(P_B)^{0.5}[S]^2 \tag{12.155}$$

Next, we need an expression for [S]. We get it from a site balance let's define S_0 as the total number of sites available to adsorb gas (i.e., black dots in Figure 12.33). Notice that the black dots can be empty or they can be covered by A or B. Therefore

$$S_0 = [S] + [A_{ad}] + [B_{ad}] \tag{12.156}$$

Substituting $[A_{ad}]$ and $[B_{ad}]$ from equations (12.153) and (12.154) into (12.156) yields

$$S_0 = [S] + K_A P_A [S] + (K_B)^{0.5} (P_B)^{0.5} [S] \tag{12.157}$$

Solving equation (12.157) for [S] yields

$$[S] = \frac{S_0}{1 + K_A P_A + (K_B)^{0.5} (P_B)^{0.5}} \tag{12.158}$$

Substituting (12.158) into (12.155) yields the Langmuir–Hinshelwood–Hougen–Watson rate equation:

$$r_c = \frac{k_{151}K_A(K_B)^{0.5}(S_0)^2P_A(P_B)^{0.5}}{(1 + K_A P_A + (K_B)^{0.5}(P_B)^{0.5})^2} \tag{12.159}$$

We work out more examples in solved Examples 12.B and 12.C. The reader should examine those examples before proceeding.

12.17.3 Qualitative Features

Next, we want to discuss the predictions of the model. Figure 12.35 shows a plot of the rate of the $A \Rightarrow C$ reaction as a function of the reactant pressure calculated from equation (12.143) with $k_4 = 0$. Notice that the rate of reaction goes up and then levels off. Furthermore, as the partial pressure of B rises, the rate goes down even though we are considering the reaction $A \Rightarrow C$, so B is not participating in the reaction.

Notice that the trends in Figure 12.35 are quite different from the trends seen with gas-phase reactions. In the gas phase, the rate would increase with increasing A concentration and never level off. A species such as B, which is not participating in the reaction, would have no effect on the rate.

It is useful to compare the results in Figure 12.35 to the experimental results in Figure 2.14. Notice that the experimental results follow the trends expected from equation (12.143). In fact, the lines in Figure 2.14 were calculated from equation (12.143). Therefore, it seems that the experiments do follow the trends in equation (12.143). Clearly, the kinetics of catalytic reactions look quite different from the kinetics of gas-phase reactions even though the mechanisms of the two reactions look quite similar.

The reason why the rate shows this weird behavior is that the concentration of A on the catalyst does not have a simple relationship to the partial pressure of A. Figure 12.36 is a plot of $[A_{ad}]$, the concentration of A on the catalyst, calculated from the equation (12.141). Notice that the concentration of A on the catalyst increases as the partial pressure of A increases, and then levels off. As we increase the partial pressure of B, the surface concentration of A on the catalyst decreases, even though there is no direct reaction between A and B.

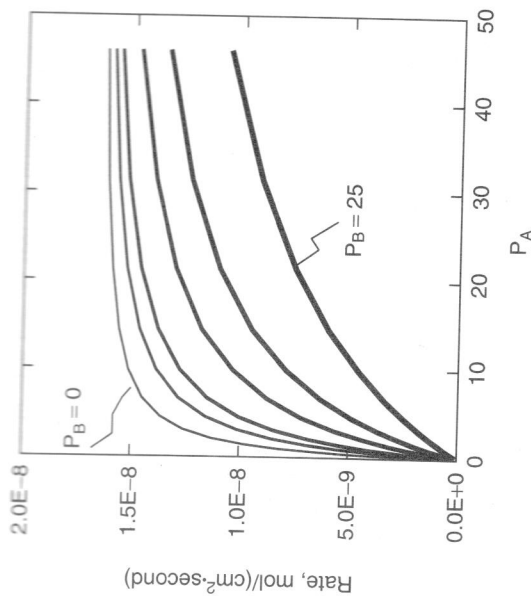


Figure 12.35 A plot of the rate of the reaction $A \rightarrow C$ calculated from equation (12.143) with $k_d = 0$, $P_B = 0$, $P_B = 0$, 1, 2, 5, 10 and 25, $K_A = K_B = 1$.

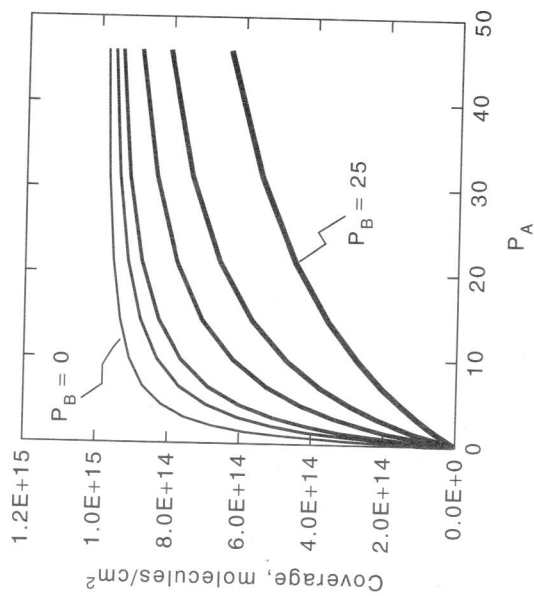


Figure 12.36 A plot of $[A_{ads}]$ calculated from the Langmuir adsorption isotherm, equation (12.141), with $K_A = 1$, $K_B = 1$, $P_B = 0$, 1, 2, 5, 10, 25.

This happens because there are only a finite number of sites on the catalyst to hold gas and A and B are competing for those sites. At low pressures, there are plenty of bare sites, so A simply adsorbs. However, at higher A pressures, the surface will start to fill up with gas. In that case, when one increases the partial pressure of A in the gas phase, one does not put that much more A onto the surface.

I find it useful to consider another quantity, θ_A , defined by

$$\theta_A = \frac{[A_{ad}]}{S_0} \quad (12.160)$$

where θ_A is the fraction of the sites on the catalyst that are covered with A. Substituting equation (12.141) into equation (12.160) shows

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B} \quad (12.161)$$

A similar derivation for B shows

$$\theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B} \quad (12.162)$$

Equation (12.161) is called the *Langmuir adsorption isotherm*. It was first derived by Langmuir (1912).

Figure 12.37 is a plot of θ_A as a function of P_A for various values of P_B . Notice that as θ_A approaches 1.0, a change in the partial pressure of A does not change the surface concentration of A significantly, because one cannot squeeze more A molecules onto the surface. Further, when P_B increases at constant P_A , the surface concentration of A decreases!

Molecule B takes up some of the surface sites and thereby partially blocks the adsorption of A. Consequently, as the partial pressure of B rises, the surface concentration of A decreases.

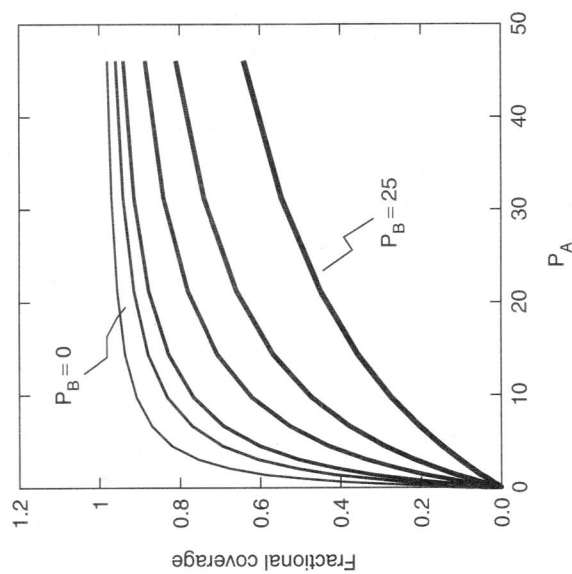


Figure 12.37 A plot of the Langmuir adsorption isotherm.

go to condense toward A, equation (12.167) arises because, with a condensable gas, you can get what is called a *multilayer*, where additional layers of gas condense on top of the first layer of gas.

Experimentally, one usually gets better kinetics with the Langmuir adsorption isotherm than with any other models. However, there are exceptions. See Masel (1996) for details.

12.17.5 Extension to More Complex Reactions

So far, we have discussed only the reaction $A \Rightarrow C$, but it is helpful to consider a slightly more complicated case:



This case was first considered by Langmuir [1919]. Langmuir assumed that the reaction followed a Langmuir-Hinshelwood mechanism:



Langmuir also assumed that step (3) in reaction (12.169) was much slower than the rest, so the surface concentrations of A and B maintained a dynamic equilibrium. If reaction 3 is elementary, then r_c , the rate of formation of C, is equal to

$$r_c = k_3[A_{ad}][B_{ad}] \quad (12.170)$$

where $[A_{ad}]$ and $[B_{ad}]$ are the concentrations of A and B on the surface of the catalyst in molecules/cm² and k_3 is the rate constant for reaction 3. If it is assumed that there are a fixed number of sites, S_0 , to hold gas then equation (12.168) can be rewritten

$$r = k_{AB}\theta_A\theta_B \quad (12.171)$$

where θ_A and θ_B are the fractional coverage of A and B, that is

$$\theta_A = \frac{[A_{ad}]}{S_0}, \quad \theta_B = \frac{[B_{ad}]}{S_0} \quad (12.172)$$

and $k_3(S_0)^2 = k_{AB}$. Langmuir then assumed that the adsorption of A and B would follow a Langmuir adsorption isotherm from equations (12.161) and (12.162) to obtain

$$r_c = \frac{k_{AB}K_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B)^2} \quad (12.173)$$

Equation (12.173) is the key result in this section. One should memorize it before proceeding.

Figure 12.38 shows a plot of the r_c/k_{AB} as a function of P_A calculated from equation (12.173) with $K_A = K_B = 1$. Notice that the rate goes up with increasing P_A , reaches a maximum, and then declines. The results are in qualitative agreement with the data in

Next, it is useful to go back and consider the implication of these results for the reaction:



According to equation (12.124), when $K_A = 0$

$$r_c = k_3 [A_{ad}] \quad (12.164)$$

Therefore, the rate is proportional to the concentration of A on the catalyst. Figure 12.36 shows a plot of the concentration of A on the surface. Notice that at high A pressures, $[A_{ad}]$ is almost independent of P_A . Consequently, according to (12.163), increases in P_A do not significantly enhance the rate of reaction (12.163). Similarly, the presence of B reduces $[A_{ad}]$. Consequently, the rate of reaction (12.163) goes down. The result is that the presence of B decreases the rate of the reaction even though B does not directly participate in the reaction.

Notice, however, that according to equation (12.162), the fractional coverage of B goes to zero when P_A is large. Therefore, B will not affect the rate at high enough A partial pressures.

Experimentally, one usually observes such trends, which is why equation (12.143) has prove to be so useful.

12.17.4 Alternative Isotherms

There is one other detail. When you fit real adsorption data, you sometimes have to use an equation for θ other than the Langmuir adsorption isotherm. In the literature, there are a number of adsorption isotherms, where an *adsorption isotherm* is defined as an equation or plot of $[A_{ad}]$ versus P_A . Masel (1996) lists several isotherms. The most important are the Toth equation

$$\theta_A = \left(\frac{K_A P_A^{C_{Toth}}}{1 + K_A P_A^{C_{Toth}}} \right)^{1/C_{Toth}} \quad (12.165)$$

and the multisite model:

$$\theta_A = \sum_{i=1}^n \left(\frac{X_i K_i P_A}{1 + K_i P_A} \right) \quad (12.166)$$

In equations (12.165) and (12.166) i is a sum over different sites in a sample and C_{Toth} , X_i , K_i are parameters that are adjusted to fit data as described in Chapter 4 of Masel (1996). The Toth equation arises because of attractive or repulsive interactions between molecules. The multisite model works because there can be different sites (i.e., places where reactants can adsorb) on a catalyst with different activities. For condensable substances (e.g., H_2O), people sometimes use what is called the Brunauer-Emmett-Teller (BET) equation:

$$[A_{ad}] = \frac{S_0 C_B \left(\frac{P_A}{P_A^S} \right)}{\left(1 - \frac{P_A}{P_A^S} \right) \left[1 + (C_B - 1) \frac{P_A}{P_A^S} \right]} \quad (12.167)$$

where $[A_{ad}]$ equals the concentration of A on the catalyst, S_0 is the concentration of sites on the catalyst, P_A is the partial pressure of A, and P_A^S is the pressure you would have to

Physically, what is happening is that according to equation (12.161), when P_A increases, more A will adsorb. As a result, θ_A will increase. However, according to equation (12.162), when P_A increases, θ_B decreases because there are fewer vacant sites to hold B (see Figure 12.39). Now consider the product of θ_A and θ_B in equation (12.171). Note that since θ_A goes up and θ_B goes down, the product of the two can increase or decrease with increasing pressure of A. If the fractional decrease in θ_B is smaller than the fractional increase in θ_A , the net rate will increase. However, if the fractional decrease in θ_B exceeds the fractional increase in θ_A , the net rate will decrease. Consequently, an increase in the partial pressure of A will not necessarily increase the rate of the reaction between A and B, and it may decrease it.

12.17.6 Further Extensions

One can extend these ideas to a wide variety of reactions. For example, consider the case where reaction (12.168) is run in the presence of a species D_2 that dissociatively adsorbs on the catalyst and blocks sites but does not otherwise participate in the reaction. One can write equilibrium constants for A and B as before:

$$\frac{[A_{ad}]}{P_A[S]} = K_A \tag{12.174}$$

$$\frac{[B_{ad}]}{P_B[S]} = K_B \tag{12.175}$$

Now let's assume that D_2 dissociatively adsorbs to form two D atoms, that is, that during the adsorption process, D follows



At equilibrium:

$$\frac{[D_{ad}]^2}{P_{D_2}(S_0)^2} = K_D \tag{12.177}$$

where $[D_{ad}]$ is the concentration of adsorbed D atoms, P_{D_2} is the partial pressure of D_2 , S_0 is the number of sites in the catalyst, and K_D is the equilibrium constant for the adsorption of D. The site balance becomes

$$S_0 = [S] + [A_{ad}] + [B_{ad}] + [D_{ad}] \tag{12.178}$$

Substituting equations (12.174), (12.175), and (12.177) into equation (12.178) and rearranging yields

$$[S] = \frac{S_0}{1 + K_A P_A + K_B P_B + (K_D P_{D_2})^{1/2}} \tag{12.179}$$

Substituting equation (12.179) into Equations (12.174) and (12.175), and then substituting the result into equation (12.170), yields

$$R_C = \frac{k_{AB} K_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B + (K_D P_{D_2})^{1/2})^2} \tag{12.180}$$

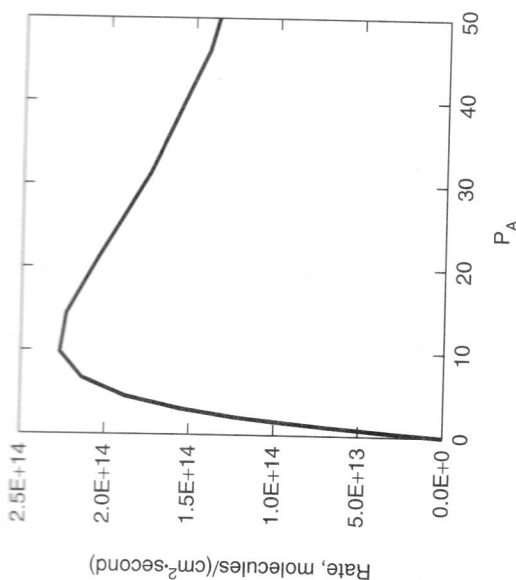


Figure 12.38 A plot of the rate calculated from equation (12.173) with $K_B P_B = 10$.

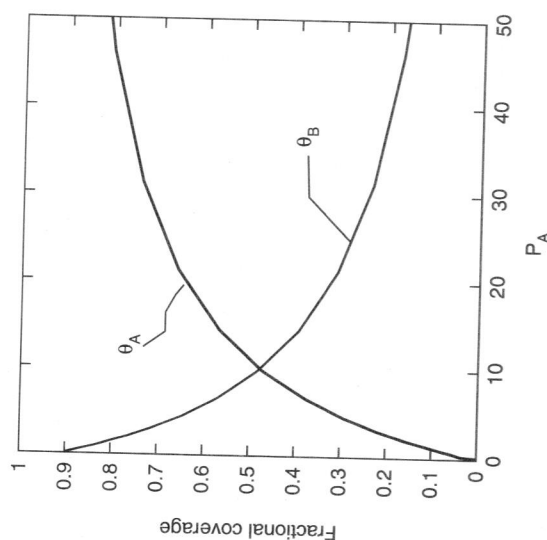


Figure 12.39 The changes in θ_A and θ_B as a function of P_A with $K_B P_B = 10$.

Figure 2.17. In fact, the fit is quantitative. The lines in Figure 2.17 are actual fits to the data via equation (5.127).

Just to keep this plot in perspective, note that for a gas-phase reaction, an increase in the partial pressure of the reactants always produces an increase in the reaction rate. However, the data in Figure 2.17 and the plot in Figure 12.38 show that with a catalytic reaction, an increase in the partial pressure of the reactants may decrease, not increase, the rate.

Equation (12.180) is the rate equation for reaction (12.168) in the presence of an inert species D_2 that dissociates.

Masel (1996, Chapter 7) provides many other examples of these methods. In the problem set, we also ask the readers to do some similar examples. The derivations are simple but amazingly powerful. One can fit kinetic data for most catalytic reactions, most enzyme reactions, and many reactions in electronic materials production using equation (12.180).

12.18 SUMMARY

In summary, then, in this chapter, we described many different types of catalysts:

Homogeneous catalysts:

- Acids or bases
- Metal salts
- Enzymes
- Radical initiators
- Solvents

Heterogeneous catalysts:

- Supported metals
- Metal oxides, carbides, and sulfides
- Solid acids and bases
- Immobilized enzymes and other polymer-bound species
- Photocatalysts

We found that all catalysts work in basically the same way:

- Catalysts can be used to help initiate reactions.
- Catalysts can be used to stabilize intermediates.
- Catalysts can be used to hold the reactants in close proximity.
- Catalysts can be used to hold the reactants in the right configuration to react.
- Catalysts can be used to block side reactions.
- Catalysts can be used to modify the forces between the reactants, which changes the intrinsic barriers to reactions.
- Catalysts can be used to act as efficient means for energy transfer.

It is also important to realize that

- One needs a catalytic cycle to get a reaction to happen.
- Mass transfer limitations are more important when a catalyst is present.
- Most catalytic reactions also follow Langmuir–Hinshelwood rate laws.

In the next few chapters, we will be examining each type of catalyst in detail. However, we recommend that the reader carefully study the materials in this chapter before proceeding to Chapters 13 and 14.

12.19 SUPPLEMENTAL MATERIAL

12.19.1 Derivation of equation 12.116

In section 12.15, we provided the following approximation for the effectiveness factor for the reaction $A \Rightarrow B$ occurring in a spherical pellet of radius y_p :

$$\eta_c = \frac{1}{\Phi_p} \left(\frac{1}{\tanh(3\Phi_p)} - \frac{1}{\Phi_p} \right) \quad (12.181)$$

with Φ_p given by equation (12.117), or equivalently (for first order)

$$\Phi_p^2 = \frac{y_p^2 (-r_A^0)}{C_A^0 D_e} \quad (12.182)$$

where y_p is the diameter of the pellet ($-r_A^0$) is the reaction rate (in the absence of mass transfer), D_e is the effective diffusivity into the pellet, and C_A^0 is the concentration of reactant outside the pellet.

Equation (12.181) predicts that the actual rate of reaction is less than the rate in the absence of mass transfer resistances. The rate is reduced because the reactants are used up as they diffuse into the pellet, as shown in Figure 12.40. The average concentration of reactants in the pellet is less than the concentration in the gas phase. As a result, the rate is less than the rate one would have if the concentrations were equal to the gas-phase concentration.

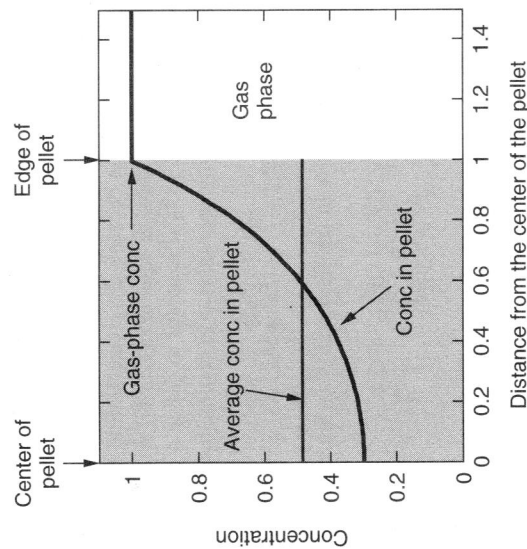


Figure 12.40 The concentration of species in a spherical catalyst pellet.

The purpose of this section is to derive equation (12.181). The effectiveness factor η_e is defined by

$$\eta_e = \frac{\text{actual rate for a catalyst pellet with mass transfer limitations}}{\text{rate in the absence of mass transfer limitations}} \quad (12.183)$$

Let's consider the reaction $A \Rightarrow B$ occurring in the spherical pellet shown in Figure 12.40.

In this section, we derive an equation for the effectiveness factor assuming that all of the mass transfer resistance is associated with diffusion of reactants into the pellet. We will also assume that the diffusion process follows Fick's law with an *effective diffusivity*, D_e . First let us derive an expression of the concentration of A diffusing into the pellet. A mass balance on A shows

$$\left(4\pi y^2 D_e \left(-\frac{dC_A}{dy} \right) \right)_{y+\Delta y} - \left(4\pi y^2 D_e \left(-\frac{dC_A}{dy} \right) \right)_y = 4\pi y^2 \Delta y (-r_A) \quad (12.184)$$

where y is the distance from the center of the pellet, C_A is the concentration of A at a distance y , Δy is the thickness of the slice, D_e is the effective diffusivity, and r_A is the rate of the $A \Rightarrow B$ reaction. The first term in equation (12.184) is the amount that diffuses into the slice. The second term in equation (12.184) is the amount that diffuses out. The last term is the amount that is used up. The negative sign in the first term expression arises because A is diffusing in the negative direction.

Taking the limit as Δy goes to zero yields

$$\frac{d^2 C_A}{dy^2} + \frac{2}{y} \frac{dC_A}{dy} + \frac{r_A}{D_e} = 0 \quad (12.185)$$

The boundary conditions on equation (12.185) are

$$\frac{dC_A}{dy} = 0 \quad \text{at } y = 0 \quad (12.186)$$

$$C_A = C_A^0 \quad \text{at } y = y_p \quad (12.187)$$

Note that equation (12.186) arises because the concentration profile must be symmetric around $y = 0$, or else the second term in equation (12.185) will grow to infinity.

In order to solve equation (12.187), it is useful to define a new variable, ζ_A , by

$$\zeta_A = \frac{y C_A}{y_p C_A^0} \quad (12.188)$$

where C_A^0 is the concentration of A in the fluid and y_p is the radius of the pellet.

One can show

$$\frac{C_A^0 y_p}{y} \frac{d^2 \zeta_A}{dy^2} = \frac{d^2 C_A}{dy^2} + \frac{2}{y} \frac{dC_A}{dy} \quad (12.189)$$

Equation (12.185) becomes

$$\left(\frac{C_A^0 y_p}{y} \right) \frac{d^2 \zeta_A}{dy^2} + \frac{r_A}{D_e} = 0 \quad (12.190)$$

For simplicity, we will assume

$$r_A = -k_A C_A \quad (12.191)$$

Substituting equations (12.188) and (12.191) into equation (12.190) yields

$$\frac{d^2 \zeta_A}{dy^2} - \frac{k_A}{D_e} \zeta_A = 0 \quad (12.192)$$

The solution of equation (12.192) is

$$\zeta_A = \frac{\sinh \left(\sqrt{\frac{k_A}{D_e}} y^2 \right)}{\sinh \left(\sqrt{\frac{k_A}{D_e}} y_p \right)} \quad (12.193)$$

Converting equation (12.193) to standard form yields

$$C_A = C_A^0 \frac{y_p}{y} \frac{\sinh(3\Phi_P/y_p)}{\sinh(3\Phi_P)} \quad (12.194)$$

where Φ_P is called the Thiele modulus defined by

$$\Phi_P = \frac{y_p}{3} \sqrt{\frac{k_A}{D_e}} \quad (12.195)$$

Next, we want to compute how much product is consumed by the pellet. There are two ways to do that. One could integrate the rate over the volume of the pellet. However, we can also calculate how much A is diffusing into the pellet and note that at steady state the amount of A consumed by the pellet equals the amount of A that diffuses into the pellet. The algebra is simpler if we choose the latter derivation. From the definition of the diffusivity, we have

$$(A \text{ consumed}) = -4\pi y_p^2 D_e \frac{dC_A}{dy} \quad (12.196)$$

Next, let's define r_A^{mr} , the average rate of reaction per unit volume of pellet. From a mass balance

$$(A \text{ consumed}) = \frac{4\pi}{3} y_p^3 r_A^{mr} \quad (12.197)$$

Combining equations (12.196) and (12.197) yields

$$r_A^{mr} = -\frac{3D_e}{y_p} \left(\frac{dC_A}{dy} \right)_{y=y_p} \quad (12.198)$$

Substituting equation (12.194) into equation (12.198) yields

$$r_A^{mr} = -\frac{3D_e C_A^0}{y_p} \left[\frac{3\Phi_P \cosh(3\Phi_P)}{y_p \sinh(3\Phi_P)} - \left(\frac{y_p}{(y_p)^2} \right) \frac{\sinh(3\Phi_P)}{\sinh(3\Phi_P)} \right] \quad (12.199)$$

Factoring out $3\Phi_P/y_P$ from the big bracket on the left of equation (12.199) yields

$$r_A^{nr} = \frac{3D_c C_A^0}{y_P} \left(\frac{3\Phi_P}{y_P} \right) \left(\frac{1}{\tanh(3\Phi_P)} - \frac{1}{3\Phi_P} \right) \quad (12.200)$$

Further rearranging yields

$$r_A^{nr} = - \left(\frac{9D_c}{y_P^2} \right) (C_A^0)(\Phi_P) \left(\frac{1}{\tanh(3\Phi_P)} - \frac{1}{3\Phi_P} \right) \quad (12.201)$$

Note that from equation (12.195)

$$\frac{1}{\Phi_P^2} = \left(\frac{9D_c}{y_P^2} \right) \left(\frac{1}{k_A} \right) \quad (12.202)$$

Substituting equation (12.202) into equation (12.201) yields

$$r_A^{nr} = - \left(\frac{k_A}{\Phi_P^2} \right) C_A^0 \Phi_P \left(\frac{1}{\tanh(3\Phi_P)} - \frac{1}{3\Phi_P} \right) \quad (12.203)$$

The effectiveness factor η_e is defined by

$$\eta_e = \frac{r_A^{nr}}{r_A} \quad (\text{no mass transfer limitation}) \quad (12.204)$$

where from equation (12.191)

$$r_A \quad (\text{no mass transfer limitation}) = -k_A C_A^0 \quad (12.205)$$

Substituting equation (12.203) and (12.205) into equation (12.204) yields

$$\eta_e = \frac{1}{\Phi_P} \left(\frac{1}{\tanh(3\Phi_P)} - \frac{1}{3\Phi_P} \right) \quad (12.206)$$

Equation (12.206) was cited in Section 12.15.

In the homework set, we ask the reader to do a similar derivation for diffusion into a flat plate of thickness $2L$. The result is

$$\eta_e = \frac{\tanh \Phi_P}{\Phi_P} \quad (12.207)$$

where

$$\Phi_P = L_1 \sqrt{\frac{k_A}{D_c}} \quad (12.208)$$

Similarly, one can integrate equation (12.185) for other rate forms (see also Figure 12.41).

$$r_A = kC_A^n \quad (12.209)$$

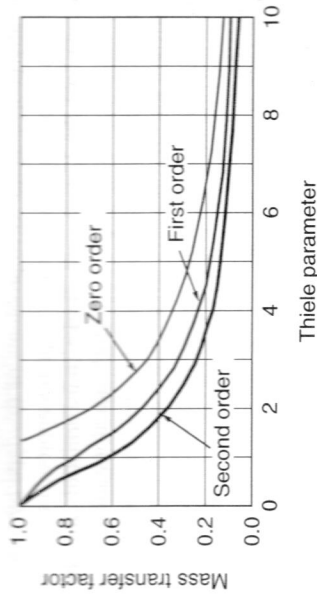


Figure 12.41 A plot of the effectiveness factor for reaction in a flat plate where the rate follows equations (12.207) and (12.208).

and

$$r_A = \frac{k_2 C_A}{(1 + k_2 C_A)^m} \quad (12.210)$$

In all cases equation (12.206) is an excellent approximation whenever the factor is greater than about 2.

12.20 SOLVED EXAMPLES

Example 12.A **Fitting Data to Langmuir–Hinshelwood and Michaelis–Menten Rate Forms** Steger and Masel (1998) examined the etching of copper with hexafluoropentanedione ($CF_3COCH_2COCF_3$). The main reaction is



Table 12.A.1 shows some data for the rate of copper etching via the reaction. Fit the data to the Langmuir–Hinshelwood expression:

$$R_e = \frac{k_1 P_{O_2}^{0.5}}{1 + K_2 P_{O_2}^{0.5}} \quad (12.A.2)$$

where R_e is the etch rate, P_{O_2} is the partial pressure of oxygen, and k_1 and K_2 are constants.

Table 12.A.1 The rate of copper etching measured by Steger and Masel

R_e $\mu\text{m/minute}$	P_{O_2} , torr	R_e $\mu\text{m/minute}$	P_{O_2} , torr	R_e $\mu\text{m/minute}$	P_{O_2} , torr
0.3	0.1	0.8	1.5	1.2	7.5
0.5	0.3	0.9	2.0	1.3	10.0
0.6	0.5	1.0	3.0	1.4	15.0
0.8	1.0	1.1	5.0	1.5	20.0

Solution Generally people try to solve problems of this type by transforming equation (12.A.2) to a linear form and then using a least-squares approach to fit the data. There are two key transformations: the Lineweaver–Burke transformation and the Eadie–Hofstee transformation as discussed in example 3.A. Both transformations were developed by biochemists to fit data to the Michaelis–Menten equation and then were adopted by catalytic chemists.

The Lineweaver–Burke transformation rearranges equation (12.A.2) by taking one over both sides:

$$\frac{1}{R_e} = \frac{1}{k_1 P_{O_2}^{0.5}} + \frac{K_2}{k_1} \quad (12.A.3)$$

Therefore a plot of $1/R_e$ versus $P_{O_2}^{-0.5}$ should be linear.

The Eadie–Hofstee transformation can be derived by multiplying equation (12.A.2) by $(1 + P_{O_2}^{0.5})$:

$$R_e + R_e K_2 P_{O_2}^{0.5} = k_1 P_{O_2}^{0.5} \quad (12.A.4)$$

Dividing equation (12.A.4) by $P_{O_2}^{0.5}$ yields

$$\frac{R_e}{P_{O_2}^{0.5}} = k_1 - R_e K_2 \quad (12.A.5)$$

Therefore the plot of $R_e/P_{O_2}^{0.5}$ versus R_e should be linear.

One can also rearrange the Lineweaver–Burke transformation as

$$\frac{P_{O_2}^{0.5}}{R_e} = \frac{1}{k_1} + \frac{K_2}{k_1} P_{O_2}^{0.5}$$

Therefore the plot of $P_{O_2}^{0.5}/R_e$ versus $P_{O_2}^{0.5}$ should be linear.

If one had perfect data measured to several significant figures, one would get the same result, independent of whether one plotted the data as shown in equation (12.A.3), (12.A.5), or (12.A.6). However, in actual practice the three methods give slightly different results. Let's illustrate that point using the data in Table 12.A.1. Figure 12.A.1 shows a plot of the data using three methods. Notice that all the plots look linear, which suggests that all three methods work.

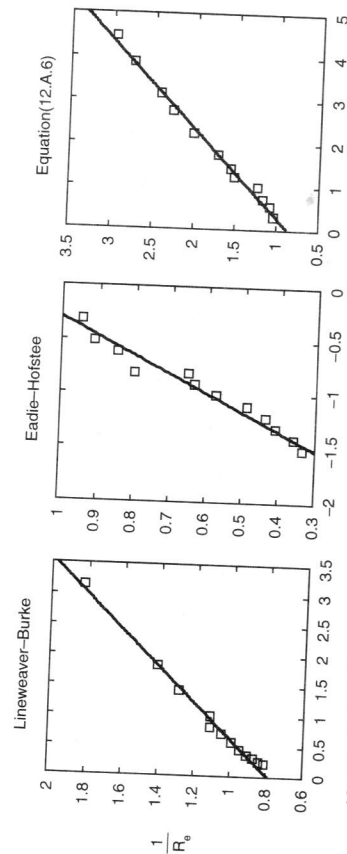


Figure 12.A.1 A plot of the data in Table 12.A.1 according to equations (12.A.3), (12.A.5), and (12.A.6).

The plots are not completely revealing, though, so one needs numbers to compare the results.

I have analyzed the data with the help of the spreadsheet in Table 12.A.2. In the spreadsheet, column A is the pressure, column B is the rate, column C is one over the square root of the pressure, column D is one over the rate, column E is minus the rate, column F is the rate over the square root of the pressure, column G is the square root of the pressure, and column H is the square root of the pressure divided by the rate.

Table 12.A.3 shows the numerical values in the spreadsheet.

In the Lineweaver–Burke method, one fits the data to equation (12.A.3). Column C should be linear with column D. In fact, it is, and the regression output (cells D16 and D17) show

$$\frac{1}{R_e} = \frac{0.879}{P_{O_2}^{0.5}} + 0.477 \quad (12.A.7)$$

A comparison of equations (12.A.3) and (12.A.7) yields

$$\frac{1}{k_1} = 0.879 \quad (12.A.8)$$

or

$$k_1 = \frac{1}{0.879} = 1.137 \quad (12.A.9)$$

Similarly, comparison of equations (12.A.3) and (12.A.7) shows

$$\frac{K_2}{k_1} = 0.477 \quad (12.A.10)$$

or

$$K_2 = 0.477 \times k_1 = 0.477 \times 1.137 = 0.544 \quad (12.A.11)$$

In the Eadie–Hofstee method, one fits the data to equation (12.A.5). Column E should be linear as column F. The regression output 14 (cells F16 and F17) show.

$$\frac{R_e}{P_{O_2}^{0.5}} = 1.166 - 0.577 \times R_e \quad (12.A.12)$$

Therefore

$$k_1 = 1.166 \quad (12.A.13)$$

$$K_2 = 0.577 \quad (12.A.14)$$

Similarly, one can fit the data to equation (12.A.6). Column G should be linear with column H. The regression output 14 (cells H16 and H17) shows.

$$\frac{P_{O_2}^{0.5}}{R_e} = 0.869 + 0.490 \times P_{O_2}^{0.5} \quad (12.A.15)$$

Therefore

$$\frac{1}{k_1} = 0.869 \quad (12.A.16)$$

	A	B	C	D	E	F	G	H
01			Lineweaver-Burke	Eadie-Hoffstee	Equation (12.A.6)			
02	pressure	rate	1/p ^{0.5}	-rate	rate/p ^{0.5}	p ^{0.5}	p ^{0.5} /rate	
03	0.1	0.3	3.162278	3.333333	-0.3	0.948683	0.316228	1.054093
04	0.3	0.5	1.825742	2	-0.5	0.912871	0.547723	1.095445
05	0.5	0.6	1.414214	1.666667	-0.6	0.848528	0.707107	1.178511
06	1	0.8	1	1.25	-0.8	0.8	1	1.25
07	1.5	0.8	0.816497	1.25	-0.8	0.653197	1.224745	1.530931
08	2	0.9	0.707107	1.111111	-0.9	0.636396	1.414214	1.571348
09	3	1	0.57735	1	-1	0.57735	1.732051	1.732051
10	5	1.1	0.47214	0.909091	-1.1	0.491935	2.236068	2.032789
11	7.5	1.2	0.365148	0.833333	-1.2	0.438178	2.738613	2.282177
12	10	1.3	0.316228	0.769231	-1.3	0.411096	3.162278	2.432521
13	15	1.4	0.258199	0.714286	-1.4	0.361478	3.872983	2.766417
14	20	1.5	0.223607	0.666667	-1.5	0.33541	4.472136	2.981424
15								
16			slope	0.879058	slope	0.576817	slope	0.489952
17			Intercept	0.477853	Intercept	1.165903	Intercept	0.869251
18			r ²	0.994711	r ²	0.961547	r ²	0.992587

Table 12.A.3 The numerical values in the spreadsheet used to fit the rate data by the various methods

	A	B	C	D	E	F	G	H
01			Lineweaver-Burke	Eadie-Hoffstee	Equation (12.A.6)			
02	pressure	rate	1/p ^{0.5}	-rate	rate/p ^{0.5}	p ^{0.5}	p ^{0.5} /rate	
03	0.1	0.3	=1/A3^0.5	=B3	=+B3/(A3^0.5)	=+A3^0.5	=+G3/B3	
04	0.3	0.5	=1/A4^0.5	=B4	=+B4/(A4^0.5)	=+A4^0.5	=+G4/B4	
05	0.5	0.6	=1/A5^0.5	=B5	=+B5/(A5^0.5)	=+A5^0.5	=+G5/B5	
06	1	0.8	=1/A6^0.5	=B6	=+B6/(A6^0.5)	=+A6^0.5	=+G6/B6	
07	1.5	0.8	=1/A7^0.5	=B7	=+B7/(A7^0.5)	=+A7^0.5	=+G7/B7	
08	2	0.9	=1/A8^0.5	=B8	=+B8/(A8^0.5)	=+A8^0.5	=+G8/B8	
09	3	1	=1/A9^0.5	=B9	=+B9/(A9^0.5)	=+A9^0.5	=+G9/B9	
10	5	1.1	=1/A10^0.5	=B10	=+B10/(A10^0.5)	=+A10^0.5	=+G10/B10	
11	7.5	1.2	=1/A11^0.5	=B11	=+B11/(A11^0.5)	=+A11^0.5	=+G11/B11	
12	10	1.3	=1/A12^0.5	=B12	=+B12/(A12^0.5)	=+A12^0.5	=+G12/B12	
13	15	1.4	=1/A13^0.5	=B13	=+B13/(A13^0.5)	=+A13^0.5	=+G13/B13	
14	20	1.5	=1/A14^0.5	=B14	=+B14/(A14^0.5)	=+A14^0.5	=+G14/B14	
15								
16			slope	=SLOPE(D3:D14, C3:C14)	=SLOPE(F3:F14, E3:E14)	=SLOPE(H3:H14, G3:G14)		
17			Intercept	=RSQ(D3:D14, D14, C3:C14)	=INTERCEPT(D3: D14, C3: C14)	=INTERCEPT(H3: H14, G3: G14)		
18			r ²	=RSQ(D3:D14, C3:C14)	=RSQ(F3:F14, E3:E14)	=RSQ(H3:H14, G3:G14)		

Table 12.A.2 The formulas used to fit the rate data by the various methods

$$k_1 = 1.150$$

$$(12.A.17)$$

Similarly

$$\frac{K_2}{k_1} = 0.490$$

$$(12.A.18)$$

or

$$K_2 = 0.490 \times k_1 = 0.490 \times 1.150 = 0.564$$

$$(12.A.19)$$

Table 12.A.4 summarizes these results. Notice that the three methods give different values of the coefficients although the differences are not large.

Figure 12.A.2 shows a replot of the data on a semilog scale. In this particular case there is almost no difference between the methods.

In the homework set we will ask the reader to show that the Lineweaver–Burke plot is sensitive to errors. Physically, when one uses the Lineweaver–Burke method for fitting to $1/Re$ rather than Re , $1/Re$ is very sensitive to noise at low concentrations. As a result, Lineweaver–Burke plots sometimes fail.

If you try to derive your own method, be careful to compare errors on Re not $1/Re$, or else you will do a poor job of fitting real data.

In my experience, it is better to avoid the linear methods and use nonlinear least-squares method instead. The nonlinear least-squares method can be done using the solver function in Microsoft Excel or Lotus 1-2-3.

Table 12.A.4 Fits of the data to equations (12.A.3), (12.A.5), and (12.A.6)

	Lineweaver–Burke	Eadie–Hofstee	Equation (12.A.6)
Slope	0.879	0.577	
Intercept	0.477	1.166	0.490
Regression coefficient	0.9994711	0.961547	0.869
k_1	1.137	1.166	0.992587
K_2	0.544	0.577	1.150
			0.564

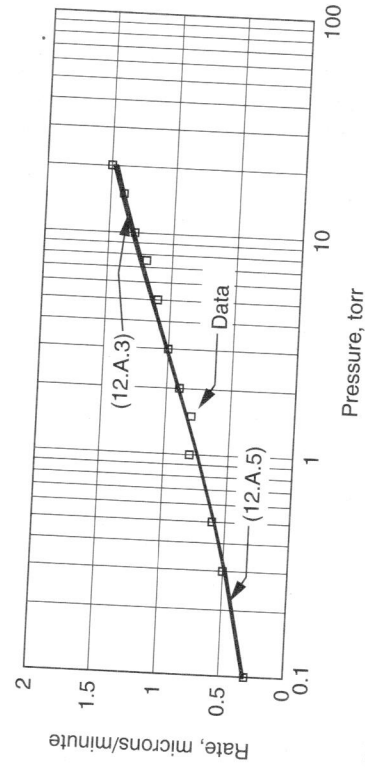


Figure 12.A.2 A plot of the data in Table 12.A.1 fit by using the Lineweaver–Burke method and the Eadie–Hofstee method.

Here is the spreadsheet I set up to do the calculations:

	A	B	C	D	E
5	pressure	rate	rate calculated from equation(12.A.2)	error^2	abs(error)
6	0.1	0.3	=C\$19*(\$A6^0.5)/(1+C\$20*(\$A6^0.5))	=(C6-\$B6)^2	=ABS(C6-\$B6)
7	0.3	0.5	=C\$19*(\$A7^0.5)/(1+C\$20*(\$A7^0.5))	=(C7-\$B7)^2	=ABS(C7-\$B7)
8	0.5	0.6	=C\$19*(\$A8^0.5)/(1+C\$20*(\$A8^0.5))	=(C8-\$B8)^2	=ABS(C8-\$B8)
9	1	0.8	=C\$19*(\$A9^0.5)/(1+C\$20*(\$A9^0.5))	=(C9-\$B9)^2	=ABS(C9-\$B9)
10	1.5	0.8	=C\$19*(\$A10^0.5)/(1+C\$20*(\$A10^0.5))	=(C10-\$B10)^2	=ABS(C10-\$B10)
11	2	0.9	=C\$19*(\$A11^0.5)/(1+C\$20*(\$A11^0.5))	=(C11-\$B11)^2	=ABS(C11-\$B11)
12	3	1	=C\$19*(\$A12^0.5)/(1+C\$20*(\$A12^0.5))	=(C12-\$B12)^2	=ABS(C12-\$B12)
13	5	1.1	=C\$19*(\$A13^0.5)/(1+C\$20*(\$A13^0.5))	=(C13-\$B13)^2	=ABS(C13-\$B13)
14	7.5	1.2	=C\$19*(\$A14^0.5)/(1+C\$20*(\$A14^0.5))	=(C14-\$B14)^2	=ABS(C14-\$B14)
15	10	1.3	=C\$19*(\$A15^0.5)/(1+C\$20*(\$A15^0.5))	=(C15-\$B15)^2	=ABS(C15-\$B15)
16	15	1.4	=C\$19*(\$A16^0.5)/(1+C\$20*(\$A16^0.5))	=(C16-\$B16)^2	=ABS(C16-\$B16)
17	20	1.5	=C\$19*(\$A17^0.5)/(1+C\$20*(\$A17^0.5))	=(C17-\$B17)^2	=ABS(C17-\$B17)
18					
19		k_1	1.156678444795306 (calculated via solver)	=SUM(D6:D17)	=SUM(E6:E17)
20		K_2	0.570642862949246 (calculated via solver)		

In the spreadsheet, c19 = k_1 , c20 = K_2 , column C, contains the rates were calculated from equation (12.A.2). Column D contains the individual errors squared. Cell d19 is the sum of the squares of the errors. When I set up the spreadsheet, I guessed $k_1 = 1$ and $K_2 = 0.5$ and used the solver function in Excel to minimize the d19 by varying c19 and c20. The result is that Excel calculated that the best k_1 is 1.157 and the best K_2 is 0.571.

There is one subtlety in the calculation. Notice that I calculated the error squared in column D of the spreadsheet. If you suspect that you have bad points in the calculation, it is better to instead minimize the absolute value of the error. Column E in the spreadsheet shows the absolute value of the error. Again, one can use the solver function in Excel

to minimize the d19 by varying c19 and c20. The result is that Excel calculated that the best k_1 is 1.131 and the best K_2 is 0.554. Additional details are in Problem 3.A.

Example 12.B Simple Langmuir Derivation The reaction $A + B \Rightarrow C$ obeys



Derive an equation for the rate of formation of C as a function of the partial pressures of A and B. Assume that reaction 3 is rate-determining.

Solution

$$r_C = k_3[A_{ad}][B_{ad}] \quad (12.B.1)$$

Assume that reaction 1 is in equilibrium:

$$\frac{[A_{ad}]}{SP_A} = K_1 \quad (12.B.2)$$

Similarly for reaction 2

$$\frac{[B_{ad}]}{SP_B} = K_2 \quad (12.B.3)$$

Combining (12.B.1)–(12.B.3) yields

$$r_C = K_1 K_2 k_3 P_A P_B S^2 \quad (12.B.4)$$

I need S to complete solution; I get it from a site balance:

$$S_0 = S + [A_{ad}] + [B_{ad}] \quad (12.B.5)$$

Combining (12.B.2), (12.B.3), and (12.B.5) yields

$$S_0 = S + SK_1 P_A + K_2 P_B \quad (12.B.6)$$

Solving (12.B.6) for S, we obtain

$$S = \frac{S_0}{1 + K_1 P_A + K_2 P_B} \quad (12.B.7)$$

Combining equations (12.B.4) and (12.B.7) yields

$$r_C = \frac{K_1 K_2 k_3 P_A P_B (S_0)^2}{(1 + K_1 P_A + K_2 P_B)^2} \quad (12.B.8)$$

Example 12.C Derivation of a Langmuir–Hinshelwood rate equation Tanaka (1960) proposed that the decomposition of silane, SiH_4 , on a silicon wafer followed the following mechanism:



Derive a Langmuir–Hinshelwood–Hougan–Watson rate equation for the reaction, assuming that reaction (12.C.2) is rate-determining, and irreversible.

Solution If reaction (12.C.2) is rate-determining, then the rate of silicon deposition, r_{Si} , is given by

$$r_{Si} = k_2 [SiH_{4(ad)}] [S] \quad (12.C.5)$$

Following Hougan and Watson (1943), we will assume that reactions (12.C.1), (12.C.3), and (12.C.4) are in equilibrium.

$$\frac{[SiH_{4(ad)}]}{[S] P_{SiH_4}} = K_{SiH_4} \quad (12.C.6)$$

$$\frac{[SiH_{3(ad)}]}{[S] P_{H_2}^{3/2} [Si]} = K_{SiH_3} \quad (12.C.7)$$

$$\frac{[H_{(ad)}]}{[S] P_{H_2}^{1/2}} = K_H \quad (12.C.8)$$

where K_{SiH_4} , K_{SiH_3} and K_H are the equilibrium constants for reactions (12.C.1), (12.C.3) and (12.C.4), respectively.

Combining equations (12.C.5) and (12.C.6) yields

$$r_{Si} = k_2 K_{SiH_4} P_{SiH_4} [S]^2 \quad (12.C.9)$$

We get [S] from a site balance:

$$S_0 = [S] + [SiH_{4(ad)}] + [SiH_{3(ad)}] + [H_{(ad)}] \quad (12.C.10)$$

where S_0 is the total number of surface sites. Note that if you have a growing water, then, after you deposit a silicon atom, the silicon atom is a site for further adsorption. Adsorbed silicon does not use up sites. Therefore, there is no $[Si_{ad}]$ term in equation (12.C.10). Instead $[Si] = S_0$. Substituting equations (12.C.6)–(12.C.8) into equation (12.C.10) yields

$$S_0 = [S] + K_{SiH_4} [S] P_{SiH_4} + K_{SiH_3} [S] P_{H_2}^{3/2} [Si] + [K_H] [S] P_{H_2}^{1/2} \quad (12.C.11)$$

Noting that $[Si] = S_0$ and solving for [S] yields

$$[S] = \frac{S_0}{1 + K_{SiH_4} P_{SiH_4} + K_{SiH_3} P_{H_2}^{3/2} S_0 + K_H P_{H_2}^{1/2}} \quad (12.C.12)$$

Substituting equation (12.C.12) into equation (12.C.9) yields

$$r_{Si} = \frac{k_2 K_{SiH_4} P_{SiH_4} S_0^2}{\left(1 + K_{SiH_4} P_{SiH_4} + K_{SiH_3} P_{H_2}^{3/2} S_0 + K_H P_{H_2}^{1/2}\right)^2} \quad (12.C.13)$$

Equation (12.C.13) is the Langmuir–Hinshelwood–Hougan–Watson rate equation for silicon deposition.

Example 12.D Distinguishing between Mechanisms Assume that the decomposition of silane instead obeys



Reaction (12.D.2) is rate-determining. How would you tell the difference between this mechanism and the mechanism in Example 12.C: (a) spectroscopically or (b) on the basis of kinetic analysis.

Solutions There are two different solutions: a spectroscopic solution and a kinetic solution.

(a) The spectroscopic solution is to do spectroscopy of the surface, and see what species are present. For example, if reaction (12.C.2) is rate-determining, then there should be SiH_4 on the surface; if reaction (12.D.2) is rate-determining, adsorbed hydrogen atoms should be seen. There are some uncertainties because the concentrations could be low. However, one can often find conditions where the reactants in the rate-determining step are on the surface of the water. One can then use IR (infrared) to see which species are present. If silane is present, reaction (12.C.2) is rate-determining. If hydrogen atoms are present, then (12.D.2) is rate-determining. If both are present, no reaction is rate-determining.

(b) You can try to determine which mechanism is better by seeing whether equation (12.C.13) or the equivalent expression, reactions (12.D.1) and (12.D.2), work better.

First let us derive an equation for the rate, assuming that reaction (12.D.2) is rate-determining. According to the analysis in Chapter 4, $r_{12.C.2}$, the rate of reaction (12.D.2), is given by

$$r_{12.C.2} = k_{2C}[\text{H}_{(\text{ad})}]^2 \quad (12.D.3)$$

If reaction 12.D.1 is in equilibrium, then

$$\frac{[\text{H}_{(\text{ad})}]^4}{[\text{S}]^4 P_{\text{SiH}_4}} = K_{12.C.1} \quad (12.D.4)$$

where $K_{12.C.1}$ is the equilibrium constant for reaction (12.D.1).

Rearranging equation (12.D.4) shows

$$[\text{H}_{(\text{ad})}] = [\text{S}](K_{12.C.1})^{0.25} (P_{\text{SiH}_4})^{0.25} \quad (12.D.5)$$

Substituting (12.D.5) into (12.D.3) yields

$$r_{12.C.2} = k_{2C}[\text{S}]^2 (K_{12.C.1})^{0.5} P_{\text{SiH}_4}^{0.5} \quad (12.D.6)$$

Again, we calculate $[\text{S}]$ from the balance:

$$S_0 = [\text{S}] + [\text{H}_{(\text{ad})}] \quad (12.D.7)$$

where S_0 is the total number of sites on the surface.

Substituting (12.D.5) into (12.D.7) and rearranging shows

$$[\text{S}] = \frac{S_0}{1 + (K_{12.C.1})^{0.25} (P_{\text{SiH}_4})^{0.25}} \quad (12.D.8)$$

Combining equations (12.D.6) and (12.D.8) yields

$$r_{12.C.2} = \frac{k_{2C} S_0^2 (K_{12.C.1})^{1/2} (P_{\text{SiH}_4})^{0.5}}{(1 + (K_{12.C.1})^{0.25} (P_{\text{SiH}_4})^{0.25})^2} \quad (12.D.9)$$

Now the question is how to do experiments to distinguish between equations (12.C.13) and (12.D.9). The easier way to find out is to put both rate equations in a spreadsheet and look for differences.

For the purposes here, it is useful to consider a case where P_{H_2} is negligible in the denominator of equation (12.C.13). In that case (12.C.13) becomes

$$r_{\text{Si}} = \frac{k_2 K_{\text{SiH}_4} P_{\text{SiH}_4} S_0^2}{(1 + K_{\text{SiH}_4} + P_{\text{SiH}_4})^2} \quad (12.D.10)$$

Table 12.D.1 shows a spreadsheet that I used to illustrate the difference between equations (12.C.14) and (12.D.9). In the spreadsheet I set column A to the pressure, column B to the rate calculated from equation (12.C.14), and column C to be the rate from equation (12.D.9). I picked $S_0 = 1$, $k_2 = 1$, $K_{\text{SiH}_4} = 1$. I then calculated an error in column D, and used the solver function of the spreadsheet to find values of k_{2C} and $K_{12.C.1}$ to minimize cell D\$4, the total difference between the values of the rate was calculated from equations (12.D.9) and (12.C.14).

Figure 12.D.1 shows a plot of the data. Notice that the two curves look similar at low pressure, but there are significant differences at high pressure. Equation (12.D.9) rises over the range of pressure shown. One can show that the rate eventually saturates at high pressures. In contrast, equation (12.C.14) reaches a maximum and then declines.

Figure 12.D.1 tells us how to run experiments to distinguish between the mechanisms. One runs the reaction over a wide range of pressure, and looks to see how the rate varies. If the rate reaches a maximum and declines, then equation (12.C.14) will be better. If the

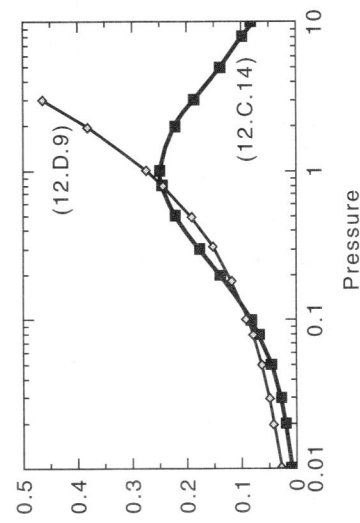


Figure 12.D.1 A plot of the rate calculated via equations (12.C.14) and (12.D.9).

Table 12.D.1 The formulas in the spreadsheet used to create Figure 12.D.1

A	B	C	D
01 KSiH4=	1		
02 k2s0=	1		
03 K12.c.1=	6.295E - 08		
04 k2s0C=	1115.97		
05 pressure	12. B. 14		=SUM(D6:D16)
06 0.01	=k2s0* KSiH4* \$A6 / (1+KSiH4* \$A6)^2	12. C.9	error
07 0.02	=k2s0* KSiH4* \$A7 / (1+KSiH4* \$A7)^2	=k2s0C* (ABS(K12.c.1) \$A6)^0.5 / (1+ABS(K12.c.1) \$A6)^0.25)^2	=ABS(B6 - C6)^2
08 0.03	=k2s0* KSiH4* \$A8 / (1+KSiH4* \$A8)^2	=k2s0C* (ABS(K12.c.1) \$A7)^0.5 / (1+ABS(K12.c.1) \$A7)^0.25)^2	=ABS(B7 - C7)^2
09 0.05	=k2s0* KSiH4* \$A9 / (1+KSiH4* \$A9)^2	=k2s0C* (ABS(K12.c.1) \$A8)^0.5 / (1+ABS(K12.c.1) \$A8)^0.25)^2	=ABS(B8 - C8)^2
10 0.08	=k2s0* KSiH4* \$A10 / (1+KSiH4* \$A10)^2	=k2s0C* (ABS(K12.c.1) \$A9)^0.5 / (1+ABS(K12.c.1) \$A9)^0.25)^2	=ABS(B9 - C9)^2
11 =10^A6	=k2s0* KSiH4* \$A11 / (1+KSiH4* \$A11)^2	=k2s0C* (ABS(K12.c.1) \$A10)^0.5 / (1+ABS(K12.c.1) \$A10)^0.25)^2	=ABS(B10 - C10)^2
12 =10^A7	=k2s0* KSiH4* \$A12 / (1+KSiH4* \$A12)^2	=k2s0C* (ABS(K12.c.1) \$A11)^0.5 / (1+ABS(K12.c.1) \$A11)^0.25)^2	=ABS(B11 - C11)^2
13 =10^A8	=k2s0* KSiH4* \$A13 / (1+KSiH4* \$A13)^2	=k2s0C* (ABS(K12.c.1) \$A12)^0.5 / (1+ABS(K12.c.1) \$A12)^0.25)^2	=ABS(B12 - C12)^2
14 =10^A9	=k2s0* KSiH4* \$A14 / (1+KSiH4* \$A14)^2	=k2s0C* (ABS(K12.c.1) \$A13)^0.5 / (1+ABS(K12.c.1) \$A13)^0.25)^2	=ABS(B13 - C13)^2
15 =10^A10	=k2s0* KSiH4* \$A15 / (1+KSiH4* \$A15)^2	=k2s0C* (ABS(K12.c.1) \$A14)^0.5 / (1+ABS(K12.c.1) \$A14)^0.25)^2	=ABS(B14 - C14)^2
16 =10^A11	=k2s0* KSiH4* \$A16 / (1+KSiH4* \$A16)^2	=k2s0C* (ABS(K12.c.1) \$A15)^0.5 / (1+ABS(K12.c.1) \$A15)^0.25)^2	=ABS(B15 - C15)^2
17 =10^A12	=k2s0* KSiH4* \$A17 / (1+KSiH4* \$A17)^2	=k2s0C* (ABS(K12.c.1) \$A16)^0.5 / (1+ABS(K12.c.1) \$A16)^0.25)^2	=ABS(B16 - C16)^2
18 =10^A13	=k2s0* KSiH4* \$A18 / (1+KSiH4* \$A18)^2	=k2s0C* (ABS(K12.c.1) \$A17)^0.5 / (1+ABS(K12.c.1) \$A17)^0.25)^2	=ABS(B17 - C17)^2
19 =10^A14	=k2s0* KSiH4* \$A19 / (1+KSiH4* \$A19)^2	=k2s0C* (ABS(K12.c.1) \$A18)^0.5 / (1+ABS(K12.c.1) \$A18)^0.25)^2	=ABS(B18 - C18)^2
20 =10^A15	=k2s0* KSiH4* \$A20 / (1+KSiH4* \$A20)^2	=k2s0C* (ABS(K12.c.1) \$A19)^0.5 / (1+ABS(K12.c.1) \$A19)^0.25)^2	=ABS(B19 - C19)^2
21 =10^A16	=k2s0* KSiH4* \$A21 / (1+KSiH4* \$A21)^2	=k2s0C* (ABS(K12.c.1) \$A20)^0.5 / (1+ABS(K12.c.1) \$A20)^0.25)^2	=ABS(B20 - C20)^2
			=ABS(B21 - C21)^2

rate goes up and saturates, then equation (12.D.9) will be better. If the rate merely rises, then one cannot simply distinguish between the rate equations. On occasion one can still use the F test in Example 3.C to distinguish between the mechanisms. However, without a difference in trend, it is often difficult to reach a definite conclusion.

Example 12.E Constructing Sachtler-Fahrenfort and Tanaka-Tamaru Plots
 Table 12.E.1 contains some data for the rate of ethylene hydrogenation on a number of metals at 0 C. Next, let's construct a Sachtler-Fahrenfort plot of the data.

Table 12.E.1 The spreadsheet for Example 12.E

	A	B	C	D	E	F	G
4	Metal	rate	ΔH _f Of Oxide	Oxygens in oxide	Metal atoms in oxide	ΔH _f per mole of oxide	ΔH _f per mole of metal
5	Pt	1.0E+16	-9.7	1	1	=\$C5/D5	=\$C5/E5
6	Pd	3.0E+16	-20.4	1	1	=\$C6/D6	=\$C6/E6
7	Ir	3.0E+16	-40.1	2	1	=\$C7/D7	=\$C7/E7
8	Rh	3.0E+17	-21.7	1	1	=\$C8/D8	=\$C8/E8
9	Ru	9.0E+18	-52.5	2	1	=\$C9/D9	=\$C9/E9
10	Cu	8.3E+10	-39.8	1	2	=\$C10/D10	
11	Cu	8.3E+10	-37.1	1	1		=\$C11/E11
12	Co	3.0E+16	-57.2	1	1	=\$C12/D12	=\$C12/E12
13	Ni	1.0E+14	-58.4	1	1	=\$C13/D13	=\$C13/E13
14	Fe	1.0E+16	-197.5	3	2	=\$C14/D14	=\$C14/E14
15	Fe	1.0E+16	-63.7	1	1		
16	W	3.0E+13	-136	2	1	=\$C16/D16	=\$C16/E16
17	Ta	3.0E+13	-499.9	5	2	=\$C17/D17	=\$C17/E17

Solutions There are two types of plots: Sachtler-Fahrenfort plots and Tanaka-Tamaru plots. Sachtler-Fahrenfort plots are graphs of the rate of reaction on a series of metal catalysts as a function of the heat of formation of the metal per mole of oxygen, while Tanaka-Tamaru plots are graphs of the rate of reaction on a series of metal catalysts as a function of the heat of formation of the metal per mole of metal.

If we wanted to construct a Sachtler-Fahrenfort plot of the data, we would calculate the heat of formation of the oxide per mole of oxygen. A spreadsheet to do the calculations is given in Table 12.E.1. Column A lists the metal; column B lists the rate. Column C is in the heat of formation of the oxide per mole from Table 12.11, while column D is the number of oxygens in the corresponding oxide. The heat of formation per mole of oxygen is given in column F. Similarly, column E gives the number of metal atoms in the oxide, while column G gives the heat of formation of the oxide per mole of metal.

The one subtlety in the analysis comes when there are two oxides of the same material. For example, copper is available as both Cu₂O and CuO. The heat of formation of Cu₂O per mole of oxygen is greater than the heat of formation of CuO per mole of oxygen. Consequently, one uses the heat of formation of Cu₂O when constructing a Sachtler-Fahrenfort plot. In contrast, the heat of formation of CuO per mole of copper is larger than the heat of formation of Cu₂O per mole of copper. Therefore, one uses the heat of formation of CuO when constructing the Tanaka-Tanaka plot.

The Sachtler-Fahrenfort plot is a graph of the rate data (i.e., column A) versus column F in the spreadsheet. The Tanaka-Tamaru plot is a graph of the rate data (i.e., column A) versus column G in the spreadsheet. The actual plot is given in Figure 12.14 in the chapter.

12.21 SUGGESTIONS FOR FURTHER READING

Introductory books on catalysis include:

- M. Boudart, *Kinetics of Heterogeneous Catalytic Reactions*, Princeton University Press, Princeton, NJ, 1984.
- G. C. Bond, *Heterogeneous Catalysis, Principles and Applications*, Clarendon Press, Oxford, UK 1987.

B. C. Gates, *Catalytic Chemistry*, Wiley, New York, 1992.

More advanced treatments include:

- H. Pines, *The Chemistry of Catalytic Hydrocarbon Conversions*, Academic Press, San Diego, 1991.
 G. V. Smith and F. Notheisz, *Heterogeneous Catalysis in Organic Chemistry*, Academic Press, San Diego, CA, 1999.
 J. M. Thomas and W. J. Thomas, *Principles and Practice of Heterogeneous Catalysis*, Wiley, New York, 1996.
 J. R. Anderson and M. Boudart eds., *Catalysis: Science and Technology*, Elsevier, Amsterdam, 1984–1998.

Mass transfer effects are well described in:

- R. I. Wijngaarden and K. R. Westertep, *Industrial Catalysts*, New York, VCH, 1998.

Enzyme catalysis is covered in

- K. Faber, *Biotransformations in Organic Chemistry*, 4th ed, Springer, NY 2000.
 A. Fersht, *Structure and Mechanism in Protein Science*, 3rd ed, W. H. Freeman 1999.

12.22 PROBLEMS

12.1 Define the following terms:

- (a) Homogeneous catalyst
 (b) Heterogeneous catalyst
 (c) Volcano plot
 (d) Isomerization
 (e) Alkylation
 (f) Cracking
 (g) Aldol condensation
 (h) Ziegler–Natta catalyst
 (i) Wilkinson catalyst
 (j) Wacker process
 (k) Hydroformylation
 (l) Monsanto carbonylation process
 (m) Oxidoreductases
 (n) NADH peroxidase
 (o) Hydrolases
 (p) Lyases
 (q) Isomerase
 (r) Langmuir adsorption isotherm

- (s) Effectiveness factor
 (t) Michaelis–Menten Kinetics
 (u) Transferases
 (v) Ligases
 (w) Menschutkin reactions
 (x) Supported metals
 (pp) Molecular adsorption
 (qq) Dissociative adsorption
 (rr) Langmuir–Hinshelwood mechanism
 (ss) Rideal–Eley mechanism
 (tt) Precursor mechanism
 (uu) Surface sites

12.2 How do catalysts change rates of reactions? List the key ways that catalysts change reactions and give an example of each of the effects.

12.3 Describe the key differences between Langmuir–Hinshelwood, Rideal–Eley, and precursor mechanisms. How would you distinguish between them experimentally.

12.4 Describe in your own words why the kinetics of surface reactions are so different from the kinetics of gas-phase reactions. What makes the kinetics different?

12.5 Summarize the various types of catalysts described in the first half of this chapter. Provide an illustration of each type of catalyst and an explanation of how the catalyst works.

12.6 Visit the Websites of some of the large catalyst manufacturers:

- (a) Johnson Matthey (<http://www.matthey.com/divisions/catalytic.htm>), Engelhard (<http://www.engelhard.com/>), W. R. Grace (<http://www.gracedavison.com/>), United Catalysts Süd-chemie (<http://www.unitedcatalysts.com/>). Find a list of catalysts that they offer and describe what the catalysts do. Then go to the Shell and Exxon sites, search the word catalyst, and see what you find.

- (b) Visit the Websites of the major enzyme manufacturers: Novozymes (<http://www.novozymes.dk/>), Genencor (<http://www.genencor.com/>), Royal Gist Brochades (<http://www.gist-brochades.com/>). What do you find?

12.7 Describe in your own words when Sabatier's principle works.

- (a) When do you get a maximum as in Figure 12.12?

- (b) When does the rate continue to increase as in Figure 12.11?

- (c) How would changes in the intrinsic barriers to reaction affect a volcano plot?

12.8 Find five examples of catalytic reactions in your home or your car. Be sure to consider reactions in your oven, your washing machine, your stomach, your intestines, and so on.

12.9 Diagram the catalytic cycle for

- (a) Ethylene hydrogenation catalyzed by the Wilkinson catalyst.

- (b) Platinum-catalyzed ethylene hydrogenation

- (c) The copper-catalyzed reaction: $\text{Fe}^{2+} + \text{V}^{4+} \Rightarrow \text{Fe}^{3+} + \text{V}^{3+}$

- (d) The dehydration of ethanol

- (e) Hydrogen oxidation on a fuel cell

- (f) Free-radical polymerization of styrene

- (g) Photocatalysis of CO oxidation

- (kk) Photocatalysts

- (ll) Langmuir–Hinshelwood kinetics

- (mm) Sabatier's principle

- (nn) Adsorption

- (oo) Adsorbate

12.10 Your stomach contains a solution of hydrochloric acid that is buffered to a pH of 2.0. On the basis of the results in this chapter

- (a) What would you expect the acid to do to?
 - (1) Proteins
 - (2) Fats
 - (3) Sugars and starches
 - (4) Invading bacteria
- (b) Your saliva contains the enzyme lingual amylase. Look in the protein database or a biochemistry book and find out what each enzyme does to the substances listed in items (1)–(4) (above). What is the main mode of enzyme action?
- (c) Your intestines contain α -amylase, trypsin, chymotrypsin, and elastase. Look in the protein database and find out what each enzyme does to the substances in items (1)–(4). What is the main mode of enzyme action?

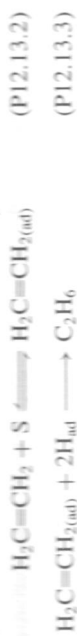
12.11 Enzymes are widely used in detergents. The enzymes catalyze the hydrolysis of stains.

- (a) Look in the protein database and find enzymes that would be active for the hydrolysis of
 - (1) Proteins
 - (2) Fats
 - (3) Sugars and starches
 - (4) Cellulose
- (b) Detergents have a pH of about 8.5. Would any of the compounds you found be stable at a pH of 8.5?
- (c) Look at some of the Websites for the commercial enzyme manufacturers: Novozymes (<http://www.novozymes.dk/>), Genencor (<http://www.genencor.com/>). What do they tell you about their enzymes?
- (d) The following is a noninclusive list of some of the major commercial detergent enzymes: Alcalase, Esperase, Maxatase, Optimase, Durazym, Kazusase, Opticlean, Savinase, Celluzyme, Duramyl. Look up each of the enzymes and see what they do.

12.12 In Example 12.A we used a variety of methods to fit Steger and Masel's data to rate equations.

- (a) Set up the spreadsheets yourself and reproduce the findings
- (b) Assume that Steger and Masel misrecorded the data so the rate was 0.03 at a pressure of 0.1 torr. Reanalyze the data. How well does each of the methods do?
- (c) What do the results in this problem tell you about the sensitivity of the various methods to errors?

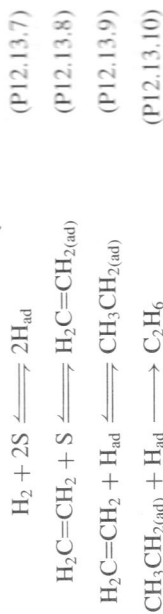
12.13 Ethylene hydrogenation was one of the first catalytic reactions to be studied in detail. Langmuir and Hinshelwood (1918) proposed that the reaction went via a Langmuir–Hinshelwood reaction:



Rideal and Eley proposed a Rideal–Eley mechanism:



Houriti and Polanyi proposed a third mechanism:



(a) Derive a rate equation for each mechanism.

(b) What experiments would you do to distinguish between the mechanisms? For the purpose of this problem, assume that you are working in 1920 and do not know how to measure the surface concentration of species.

(c) Repeat part (b) assuming that you can measure surface concentrations

12.14 The synthesis of ethylene (C_2H_4) is one of the largest chemical processes in the United States.

- (a) Find a reasonable mechanism for the conversion of ethane (CH_3CH_3) into ethylene and hydrogen.
- (b) What other products would you expect?
- (c) Use the steady-state approximation to derive an expression for the rate of the overall reaction.
- (d) Estimate the preexponentials and activation barriers for each of the reactions.
- (e) How could you catalyze the reaction? Pick one homogeneous catalyst and one heterogeneous catalyst and explain how they would work. Do not pick the catalysts from part (f) or (g) (in this problem) or Problem 12.6.
- (f) In industrial practice, people use water and a zeolite (a solid catalyst) as catalysts. The water dissociates on the zeolite to yield OH and H. The water also reacts with carbon deposited on the pores of the zeolite. Explain how the water/zeolite mixture would catalyze the reaction.
- (g) In Section 12.1.1 we noted that I_2 can catalyze the decomposition of ethane. How would that work?
- (h) Find a reasonable mechanism for the decomposition of ethane in the presence of iodine.
- (i) Estimate all of the preexponentials and rate constants for the reaction in part (h).

Table P12.18 The rate of ethane hydrogenolysis at 523 K and 10 atm over an number of supported metal catalysts

Substance	Rate Molecules/cm ² /sec	Substance	Rate Molecules/(cm ² ·second)
Co	9 × 10 ¹²	Rh	2 × 10 ¹⁴
Ni	4 × 10 ¹⁴	Pd	2 × 10 ⁹
Cu	> 1 × 10 ⁶	Os	2 × 10 ¹⁶
Ru	6 × 10 ¹⁴	Ir	5 × 10 ¹³
Re	2 × 10 ¹³	Pt	2 × 10 ⁹

Source: Data of J. H. Sinfelt, *Adv Catalysis*, **23**, 91 (1973a,b), *J. Catalysis*, **29**, 308 (1973).

(d) Experimentally, none of these other metals actually shows significant catalytic activity. What do you conclude from that?

12.19 The reaction $2\text{CH}_3\text{CH}_2\text{OH} \Rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + 2\text{H}_2\text{O}$ is being run in an acid catalyst.

- (a) Find a feasible mechanism for the reaction.
- (b) What side products do you expect?
- (c) If you run the reaction in a zeolite, could you eliminate some of the side products?
- (d) What zeolite would you choose?

12.20 Imbert, Gnep, and Guisset, (1997) *J. Catalysis*. **172**, 307 examined the isomerization of creosol, $\text{CH}_3(\text{C}_6\text{H}_4)\text{OH}$.

- (a) Find a feasible mechanism for the reaction
- (b) What side products do you expect?
- (c) If you run the reaction in a zeolite, could you eliminate some of the side products?
- (d) What zeolite would you choose?

(e) Imbert et al. actually ran the reaction in ZSM-5. They found that initially they got mainly *para*-creosol. However, after they ran the reaction for a long time so that there was plenty of time for all species to diffuse in and out of the catalyst, *meta*-creosol was the major product. How can you account for these observations?

12.21 Iiao, Yamamoto, Segawa (1996). *Journal of Catalysis*. **161**, 20 examined the reaction between methanol and ammonia to yield methylamine.

- (a) What general class of reaction would the addition of a methyl group to ammonia fall under?
- (b) What type of catalyst would you use?
- (c) What side products would you expect?
- (d) What would you do to avoid the formation of dimethyl and trimethyl amine?
- (e) Look at the lists of catalysts in this chapter. Which one is properly sized to avoid the formation of dimethyl and trimethyl amine?
- (f) How do your predictions in a), b), c) compare to Iiao, Yamamoto, Segawa's findings?

(j) Use the steady-state approximation to derive an equation for the rate of reaction for the mechanism in part (h).

(k) Show that the rate is higher than in the case in part (a).

12.15 Repeat Problem 12.14, parts (g)–(k) using acetaldehyde as a catalyst. Could ethanol also be used as a catalyst. (*Hint*: What products are formed when ethanol decomposes?)

12.16 What type of catalyst would you use for the following reaction:

- (a) Hydrogenation of corn oil to form margarine
- (b) Oxidation of carbon monoxide in your home furnace
- (c) Hydrogenation of furfurylamine
- (d) Hydrolysis of protein stains on clothes
- (e) Production of methylamine from methanol and ammonia
- (f) Transformation of 2,4-pentanedione into 3-methyl-2-cyclopentanone
- (g) Partial oxidation of C₃–C₆ olefins
- (h) Softening of a pair of jeans by hydrolyzing the cellulose.

12.17 Jennings (1991) summarized the available data for ammonia synthesis on a number of catalysts. Table P12.17 summarizes the data.

- (a) How well do these data follow a Sachtler–Fahrenfort plot?
- (b) On the basis of your findings, what other materials would be good catalysts for ammonia synthesis?
- (c) In reality, lead and other substances you would guess from Table 6.5 are not good catalysts for the reaction. What does that tell you?

12.18 Sinfelt and co-workers did a considerable amount of data on ethane hydrogenolysis. Table P12.18 gives a selection of their results.

- (a) How well do these data follow a Sachtler–Fahrenfort plot and Tanaka–Tamaru plot?
- (b) Are there any points way off of the curve? What do you make of that?
- (c) On the basis of your plots and the data in Table 12.11, what other substances would you expect to be active for this reaction?

Table P12.17 The relative rate of ammonia synthesis over a number of catalysts

Metal	Relative Rate	Heat of Adsorption of Nitrogen, kcal/mol of nitrogen atoms
Ru	1.0	-30
Fe	0.01	-42
Rh	0.005	-27
Re	1 × 10 ⁻⁵	-99
Pt	1 × 10 ⁻⁷	-71

Note: Heat of adsorption of N₂ = 3* energy in Table 6.5.

Source: Data from Jennings (1991).

Hauptfear, Olson and Schmidt (1994), *Journal of the Electrochemical Society*, **141**, 1943 examined the kinetics of SiO₂ deposition from tetraethylorthosilicate, (CH₃CH₂O)₄Si also called TEOS. The main reaction is:



- (a) Derive a Langmuir-Hinshelwood rate equation for the reaction, assuming that the mechanism of the reaction is $\text{TEOS} \rightleftharpoons \text{TEOS}_{(\text{ad})} \rightarrow \text{products}$.
- (b) Hauptfear, et al. found that the rate of decomposition is reduced when ethylene is fed into the reactor even though the reaction is irreversible. Show that your rate equation predicts that the ethylene will slow down the reaction.
- (c) Would the ethylene affect the activation barrier for the reaction. In other words, would a plot of log rate versus $1/T$ change? Try to be quantitative.
- (d) What effect would you expect acetylene to have on the reaction rate? How about ammonia?

12.23 In Table 2.9 we said that the hydrogenation of ethylene over a nickel catalyst obeys

$$r_{\text{C}_2\text{H}_4} = \frac{k_1 S_0 K_2 K_3 P_{\text{H}_2} P_{\text{C}_2\text{H}_4}}{(1 + K_2 P_{\text{H}_2} + K_3 P_{\text{C}_2\text{H}_4})^2} \quad (\text{P12.23.1})$$

The objective of this problem is to work out the behavior of equation (P12.23.1). Assume

$$k_1 = 10^{13} / \text{second} \times \exp(-18 \text{ kcal/mol}) / k_{\text{B}} T,$$

$$K_2 = 10^{-11} / \text{atm} \times \exp(16 \text{ kcal/mol}) / k_{\text{B}} T,$$

$$K_3 = 10^{-10} / \text{atm} \times \exp(14 \text{ kcal/mol}) / k_{\text{B}} T, S_0 = 10^{15} \text{ molecules/cm}^2$$

- (a) Plot the rate as a function of the C₂H₄ pressure at 300 K. Assume an H₂ pressure of 1 atm and consider C₂H₄ pressures from 0.5 to 10 atm.
- (b) Why does the rate decline at high C₂H₄ pressures?
- (c) Plot the rate as a function of temperature for temperatures between 200 and 500 K. Assume a C₂H₄ pressure of 1 atm and a H₂ pressure of 1 atm.
- (d) Why does the rate decline at high pressures?

12.24 The decomposition of urea in the presence of an enzyme called *urease* follows the following rate law:

$$r_{\text{urea}} = -\frac{k_1 K_2 [\text{urea}]}{1 + K_2 [\text{urea}]}$$

Table P12.24 shows rate data for the reaction.

- (a) Fit the data to the rate law using a Lineweaver-Burke plot, the Eadie-Hofstee plot, and a nonlinear fit to the data. (*Hint*: Look back to Examples 3.A and 12.A.)
- (b) Why do the different methods give you such different numbers?
- 12.25** Vannice and Poondi (1997), *J. Catalysis*, **169**, 166 examined benzyl alcohol hydrogenation over on a number of supported platinum catalysts. They found that the main reaction was hydrogenation of the benzyl alcohol to toluene.

Table P12.24 Rate data for Problem 12.24

Urea Concentration, mol/liter	Rate, mol/(liter-minute)	Urea Concentration, mol/liter	Rate, mol/(liter-minute)
0.0001	200	0.03	10,400
0.0003	700	0.05	10,800
0.0005	1200	0.1	11,000
0.001	2000	0.3	11,500
0.003	4500	0.5	12,000
0.005	6300	1	12,100
0.01	8300	2	12,100

- (a) Write down a balanced overall reaction.
- (b) Propose a feasible mechanism for the reaction.
- (c) Derive a Langmuir-Hinshelwood rate equation for the reaction assuming that the rate-determining step is the addition of the second hydrogen to benzaldehyde.
- (d) How well does your expression fit the rate data in Table P12.25?
- (e) Next, derive an expression for the production of side products. Assume that the rate-determining step is the addition of another hydrogen.
- (f) Vannice et al. found that when they poisoned the catalyst with TiO₂ they were able to enhance the rate. Explain this result.

12.26 Sauer and Ollis, (1994), *J. Catalysis*, **149**, 81 examined the photooxidation of acetone on a TiO₂ catalyst. Under the conditions used by these investigators, the main reaction was



Assume that the reaction occurs via the following mechanisms:



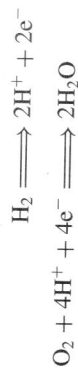
where S is an active site on the catalyst and h⁺ is a hole generated by a photon.

Table P12.25 Rate data for problem 12.25

Benzyl Alcohol Pressure, atm	Hydrogen Pressure, atm	Rate μmol/second	Benzyl Alcohol		Rate μmol/second
			Pressure, atm	Pressure, atm	
0.004	1.00	0.66	0.004	0.80	0.64
0.008	1.00	0.65	0.004	0.67	0.62
0.008	1.00	0.64	0.004	0.67	0.58
0.004	1.00	0.78	0.004	0.53	0.55
0.004	0.85	0.61	0.004	0.53	0.48
0.004	0.80	0.72	0.004	0.38	0.48
0.004	0.80	0.77	0.004	0.38	0.42

- (a) Derive equations for the rate of reaction assuming that reaction (P12.26.1) is rate-determining.
- (b) Derive equations for the rate of reaction assuming that reaction (P12.26.2) is rate-determining.
- (c) Derive equations for the rate of reaction assuming that reaction (P12.26.3) is rate-determining.
- (d) Table P12.26 shows some rate data extrapolated from Sauer and Ollis' results. Use an F test as described in Example 3.B to determine which rate equation fits best.

12.27 In Section 12.13 we presented the mechanism of hydrogen oxidation in a fuel cell. However, that mechanism works with only one kind of fuel cell: a fuel cell with a polymer electrolyte. The electrolyte is active at 60°C.

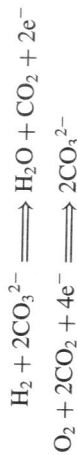


However, under other conditions, alternative mechanisms occur:

With an alkaline electrolyte at 120°C



With a molten carbonate at 600°C



With a molten salt at 900°C



Table P12.26 Rate data for Problem 12.26

Acetone Concentration, mg/m ³	Rate, mg/(cm ³ ·minute)	Acetone Concentration, mg/m ³	Rate, mg/(cm ³ ·minute)	Acetone Concentration, mg/m ³	Rate, mg/(cm ³ ·minute)
0	0	25	0.08	150	0.25
3	0.01	30	0.10	170	0.26
4	0.02	40	0.12	200	0.27
5	0.02	50	0.14	250	0.29
7	0.03	70	0.17	300	0.3
10	0.04	100	0.21	350	0.032
15	0.06	130	0.23	400	0.32

(a) Guess a feasible mechanism for each of the reactions on a platinum catalyst. (*Hint:* The reactions above are not elementary reactions. Find elementary reactions that occur on platinum. There should be a different mechanism on the anode and cathode. See Figure 5.10 for ideas.)

(b) Diagram the catalytic cycle for each reaction. Be sure to consider the production and destruction of the catalytic site. (*Hint:* In each case there is one catalytic cycle on the anode and one on the cathode.)

(c) How is electricity generated?

(d) Look up the half-cell potential for each of these reactions. How much voltage will you produce?

12.28 The production of indindiol is one of the key steps in the manufacture of an AIDS drug called Trixovan (see Figure P12.28). The objective of this project is for you to propose ways to make indindiol.

(a) One scheme to make the product is to oxidize indene with hydrogen peroxide. Search the protein database to find an enzyme that would catalyze the simultaneous addition of two OH groups.

(b) An alternative scheme is to add iodine across the double bond in indene to form an indene diiodide and then hydrolyze the product (replace iodine with water). What kind of catalyst would you use to catalyze the addition of iodine?

(c) What type of catalyst would you use to catalyze the hydrolysis reaction? (*Hint:* What type of catalyst works for the reverse reaction, i.e., dehydration?)

(d) Repeat (b) and (c) when the first step is to phosphorylate the indene.

12.29 The reaction $\text{CH}_3\text{CH}_2\text{OH} + \text{NAD}^+ \rightleftharpoons \text{CH}_3\text{CHO} + \text{NADH} + \text{H}^+$ is critical to the destruction of alcohol in the human body.

(a) Look up NAD and NADH in a biochemistry book. What are they?

(b) Look in the protein database and find an enzyme that would catalyze the reaction in your liver.

(c) Assume that the reaction follows the mechanism:

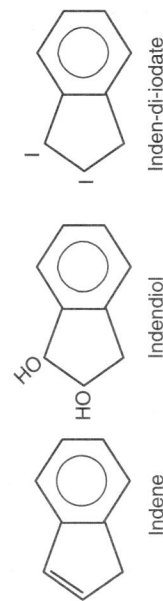
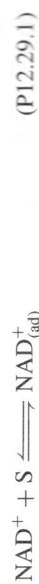


Figure P12.28 Structures of some of the intermediates used in the production of Trixovan.

where $[\text{CH}_3\text{CH}_2\text{OH}:\text{NAD}]_{\text{ad}}^+$ is a NAD, ethanol complex and S is a site on the enzyme. Derive an equation for the rate of the reaction assuming that reaction (P12.29.3) is rate-determining.

- (d) How do your kinetics differ from Langmuir-Hinshelwood kinetics?
- (e) Look up a biochemistry book, and find out how much of the NAD^+ is available in a typical human being?
- (f) Does the amount of NAD^+ vary with the weight of the individual?
- (g) Use your findings to suggest a possible hangover cure.
- (h) Would a vitamin work?

12.30

The *US Chemical Industry Statistical Handbook for 1997* gives a chart showing the feedstocks used to produce all of the major chemicals in the United States. Figure P12.30 shows part of the benzene chain, specifically, the chemicals produced starting with benzene. The chart includes the major organic chemicals used in the process, but not hydrogen, oxygen, CO, or water.

- (a) Look at each step (i.e., arrow) and write a balanced reaction for the step, adding hydrogen oxygen, water, or CO as needed.
- (b) Use your knowledge from Chapter 5 to suggest a possible mechanism for each reaction.
- (c) Suggest a possible catalyst or series of catalysts for each step.
- (d) Look in the chemical processes handbook. How do your guesses for catalysts compare to the ones actually used?

12.31 In the human body, cells use the reaction



to trap glucose in cells. The kinetics of the reaction varies between various tissues. Your heart and brain use an enzyme called *hexokinase*. Your liver uses a different enzyme called *glucokinase*.

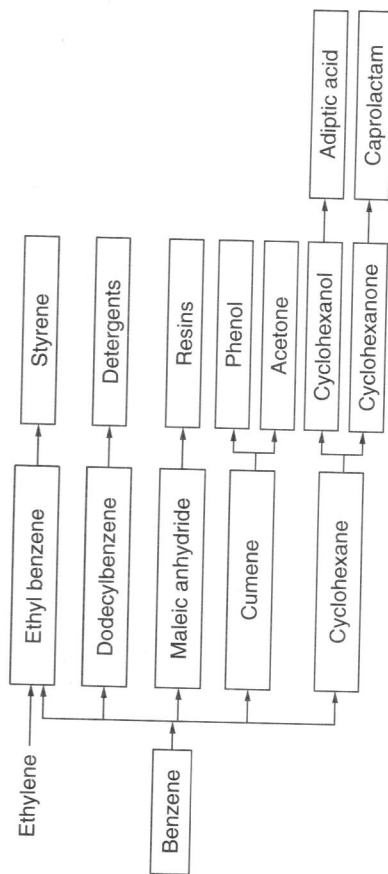


Figure P12.30 A part of the benzene chain for the production of industrial chemicals. [Adapted from *The U.S. Chemical Industry Statistical Handbook for 1997* and Dr. D. L. Burdick and Dr. W. L. Leffler, *Petrochemical Chart*.]

Table P12.31 The reactivity of hexokinase and glucokinase for phosphorylating glucose

Blood Glucose, mmol/liter	Rate with Hexokinase, mmol/hour	Rate with Glucokinase, mmol/hour	Blood Glucose, mmol/liter	Rate with Hexokinase, mmol/hour	Rate with Glucokinase, mmol/hour
0.05	0.3	0.02	3.0	0.97	0.7
0.1	0.5	0.03	4.0	1.0	0.9
0.3	0.75	0.10	5.0	1.0	1.0
0.5	0.8	0.15	6.0	1.0	1.1
1.0	0.9	0.3	7.0	1.0	1.2
2.0	0.95	0.5	10.0	1.0	1.4

(a) Fit the data in Table P12.31 to Michaelis-Menten kinetics.

(b) How do the results above help your brain and heart to survive famine? What happens as the blood glucose level drops? Where does the glucose go? To your heart or to your liver?

(c) Now assume that there is an excess of glucose in your bloodstream. What happens? (Note: 5 mmol/liter is a normal glucose level in humans.)

12.32 In Section 12.5 we found that NO_2 can catalyze the decomposition of ethane. NO_2 catalysis occurs at low temperature, where there are not many radicals in the system. However, at higher temperatures, NO_2 can instead inhibit the decomposition of ethane. The main mechanism is for the NO_2 to trap the radicals in the system (i.e., NO_2 reacts with the radicals to form stable species). The objective of this problem is to develop a criterion to see whether NO_2 will enhance or inhibit ethane decomposition.

(a) Write a complete mechanism for ethane decomposition including the fact that NO_2 can initiate the mechanism as discussed in Section 12.5 and that NO_2 can trap the hydrogen atoms and ethyl radicals.

(b) Use the steady-state approximation to develop a rate equation for the reaction.

(c) Use the results in Chapters 5, 7, and 11 to guess a preexponential and an activation barrier for each step.

(d) Use your results to calculate the rate of ethane decomposition at 500, 800, and 1200 K, assuming that you have a reactor filled with 1 atm of ethane and 0.01 atm of NO_2 .

(e) How do your results compare to the case in Figure 12.9?

12.33 Blaser, Jalett, Garland, Studer, Thies, and Wirthjani (1998). *J. Catalysis*. **173**, 282 examined the kinetics of the hydrogenation of ethyl pyruvate ($\text{CH}_3\text{COCOOC}_2\text{H}_5$) to ethyl lactate ($\text{CH}_3\text{CHOHCOOC}_2\text{H}_5$) on a 5% Pt/ Al_2O_3 catalyst in toluene in both presence and absence of a chiral modifier.

(a) What is the stoichiometry of the reaction? Provide a balanced overall reaction.

(b) Propose a feasible mechanism for the reaction.

(c) Blaser et al. propose that in the absence of the chiral modifier, the rate-determining step in the reaction is the addition of an adsorbed hydrogen to an adsorbed ethyl pyruvate. Derive a Langmuir-Hinshelwood rate equation for the reaction, assuming that this mechanism is correct.

- (d) Blaser et al. also propose that in the presence of the chiral modifier, the addition of the first hydrogen to the ethyl pyruvate rate is rapid, while the addition of a second hydrogen to the adsorbed ethyl pyruvate is rate-determining. Derive a Langmuir-Hinshelwood rate equation for the reaction assuming that this mechanism is correct.

(e) What types of experiments would you do to distinguish between your rate equations in c) and d)?

(f) Which equation fits the data in Table P12.33 better?

12.34 Schürch, et al. (1998). *J. Catalysis*. **173**, 187 examined the role of certain amines in modifying the stereospecificity of ethyl pyruvate ($\text{CH}_3\text{COCOOC}_2\text{H}_5$) hydrogenation to ethyl lactate ($\text{CH}_3\text{CHOHCOOC}_2\text{H}_5$) on a 5% Pt/ Al_2O_3 catalyst.

- (a) If you were trying to modify the stereospecificity of a reaction, what would you do? (*Hint*: Draw an analogy to the production of isotactic polyethylene.)
- (b) Amines bind moderately strongly to platinum. How could the amine work?
- (c) If you were designing the modifiers, what other species would you choose? Look specifically at thiols since they bind even more strongly to platinum.
- (d) Would you anticipate side reactions? (*Hint*: What other reactions would the platinum do? What other reactions would the alumina do?)

12.35 Keane, (1997). *Journal of the Chemical Society-Faraday Transactions*. **93**, 2001 examined the hydrogenation of methylacetoacetate (MAA) ($\text{CH}_3\text{COCH}_2\text{COOCH}_3$) to methyl 3-hydroxybutyrate ($\text{CH}_3\text{CHOHCH}_2\text{COOCH}_3$) over a Ni/SiO₂ catalyst.

- (a) What is the reaction? Provide a balanced equation.
- (b) Derive a Langmuir-Hinshelwood rate equation for the reaction assuming that the addition of the first hydrogen is rate-determining
- (c) Derive a Langmuir-Hinshelwood rate equation for the reaction assuming that the addition of the second hydrogen is rate-determining.
- (d) Which equation fits the data in Table P12.35 better?
- (e) Why is there a maximum rate at intermediate MAA concentrations?

12.36 Many different catalysts can decompose H_2O_2 : catalyze from potatoes, MnO_2 , iron, and iron oxide. Put a 30% solution of H_2O_2 into a Petri dish, than add

Table P12.33 Rate data for problem 12.33 - rates/gram of catalyst

Rate, mmol/ (gm-hour)	H_2 Pressure, bar	Ethyl Pyruvate		Rate mmol/ (gm-hour)	H_2 Pressure, bar	Ethyl Pyruvate	
		Concentration, mol/liter	Concentration, mol/liter			Concentration, mol/liter	Concentration, mol/liter
0	21	0	17	10	10	3	3
20	21	0.3	24	20	20	3	3
20.5	21	1	30	30	30	3	3
25	21	2.5	34	40	40	3	3
24	21	3	42	60	60	3	3
23	21	4.2	48	80	80	3	3
18	21	6.8	54	100	100	3	3
15	21	9.0	68	160	160	3	3

Table P12.35 Rate data for Problem 12.34

Rate, mmol/ (liter-minute)	MAA		H_2 pressure, atm	Rate, mmol/ (liter-minute)	MAA		H_2 pressure, atm
	Concentration, mmol/liter	Concentration, mmol/liter			Concentration, mmol/liter	Concentration, mmol/liter	
2.1	1	1	1.0	2.0	1	1	0.5
7.9	5	5	1.0	7.2	5	5	0.5
11.5	10	10	1.0	10.0	10	10	0.5
13.5	30	30	1.0	11.0	30	30	0.5
12.8	40	40	1.0	10.2	40	40	0.5
20	50	50	1.0	9.4	50	50	0.5
10.4	70	70	1.0	8.0	70	70	0.5
8.5	100	100	1.0	6.4	100	100	0.5

Note: The 0.5-atm data were made up for this problem. Keane actually measured at only 1 atm.

a slice of potato, some MnO_2 , a clean nail, and a rusty nail. Which substance decomposes the H_2O_2 the quickest?

12.37 Consider a first-order reaction occurring in a 5-mm-diameter spherical catalyst pellet.

- (a) Calculate the effectiveness factor for the reaction. Data: $k_1 = 8/\text{second}$, $D_e = 0.8 \text{ cm}^2/\text{second}$.
- (b) How would the effectiveness factor change if you changed to 2-mm-diameter spherical catalyst pellets?
- (c) How would the effectiveness factor change for 4-mm-diameter pellets with a k_e of 1/min?

12.38 As noted in Problem 12.11, enzymes are commonly added to detergents to eliminate stains. The detergents work best in cold water. The object of this problem is to quantify the idea that the enzymes work best in cold water.

(a) Consider removing a food stain from your shirt. Food stains contain proteins that take a week to set. Guess at a kinetic expression for the setting of the stain assuming the activation barrier to be 26 kcal/mol, that is, the value from Figure 2.8, assuming that the half-life is a week.

(b) Now consider the reaction between the stain and the enzyme. Develop a kinetic expression for the reaction between the enzyme and the stain. Assume that

- (1) The reaction between the enzyme is catalyzing the hydrolysis of the protein in the stain,
- (2) The reaction follows a Rideal-Eley mechanism; that is, the enzyme binds to the stain, then water is added without binding to the enzyme,
- (3) The binding energy (i.e., ΔG_{ad}) between the protein and the enzyme is 25 kcal/mol,
- (4) The reaction has a preexponential of $10^{13}/\text{second}$ and an activation barrier of 18 kcal/mol.
- (5) $S_0 = 1$ enzyme site/1000 linkages in the stain.

(c) At this point, you have two parallel reactions. Integrate the rate equations to calculate the concentration of the stain, the portion of the stain that is set, and the portion of the stain that is hydrolyzed as a function of time.

- (d) Plot your results as a function of time at $T = 273, 290, 300, 340$ K. What fraction of the stain is set in each case?

12.39 In the supplemental material, we derived an equation for the effectiveness factor for diffusion into a flat plate. The objective of this problem is to derive an expression for the diffusion into a flat slab of thickness $2L$. Assume that the top and bottom of the slab are surrounded by gas and that the slab is infinite in the x and y directions.

- (a) Use a shell balance to show that the slab obeys

$$D_e \frac{d^2 C_A}{dz^2} + r_A = 0 \quad (\text{P12.39.1})$$

where z is the distance from the center of the slab, C_A is the concentration of the reactant, and r_A is the rate of formation of the reactant A.

- (b) Substitute in a first-order rate law to derive a differential equation for the concentration in the slab.
 (c) What are the boundary conditions for your rate equation?
 (d) Show that the solution of the differential equation is

$$C_A = C_A^0 \left(\frac{\cosh(\Phi_P z/L)}{\cosh(\Phi_P)} \right) \quad (\text{P12.39.2})$$

with

$$\Phi_P = L \sqrt{\frac{k_A}{D_e}} \quad (\text{P12.39.3})$$

- (e) Now use your results to derive an equation for the effectiveness factor.

- (f) Make a plot of the effectiveness factor as a function of the Thiele modulus. How do your results compare to those for a spherical catalyst pellet?

12.40 Chen, Lu Pradier, Paul and Flodstrom (1997), *J. Catalysis*, **177**, 3, examined the effect of SO_2 on the reduction of NO by butene over a platinum catalyst. They found that small additions of SO_2 enhanced the rate of reaction, while large amounts of SO_2 stopped the reaction.

- (a) Use a Langmuir–Hinshelwood rate expression to show how large amounts of SO_2 could stop the reaction.
 (b) Now consider small amounts of SO_2 . Small amounts of SO_2 act as a poison to weaken the bonds between the reactants and the platinum. How could that increase the rate of reaction?
 (c) SO_2 also creates acid sites. How would that affect the reaction?

More Advanced Problems

12.41 Gouverneur, Houk, Pascual-Teresa, Beno, Janda, and Lerner (1993), *Science* **262**, 204 produced catalytic antibodies to control the percentage of cis and trans isomers in a series of Diels–Alder reactions. Their technique is to calculate the transition state geometry, find a “hapten” that has a geometry that closely mimics the

transition state, and then create antibodies to the hapten. The antibody strongly binds the transition state and so acts like a catalyst for the reaction.

- (a) In the paper they use RHF/3-21G methods to calculate the transition state geometry for the reaction. Recalculate the transition state geometry at the MP2/6-31G* level. To simplify things, replace the part of the diene past the nitrogen with a hydrogen. How much does the geometry change? See Longcharich, Brown and Houk (1989), *J. Organic Chem*, **54**, 1129 for more details of the transition state calculation.

- (b) How would the changes in the geometry of the transition state affect the conclusions in the paper? Is the real transition state geometry closer or farther away from the hapten geometry?

12.42 Korre, Klein, and Quann (1997), *Industrial & Engineering Chemistry Research*, **36**, 2041 say that they used “inhibition studies” to examine “the kinetics of naphthalene and phenanthrene hydrocracking over a presulfided NiW/USY catalyst in an 1-L batch autoclave at $P_{\text{H}_2} = 68.1$ atm and $T = 350$ degrees C.”

- (a) What is the overall reaction? Write a balanced equation for the reactants and major products.
 (b) Describe the catalyst. What do you know about the structure of the catalyst from the properties given in the paper?
 (c) How was selective inhibition used to help determine kinetics?
 (d) Korre, et al. conclude that the reaction occurs on two sites. What is the evidence for this conclusion? Do you agree with the conclusion?

12.43 Prins, Jian, and Flechsenhar (1997a,b), *Polyhedron*, **16**, 3235, (1997), *Journal of Catalysis*, **168**, 491 examined the kinetics and mechanism of aniline hydrodenitrogenation. They find that the data are not easily fit by a Langmuir–Hinshelwood rate expression, but a multisite model works.

- (a) Use the multisite model to derive an expression for the hydrodenitrogenation of aniline.
 (b) Read Prins’ paper. What evidence does he provide for the multisite model? Is the evidence convincing?

12.44 HJ. Bart W. Kaltenbrunner and H. Landschutzer, examined the kinetics of the esterification of acetic acid with propyl alcohol catalyzed by the ion exchange resin Dowex Monosphere at 650°C . The mixture is very nonideal.

- (a) How do Bart et al. account for the nonideal mixing properties in their kinetic model? Do the changes make sense? In other words, does it make sense to modify the kinetic equations in this way?

- 12.45** Read the following papers and report on the findings; and then devise a possible homework problem based on the results.

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