

CHAPTER SEVEN

HETEROGENEOUS PROCESSES, CATALYSIS, AND ADSORPTION

HETEROGENEOUS PROCESSES

The reaction rates and reactor designs considered thus far have been for homogeneous reactions. The remainder of the book is devoted to heterogeneous systems, particularly those involving fluid and solid phases. Such heterogeneous systems are very important because most chemical reaction processes require a solid catalyst. Accordingly, the main objective of the next three chapters is an understanding of the kinetics of reactions of fluids on solid catalysts. In this first of the three chapters, the essential differences between homogeneous and heterogeneous rates are presented. This is followed by a discussion of the general aspects of catalysis and adsorption. Chapter 8 is concerned with solid catalysts, particularly their physical properties, because these properties affect mass and energy transport within catalyst particles. Also included in Chap. 8 is a discussion of theories of behavior of solid catalysts and practical aspects such as preparation, life, etc. Then in Chap. 9 we discuss kinetics and rate equations for fluid-phase reactions occurring at the surface of solid catalysts. With this preparation we are in position to consider transport effects in heterogeneous processes (Chaps. 10 and 11) and reactor design (Chap. 13).

There are heterogeneous reactions other than those involving solid catalysts, for example, reactions between gases and solids such as in the reduction of metallic ores. Such gas-solid, noncatalytic reactions are taken up in Chap. 14. Also, there are important heterogeneous processes not involving solid phases. Examples

are alkylation (liquid-liquid systems) and absorption and reaction processes such as the separation of CO_2 and H_2S from gases with amine solutions. These kinds of heterogeneous processes will be considered, but the major emphasis will be on fluid-solid catalytic reactions.

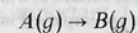
The phase boundaries inherent in heterogeneous systems require that transport processes (mass and energy transfer) as well as the intrinsic reaction rate be accounted for in reactor design. Consider the case of a gaseous reaction mixture and a solid catalyst. It is advantageous to use the same conservation equations for reactor design that were given in Chap. 3. Then much of our previous work on homogeneous systems (Chaps. 3, 4, and 5) will be applicable. This can be done if the reaction rate is expressed in terms of the bulk concentration and temperature of the gas phase. Such rates will include the effects of transport processes. In Equation (3-1) the rate term is based upon a volume element of reactor. If the volume element includes a heterogeneous region of reaction fluid and solid catalyst particles, the proper rate will incorporate mass and energy transfer from fluid to solid surface and within the particles (catalyst particles are normally porous). Such rates are called *global* or *overall* rates and their use allows us to apply many of the design equations given in Chaps. 3 to 5. In order to express the global rate in terms of bulk properties, expressions must be formulated for each of the steps in the overall process. The sequence of steps for converting reactants to products is:

1. Transport of reactants from the bulk fluid to the fluid-solid interface (external surface of catalyst particle)
2. Intraparticle transport of reactants into the catalyst particle (if it is porous)
3. Adsorption of reactants at interior sites of the catalyst particle
4. Chemical reaction of adsorbed reactants to adsorbed products (surface reaction—the intrinsic chemical step)
5. Desorption of adsorbed products
6. Transport of products from the interior sites to the outer surface of the catalyst particle
7. Transport of products from the fluid-solid interface into the bulk-fluid stream

At steady state the rates of all the individual steps will be the same. This equality can be used to develop a global rate equation in terms of the concentrations and temperatures of the bulk fluid. The derivation of such equations will be considered in detail in Chaps. 10 to 12, but a very simple treatment is given next to illustrate the nature of the problem.

7-1 Global Rates of Reaction

Consider an irreversible gas-phase reaction



which requires a solid catalyst C . Suppose that the temperature is constant and that the reaction is carried out by passing the gas over a bed of *nonporous* particles of C . Since the catalyst is nonporous, steps 2 and 6 are not involved. The problem

is to formulate the rate of reaction per unit volume† of the bed—that is, the *global rate for a catalyst particle*, r_v —in terms of the temperature and concentration of A in the bulk-gas stream. Note that these are the quantities that are measurable or can be specified (as design requirements), rather than the temperature and concentration at the gas-particle interface. Global rates of catalytic reactions are usually expressed per unit mass of catalyst, i.e., r_p . These are easily converted to rates r_v per unit volume by multiplying them by the bulk density ρ_B of the bed of catalyst particles.

The overall conversion of A to B in the bulk gas for this case of nonporous catalyst occurs according to steps 1, 3 to 5, and 7 in series. Let us further simplify the problem by supposing that steps 3 to 5 may be represented by a single first-order rate equation. Then the overall reaction process may be described in three steps: gas A is transported from the bulk gas to the solid surface, the reaction occurs at the interface, and finally, product B is transported from the catalyst surface to the bulk gas. Since the reaction is irreversible, the concentration of B at the catalyst surface does not influence the rate. This means that r_p can be formulated by considering only the first two steps involving A . Since the rates of these two steps will be the same at steady state, the disappearance of A can be expressed in two ways: either as the rate of transport of A to the catalyst surface,

$$r_p = k_m a_m (C_b - C_s) \quad (7-1)$$

or as the rate of reaction at the catalyst surface,

$$r_p = k C_s \quad (7-2)$$

In Eq. (7-1) k_m is the usual mass-transfer coefficient based on a unit of transfer surface, i.e., a unit of external area of the catalyst particle. In order to express the rate per unit mass‡ of catalyst, we multiply k_m by the external area per unit mass, a_m . In Eq. (7-2) k is the reaction-rate constant per unit mass of catalyst. Since a positive concentration difference between bulk gas and solid surface is necessary to transport A to the catalyst, the surface concentration C_s will be less than the bulk-gas concentration C_b . Hence Eq. (7-2) shows that the rate is less than it would be for $C_s = C_b$. Here the effect of the mass-transfer resistance is to reduce the rate. Figure 7-1 shows schematically how the concentration varies between bulk gas and catalyst surface.

† As defined, the volume element on which r_v is based must include at least one catalyst particle; otherwise the interphase physical effects cannot be considered. Yet this rate is used in such equations as (3-18) and (3-18a) as a rate applicable to a differential volume, i.e., as a point rate. This is an approximation which arises from treating the discrete nature of a bed of catalyst particles as a continuum. It is a necessary approximation because it is not yet possible to take into account variations in heat- and mass-transfer coefficients with position on the surface of a single catalyst particle. Thus average values of these coefficients over the particle surface are employed in formulating global rates. This is the value denoted by k_m in Eq. (7-1).

‡ Instead of rate per unit mass of catalyst, Eqs. (7-1) and (7-2) could be expressed as rates per unit external surface, in which case a_m would not be needed in Eq. (7-1) and k in Eq. (7-2) would be per unit of catalyst surface. Alternately, a rate per particle could be used. We shall generally use the rate per unit mass.

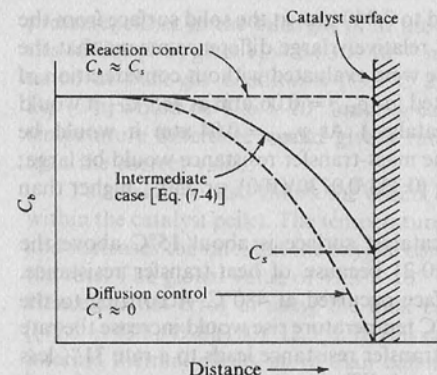


Figure 7-1 Mass transfer between fluid and catalyst surface.

The global rate can be expressed in terms of C_b by first solving for C_s from Eqs. (7-1) and (7-2); thus

$$C_s = \frac{k_m a_m}{k_m a_m + k} C_b \quad (7-3)$$

Then this result is substituted in either Eq. (7-1) or Eq. (7-2) to give

$$r_p = \frac{k k_m a_m}{k_m a_m + k} C_b = \frac{1}{1/k + 1/k_m a_m} C_b \quad (7-4)$$

This is the expression for the global rate in terms of the bulk-reactant concentration. The second equality shows that the effects of reaction and mass transfer are additive. Since the terms are in the denominator, they are *resistances* to the rate. Thus we speak of a reaction resistance ($1/k$ term) and a mass-transfer resistance ($1/k_m a_m$ term). The concentration profile in this case is shown by the solid line in Fig. 7-1. It is a very restricted illustration of a global rate, since heat-transfer effects were not considered and only external mass transfer is involved (the catalyst particle is nonporous). These restrictions are removed in the detailed treatment in Chaps. 10 and 11, but this simple example illustrates the meaning of global rates of reaction for heterogeneous systems.

A hypothetical reaction has been used to develop the previous results. It is of interest to know the magnitude of the global rate for *real* situations. Fortunately, considerable experimental data are available. Measurements† for the oxidation of SO_2 with air on a platinum catalyst, deposited on $\frac{1}{8} \times \frac{1}{8}$ -in. cylindrical pellets,‡ gave a global rate of 0.0956 g mol/(h)(g catalyst). The bulk temperature of the gas was 465°C and the gas velocity in the catalyst bed was 350 lb/(h)(ft²). The bulk composition corresponded to an SO_2 partial pressure of 0.06 atm. At these conditions both mass- and heat-transfer resistances between the bulk gas and the surface of the catalyst pellets were important. Calculations with Eq. (7-1) indicated

† R. W. Olson, R. W. Schuler, and J. M. Smith, *Chem. Eng. Progr.*, **42**, 614 (1950).

‡ The particles were of porous alumina, but the platinum was deposited on the outer surface, so that, in effect, a nonporous catalyst was used.

that the partial pressure of SO_2 dropped to 0.040 atm at the solid surface from the value of 0.06 atm in the bulk gas. This relatively large difference means that the diffusion resistance was large. If the rate were evaluated without consideration of this resistance—that is, if it were evaluated for $p_{\text{SO}_2} = 0.06$ atm at 465°C —it would be 0.333 g moles SO_2 reacted/(h)(g catalyst). At $p_{\text{SO}_2} = 0.04$ atm it would be 0.0730. Hence the error in neglecting the mass-transfer resistance would be large; that is, the rate so computed would be $(0.333/0.0730)(100)$, or 350% higher than the global rate.

Actually, the temperature at the catalyst surface is about 15°C above the bulk-gas temperature (see Example 10-2) because of heat-transfer resistance. Hence the reaction at the catalyst surface occurred at 480°C . According to the activation energy for this reaction, a 15°C temperature rise would increase the rate about 31%. Hence neglecting the heat-transfer resistance leads to a rate 31% less than the global value. If both thermal and diffusion resistances were neglected, the rate would be $(0.333/0.0956)(100)$, or 250% higher than the global rate. For this exothermic reaction the diffusion and thermal resistances have opposite effects on the rate. The example is extreme in that mass-transfer resistance was relatively large in comparison with reaction resistance. At lower temperatures and/or higher gas velocities past the catalyst pellet (higher k_m) the mass-transfer effect would be less.

Frequently external heat-transfer resistances are much larger than mass-transfer resistances, in contrast to the preceding example. As an illustration, consider the data of Maymo and Smith[†] for the oxidation of hydrogen with oxygen on a platinum-on-alumina catalyst. Rates and temperatures were measured for a single porous catalyst pellet (1.86 cm diameter) suspended in a well-mixed gas containing primarily hydrogen with a small percentage of oxygen and water vapor. Because of the turbulence in the gas, the concentration difference between bulk gas and pellet surface was negligible. However, there was a significant thermal resistance, so that the pellet-surface temperature was greater than the bulk-gas temperature. The pellet was porous with uniform distribution of platinum throughout. Hence there were internal resistances, both to mass and to heat transfer. In one particular run the measured rate of water production was 49.8×10^{-6} mol/(g catalyst)(s). This is the global value and includes the effects of both internal and external transport resistances. The bulk-gas, pellet-surface, and pellet-center temperatures were 89.9, 101, and 147.7°C , respectively. The rate of the chemical step on the surface was also measured by experiments with fine particles of catalyst for which there were no temperature or concentration differences between bulk gas and surface or interior of particle. This intrinsic rate was correlated by the equation

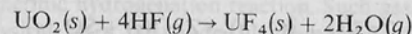
$$r_p = 0.655 p_{\text{O}_2}^{0.804} e^{-5230/R_p T} \quad (7-5)$$

where p is in atmospheres and T is in degrees Kelvin. We can evaluate the effect of the external resistance in the following way. First calculate the rate at the surface temperature ($101 + 273$ K) and $p_{\text{O}_2} = 0.0527$ atm, which is the oxygen partial

pressure, either in the bulk gas or at the pellet surface. Substituting these quantities in Eq. (7-5) gives $r_p = 54.3 \times 10^{-6}$ mol/(g catalyst)(s). If the rate were evaluated at bulk-gas conditions (89.9°C and $p_{\text{O}_2} = 0.0527$ atm), the result from Eq. (7-5) would be 43.6×10^{-6} mol/(g catalyst)(s). Hence neglecting the external-temperature difference would give a rate $[(54.3 - 43.6)/54.3](100)$, or 20%, less than the correct value.

This example also shows the effects of mass- and energy-transfer resistances within the catalyst pellet. The temperature increases toward the center of the pellet and increases the rate, but the oxygen concentration goes down, tending to reduce the rate. The global value of 49.8×10^{-6} is the resultant balance of both factors. Hence the net error in using the bulk conditions to evaluate the rate would be $[(49.8 - 43.6)/49.8](100)$, 12.5%. In this case the rate increase due to external and internal thermal effects more than balances the adverse effect of internal mass-transfer resistance. The procedure for calculating the effects of internal gradients on the rate is presented in Chap. 11.

One additional illustration is of interest. This refers to the hydrofluorination of UO_2 pellets with $\text{HF}(g)$ according to the reaction



This is a different kind of heterogeneous reaction—a gas-solid noncatalytic one. Let us examine the process at initial conditions ($t \rightarrow 0$), so that there has been no opportunity for a layer of $\text{UF}_4(s)$ to be formed around the UO_2 pellet. The process is much like that for gas-solid catalytic reactions. Hydrogen fluoride gas is transferred from the bulk gas to the surface of the UO_2 pellets and reacts at the pellet-gas interface, and H_2O diffuses out into the bulk gas. If the pellet is nonporous, all the reaction occurs at the outer surface of the UO_2 pellet, and only an external transport process is possible. Costa[†] studied this system by suspending spherical pellets 2 cm in diameter in a stirred-tank reactor. In one run, at a bulk-gas temperature of 377°C , the surface temperature was 462°C and the observed rate was $r = 6.9 \times 10^{-6}$ mol UO_2 /(s)(cm^2 reaction surface). At these conditions the concentrations of HF gas were 1.12×10^{-5} g mol/ cm^3 at the surface of the pellet and 1.38×10^{-5} g mol/ cm^3 in the bulk gas. The intrinsic rate of reaction was found to be given by

$$r = 40 C_{\text{HF}} e^{-6070/R_p T} \text{ g mol}/(\text{cm}^2)(s) \quad (7-6)$$

where T is in degrees Kelvin and C_{HF} is in gram moles per cubic centimeter. If the rate is evaluated at bulk-gas conditions, Eq. (7-6) gives 5.0×10^{-6} g mol/(s)(cm^2). Then the combined effects of an external temperature and concentration difference serve to increase the rate from 5.0×10^{-6} to 6.9×10^{-6} g mol/(cm^2)(s), or 38%. In this case the temperature at the catalyst surface is 95°C higher than the bulk-gas temperature, and this has a dominating effect on the rate of reaction. The effect of external mass-transfer resistance is to reduce the rate of this first-order reaction by $(1.38 - 1.12)/1.38$, or 19%.

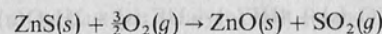
[†] J. A. Maymo and J. M. Smith, *AIChE J.*, **12**, 845 (1966).

[†] E. C. Costa and J. M. Smith, *AIChE J.*, **17**, 947 (1971).

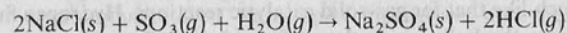
7-2 Types of Heterogeneous Reactions

All the examples in Sec. 7-1 were of the gas-solid form. As mentioned earlier this is a most important type of heterogeneous system. Most salable chemicals are prepared by converting raw materials via chemical reactions. Such reactions usually require catalysts, and these are normally solids. Since the temperatures must be high for rapid rates, the reacting fluid commonly is in the gas phase. Examples of large-scale gas-solid catalytic reactions are the major hydrocarbon transformations: cracking, reforming, dehydrogenation (for example, butadiene and butenes from butane), isomerization, desulfurization, etc. Kinetics and reactor design for such systems have naturally received major attention, and most of our emphasis on design is directed to this type of flow reactor (Chap. 13).

Gas-solid heterogeneous reactions may be noncatalytic.[†] An example is the hydrofluorination of uranium dioxide pellets referred to in Sec. 7-1. Since one reactant is in the solid phase and is consumed, the rate of reaction varies with time. Hence such processes are intrinsically dynamic, in comparison with the steady-state operation of gas-solid catalytic reactors. The process for smelting ores such as zinc sulfide,



is of this type. The conversion of CaCO_3 to CaO in the lime kiln is another example. Yet another is the process for making HCl in a transport reactor[‡] from salt particles; the reaction is



In many noncatalytic types a solid product builds up around the reacting core [for example, $\text{Na}_2\text{SO}_4(s)$ is deposited around the NaCl particles in the last illustration]. This introduces the additional physical processes of heat and mass transfer through a product layer around the solid reactant. A somewhat different form of noncatalytic gas-solid reaction is the regeneration of catalysts which have been deactivated by the deposition of a substance on the interior surface. The most common is the burning (with air) of carbon which has been gradually deposited on catalyst particles used in hydrocarbon reactions. Many of the physical and chemical steps involved here are the same as those for gas-solid catalytic reactions. The chief difference is the transient nature of the noncatalytic reaction. This type of heterogeneous reaction will be considered in Chap. 14. Another dynamic noncatalytic process is the separation or purification of gases or liquids by adsorption. Such processes are normally carried out in tubes packed with the adsorbent particles. Adsorption of the higher molecular weight hydrocarbons from gas streams in beds of activated carbon and removal of organic pollutants from water with activated carbon are examples.

A steady-state example of noncatalytic reactions is the gas-liquid form in which a gaseous reactant is absorbed in the liquid and subsequently reacts in the liquid phase. The reactor in such cases is usually a countercurrent or cocurrent absorption column of the bubble type[†] (gas bubbling through a continuous liquid phase, spray column or a tube packed with inert particles). Examples are the separation of CO_2 from a gas by adsorption and reaction in an aqueous amine solution.[‡]

Liquid-solid reactions, where the solid phase is a catalyst, is a type of heterogeneous system that is common in the chemical and petroleum industries. Alkylation with $\text{AlCl}_3(s)$ catalyst is an example. In these systems the catalyst frequently forms complexes with reactants and/or products and becomes a poorly defined solid-liquid mixture, best described as a sludge. Analytical treatment in these cases is difficult. Three-phase systems involving a gas, liquid, and solid are also encountered. Hydrogenation of liquids normally is of this type. For example, a slurry may be formed of the catalyst particles in the oil to be hydrogenated. Then hydrogen is bubbled into the slurry. These reactions are carried out in stirred-tank reactors, where the high heat capacity of the tank contents simplifies temperature control of the exothermic hydrogenation reaction. Such gas-liquid-solid systems involve several physical steps, and indeed, resistance to diffusion of dissolved hydrogen to the catalyst particle is frequently significant. The quantitative treatment of combined physical and chemical steps in such slurry reactors is considered in Chaps. 10 and 13. Polymerization systems are often of this type. For example, ethylene is polymerized by dissolving it in a solvent containing suspended catalyst particles. The trickle-bed reactor is a somewhat different form of gas-liquid-solid system. Here gas and liquid, usually in cocurrent flow, pass over a bed of catalyst particles in a fixed bed. This form is used when the volatility of the liquid is so low that complete gasification is not practical. Sulfur compounds are removed from hydrocarbon liquids in such reactors. The gas phase is primarily hydrogen. Oxidation of liquids also is carried out in trickle-bed reactors (see Chaps. 10 and 13).

Liquid-liquid reactions are sometimes encountered. Alkylation of hydrocarbons with sulfuric acid or HF as a catalyst is an example.

Solid-solid noncatalytic reactions are important in ceramics manufacture.[§] It appears that diffusion resistances may be important to some extent in all such systems. The diffusion process itself is difficult to define in solid-solid systems. At least two possibilities exist: volume diffusion in the solid and surface diffusion along interfaces and crystal boundaries.[¶] Little is known about the kinetics of solid-solid reactions at the reacting interface because most measurements include diffusion effects.

[†] C. G. Hagberg and F. X. Krupa, *Proc. 4th Int. Symp. Chem. React. Eng.*, Sec. IX, p. 408, April, 1976, Heidelberg, DECHEMA, Frankfurt.

[‡] P. V. Danckwerts, "Gas-Liquid Reactions," McGraw-Hill Book Company, New York, 1960.

[§] W. Kingery, "Kinetics of High Temperature Processes," John Wiley & Sons, Inc., New York, 1959; G. Cohn, *Chem. Rev.*, **42**, 527 (1948).

[¶] R. J. Arrowsmith and J. M. Smith, *Ind. Eng. Chem. Fund. Quart.*, **5**, 327 (1966).

[†] Julian Szekely, James W. Evans and Hong Yong Sohn, "Gas-Solid Reactions," Academic Press, New York, 1976.

[‡] A transport reactor is like a fluidized-bed reactor (Fig. 1-8), except that the fluidized particles move through and out of the reactor with the gas phase.

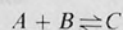
CATALYSIS

The first step in determining global rates is to examine the processes associated with the solid surface (the adsorption, desorption, and intrinsic reaction steps in the list at the beginning of the chapter). We start out with a brief qualitative discussion of the nature of catalysis and then complete this chapter with an examination of adsorption. As kinetic information began to accumulate during the last century, it appeared that the rates of a number of reactions were influenced by the presence of a material which itself was unchanged during the process. In 1836 Berzelius[†] reviewed the evidence and concluded that a "catalytic" force was in operation. Among the cases he studied were the conversion of starch into sugar in the presence of acids, the decomposition of hydrogen peroxide in alkaline solutions, and the combination of hydrogen and oxygen on the surface of spongy platinum. In these three examples the acids, the alkaline ions, and the spongy platinum were the materials which increased the rate and yet were virtually unchanged by the reaction. Although the concept of a catalytic force proposed by Berzelius has now been discarded, the term "catalysis" is retained to describe all processes in which the rate of a reaction is influenced by a substance that remains chemically unaffected.

7-3 The Nature of Catalytic Reactions

Although the catalyst remains unchanged at the end of the process, there is no requirement that the material not take part in the reaction. In fact, present theories of catalyst activity postulate that the material does actively participate in the reaction. From the concept of the energy of activation developed in Chap. 2, the mechanism of catalysis would have to be such that the free energy of activation is lowered by the presence of the catalytic material. A catalyst is effective in increasing the rate of a reaction because it makes possible an alternative mechanism, each step of which has a lower free energy of activation than that for the uncatalyzed process. Consider the reaction between hydrogen and oxygen in the presence of platinum. According to the proposed concept, hydrogen combines with the platinum to form an intermediate substance, which then reacts with oxygen to provide the final product and reproduce the catalyst. It is postulated that the steps involving the platinum surface occur at a faster rate than the homogeneous reactions between hydrogen and oxygen.

The combination or complexing of reactant and catalyst is a widely accepted basis for explaining catalysis. For example, suppose the overall reaction



is catalyzed via two active centers, or catalytic sites, X_1 and X_2 , which form complexes with A and B . The reaction is truly catalytic if the sequence of steps is

such that the centers X_1 and X_2 are regenerated after they have caused the formation of C . In a general way the process may be written

1. $A + X_1 \rightleftharpoons AX_1$
2. $B + X_2 \rightleftharpoons BX_2$
3. $AX_1 + BX_2 \rightleftharpoons C + X_1 + X_2$

Note that whereas X_1 and X_2 are occupied and regenerated a number of times, it does not necessarily follow that their catalyzing ability and/or number remain constant forever. For example, poisons can intervene to slowly remove X_1 and/or X_2 from the system, arresting the catalytic rate. What distinguishes this decline in catalytic activity from that of a noncatalytic reaction in which X_1 and X_2 are not regenerated is that the complexing-regenerating sequence occurs a great many times before X_1 and X_2 become inactive. In the noncatalytic sequence no regeneration of X occurs. Hence, while catalysts can deteriorate, their active lifetime is far greater than the time required for reaction.

A relatively small amount of catalyst can cause conversion of a large amount of reactant. For example, Glasstone[†] points out that cupric ions in the concentration of 10^{-9} mol/liter appreciably increase the rate of the oxidation of sodium sulfide by oxygen. However, the idea that a small amount of the catalyst can cause a large amount of reaction does not mean that the catalyst concentration is unimportant. In fact, when the reaction does not entail a chain mechanism, the rate of the reaction is usually proportional to the concentration of the catalyst. This is perhaps most readily understood by considering the case of surface catalytic reactions. In the reaction of hydrogen and oxygen with platinum catalyst the rate is frequently directly proportional to the platinum surface. Here a simple proportionality exists between platinum surface area and the number of centers X which catalyze the oxidation of hydrogen. While such a simple relationship may not often exist in solid-catalyzed reactions, in homogeneous catalysis there is frequently a direct proportionality between rate and catalyst concentration. For example, the hydrolysis of esters in an acid solution will depend on the concentration of hydrogen ion acting as a catalyst.

The position of equilibrium in a reversible reaction is not changed by the presence of the catalyst. This conclusion has been verified experimentally in several instances. For example, the oxidation of sulfur dioxide by oxygen has been studied with three catalysts: platinum, ferric oxide, and vanadium pentoxide. In all three cases the *equilibrium compositions* were the same.

An important characteristic of a catalyst is its effect on selectivity. An illustration is the decomposition of ethanol. Thermal decomposition gives water, acetaldehyde, ethylene, and hydrogen. If, however, ethanol vapor is suitably contacted with alumina particles, ethylene and water are the only products. In contrast, dehydrogenation to acetaldehyde is virtually the sole reaction when ethanol is reacted over a copper catalyst.

[†] J. J. Berzelius, *Jahresher. Chem.*, **15**, 237 (1836).

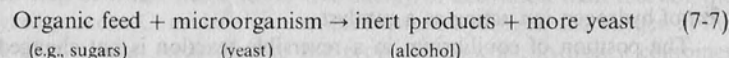
[†] S. Glasstone, "Textbook of Physical Chemistry," p. 1104, D. Van Nostrand Company, Inc., New York, 1940.

The general characteristics of catalysis may be summarized as follows:

1. A catalyst accelerates reaction by providing alternate paths to products, the activation energy of each catalytic step being less than that for the homogeneous (noncatalytic) reaction.
2. In the reaction cycle, active centers of catalysis first combine with at least one reactant and then are reproduced with the appearance of product. The freed center then recombines with reactant to produce another cycle, and so on.
3. Comparatively small quantities of catalytic centers are required to produce large amounts of product.
4. Equilibrium conversion is not altered by catalysis. A catalyst which accelerates the forward reaction in an equilibrium system is a catalyst for the reverse reaction.
5. The catalyst can radically alter selectivity.

Examples have been observed of negative catalysis, where the rate is decreased by the catalyst. Perhaps the most reasonable theory is that developed for chain reactions. In these cases it is postulated that the catalyst breaks the reaction chains, or sequence of steps, involved in the mechanism. For example, nitric oxide reduces the rate of decomposition of acetaldehyde or ethyl ether. Apparently nitric oxide has the characteristic of combining with the free radicals involved in the reaction mechanism. The halogens, particularly iodine, also act as negative catalysts in certain gaseous reactions. In the combination of hydrogen and oxygen, where a chain mechanism is probably involved, iodine presumably destroys the radicals necessary for the propagation of the chains.

Reactions in which the rate increases with *product* concentration also occur. Such reactions are termed autocatalytic. The most common examples are fermentation processes "catalyzed" by microorganisms such as yeasts, bacteria, and algae. The processes are complex but may be described approximately as a reaction between an organic feed and microorganism to produce products and more microorganisms. For example, the fermentation of sugar may be expressed:



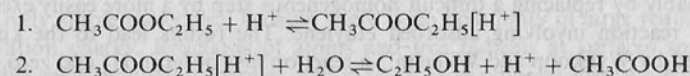
If a batch reactor initially contains a sugar solution and a small quantity of yeast, the rate will increase as the reaction proceeds, because the yeast produced is also a reactant. Ultimately, the depletion of sugar will cause the rate to reach a maximum and decrease toward zero. The microorganism does not act as a true catalyst since it is a reactant, but its presence does increase the rate. Such abnormal kinetics has been extensively treated in the literature, partly because the unusual rate vs. conversion relationship leads to interesting problems of reactor choice and optimization.^{†‡} The kinetic equations are illustrated in Prob. 7-5 for bacterial oxidation.

[†] K. B. Bischoff, *Can. J. Chem. Eng.*, **44**, 281 (1966).

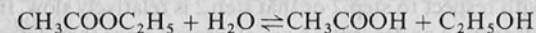
[‡] K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Company, New York, 1965.

7-4 The Mechanism of Catalytic Reactions

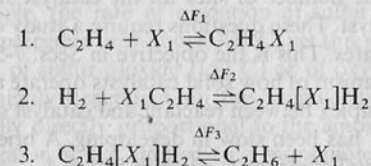
The concept that a catalyst provides an alternate mechanism for accomplishing a reaction, and that this alternate path is a more rapid one, has been developed in many individual cases. The basis for the theory is that first the catalyst and one or more of the reactants form an intermediate complex, a loosely bound compound which is unstable. This complex then takes part in subsequent reactions which result in the final products and the regenerated catalyst. Homogeneous catalysis can frequently be explained in terms of this concept. For example, consider catalysis by acids and bases. In aqueous solutions acids and bases can increase the rate of hydrolysis of sugars, starches, and esters. The kinetics of the hydrolysis of ethyl acetate catalyzed by hydrochloric acid can be explained by the following mechanism:



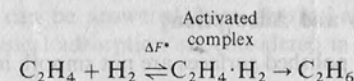
For this catalytic sequence to be rapid with respect to noncatalytic hydrolysis, the free energy of activation of reaction steps 1 and 2 must each be less than the free energy of activation for the noncatalytic reaction,



Similarly, the *heterogeneous* catalytic hydrogenation of ethylene on a solid catalyst might be represented by the steps



where X_1 is an active site on the solid catalyst and $\text{C}_2\text{H}_4[\text{X}_1]\text{H}_2$ represents the complex formed between the reactants and the catalyst. The *homogeneous* reaction, according to the absolute theory of reaction rates discussed in Chap. 2, would be written



where the free-energy change for the formation of the activated complex ΔF^* is the free energy of activation for the homogeneous reaction. The effectiveness of the catalyst is explained on the basis that the free energy of activation of each of the steps in the catalytic mechanism is less than ΔF^* .

These illustrations, particularly that for ethylene hydrogenation, are grossly oversimplified. They must be considered phenomenological models, not mechanisms. The actual mechanism of ethylene hydrogenation is quite complex. In spite of the considerable effort focused on this reaction, a mechanism satisfactory to all

investigators has yet to be offered. The system does, however, provide an opportunity to compare homogeneous and heterogeneous rates. Using published data, Boudart[†] found that the homogeneous and catalytic rates can be expressed as

$$r_{\text{hom}} = 10^{27} e^{-43,000/R_g T} \quad (7-8)$$

$$r_{\text{cat}} = 2 \times 10^{27} e^{-13,000/R_g T} \quad (\text{CuO-MgO catalyst}) \quad (7-9)$$

At 600 K the relative rates are

$$\frac{r_{\text{cat}}}{r_{\text{hom}}} = e^{(43,000 - 13,000)/600 R_g} \approx 10^{11}$$

In this case the catalyst has caused a radical reduction in overall activation energy, presumably by replacing a difficult homogeneous step by a more easily executed surface reaction involving adsorbed ethylene. The results lead to the kinetics observed by Wynkoop and Wilhelm,[‡] a reaction first order in H_2 and zero order in strongly adsorbed ethylene.

The three steps postulated for the catalytic hydrogenation of ethylene indicate that the rate may be influenced by both adsorption and desorption (steps 1 and 3) and the surface reaction (step 2). Extreme cases can be imagined: that step 1 or step 3 is slow with respect to step 2 or that step 2 is relatively slow. In the first two cases rates of adsorption or desorption are of interest since they determine the rate while in the third case the surface concentration of the adsorbed species, corresponding to equilibrium with respect to steps 1 and 3, is needed. In any event we should like to know the number of sites on the catalyst surface, or at least the surface area of the catalyst. These questions require a study of adsorption equilibrium and adsorption rates. This is the objective in Secs. 7-5 to 7-7.

The detailed mechanism of how solid catalysts operate requires knowledge of the structure of the complex between reactant and catalyst site. Understanding of this aspect to catalysis has been slow in developing. A brief review of suggested theories and experimental evidence is given in Sec. 8-4.

ADSORPTION

7-5 Surface Chemistry and Adsorption§

Even the most carefully polished surfaces are not smooth in a microscopic sense, but are irregular, with valleys and peaks alternating over the area. The regions of irregularity are particularly susceptible to residual force fields. At these locations the surface atoms of the solid may attract other atoms or molecules in the surrounding gas or liquid phase. Similarly, the surfaces of pure crystals have nonuni-

form force fields because of the atomic structure in the crystal. Such surfaces also have sites or active centers where adsorption is enhanced. Two types of adsorption may occur.

Physical adsorption[†] Physical adsorption is nonspecific and somewhat similar to the process of condensation. The forces attracting the fluid molecules to the solid surface are relatively weak, and the heat evolved during the exothermic adsorption process is of the same order of magnitude as the heat of condensation, 0.5 to 5 kcal/g mol. Equilibrium between the solid surface and the gas molecules is usually rapidly attained and easily reversible, because the energy requirements are small. The energy of activation for physical adsorption is usually no more than 1 kcal/g mol, since the forces involved in physical adsorption are weak. Physical adsorption cannot explain the catalytic activity of solids for reactions between relatively stable molecules, because there is no possibility of large reductions in activation energy. Reactions of atoms and free radicals at surfaces sometimes involve small activation energies, and in these cases physical adsorption may play a role. Also, physical adsorption serves to concentrate the molecules of a substance at a surface. This can be of importance in cases involving reaction between a chemisorbed reactant and a coreactant which can be physically adsorbed. In such a system the catalytic reaction would occur between chemisorbed and physically adsorbed reactants.

The amount of physical adsorption decreases rapidly as the temperature is raised and is generally very small above the critical temperatures of the adsorbed component. This is further evidence that physical adsorption is not responsible for catalysis. For example, the rate of oxidation of sulfur dioxide on a platinum catalyst becomes appreciable only above 300°C; yet this is considerably above the critical temperature of sulfur dioxide (157°C) or of oxygen (−119°C). Physical adsorption is not highly dependent on the irregularities in the nature of the surface, but is usually directly proportional to the amount of surface. However, the extent of adsorption is not limited to a monomolecular layer on the solid surface, especially near the condensation temperature. As the layers of molecules build up on the solid surface, the process becomes progressively more like one of condensation.

Physical-adsorption studies are valuable in determining the physical properties of solid catalysts. Thus the questions of surface area and pore-size distribution in porous catalysts can be answered from physical-adsorption measurements. These aspects of physical adsorption are considered in Chap. 8.

Chemisorption[‡] The second type of adsorption is specific and involves forces much stronger than in physical adsorption. According to Langmuir's pioneer work,[§] the adsorbed molecules are held to the surface by valence forces of the

[†] For a detailed treatment of physical adsorption see D. M. Young and A. D. Crowell, "Physical Adsorption of Gases," Butterworth & Co. (Publishers), London, 1962.

[‡] For a detailed treatment of chemisorption see D. O. Hayward and B. M. W. Trapnell, "Chemisorption," 2d ed., Butterworth & Co. (Publishers), London, 1964.

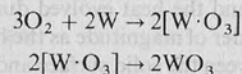
[§] I. Langmuir, *J. Am. Chem. Soc.*, **38**, 221 (1916).

[†] M. Boudart, *Ind. Chim. Belg.*, **23**, 383 (1958).

[‡] R. Wynkoop and R. H. Wilhelm, *Chem. Eng. Progr.*, **46**, 300 (1950).

[§] A discussion of the thermodynamics and kinetics of adsorption is given by Alfred Clark, "The Theory of Adsorption and Catalysis," Academic Press, New York, 1970.

same type as those occurring between atoms in molecules. He observed that a stable oxide film was formed on the surface of tungsten wires in the presence of oxygen. This material was not the normal oxide WO_3 , because it exhibited different chemical properties. However, analysis of the walls of the vessel holding the wire indicated that WO_3 was given off from the surface upon desorption. This suggested a process of the type



where $[\text{W}\cdot\text{O}_3]$ represents the adsorbed compound. Further evidence for the theory that such adsorption involves valence bonds is found in the large heats of adsorption. Observed values are of the same magnitude as the heat of chemical reactions, 5 to 100 kcal/g mol.

Taylor† suggested the name *chemisorption* for describing this second type of combination of gas molecules with solid surfaces. Because of the high heat of adsorption, the energy possessed by chemisorbed molecules can be substantially different from that of the molecules alone. Hence the energy of activation for reactions involving chemisorbed molecules can be considerably less than that for reactions involving gas-phase molecules. It is on this basis that chemisorption offers an explanation for the catalytic effect of solid surfaces.

Two kinds of chemisorption are encountered: activated and, less frequently, nonactivated. *Activated chemisorption* means that the rate varies with temperature according to a finite activation energy in the Arrhenius equation. However, in some systems chemisorption occurs very rapidly, suggesting an activation energy near zero. This is termed *nonactivated chemisorption*.‡ It is often found that for a given gas and solid the initial chemisorption is nonactivated, while later stages of the process are slow and temperature dependent (activated adsorption).

An approximate, qualitative relation between temperature and quantity adsorbed (both physically and chemically) is shown in Fig. 7-2. Chemisorption is assumed to be activated in this case. When the critical temperature of the component is exceeded, physical adsorption approaches a very low equilibrium value. As the temperature is raised, the amount of activated adsorption becomes important because the rate is high enough for significant quantities to be adsorbed in a reasonable amount of time. In an ordinary adsorption experiment involving the usual time periods the adsorption curve actually rises with increasing temperatures from the minimum value, as shown by the solid line in Fig. 7-2. When the temperature is increased still further, the decreasing equilibrium value for activated adsorption retards the process, and the quantity adsorbed passes through a maximum. At these high temperatures even the rate of the relatively slow activated process may be sufficient to give results closely approaching equilibrium. Hence the solid curve representing the amount adsorbed approaches the dashed equilibrium value for the activated adsorption process.

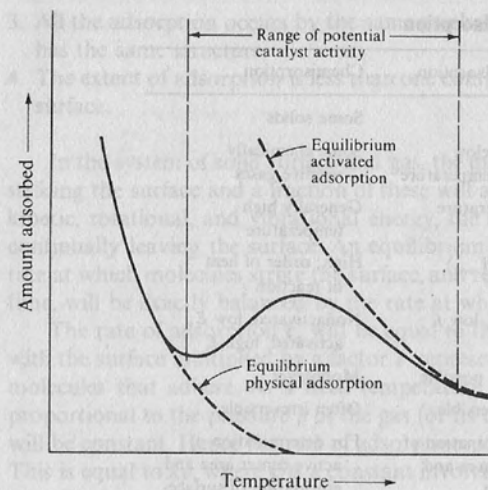


Figure 7-2 Effect of temperature on physical and activated adsorption.

It has been explained that the effectiveness of solid catalysts for reactions of stable molecules is dependent upon chemisorption. Granting this, the temperature range over which a given catalyst is effective must coincide with the range where chemisorption of one or more of the reactants is appreciable. This is indicated on Fig. 7-2 by the dashed vertical lines. There is a relationship between the extent of chemisorption of a gas on a solid and the effectiveness of the solid as a catalyst. For example, many metallic and metal-oxide surfaces adsorb oxygen easily, and these materials are also found to be good catalysts for oxidation reactions. When reactions proceed catalytically at low temperatures, Fig. 7-2 does not apply. In these cases catalysis is due to nonactivated chemisorption. Thus ethylene is hydrogenated on nickel at -78°C , at which temperature there would surely exist physical adsorption of the ethylene.

An important feature of chemisorption is that its magnitude will not exceed that corresponding to a monomolecular layer. This limitation is due to the fact that the valence forces holding the molecules on the surface diminish rapidly with distance. These forces become too small to form the adsorption compound when the distance from the surface is much greater than usual bond distances.

The differences between chemisorption and physical adsorption are summarized in Table 7-1.

In order to develop rate equations for catalytic reactions quantitative expressions for adsorption are necessary. Langmuir† proposed simple formulations for rates of adsorption and desorption of gases (applicable also to liquids) on solid surfaces. While his concern was with chemisorption, the concepts have been used for deriving a valuable relationship between the volume of a gas physically adsorbed and the surface area of the solid (see Sec. 8-1). Applied to chemisorption,

† H. S. Taylor, *J. Am. Chem. Soc.*, **53**, 578 (1931).

‡ As an illustration, chemisorption of hydrogen on nickel at low temperatures is nonactivated; see G. Padberg and J. M. Smith, *J. Catalysis*, **12**, 172 (1968).

† I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).

Table 7-1 Physical vs. chemical adsorption

Parameter	Physical adsorption	Chemisorption
Adsorbent	All solids	Some solids
Adsorbate	All gases below critical temperature	Some chemically reactive gases
Temperature range	Low temperature	Generally high temperature
Heat of adsorption	Low ($\approx \Delta H_{\text{cond}}$)	High; order of heat of reaction
Rate, activation energy	Very rapid, low E	Nonactivated, low E ; activated, high E
Coverage	Multilayer possible	Monolayer
Reversibility	Highly reversible	Often irreversible
Importance	For determination of surface area and pore size	For determination of active-center area and elucidation of surface-reaction kinetics

the Langmuir treatment provides a systematic basis for developing rates of heterogeneous catalytic reactions and we use this approach in Chap. 9. Adsorption and desorption steps in the overall conversion of reactants to products (see list at beginning of this chapter) may be very fast and hence, occur at near equilibrium. Therefore, we need also to know the equilibrium relation between the concentration of adsorbent in the gas (or liquid) and the amount adsorbed. Such equilibrium isotherms, Langmuir and other forms, are considered in Sec. 7-6 and then rates of adsorption are discussed in Sec. 7-7.

7-6 Adsorption Isotherms

A. The Langmuir treatment of adsorption The derivations may be carried out by using as a measure of the amount adsorbed either the fraction of the surface covered or the concentration of the gas adsorbed on the surface. Both procedures will be illustrated, although the second is the more useful for kinetic developments (Chap. 9). The important assumptions are as follows:[†]

1. All the surface of the catalyst has the same activity for adsorption; i.e., it is energetically uniform. The concept of nonuniform surface with active centers can be employed if it is assumed that all the active centers have the same activity for adsorption and that the rest of the surface has none, or that an average activity can be used.
2. There is no interaction between adsorbed molecules. This means that the amount adsorbed has no effect on the rate of adsorption per site.

[†] It is also supposed that each site can accommodate only one adsorbed particle.

3. All the adsorption occurs by the same mechanism, and each adsorbed complex has the same structure.
4. The extent of adsorption is less than one complete monomolecular layer on the surface.

In the system of solid surface and gas, the molecules of gas will be continually striking the surface and a fraction of these will adhere. However, because of their kinetic, rotational, and vibrational energy, the more energetic molecules will be continually leaving the surface. An equilibrium will be established such that the rate at which molecules strike the surface, and remain for an appreciable length of time, will be exactly balanced by the rate at which molecules leave the surface.

The rate of adsorption r_a will be equal to the rate of collision r_c of molecules with the surface multiplied by a factor F representing the fraction of the colliding molecules that adhere. At a fixed temperature the number of collisions will be proportional to the pressure p of the gas (or its concentration), and the fraction F will be constant. Hence the rate of adsorption per unit of bare surface will be $r_c F$. This is equal to kp , where k is a constant involving the fraction F and the proportionality between r_c and p .

Since the adsorption is limited to complete coverage by a monomolecular layer, the surface may be divided into two parts: the fraction θ covered by the adsorbed molecules and the fraction $1 - \theta$, which is bare. Since only those molecules striking the uncovered part of the surface can be adsorbed, the rate of adsorption per unit of total surface will be proportional to $1 - \theta$; that is,

$$r_a = kp(1 - \theta) \quad (7-10)$$

The rate of desorption will be proportional to the fraction of covered surface

$$r_d = k'\theta \quad (7-11)$$

The amount adsorbed at equilibrium is obtained by equating r_a and r_d and solving for θ . The result, called the *Langmuir isotherm*, is

$$\theta = \frac{kp}{k' + kp} = \frac{Kp}{1 + Kp} = \frac{v}{v_m} \quad (7-12)$$

where $K = k/k'$ is the adsorption equilibrium constant, expressed in units of (pressure)⁻¹. The fraction θ is proportional to volume of gas adsorbed, v , since the adsorption is less than a monomolecular layer. Hence Eq. (7-12) may be regarded as a relationship between the pressure of the gas and the volume adsorbed. This is indicated by writing $\theta = v/v_m$, where v_m is the volume adsorbed when all the active sites are covered, i.e., when there is a complete monomolecular layer.

The concentration form of Eq. (7-12) can be obtained by introducing the concept of an adsorbed concentration $\bar{C}$, expressed in moles per gram of catalyst. If $\bar{C}_m$ represents the concentration corresponding to a complete monomolecular layer on the catalyst, then the rate of adsorption, mol/(s)(g catalyst) is, by analogy with Eq. (7-10),

$$r_a = k_c C_g (\bar{C}_m - \bar{C}) \quad (7-13)$$

where k_c is the rate constant for the catalyst and C_g is the concentration of adsorbable component in the gas. Similarly, Eq. (7-11) becomes

$$r_d = k'_c \bar{C} \quad (7-14)$$

At equilibrium the rates given by Eqs. (7-13) and (7-14) are equal, so that

$$\bar{C} = \frac{K_c \bar{C}_m C_g}{1 + K_c \bar{C}_m} \quad (7-15)$$

where now the equilibrium constant K_c is equal to k_c/k'_c and is expressed in units of $(\text{concn})^{-1}$, centimeters per gram mole. Since $\bar{C}/\bar{C}_m = \theta$, Eq. (7-15) may also be written

$$\theta = \frac{K_c C_g}{1 + K_c C_g} \quad (7-16)$$

which is a form analogous to Eq. (7-12), since C_g is proportional to p .

Equation (7-15) predicts that adsorption data should have the general form shown in Fig. 7-3. Note that at low values of C_g (or low surface coverages θ) the expression becomes a straight line with a slope equal to $K_c \bar{C}_m$. The data points in Fig. 7-3 are for the physical adsorption of *n*-butane on silica gel ($S_g = 832 \text{ m}^2/\text{g}$) at 50°C .† The solid line represents Eq. (7-15), where

$$\bar{C}_m = 0.85 \times 10^{-3} \text{ g mol/g silica gel}$$

and the equilibrium constant of adsorption is

$$K_c = 4.1 \times 10^5 \text{ cm}^3/\text{g mol}$$

For this instance of physical adsorption Eq. (7-15) fits the data rather well. The measurements were made on mixtures of *n*-butane in helium (at 1 atm total pressure) to vary C_g . The percentage of *n*-butane in the gas corresponding to the concentration C_g is shown as a second abscissa in the figure. Also, θ is shown as a second ordinate. This was calculated from $\theta = \bar{C}/\bar{C}_m$. It is interesting to note that the isotherm is linear up to about $\theta = 0.10$, or a gas concentration of 1% *n*-butane in He. This means that the denominator in Eq. (7-15) is nearly unity at low concentrations. The region of linearity depends upon the adsorbent-adsorbate system. For example, for the same silica gel at 50°C , the linear isotherm was applicable up to 2% for adsorption of propane and to more than 4% for ethane.

Chemisorption data often do not fit Eq. (7-15). However, the basic concepts on which the Langmuir isotherm is based (the ideas of a dynamic equilibrium between rates of adsorption and desorption and a finite adsorption time) are sound and of great value in developing the kinetics of fluid-solid catalytic reactions. Equations (7-13) to (7-15) form the basis for the rate equations presented in Chap. 9.

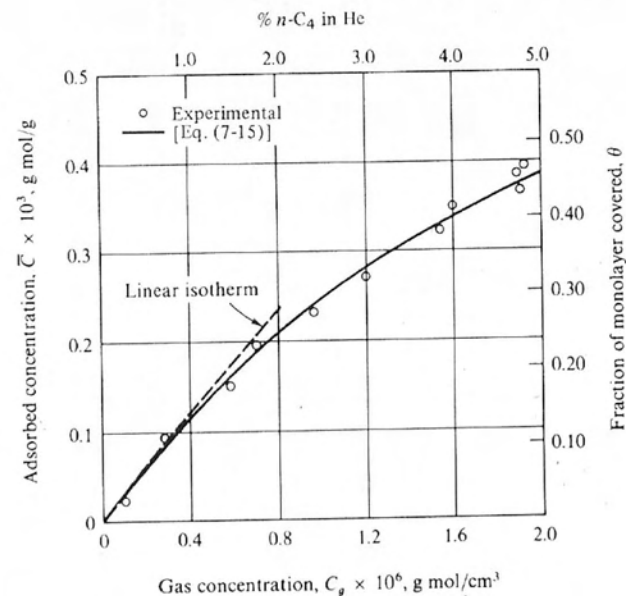


Figure 7-3 Adsorption-equilibrium data for *n*-butane on silica gel (surface area $832 \text{ m}^2/\text{g}$) at 50°C .

B. Other isotherms and heats of adsorption Experimentally, the five types of isotherms shown in Fig. 7-4 have been observed.† Note that the linear form of Eq. (7-15)

$$\bar{C} = (K_c \bar{C}_m) C_g \quad (7-17)$$

would fit all of the five isotherms at very low fluid concentrations. However, only curve I agrees with the Langmuir expression over the whole concentration range. The deviations from the Langmuir form are probably largely due to the postulates of sites of equal activity and no interaction between occupied and bare sites. It might be surmised that these assumptions correspond to a constant heat of adsorption. Indeed, it is possible‡ to derive the Langmuir isotherm by assuming that ΔH_a is independent of θ . The heat of adsorption can be evaluated from adsorption-equilibrium data. First the Clausius-Clapeyron equation is applied to the two-phase system of gas and adsorbed component on the surface:

$$\left(\frac{dp}{dT} \right)_\theta = \frac{\Delta H_a}{T(V - V_a)}$$

† D. O. Hayward and B. M. W. Trapnell, "Chemisorption," 2d ed., Butterworth & Co. (Publishers), London, 1964.

‡ K. J. Laidler, *J. Phys. Chem.*, **53**, 712 (1949).

† P. Schneider and J. M. Smith, *AIChE J.*, **14**, 769 (1968).

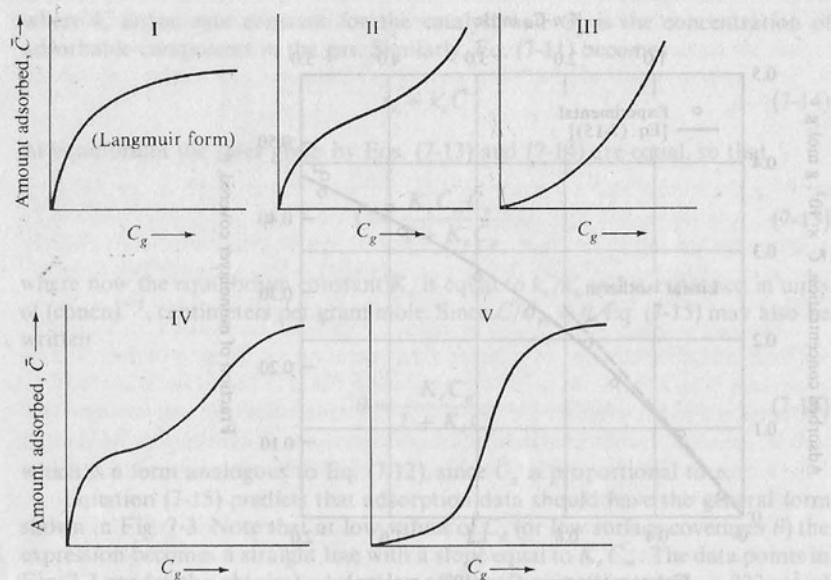


Figure 7-4 Types of adsorption isotherms.

where V and V_a are the volumes per mole of adsorbed component in the gas and on the surface, respectively. Neglecting the latter and assuming the ideal-gas law for V gives

$$\left[\frac{d(\ln p)}{dT} \right]_{\theta} = \frac{\Delta H_a}{R_g T^2} \quad (7-18)$$

For the Clausius-Clapeyron equation to be valid the process must be univariant. This means that Eq. (7-18) can be applied only for constant concentration of adsorbate on the surface, that is, constant θ . If adsorption-equilibrium data are available at different temperatures, the slopes of p -vs.- T curves at constant θ may be used with Eq. (7-18) to calculate ΔH_a . Figure 7-5, taken from Beeck,[†] shows such isosteric heats of adsorption as a function of θ for hydrogen on several metal films. These results are typical in showing a decrease in ΔH_a with increasing surface coverage. For physical adsorption, ΔH_a values are lower. For example, for nitrogen and n -butane the heats of adsorption (at essentially zero surface coverage) on a molecular sieve catalyst (synthetic zeolite, 5A type) were 4.3 and 10.3 kcal/g mol.[‡]

Two other well-known isotherms may be classified in terms of the $\Delta H_a - \theta$ dependency. The *Temkin isotherm* may be derived from the Langmuir isotherm

[†] O. Beeck, *Disc. Faraday Soc.*, **8**, 118 (1950).

[‡] N. Hashimoto and J. M. Smith, *Ind. Eng. Chem. Fundam.*, **12**, 353 (1973).

by assuming that the heat of adsorption drops linearly with increasing θ .[†] The result is

$$\theta = k_1 \ln k_2 p \quad (7-19)$$

where k_1 and k_2 are constants at a given temperature. Figure 7-5 shows that a linear decrease in ΔH_a with θ fits some data for H_2 on metal films. Similar agreement has been obtained for N_2 chemisorbed on a promoted iron catalyst.[‡]

The *Freundlich isotherm* can be derived[§] by assuming a logarithmic decrease in ΔH_a with θ ; that is,

$$\Delta H_a = -\Delta H_0 \ln \theta \quad (7-20)$$

The isotherm itself has the form

$$\theta = c(p)^{1/n} \quad (7-21)$$

where n has a value greater than unity. Owing to its flexibility, the Freundlich isotherm usually fits experimental data over a reasonable range of concentrations. For example, hydrogen gas on tungsten[¶] and sulfur dioxide (in aqueous solution) on activated carbon.^{††} In the latter system, the concentration form of Eq. (7-21) at 23°C was found to be

$$C_{SO_2} = 0.180[(C_L)_{SO_2}]^{1/1.88} \quad (7-22)$$

[†] A. Frumkin and A. Slygin, *Acta Physico chim.*, **3**, 791 (1935); S. Brunauer, K. S. Love, and R. G. Keenan, *J. Am. Chem. Soc.*, **64**, 751 (1942).

[‡] P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **56**, 35 (1934).

[§] G. Halsey and H. S. Taylor, *J. Chem. Phys.*, **15**, 624 (1947).

[¶] R. M. W. Trapnell, *Proc. Roy. Soc. (London)*, **A206**, 39 (1951).

^{††} Hiroshi Komiyama and J. M. Smith, *AIChE J.*, **21**, 664 (1975).

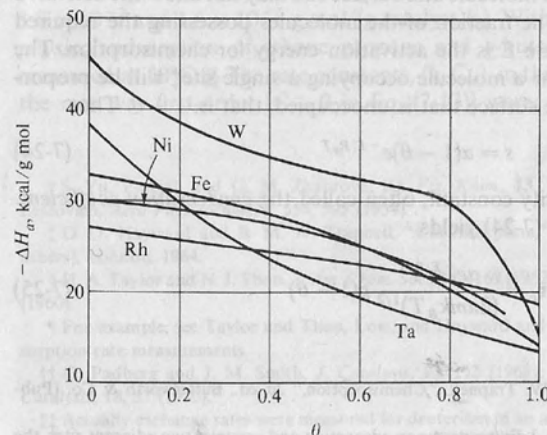


Figure 7-5 Heats of adsorption vs. surface coverage for hydrogen on metal films.

where

C_L = concentration of SO_2 in water, g mol/cm³

$\bar{C}$ = adsorbed concentration of SO_2 , g mol/(g of carbon)

In conclusion, note two points. First, the Freundlich isotherm can be reduced to either the Langmuir or the Temkin form by proper simplification. It may be considered a general empirical form encompassing the other more specific types. Second, a single isotherm of the Langmuir or Temkin type cannot be expected to fit data over the entire range of θ .

7-7 Rates of Adsorption

As already noted we are going to use the Langmuir formulation [Eqs. (7-10) and (7-11)] for adsorption rates in Chap. 9 to derive rate expressions for catalytic reactions. Also as noted, the Langmuir formulation is seldom substantiated over a wide range of adsorbent concentrations. Therefore, it is useful to examine what is known about adsorption rates and compare this information with the Langmuir postulates.

The rate at which molecules of a gas strike a surface, in molecules/(s)(cm² surface), is $p/(2\pi mk_B T)^{1/2}$. If s is the fraction of the collisions which result in chemisorption, that is, the *sticking probability*, the rate of adsorption is

$$r_a = \frac{sp}{(2\pi mk_B T)^{1/2}} \quad (7-23)$$

where p is the gas pressure and m is the mass of the molecule. As Hayward and Trapnell point out,[†] $s < 1$ for several reasons. Two are particularly important: only those molecules possessing the required activation energy can be chemisorbed, and molecules possessing the necessary energy may not be chemisorbed because the configuration of molecule and surface site may not allow the activated complex to be traversed. The fraction of the molecules possessing the required energy will be $e^{-E/R_g T}$, where E is the activation energy for chemisorption. The configuration probability for a molecule occupying a single site[‡] will be proportional to the fraction of the surface that is unoccupied, that is, $1 - \theta$. Thus

$$s = \alpha(1 - \theta)e^{-E/R_g T} \quad (7-24)$$

where α is the proportionality constant, often called the *condensation coefficient*. Combining Eqs. (7-23) and (7-24) yields

$$r_a = \frac{\alpha e^{-E/R_g T}}{(2\pi mk_B T)^{1/2}} p(1 - \theta) \quad (7-25)$$

[†] D. O. Hayward and B. M. W. Trapnell, "Chemisorption," 2d ed., Butterworth & Co. (Publishers), London, 1964.

[‡] If a molecule (for example, O_2) dissociates upon adsorption and occupies two adjacent sites, the configuration probability will be $(1 - \theta)^2$, at least for small values of θ .

This ideal expression for the rate of adsorption does not usually agree with experimental data. Observed rates decrease so rapidly with increasing coverage θ that they can be explained only if the activation energy increases with θ . Also, the condensation coefficient may vary with θ . These variations may be caused by surface heterogeneity; that is, the activity of the sites varies, so that different sites possess different values of α and E . The most active sites would have the lowest activation energy and would be occupied first. In addition, interaction forces between occupied and unoccupied sites can cause deviations. In any event, it is necessary to rewrite Eq. (7-25) showing α and E as functions of θ :

$$r_a = \frac{\alpha(\theta)e^{-E(\theta)/R_g T}}{(2\pi mk_B T)^{1/2}} p(1 - \theta) \quad (7-26)$$

Comparing the Langmuir equation, Eq. (7-10), with Eq. (7-26) shows that k in Eq. (7-10) is a function of surface coverage. However, the reason α and E are functions of θ is that the first two postulates of the Langmuir treatment (Sec. 7-6, A) are not satisfied experimentally; that is, in real surfaces all sites do not have the same activity, and interactions do exist.

For many cases of chemisorption the variation in rate with surface coverage can be accounted for entirely in the exponential term of Eq. (7-26), because $\alpha(\theta)$ and $1 - \theta$ are so much weaker functions. This leads to the result (for constant temperature)

$$r_a = \beta p e^{-\gamma \theta} \quad (7-27)$$

commonly known as the *Elovich equation*.[†] Equation (7-27) can be obtained[‡] from Eq. (7-26) by assuming that α is constant and that E is a linear function of θ . It can also be derived by supposing that E is constant but that the number of sites is a function of the coverage and of the temperature.[§]

Experimental data for rates of *chemisorption* are meager.[¶] By pulse-response measurements^{††} adsorption rates of hydrogen^{‡‡} on commercial nickel and cobalt (on Kieselguhr) catalysts at temperatures of about 297 K were found to be 1.0×10^{-2} and 1.6×10^{-3} g mol/(g catalyst)(s). With a similar technique rates of *physical* adsorption of ethane propane and *n*-butane on silica gel have been measured at 50°C.^{§§} The rate constants, $(k_c \bar{C}_m)$, in the concentration range where the rate was first-order [$C \rightarrow 0$ in Eq. (7-13)] were: 167 cm³/(s)(g silica gel) for

[†] S. Yu. Elovich and G. M. Zhabrova, *Zh. Fiz. Khim.*, **13**, 1761 (1939); S. Roginsky and Ya. Zeldovich, *Acta Physicochim.*, **1**, 554, 595 (1934).

[‡] D. O. Hayward and B. M. W. Trapnell, "Chemisorption," 2d ed., Butterworth & Co. (Publishers), London, 1964.

[§] H. A. Taylor and N. J. Thon, *J. Am. Chem. Soc.*, **74**, 4169 (1952); M. J. D. Low, *Chem. Rev.*, **60**, 267 (1960).

[¶] For example, see Taylor and Thon, Low, and Hayward and Trapnell for summaries of chemisorption rate measurements.

^{††} G. Padberg and J. M. Smith, *J. Catalysis*, **12**, 172 (1968); J. C. Adrian and J. M. Smith, *J. Catalysis*, **18**, 57 (1970).

^{‡‡} Actually exchange rates were measured for deuterium in an atmosphere of hydrogen so that the catalyst surface was saturated with hydrogen.

^{§§} P. Schneider and J. M. Smith, *AIChE J.*, **14**, 762 (1968).

C_2H_6 , 255 for C_3H_8 , and about 1500 for $n-C_4H_{10}$. The increase in rate constant with increasing molecular weight is expected since heavier hydrocarbons are more easily and rapidly adsorbed. Transition-state theory (presented in Sec. 2-6 for homogeneous gas-phase reactions) has been applied to the prediction of the condensation coefficient. Lack of precise knowledge about the structure of the activated complex on the solid surface hinders these calculations and the evaluation of numerical values for the rates.

Before we leave the topic of rates it is important to mention the desorption step. Since desorption is normally an endothermic process,[†] it will have a significant activation energy (see Fig. 2-1). Thus desorption will be an activated process even when adsorption is not. If ΔH_a is the heat of adsorption on the site, the activation energies are related by

$$E_d = E_a - \Delta H_a \quad (7-28)$$

Rates of chemisorption of hydrogen on a given nickel catalyst were found to be nonactivated ($E_a \sim 0$) but the desorption activation energy was 13.8 kcal/g mol, about the same magnitude as the heat of adsorption (-13.5 kcal/g mol).[‡] For hydrogen adsorption on a cobalt/Kieselguhr catalyst, the chemisorption also was nonactivated with $E_d = 5.2$ kcal/(g mol).[§]

PROBLEMS

7-1 In a sketch similar to Fig. 7-1 show schematically the concentration profiles for a first-order reversible catalytic reaction. Consider three cases: (a) reaction control, (b) diffusion control, and (c) an intermediate case.

7-2 Explain why mass-transfer resistance reduces the global rate more at higher temperatures than at lower temperatures. Assume no heat-transfer resistance.

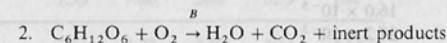
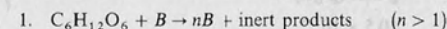
7-3 For endothermic reactions, do mass- and heat-transfer resistances have complementary or counterbalancing effects on the global rate?

7-4 A gaseous reaction with a solid catalyst is carried out in a flow reactor. The system is isothermal, but it is believed that mass-transfer resistances are important. (a) Would increasing the turbulence in the gas region next to the catalyst surface increase or decrease the global rate? (b) If the system is not isothermal and the reaction is exothermic, would increasing the turbulence increase or decrease the global rate?

7-5 There is a growing need to obtain a better understanding of reactions involving bacteria. For example, most all-sewage disposal plants for purifying municipal wastewater are based upon bacterial oxidation (activated sludge process). A special characteristic of bacterial oxidation is that the bacteria not only catalyze the oxidation of carbonaceous compounds, but also the carbon compound provides "fuel" for growth of the bacteria. As an illustration, consider a stirred-tank reactor operating continuously at steady state and at constant temperature. The feed consists of an aqueous solution of glucose

(the carbonaceous material) which does not contain bacteria. The concentration of glucose in the feed is S_0 , and its volumetric flow rate into the reactor is Q . The mixture in the tank contains bacteria in a concentration B , and the product stream has a flow rate equal to Q . This product stream contains bacteria and glucose in concentrations B and S (both in mg/liter).

The two major reactions may be written (in a highly simplified manner) as follows:



The Michaelis-Menten[†] rate equations have been found to fit some types of bacterial oxidations. For conditions where the oxygen supply is adequate, the equations can be written for reactions 1 and 2 as

$$R_x = \frac{\mu_m S}{K + S} (B)$$

$$R_s = \left(\frac{1}{Y} \right) \frac{\mu_m S}{K + S} (B)$$

where μ_m and K are rate constants.

R_x = rate of formation of bacteria (cell mass), mg/(liter)(h)

R_s = rate of disappearance of glucose (substrate), mg/(liter)(h)

R_x represents the growth of bacteria according to reaction 1, while

R_s is the total rate of disappearance of glucose by both reactions.

Notice that reaction 2 is catalyzed by the bacteria. The symbol Y represents the yield, or ratio of rates of production of bacteria to the total rate of consumption of glucose. Other symbols are defined in part D.

A. For steady-state operation, derive a relationship between Q/V (called the dilution rate, D) and the concentration S of glucose in the product stream.

B. If S is very large with respect to K , corresponding to a very large excess of glucose in the feed stream, how is the relationship of part A simplified?

C. The result obtained in part B gives a specific relation between the dilution rate D and the rate constant, or constants. If the actual dilution rate is increased above the value given by this specific relation, for example by increasing the flow rate, what would happen to the bacteria in the reactor?

D. For a particular case, the following data apply:

$$Q = 1.0 \text{ liters/h}$$

$$V = \text{volume of stirred tank reactor} = 4 \text{ liters}$$

$$\mu_m = \text{rate constant} = 0.5 \text{ (h)}^{-1}$$

$$K_s = \text{constant in the rate equation} = 15 \text{ mg/liter}$$

$$S_0 = 80 \text{ mg/liter} = \text{concn of glucose in feed}$$

$$Y = \text{yield (assume constant)} = 0.5$$

Calculate the following (for steady-state operation):

1. the concentration of glucose in the product stream leaving the reactor
2. the concentration of bacteria in the product stream leaving the reactor

E. For the conditions of part D, what would be the maximum volumetric flow rate that could be used and yet avoid the problem referred to in part C?

[†] A few chemisorption processes appear to be endothermic, so that desorption in these instances would be exothermic. See J. M. Thomas and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis," p. 30, Academic Press Inc., New York, 1967.

[‡] G. Padberg and J. M. Smith, loc. cit.

[§] J. C. Adrian and J. M. Smith, loc. cit.

[†] L. Michaelis and M. L. Menten, *Biochem. Z.*, **49**, 333 (1913).

7-6 The following data were obtained at 70°C for the equilibrium adsorption of *n*-hexane on silica gel particles.

Partial pressure of C_6H_{14} in gas, atm	C_6H_{14} adsorbed, g mol/(g gel)
0.0020	10.5×10^{-5}
0.0040	16.0×10^{-5}
0.0080	27.2×10^{-5}
0.0113	34.6×10^{-5}
0.0156	43.0×10^{-5}
0.0206	47.3×10^{-5}

(a) Determine how well the Langmuir isotherm fits these data. Establish the values of the constants C_m and K_c by least-mean-squares analysis of the linearized form of Eq. (7-15):

$$\frac{C_g}{C} = \frac{1}{K_c C_m} + \frac{C_g}{C_m}$$

Note that a straight line should be obtained if C_g/C is plotted against C_g .

(b) Up to what gas concentration is the isotherm linear?

7-7 Repeat Prob. 7-6 for the following data for the equilibrium adsorption of C_6H_6 on the same silica gel at 110°C.

Partial pressure of C_6H_6 in gas, atm	C_6H_6 adsorbed, g mol/(g gel)
5.0×10^{-4}	2.6×10^{-5}
1.0×10^{-3}	4.5×10^{-5}
2.0×10^{-3}	7.8×10^{-5}
5.0×10^{-3}	17.0×10^{-5}
1.0×10^{-2}	27.0×10^{-5}
2.0×10^{-2}	40.0×10^{-5}

7-8 Can the Freundlich isotherm, Eq. (7-21), represent the physical-adsorption data for *n*-hexane given in Prob. 7-6? What are the appropriate values of c and n ?

7-9 Will the Temkin isotherm fit the *n*-hexane data shown in Prob. 7-6?

7-10 Ward† studied the chemisorption of hydrogen on copper powder and found the heat of adsorption to be independent of surface coverage. Equilibrium data from experiments at 25°C are as follows:

Hydrogen pressure, mm Hg	1.05	2.95	5.40	10.65	21.5	45.1	95.8	204.8
Volume adsorbed, cm ³ at 0°C and 1 atm	0.239	0.564	0.659	0.800	0.995	1.160	1.300	1.471

What kind of isotherm fits these results?

† A. F. H. Ward, *Proc. Roy. Soc. (London)*, **A133**, 506 (1931).

7-11 Brunauer et al.† concluded that the Temkin isotherm, Eq. (7-19), explained equilibrium chemisorption data for N_2 on an ammonia-synthesis catalyst (promoted iron powder). Data taken at 396°C are as follows:

Nitrogen pressure, kPa	3.33	7.06	20.0	52.9	102
Volume adsorbed, $\times 10^6$, m ³ at 273 K and 101.3 kPa	2.83	3.22	3.69	4.14	4.55

Can Brunauer's conclusion be reached by plotting the data according to linearized forms of the Langmuir, Temkin, and Freundlich isotherms? Explain your answer.

7-12 Plot the isosteric heat of adsorption vs. the amount adsorbed from the following data of Shen and Smith‡ for benzene on silica gel.

Partial pressure of benzene, atm	Moles adsorbed/g gel $\times 10^5$			
	70°C	90°C	110°C	130°C
5.0×10^{-4}	14.0	6.7	2.6	1.13
1.0×10^{-3}	22.0	11.2	4.5	2.0
2.0×10^{-3}	34.0	18.0	7.8	3.9
5.0×10^{-3}	68.0	33.0	17.0	8.6
1.0×10^{-2}	88.0	51.0	27.0	16.0
2.0×10^{-2}		78.0	42.0	26.0

7-13 Show that the Elovich equation for the rate of chemisorption can be integrated with respect to surface coverage (at constant pressure of the adsorbing gas) to give

$$\theta = a \ln(1 + bt)$$

where t is the time from the start of the adsorption process and a and b are constants. If the activation energy for chemisorption is a linear function of surface coverage, according to $E = E_0 + c\theta$, derive the integrated form of the Elovich equation.

† S. Brunauer, K. S. Love, and R. G. Keenan, *J. Am. Chem. Soc.*, **64**, 751 (1942).

‡ John Shen and J. M. Smith, *Ind. Eng. Chem. Fundam.*, **7**, 100 (1968).

7-14 Ward† studied the chemisorption of hydrogen on small copper particles at 25°C. His data for one run are:

Hydrogen pressure cm of Hg	Vol. of hydrogen adsorbed, cm ³ at 25°C and 1 atm
0.019	0.042
0.066	0.138
0.097	0.163
0.101	0.161
0.110	0.171
0.190	0.221
0.265	0.256
0.405	0.321
0.555	0.371
0.750	0.411
0.815	0.421
1.19	0.471
1.75	0.550

Do these data fit the Langmuir isotherm or the Freundlich isotherm?

SOLID CATALYSTS

In Chap. 7 general concepts of catalysis were discussed. Now we want to examine solid catalysts specifically. Such catalysts depend for their activity in part, at least, on the extent of surface area. It is difficult to obtain outer surface areas of more than 1 m²/g by subdividing nonporous solids into small particles (see Example 8-1). To be effective, most catalytic solids must have surface areas in the 5 to 1000 m²/g range. Hence, solid catalysts are normally porous. For such materials the geometrical properties of the pores can affect the global reaction rate. The objective of the first part of this chapter is to present methods of measuring the pertinent physical (geometric) properties. Following this is a discussion of theories of the catalytic behavior of solids along with a listing of typical catalysts for various types of reactions. Finally, practical aspects, such as catalyst preparation, poisons, and parameters, are treated.

The importance of surface area for catalytic activity is immediately evident by considering nickel. This metal is an active catalyst under certain conditions for oxidation and hydrogenation because it absorbs oxygen and hydrogen. The surface area of a solid has a pronounced effect on the amount of gas adsorbed and on its activity as a catalyst. For example, if a sample of fresh Raney nickel, which is highly porous and has a large surface, is held in the hand, the heat due to adsorption of oxygen can be felt immediately. No evidence of heat is apparent when a single piece of nonporous nickel of the same mass is held. This relationship between surface area and extent of adsorption has led to the development of highly porous materials with areas as high as 1500 m²/g. Sometimes the catalytic material itself can be prepared in a form with large surface area. When this is not possible, materials which can be so prepared may be used as a *carrier* or *support* on which the catalytic substance is dispersed. Silica gel and alumina are widely used as supports.

† A. F. H. Ward, *Proc. Roy. Soc. (London)*, **A133**, 506 (1931).