

is 2.37 g/cm^3 . The surface area of the first sample is $467 \text{ m}^2/\text{g}$ and that of the second is $372 \text{ m}^2/\text{g}$. Which sample has the larger mean pore radius?

8-10 Mercury porosimeter data are tabulated below for a 0.400-g sample of UO_2 pellet. At the beginning of the measurements ($p = 1.77 \text{ lb/in.}^2$ abs) the mercury displaced by the sample was 0.125 cm^3 . At this low pressure no pores were penetrated. Data obtained with a pycnometer gave a true density of the solid phase of $\rho_s = 7.57 \text{ g/cm}^3$.

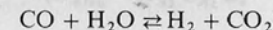
Calculate the total porosity of the pellet and the porosity due to pores of larger than 250 \AA radius. Also plot the pore-volume distribution for the pores larger than 250 \AA radius, using the coordinates of Fig. 8-5.

Pressure, lb/in. ²	196	296	396	500	600	700	800	900		
Mercury penetration, cm ³	0.002	0.004	0.008	0.014	0.020	0.026	0.032	0.038		
			1000	1200	1400	1800	2400	2800	3400	5000
			0.044	0.052	0.057	0.062	0.066	0.066	0.067	0.068

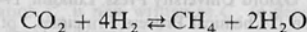
RATE EQUATIONS FOR
FLUID-SOLID CATALYTIC REACTIONS

An intermediate procedure, the Langmuir-Hinshelwood formulation, will be followed, for the most part, in this book. The fundamental concepts on which the Langmuir rate and isotherm expressions are based appear sound, although, as we have seen, some of the assumptions are not realistic. The first-order rate equations, which are the most commonly used, are based on the assumption that the rate of reaction is proportional to the concentration of the reactant. This assumption will be used in the sections that follow. However, this assumption, agreement of the resultant rate equation does not mean that the reaction

The nonuniformity of catalyst surfaces and lack of accurate knowledge of the structure of chemisorbed species and their concentrations have been emphasized in Chaps. 7 and 8. In view of these uncertainties it is debatable how much detail should be postulated in formulating equations for rates of reaction. The most simple approach, wholly empirical, would be to use the power-law form of the rate equation, employed for homogeneous reactions, that is, Eq. (2-9). The values of the exponents on the concentrations, the apparent orders of the reaction, are determined by fitting the equation to the data. This approach ignores all the problems associated with adsorption and catalytic surfaces and provides no information about how the reaction occurs. Frequently, but not always, such an equation can correlate experimental rates just as accurately, and with fewer adjustable parameters, than more elaborate methods. When the objective is reactor design, where calculations of engineering accuracy are going to be made with the rate equation, the simplicity of the power-law form is advantageous. Hence, it has been used widely in industrial reactor design. As examples, such equations have been used to represent kinetics data for the water-gas shift reaction using iron oxide catalysts†



and for the methanation reaction



on a $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst.‡

† H. Bohlbro, "An Investigation on the Kinetics of the Conversion of Carbon Monoxide with Water Vapor Over Iron Oxide Catalysts", 2d ed. Gjellerup, Copenhagen, 1969.

‡ P. J. Lunde and F. L. Kester, *J. Catal.*, **30**, 423 (1973).

At the other extreme, we might separate the adsorption and surface reaction steps. Then use rate equations like Eq. (7-25) for the adsorption rate, and postulate forms of the adsorbed species and reaction mechanism to formulate the rate of the surface reaction. The necessity for the occurrence of chemisorption as an explanation of catalytic activity provides strong support for separating the adsorption-desorption and surface processes. However, the θ function in Eq. (7-25) and many aspects of the surface reaction are unknown. Therefore, the resultant equations are not only extremely complex but dependent upon so many assumptions that the results may be no more meaningful than the power-law approach.

An intermediate procedure, the Langmuir-Hinshelwood formulation[†] will be followed, for the most part, in this book.[‡] The fundamental concepts on which the Langmuir rate and isotherm expressions are based appear sound, although, as we have seen, some of the assumptions are incorrect. The first-order relationship between gas concentration C_g , adsorbed concentration \bar{C} , and total concentration on the surface \bar{C}_m in the Langmuir approach [Eqs. (7-13) to (7-15)] permit great simplification in formulating rate equations. Therefore these equations for adsorption and desorption along with simple first- and second-order expressions for the surface reaction, will be used in the sections that follow. Because of these assumptions, agreement of the resultant rate equation does not mean that the reaction mechanism resulting from the assumptions has been proven. Establishing a mechanism, as distinguished from developing a rate equation, requires information about the adsorbed species and how they react. Sufficient information of this type cannot normally be obtained from measurements of reaction rates alone. The advantages of the Langmuir-Hinshelwood method are: (1) the resultant rate equation may be extrapolated more accurately to concentrations beyond the range of experimental measurements used, and (2) the method does take into account adsorption and surface reactions (which must occur) in a consistent manner.

9-1 Rates of Adsorption, Desorption, Surface Reaction

In this section equations are presented for the rates of adsorption, surface reaction, and desorption. In Sec. 9-2 these equations will be combined to give expressions for the rate in terms of fluid concentrations; that is, concentrations on the surface (denoted by \bar{C}) will be eliminated.

[†] This approach to kinetics of fluid-solid catalytic reactions was proposed by C. N. Hinshelwood ("Kinetics of Chemical Change," Oxford University Press, London, 1940) and developed in detail by O. A. Hougen and K. M. Watson ("Chemical Process Principles," pt. 3, "Kinetics and Catalysis," John Wiley & Sons, Inc., New York, 1947).

[‡] For critical evaluations of various methods of formulating rate equations see the reviews: Sol W. Weller, "Chemical Reaction Engineering Reviews," *Adv. Chem. Ser.*, 148, p. 26, Amer. Chem. Soc., Washington D.C. (1945) and M. Boudart, *AIChE J.*, 18, 465 (1972). Also the engineering viewpoint toward catalysis and rate equations is well presented by O. A. Hougen, *Ind. Eng. Chem.* 53 (7), 509 (1961).

Adsorption The net rate of adsorption of a component A is given by the difference between Eqs. (7-13) and (7-14), written as[†]

$$r_a = k_a C_A (\bar{C}_m - \bar{C}) - k'_a \bar{C}_A = k_a \left[C_A (\bar{C}_m - \bar{C}) - \frac{1}{K_A} \bar{C}_A \right]$$

where $\bar{C}_m - \bar{C}$ represents the concentration of vacant sites, \bar{C}_v . If only A were adsorbed, then $\bar{C}_m - \bar{C}$ would equal $\bar{C}_m - \bar{C}_A$. However, other components of the reaction may be adsorbed, so that it is necessary to write $\bar{C}_m - \bar{C} = \bar{C}_v$, where \bar{C}_v is the concentration of vacant sites per unit mass of catalyst. Then r_a is given by

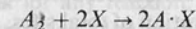
$$r_a = k_a \left(C_A \bar{C}_v - \frac{1}{K_A} \bar{C}_A \right) \quad (9-1)$$

In this equation C_A is the concentration of A in the gas phase at the catalyst surface. If the intrinsic adsorption rate (k_a) is large with respect to other steps in the overall conversion process, the concentration of A on the catalyst surface will be in equilibrium with the concentration of A in the gas phase. The net rate of adsorption, from Eq. (9-1), approaches zero, and the equilibrium concentration of A is given by the expression

$$(\bar{C}_A)_{eq} = K_A C_A \bar{C}_v \quad (9-2)$$

where K_A designates the adsorption equilibrium constant for A .

Note that this result would reduce to the Langmuir isotherm, Eq. (7-15); if only A were adsorbed. Equations (9-1) and (9-2) are applicable when A occupies one site. Often in chemisorption a diatomic molecule, such as oxygen, will dissociate upon adsorption with each atom occupying one site. Formally, dissociative adsorption may be written



For this case the net rate of adsorption is

$$r_a = k_a \left(C_{A_2} \bar{C}_v^2 - \frac{1}{K_{A_2}} \bar{C}_A^2 \right) \quad (9-3)$$

At equilibrium the concentration of atomically adsorbed A is[‡]

$$(\bar{C}_A)_{eq} = K_{A_2}^{1/2} C_{A_2}^{1/2} \bar{C}_v \quad (9-4)$$

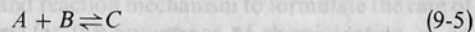
[†] The gas phase concentration C_g is now written as C_A to denote component A . Also, the rate constant k_s is written as k_a to denote adsorption.

[‡] If A_2 is the only adsorbable gas, then $\bar{C}_v = \bar{C}_m - \bar{C}_A$, and Eq. (9-4) becomes

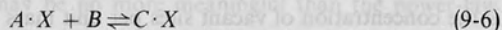
$$(\bar{C}_A)_{eq} = \frac{K_{A_2}^{1/2} C_{A_2}^{1/2} \bar{C}_m}{1 + K_{A_2}^{1/2} C_{A_2}^{1/2}} \quad \text{or} \quad \bar{\theta}_A = \frac{K_{A_2}^{1/2} C_{A_2}^{1/2}}{1 + K_{A_2}^{1/2} C_{A_2}^{1/2}}$$

in comparison with Eqs. (7-15) and (7-16) for molecularly adsorbed A_2 .

Surface reaction The mechanism assumed for the surface process will depend on the nature of the reaction. Suppose that the overall reaction is of the type



An immediate question concerning the surface process is whether the reaction is between an adsorbed molecule of A and a gaseous molecule of B at the surface or between adsorbed molecules of both A and B on adjacent active centers. In the former case the process might be represented by the expression



If the concentration of adsorbed product C on the surface is \bar{C}_C , in moles per unit mass of catalyst (analogous to \bar{C}_A), the net rate of this step would be

$$r_s = k_s \bar{C}_A \bar{C}_B - k'_s \bar{C}_C = k_s \left(\bar{C}_A \bar{C}_B - \frac{1}{K_s} \bar{C}_C \right) \quad (9-7)$$

In this equation we suppose that the rate of the forward reaction is first order in A on the solid surface and first order in B in the gas phase. Similarly, the rate of the reverse process is first order in C on the surface.

If the mechanism is a reaction between adsorbed A and adsorbed B , the process may be represented by the expression



Here only those A molecules will react which are adsorbed on sites immediately adjacent to adsorbed B molecules. Hence the rate of the forward reaction should be proportional to the concentration of the pairs of adjacent sites occupied by A and B . The concentration of these pairs will be equal to \bar{C}_A multiplied by the fraction of the adjacent sites occupied by B molecules. This fraction is proportional to the fraction of the total surface occupied by B molecules, i.e., to θ_B .† If \bar{C}_m is defined as the molal concentration of total sites, then $\theta_B = \bar{C}_B / \bar{C}_m$. The rate of the forward reaction, according to Eq. (9-8), will be

$$r = k_s \bar{C}_A \frac{\bar{C}_B}{\bar{C}_m}$$

The reverse rate is proportional to the pairs of centers formed by adsorbed product C molecules and adjacent vacant centers,

$$r' = k'_s \bar{C}_C \frac{\bar{C}_v}{\bar{C}_m}$$

Combining these two expressions gives the net surface rate by the mechanism of Eq. (9-8),

$$r_s = \frac{1}{\bar{C}_m} (k_s \bar{C}_A \bar{C}_B - k'_s \bar{C}_C \bar{C}_v) = \frac{k_s}{\bar{C}_m} \left(\bar{C}_A \bar{C}_B - \frac{1}{K_s} \bar{C}_C \bar{C}_v \right) \quad (9-9)$$

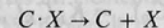
† This is correct only if the fraction of the surface occupied by A molecules is small. It would be more accurate to postulate that the fraction of the adjacent centers occupied by B is equal to $\theta_B / (1 - \theta_A)$. For small values of θ_A the two results are nearly the same.

If the surface step is intrinsically fast with respect to the others, the process would occur at equilibrium, and Eq. (9-7) or Eq. (9-9) could be used to relate the concentrations of the reactants and products on the catalyst surface. For example, if the chosen mechanism is Eq. (9-8), the concentration of product C is given by Eq. (9-9) with $r_s = 0$; that is,

$$K_s = \left(\frac{\bar{C}_v \bar{C}_C}{\bar{C}_A \bar{C}_B} \right)_{\text{eq}} \quad (9-10)$$

where K_s is the equilibrium constant for the surface reaction.

Desorption The mechanism for the desorption of the product C may be represented by the expression



The rate of desorption will be analogous to Eq. (9-1) for the adsorption of A ,

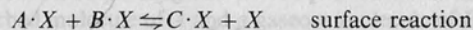
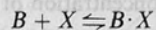
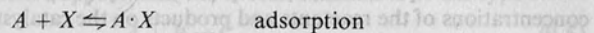
$$r_d = k'_d \bar{C}_C - k_d C_c \bar{C}_v = -k_d \left(C_c \bar{C}_v - \frac{1}{K_C} \bar{C}_C \right) \quad (9-11)$$

9-2 Rate Equations in terms of Fluid-Phase Concentrations at the Catalyst Surface

At steady state the rates of adsorption r_a , surface reaction r_s , and desorption r_d are equal. To express the rate solely in terms of fluid concentrations, the adsorbed concentrations \bar{C}_A , \bar{C}_B , \bar{C}_C , and \bar{C}_v must be eliminated from Eqs. (9-2) to (9-11). In principle, this can be done for any reaction, but the resultant rate equation involves all the rate constants k_i and the equilibrium constants K_i . Normally neither type of constant can be evaluated independently.† Both must be determined from measurements of the rate of conversion from fluid reactants to fluid products. However, there are far too many constants, even for simple reactions, to obtain meaningful values from such overall rate data. The problem can be simplified by supposing that one step in the overall reaction controls the rate. Then the other two steps occur at near-equilibrium conditions. This greatly simplifies the rate expression and reduces the number of rate and equilibrium constants that must be determined from experiment. To illustrate the procedure

† It might be supposed that rate and equilibrium constants for adsorption or desorption could be established from pure-component adsorption data on the components involved. However, such results rarely agree with the values of the constants determined from rate data for the reaction. Interaction effects between components, other inadequacies of the Langmuir theory, and the assumption of a single controlling step, explain the deviation. An exception to this conclusion is provided by Kabel and Johanson [*AIChE J.* 8, 621 (1962)] in their study of the vapor-phase dehydration of ethanol to diethyl ether over an acid catalyst (the acid form of Dowex 50, a sulfonated styrene-divinylbenzene copolymer). Evaluation of the adsorption equilibrium constants from fitting rate data and from independent, adsorption-equilibrium measurements gave nearly the same values.

equations for the rate will be developed, for various controlling steps, for the reaction system



Surface reaction controlling The concentrations \bar{C}_A , \bar{C}_B , and \bar{C}_C will be those corresponding to equilibrium for the adsorption and desorption steps. Equation (9-2) gives the equilibrium value for \bar{C}_A . Similar results for \bar{C}_B and \bar{C}_C are

$$(\bar{C}_B)_{\text{eq}} = K_B C_B \bar{C}_v \quad (9-12)$$

$$(\bar{C}_C)_{\text{eq}} = K_C C_C \bar{C}_v \quad (9-13)$$

Substituting these results in Eq. (9-9) for the surface rate gives

$$r = \frac{k_s}{\bar{C}_m} \left(K_A K_B C_A C_B \bar{C}_v^2 - \frac{K_C}{K_s} C_C \bar{C}_v^2 \right) \quad (9-14)$$

The concentration of vacant sites can be expressed in terms of the total concentration of sites \bar{C}_m ,

$$\bar{C}_m = \bar{C}_v + \bar{C}_A + \bar{C}_B + \bar{C}_C \quad (9-15)$$

Since \bar{C}_A (or \bar{C}_B and \bar{C}_C) corresponds to the equilibrium value for adsorption, Eqs. (9-2), (9-12), and (9-13) can be combined with Eq. (9-15) to yield

$$\bar{C}_v = \frac{\bar{C}_m}{1 + K_A C_A + K_B C_B + K_C C_C} \quad (9-16)$$

Now Eqs. (9-14) and (9-16) can be combined to give a relatively simple expression for the rate in terms of fluid-phase concentrations,

$$r = k_s \bar{C}_m \frac{K_A K_B C_A C_B - (K_C/K_s) C_C}{(1 + K_A C_A + K_B C_B + K_C C_C)^2} \quad (9-17)$$

This result can be further reduced by using the relationship between the several equilibrium constants K_A , K_B , K_C , and K_s . If the equilibrium constant for the overall reaction is denoted by K , then

$$K = \left(\frac{C_C}{C_A C_B} \right)_{\text{eq}} \quad (9-18)$$

This is the conventional K for a homogeneous reaction computed from thermodynamic data, as outlined in Chap. 1. It may be related to the adsorption and surface-reaction equilibrium constants by the equilibrium equations for each of these processes, Eqs. (9-2), (9-12), and (9-13). Thus

$$K = \frac{\bar{C}_C / K_C \bar{C}_v}{(\bar{C}_A / K_A \bar{C}_v)(\bar{C}_B / K_B \bar{C}_v)} = \frac{K_A K_B}{K_C} \left(\frac{\bar{C}_v \bar{C}_C}{\bar{C}_A \bar{C}_B} \right)_{\text{eq}} \quad (9-19)$$

According to Eq. (9-10), the last group of surface concentrations is K_s , and so

$$K = \frac{K_A K_B}{K_C} K_s \quad (9-20)$$

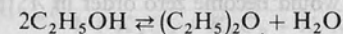
Substituting this relationship in Eq. (9-17) gives the final expression for the rate in terms of fluid-phase concentrations,

$$r = k_s \bar{C}_m K_A K_B \frac{C_A C_B - (1/K) C_C}{(1 + K_A C_A + K_B C_B + K_C C_C)^2} \quad (9-21)$$

It is well at this point to review the chief premises involved in Eq. (9-21):

1. It is supposed that the surface reaction controls the rate of the three steps.
2. The equation applies to the simple reaction $A + B \rightarrow C$. Furthermore, it is assumed that the surface step is an elementary reaction between an adsorbed molecule of A and an adsorbed molecule of B .
3. The adsorption rates are given by the Langmuir-Hinshelwood theories referred to earlier.

An application of Eq. (9-21) is the study of ethanol dehydration in the vapor phase using a sulfonated styrene-divinylbenzene polymer as a catalyst.† The reaction is



Experimental rate data agreed well with the Langmuir-Hinshelwood concept based upon a rate-controlling, reversible, surface reaction between two adsorbed molecules of ethanol. For this reaction Eq. (9-21) takes the form:

$$r = k_s \bar{C}_m K_A^2 \frac{C_A^2 - (1/K) C_W C_E}{(1 + K_A C_A + K_W C_W + K_E C_E)^2}$$

where subscripts A , W , and E refer to ethanol, water, and ether.

Consider a reaction for which the adsorption is weak for all components. The denominator of Eq. (9-21) approaches unity, and the rate expression reduces to the homogeneous form

$$r = k_s \bar{C}_m K_A K_B \left(C_A C_B - \frac{1}{K} C_C \right)$$

or

$$r = k \left(C_A C_B - \frac{1}{K} C_C \right) \quad (9-22)$$

The decomposition of formic acid on several catalytic surfaces follows such behavior.‡ Here there is only one reactant, so that the rate becomes first order in concentration of formic acid.

† R. L. Kabel and L. N. Johanson, *AIChE J.* **8**, 621 (1962).

‡ C. N. Hinshelwood and B. Topley, *J. Chem. Soc.*, **123**, 1014 (1923).

If the product of a reaction is strongly adsorbed and the reactant adsorption is weak, the term $K_C C_C$ is much larger than all others in the denominator. If the reaction is also irreversible, Eq. (9-21) becomes

$$r = k_s \bar{C}_m K_A K_B \frac{C_A C_B}{(K_C C_C)^2}$$

Suppose there was only one reactant; that is, the reaction was of the form $A \rightarrow C$. The denominator term would be raised to a power of unity instead of being squared, so that

$$r = k_s \bar{C}_m K_A \frac{C_A}{K_C C_C} \quad (9-23)$$

This result shows the retarding effect that a strongly adsorbed product can have on the rate. The decomposition of ammonia on a platinum wire has been found in one instance to follow this form of rate equation; i.e., hydrogen is strongly adsorbed and ammonia is only weakly adsorbed,[†] so that

$$r = k \frac{C_{\text{NH}_3}}{C_{\text{H}_2}}$$

Again consider a reaction of the form $A \rightarrow C$, but suppose that C is only weakly adsorbed, while A is very strongly adsorbed. Then the rate expression, in analogy with Eq. (9-23), would become zero order in A ; that is

$$r = k_s \bar{C}_m K_A \frac{C_A}{K_A C_A} = k \quad (9-24)$$

These special cases for the surface reaction controlling the rate all follow from the form of the Langmuir isotherm. Weak adsorption corresponds to small values of θ or \bar{C}_A , and Eq. (7-16) shows that \bar{C}_A is first order in C_A , as predicted by Eq. (9-22). When the adsorption is very strong, the critical parameter is the concentration of vacant sites remaining for adsorption of reactant. Equation (9-16) shows that this is inversely proportional to C_C , in agreement with Eq. (9-23).

Adsorption or Desorption Controlling Still retaining the simple reaction $A + B \rightleftharpoons C$, let us now suppose that the adsorption of A is the slow step. Then the adsorption of B , the surface reaction, and the desorption of C will occur at equilibrium. The rate can be formulated from the adsorption equation (9-1). The adsorbed concentration \bar{C}_A in this expression is obtained from the equilibrium equations for the surface rate [Eq. (9-10)], adsorption of B [Eq. (9-12)], and desorption of C [Eq. (9-13)]. Thus

$$\bar{C}_A = \frac{\bar{C}_v \bar{C}_C}{K_s \bar{C}_B} = \frac{\bar{C}_v (K_C C_C \bar{C}_v)}{K_s (K_B C_B \bar{C}_v)} = \frac{\bar{C}_v K_C C_C}{K_s K_B C_B}$$

[†] C. N. Hinshelwood and R. E. Burk, *J. Chem. Soc.*, **127**, 1105 (1925). Although there are two products in the decomposition, the nitrogen is only slightly adsorbed and does not appear in the rate equation.

From the relationship of the several equilibrium constants, Eq. (9-20), the expression for \bar{C}_A may be simplified to

$$\bar{C}_A = \frac{K_A \bar{C}_v C_C}{K_C C_B} \quad (9-25)$$

Substituting this value of \bar{C}_A in the rate-controlling equation (9-1) gives

$$r = k_a \bar{C}_v \left(C_A - \frac{1}{K} \frac{C_C}{C_B} \right) \quad (9-26)$$

The expression for \bar{C}_v can be formulated from Eq. (9-15), the equilibrium values of \bar{C}_B and \bar{C}_C from Eqs. (9-12) and (9-13), and \bar{C}_A from Eq. (9-25). With this expression for \bar{C}_v substituted in Eq. (9-26), the final rate equation for adsorption of A controlling the process is

$$r = \frac{k_a \bar{C}_m [C_A - (1/K)(C_C/C_B)]}{1 + K_B C_B + (K_A/K)(C_C/C_B) + K_C C_C} \quad (9-27)$$

If, instead of adsorption, the rate of desorption of product C controls the whole reaction, the expression for r should be formulated from Eq. (9-11). The adsorption and surface steps will occur at equilibrium conditions. Substituting the equilibrium values of \bar{C}_C and \bar{C}_v in Eq. (9-11) leads to the result

$$r = k_d \bar{C}_m K \frac{C_A C_B - (1/K) C_C}{1 + K_A C_A + K_B C_B + K_C K_A C_B} \quad (9-28)$$

9-3 Qualitative Analysis of Rate Equations

The procedure for developing rate expressions in terms of fluid properties according to the Langmuir concepts has been illustrated for a single reaction. Yang and Hougen[†] have considered various kinds of reactions and mechanisms and examined the results when adsorption, desorption, or surface reaction controls the rate. By dividing the final equation into a kinetic coefficient [for example, $k_d \bar{C}_m K$ in Eq. (9-28)], a driving force [$C_A C_B - (1/K) C_C$], and an adsorption term ($1 + K_A C_A + K_B C_B + K_C K_A C_B$), they were able to prepare tables from which the rate equation for a specific situation could be quickly assembled.[‡]

Equations such as (9-21), (9-27), and (9-28) will have value if they can be used to predict the rate over a wide range of conditions and hence be suitable for designing reactors. To be useful as working expressions the various constants (kinetics and equilibrium) must be given numerical values.[§] It has not proved possible, except in isolated instances, to obtain reliable K values from separate

[†] K. H. Yang and O. A. Hougen, *Chem. Eng. Progr.*, **46**, 146 (1950).

[‡] See also J. M. Thomas and W. J. Thomas, in "Introduction to the Principles of Heterogeneous Catalysis," pp. 458-459, Academic Press Inc., New York, 1967, for rate equations assembled in tabular form for various controlling mechanisms for the two reactions $A \rightleftharpoons B$ and $A + B \rightleftharpoons C$.

[§] Equations (9-21), (9-27), and (9-28) were developed for constant-temperature conditions. Hence the various specific rates k and equilibrium constants K are termed constants. They are, in theory, constant with respect to pressure (or concentration) and conversion but change with temperature.

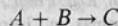
adsorption measurements. Hence all the constants must be determined from experimental kinetic data. This means, for example, that $k_d \bar{C}_m$, K_A , K_B , and K_C in Eq. (9-28) would be obtained from rate measurements. Since four-constant equations offer considerable flexibility, it is frequently possible to fit experimental data with several equations, each based on a different mechanism and assumption regarding the step which is controlling. The advantage of this method of formulating rate reactions is the systematic way in which the pertinent parameters are introduced. It is a mechanized procedure which permits little flexibility and provides little insight into the actual mechanism of heterogeneous catalytic reactions. Progress in mechanism studies for specific reactions has been summarized by Thomas and Thomas.[†] Interesting comparisons of concepts and correlations for homogeneous and heterogeneous catalytic reactions are presented by Boudart.[‡]

The quantitative interpretation of kinetic data in terms of this type of rate equation is illustrated in Sec. 9-4. Before we proceed to the evaluation of constants in rate equations, let us consider some of the implications of the rate expressions from a qualitative standpoint.

The adsorption terms in the denominator are all different. For surface rate controlling, adsorption equilibrium groups ($K_i C_i$) are included for each component, and the entire term is squared because reaction is between adsorbed A and adsorbed B . For adsorption of A controlling, no group for the adsorption of A is present, and the entire term is to the first power. For desorption controlling, no group for product C is in the adsorption term. These differences result in separate relationships between the pressure (for a gaseous reaction) and the rate. Hence the treatment of data as a function of pressure provides a useful method for distinguishing between equations. Temperature is not so useful a variable as pressure because all the constants are strong functions of temperature, and many of the same ones are part of each equation. The primary value of temperature is to determine the energies of activation for the adsorption and surface processes. Measurements at different conversion levels, obtained by varying the flow rate in a continuous reactor, can be used to evaluate various equations. However, as the conversion changes, the various concentrations (or partial pressures for a gaseous reaction) do not change independently, but in a specific way determined by the reaction stoichiometry. As with homogeneous reactions, initial rate data can be helpful. The reactants and their concentrations are known accurately, and the reverse reaction (and product concentrations) can be ignored. In a continuous-flow tubular reactor, initial rates would be evaluated from runs at low conversions (e.g., in a differential reactor) for various feed concentrations.

Quantitative treatment of conversion-vs.-rate data is illustrated in Examples 9-2 and 9-3. The importance of total pressure as a variable to evaluate forms of rate equations is shown in the following example.

Example 9-1 A solid-catalyzed gaseous reaction has the form



[†] See also J. M. Thomas and W. J. Thomas, in "Introduction to the Principles of Heterogeneous Catalysis," pp. 458-459, Academic Press Inc., New York, 1967, for rate equations assembled in tabular form for various controlling mechanisms for the two reactions $A \rightleftharpoons B$ and $A + B \rightleftharpoons C$.

[‡] Michel Boudart, "Kinetics of Chemical Processes," chaps. 8 and 9, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1968.

Sketch curves of the *initial* rate (rate at zero conversion) vs. the total pressure for the following cases:

- The mechanism is the reaction between adsorbed A and adsorbed B molecules on the catalyst. The controlling step is the surface reaction.
- The mechanism is the same as (a), but adsorption of A is controlling.
- The mechanism is the same as (b), but desorption of C is controlling. Assume that the overall equilibrium constant is large with respect to the adsorption equilibrium constants.
- The mechanism is a reaction between adsorbed A and B in the gas phase. The controlling step is the surface reaction.

In each instance suppose that the reactants are present in an equimolar mixture.

SOLUTION For a gaseous reaction the concentration C_i of any component i is proportional to its partial pressure; for an ideal-gas mixture $C_i = p_i/R_g T$. Hence at constant temperature partial pressures may be substituted for C_i in the rate equations, causing a change only in the value of the constants. At zero conversion the pressure of product C is zero, and for an equimolar mixture

$$p_A = p_B = \frac{1}{2} p_t$$

For the first three cases Eqs. (9-21), (9-27), and (9-28) are the appropriate rate equations.

(a) At initial conditions Eq. (9-21) simplifies to

$$r_0 = k_s \bar{C}_m K_A K_B \frac{\frac{1}{4} p_t^2 / (R_g T)^2}{[1 + \frac{1}{2}(K_A + K_B) p_t / R_g T]^2}$$

By combining constants we may write this expression as

$$r_0 = \frac{a p_t^2}{(1 + b p_t)^2} \quad (A)$$

where a and b are the resulting overall constants.

(b) In a similar manner Eq. (9-27) for the adsorption of A controlling may be reduced to the form

$$r_0 = k_a \bar{C}_m \frac{\frac{1}{2} p_t / R_g T}{1 + \frac{1}{2} K_B p_t / R_g T} = \frac{a' p_t}{1 + b' p_t} \quad (B)$$

(c) Equation (9-28), for the case where desorption of C is controlling, may be written

$$r_0 = k_d \bar{C}_m K \frac{\frac{1}{4} p_t^2 / (R_g T)^2}{1 + \frac{1}{2}(K_A + K_B) p_t / R_g T + \frac{1}{4} K_C K p_t^2 / (R_g T)^2}$$

If the equilibrium constant K is large with respect to K_A , K_B , and K_C , only the last term in the denominator is important, and the result is

$$r_0 = \frac{k_d \bar{C}_m}{K_C} = a'' \quad (C)$$

Equation (A) for surface reaction controlling shows that the initial rate will be proportional to the square of the pressure at low pressures and will approach a constant value at high pressures. This type of relation is shown in Fig. 9-1a. The case for adsorption controlling is indicated in Fig. 9-1b, and that for desorption controlling is shown in Fig. 9-1c. If the equilibrium constant were not very large for case (c), the initial rate equation would be as shown in Fig. 9-1a.

(d) For this case the rate equation can be obtained from Eq. (9-7). Combining this with Eqs. (9-2) and (9-13) for the equilibrium values for \bar{C}_A and \bar{C}_C gives

$$r = k_s \bar{C}_v \left(K_A C_A C_B - \frac{K_C}{K_s} C_C \right)$$

Since there is no adsorption of B in this instance, Eq. (9-16) for \bar{C}_v becomes

$$\bar{C}_v = \frac{\bar{C}_m}{1 + K_A C_A + K_C C_C}$$

The relationship of the equilibrium constants [Eq. (9-20)] is

$$K = \frac{K_A K_s}{K_C}$$

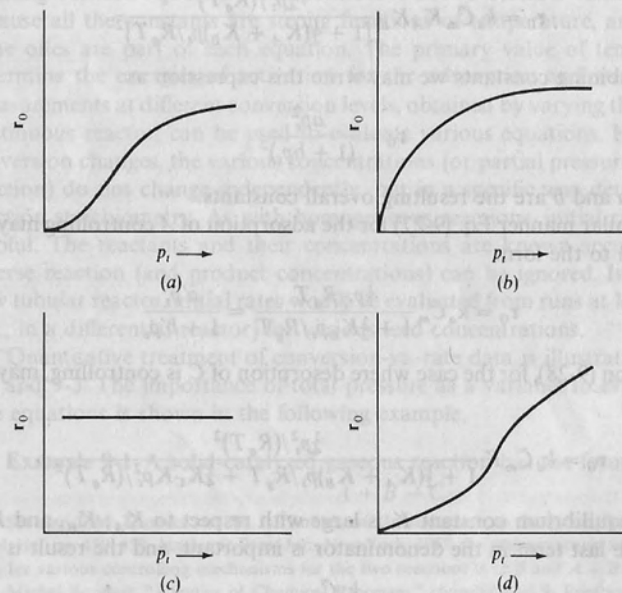


Figure 9-1 Initial rate vs. total pressure for reaction $A + B \rightarrow C$.

Substituting these two expressions into the rate equation yields

$$r = k_s K_A \bar{C}_m \frac{C_A C_B - (1/K) C_C}{1 + K_A C_A + K_C C_C} \quad (D)$$

Equation (D) is the appropriate expression for the surface rate controlling, with no adsorption of B . At initial conditions, and replacing concentrations with partial pressures, it becomes

$$r_0 = k_s K_A \bar{C}_m \frac{\frac{1}{4} p_t^2 / (R_g T)^2}{1 + \frac{1}{2} K_A p_t / R_g T} = \frac{a'' p_t^2}{1 + b''' p_t} \quad (E)$$

A schematic diagram of Eq. (E) shows the rate proportional to p_t at high pressures (Fig. 9-1d).

Suppose that experimental rate data for the reaction $A + B \rightarrow C$ were obtained over a wide range of total pressures, all at the same temperature. Comparison of a plot of the observed results with curves such as shown in Fig. 9-1 would be of value in establishing the most accurate rate equation. However, it is sometimes difficult to cover a wide enough range of pressures to observe all the changes in shape of the curves.

9-4 Quantitative Interpretation of Kinetics Data

To evaluate the rate and adsorption equilibrium constants in equations such as (9-21) rate data are needed as a function of concentrations in the fluid phase. Data are required at a series of temperatures in order to establish the temperature dependency of these constants. The proper concentrations to employ are those directly adjacent to the site. In the treatment that follows we shall suppose that these local concentrations have been established from the measurable concentrations in the bulk stream by the methods to be given in Chaps. 10 and 11. Our objective here is to find the most appropriate rate equation for the chemical steps at a catalyst site.

Statistical methods are required to obtain the best fit of the equation to the kinetic data. Minimizing the deviations between the observed rate and that predicted from the equation is straightforward as long as the constants are linearly related in the rate equation.† When nonlinearities exist the analysis is more complicated, but the general procedure is the same and consists of the following steps:

1. Assume various mechanisms and controlling steps for each mechanism. Develop a rate equation for each combination of mechanism and controlling step.
2. Determine the numerical values of the constants which give the best fit of each equation to the observed rate data.
3. Choose the equation which best fits the data and agrees with available independent information about the reaction.

† O. A. Hougen and K. M. Watson, "Chemical Process Principles," vol. III, "Kinetics and Catalysis," John Wiley & Sons, Inc., New York, 1948.

Nonlinearities in the relations for the constants complicate step 2. However, powerful iterative methods have been developed† for finding the best values of the constants, and numerous applications are available.‡ Kinetics data§ for the hydrogenation of ethylene and propylene with a Pt/Al₂O₃ catalyst is an example of a dual-site mechanism analyzed many times¶†† by the Langmuir-Hinshelwood approach.

The method of evaluating the various constants is partially illustrated for a linear case in Example 9-2.

Example 9-2 Olson and Schuler‡‡ determined reaction rates for the oxidation of sulfur dioxide, using a packed bed of platinum-on-alumina catalyst pellets. A differential reactor was employed, and the partial pressures as measured from bulk-stream compositions were corrected to fluid-phase values at the catalyst surface by the methods described in Chap. 10 (see Example 10-1). The total pressure was about 790 mmHg.

From previous studies§§ and the qualitative nature of the rate data, a suitable combination appeared to be a controlling surface reaction between adsorbed atomic oxygen and adsorbed sulfur dioxide. In order to determine all the constants in the rate equation for this mechanism, it is necessary to vary each partial pressure independently in the experimental work. Thus measuring the rate of reaction at different total pressures but at constant composition is not sufficient to determine all the adsorption equilibrium constants. Similarly, if the data are obtained at constant composition of initial reactants but varying conversions, the partial pressures of the individual components do not vary independently. However, in these cases it is possible to verify the validity of the rate equation even though values of the separate adsorption equilibrium constants cannot be ascertained. Olson and Schuler studied the effect of conversion alone. Some of their data at 480°C (interpolated for even intervals of reaction rates) are given in Table 9-1.

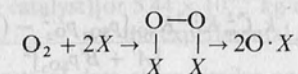
Derive the rate equation suggested from the assumed mechanism and test how well it fits the experimental rate data.

SOLUTION To develop an expression for the rate of reaction we must postulate the method of obtaining adsorbed atomic oxygen. If it is supposed that molecular oxygen is first adsorbed on a pair of vacant centers and that this

Table 9-1

r, g mol/(h)(g catalyst)	Partial pressure (atm) at catalyst surface		
	SO ₃	SO ₂	O ₂
0.02	0.0428	0.0255	0.186
0.04	0.0331	0.0352	0.190
0.06	0.0272	0.0409	0.193
0.08	0.0236	0.0443	0.195
0.10	0.0214	0.0464	0.196
0.12	0.0201	0.0476	0.197

product then dissociates into two adsorbed atoms, the process may be written



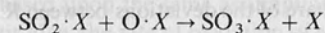
Since the surface reaction is controlling, the adsorption of oxygen must be at equilibrium. Then the concentration of adsorbed atomic oxygen is given by the equilibrium equation

$$K_{\text{O}} = \frac{C_{\text{O}}^2}{p_{\text{O}_2} \bar{C}_v^2}$$

where \bar{C}_{O} represents the concentration of adsorbed atomic oxygen and \bar{C}_v represents the concentration of vacant centers. Solving this expression for \bar{C}_{O} yields

$$\bar{C}_{\text{O}} = K_{\text{O}}^{1/2} p_{\text{O}_2}^{1/2} \bar{C}_v \quad (\text{A})$$

The surface-reaction step is represented by



$$r_s = k_s \left(C_{\text{SO}_2} \bar{C}_{\text{O}} - \frac{1}{K_s} \bar{C}_{\text{SO}_3} \bar{C}_v \right) \quad (\text{B})$$

The concentrations of SO₃ and SO₂ adsorbed on the catalyst are given by the conventional equilibrium expressions

$$\bar{C}_{\text{SO}_3} = K_{\text{SO}_3} p_{\text{SO}_3} \bar{C}_v \quad \bar{C}_{\text{SO}_2} = K_{\text{SO}_2} p_{\text{SO}_2} \bar{C}_v \quad (\text{C})$$

Substituting the values of \bar{C}_{O} , \bar{C}_{SO_2} , and \bar{C}_{SO_3} in Eq. (B) gives

$$r_s = k_s \left(K_{\text{O}}^{1/2} K_{\text{SO}_2} p_{\text{SO}_2} p_{\text{O}_2}^{1/2} - \frac{K_{\text{SO}_3}}{K_s} p_{\text{SO}_3} \right) \bar{C}_v^2 \quad (\text{D})$$

The total concentration of centers is the summation

$$\bar{C}_m = \bar{C}_v + K_{\text{O}}^{1/2} p_{\text{O}_2}^{1/2} \bar{C}_v + K_{\text{SO}_2} p_{\text{SO}_2} \bar{C}_v + K_{\text{SO}_3} p_{\text{SO}_3} \bar{C}_v + K_{\text{N}_2} p_{\text{N}_2} \bar{C}_v \quad (\text{E})$$

† G. E. P. Box and W. G. Hunter, *Technometrics*, 3, 311 (1962); W. G. Hunter and R. Mezaki, *AIChE J.*, 10, 315 (1964); J. R. Kittrell, W. G. Hunter, and R. Mezaki, *AIChE J.*, 10, 1014 (1964); J. R. Kittrell, W. G. Hunter, and C. C. Watson, *AIChE J.*, 11, 105 (1965) and 12, 5 (1966).

‡ See Sol W. Weller, "Chemical Reaction Engineering Reviews," *Adv. Chem. Ser.*, 148, p. 26, Amer. Chem. Soc. Washington D.C. (1975).

§ G. B. Rogers, M. M. Lih, and O. A. Hougen, *AIChE J.*, 12, 369 (1966).

¶ R. Mezaki, *J. Catal.*, 10, 238 (1966).

†† S. Kolboe, *J. Catal.*, 24, 40 (1972).

‡‡ R. W. Olson, R. W. Schuler, and J. M. Smith, *Chem. Eng. Progr.*, 46, 614 (1950).

§§ O. Uyehara and K. M. Watson, *Ind. Eng. Chem.*, 35, 541 (1943).

The last term is included to take into account the possibility that N_2 may be adsorbed on the catalyst. Eliminating C_v from Eq. (D) by introducing Eq. (E) and noting that $K_O^{1/2}K_{SO_2}K_S/K_{SO_3} = K$, we may write Eq. (D) as

$$r = \frac{k_s \bar{C}_m^2 K_O^{1/2} K_{SO_2} [p_{SO_2} p_{O_2}^{1/2} - (1/K) p_{SO_3}]}{[1 + K_{SO_2} p_{SO_2} + K_O^{1/2} p_{O_2}^{1/2} + K_{SO_3} p_{SO_3} + K_{N_2} p_{N_2}]^2} \quad (F)$$

Because the partial pressures of sulfur dioxide and sulfur trioxide are both small, the value of p_{N_2} will not vary significantly with conversion. Hence $K_{N_2} p_{N_2}$ may be regarded as a constant in Eq. (F). Since conversion was the only variable causing the composition to change, p_{O_2} and p_{SO_3} and p_{SO_2} are not independent, but are related to the initial, constant composition and the conversion. Hence p_{O_2} in the denominator of Eq. (F) can be expressed in terms of conversion or, more conveniently, in terms of p_{SO_3} . Thus Eq. (F) may be simplified to

$$r = \frac{k_s \bar{C}_m^2 K_O^{1/2} K_{SO_2} [p_{SO_2} p_{O_2}^{1/2} - (1/K) p_{SO_3}]}{[A' + B' p_{SO_3}]^2}$$

Combining the constants and rearranging leads to the linear form

$$R = A + B p_{SO_3} \quad (G)$$

where

$$R = \frac{p_{SO_2} p_{O_2}^{1/2} - (1/K) p_{SO_3}}{r} \quad (H)$$

Since conversion was the sole variable, individual adsorption equilibrium constants K_O , K_{SO_2} , K_{SO_3} , K_{N_2} cannot be determined. However, rate-vs.-composition data such as that in Table 9-1 can be used to evaluate the constants A and B in rate Equation (G). This is done by calculating a value of R for each of the n sets of data given in Table 9-1. Then, A and B can be determined by minimizing the square of the deviations between R and $A + B p_{SO_3}$. The equations for A and B are

$$B = \frac{\sum_i R_i p_{SO_3,i} - (\sum_i p_{SO_3,i} \sum_i R_i)/n}{\sum_i p_{SO_3,i}^2 - (\sum_i p_{SO_3,i})^2/n} \quad (I)$$

$$A = \frac{\sum_i R_i - B \sum_i p_{SO_3,i}}{n} \quad (J)$$

The summations include all n values of R and p_{SO_3} . In order to evaluate R it is necessary to know the overall equilibrium constant K . At 480°C K is estimated from the equation

$$\ln K = \frac{22,200}{R_g T} - 10.5$$

to be 73. Following this approach, and using the 6 ($n = 6$) sets of data in Table 9-1, it is found that

$$B = 12.9 \text{ (atm)}^{1/2} / [\text{g mol}/(\text{h})(\text{g catalyst})]$$

$$A = 0.176 \text{ (atm)}^{3/2} / [\text{g mol}/(\text{h})(\text{g catalyst})]$$

With these values the rate equation [from Eqs. (G) and (H)] is

$$r = \frac{p_{SO_2} p_{O_2}^{1/2} - (1/K) p_{SO_3}}{[0.176 + 12.9 p_{SO_3}]^2} \text{ g mol}/(\text{h})(\text{g catalyst}) \quad (K)$$

This expression may be used to calculate the rate at any conversion, or p_{SO_3} . For example, for the first set of data in Table 9-1

$$r = \frac{0.0255(0.186)^{1/2} - (1/73)(0.0428)}{[0.176 + 12.9(0.0428)]^2} = 0.0196 \text{ g mol}/(\text{h})(\text{g catalyst}) [\text{or } 5.44 \times 10^{-6} \text{ kg mol}/(\text{s})(\text{kg catalyst})]$$

vs. the experimental rate of 0.02 in Table 9-1

Results for the other sets of data show similar agreement, indicating that Eq. (K) represents the rate data well.

9-5 Redox Rate Equations

In some instances it is useful to formulate rate equations from known behavior of catalysts for a class of reactions. Oxidation on metal oxides is an example. It has long been demonstrated† that flowing the substance to be oxidized, without air or oxygen, over the catalyst produces some oxidized product and extracts oxygen from the metal oxide. The catalyst can be reactivated by exposure to oxygen or air. This two-step process, whereby the substance to be oxidized reduces the catalyst and then is reoxidized, is known as the redox mechanism. It leads to rate equations of the same general form as those based upon the Langmuir-Hinshelwood approach and, indeed, is based upon the same assumptions in formulating rates. According to the Langmuir idea, the rate of oxidation of a component is proportional to its concentration C in the fluid and to the concentration \bar{C}_O of the oxidized sites in the catalyst. Thus

$$r = k_1 C \bar{C}_O \quad (9-29)$$

Suppose that the rate r_o of reoxidation of the catalyst surface is directly proportional to the concentration of oxygen C_{O_2} in the fluid and to the concentration of unoxidized sites. The latter will be $\bar{C}_M - \bar{C}_O$, assuming that the extent of adsorption of other substances than oxygen is small.

$$r_o = k_2 C_{O_2} (\bar{C}_M - \bar{C}_O) \quad (9-30)$$

† A review of the literature on catalytic oxidations with extensive references is given by A. Cappelli in "Chemical Reaction Engineering Reviews," *Adv. Chem. Ser.* 148, p. 212, Amer. Chem. Soc., Washington, D.C. (1975).

For a stationary-state condition on the catalyst, and if one mole of oxygen is required for the oxidation, the two rates may be set equal to each other to give

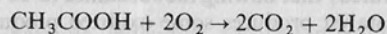
$$\bar{C}_O = \frac{(k_2 \bar{C}_M) C_{O_2}}{k_1 C + k_2 C_{O_2}} \quad (9-31)$$

Substituting this expression for \bar{C}_O in Eq. (9-29) gives the rate of oxidation:

$$r = \frac{(k_1 k_2 \bar{C}_M) C_{O_2} C}{k_1 C + k_2 C_{O_2}} = \frac{k C_{O_2} C}{k_1 C + k_2 C_{O_2}} \quad (9-32)$$

A more general form of Eq. (9-32), in which the rate of reoxidation is proportional to any power of the oxygen concentration† and any number of moles of oxygen needed for the oxidation, has been developed.‡ Equation (9-32) suggests that the rate is first order in the substance to be oxidized at low concentrations (where $k_1 C$ in the denominator would be much less than $k_2 C_{O_2}$) and zero order at high concentrations. Example 9-3 is an illustration of catalytic oxidation in the liquid phase.

Example 9-3 Reaction rates have been measured for the liquid-phase oxidation of dilute aqueous solutions of acetic acid in water, at 68 atm total pressure and at temperatures from 250°C to 280°C, in a differential, packed-bed catalytic reactor.§ Oxygen was predissolved in the solution of acetic acid in water so that only a liquid phase flowed over the bed of catalyst particles (no gas phase was present). The oxidation reaction is



The catalyst consisted of Mn, Co, and La oxides on a zinc aluminate carrier. Three catalyst particle sizes were studied. The equivalent spherical diameters were: $d_p = 0.038$ cm, $d_p = 0.054$ cm, and $d_p = 0.18$ cm.

The effect of oxygen concentration on the global rate was measured at 260°C, for $d_p = 0.054$ cm and for an average acetic acid concentration of $C_{HA} = 33.3 \times 10^{-7}$ g mol/cm³. The rates of oxidation [g mol/(s)(g catalyst)], expressed as the rate (r_{CO_2}) of production of carbon dioxide, are as follows:

Average oxygen concn. C_{O_2} , g mol/cm ³	(r_{CO_2}/C_{HA}) , cm ³ /(g)(s)
1.23×10^{-7}	2.70×10^{-2}
3.68×10^{-7}	4.29×10^{-2}
5.69×10^{-7}	5.19×10^{-2}
8.70×10^{-7}	6.30×10^{-2}

† For example, if the oxygen dissociates on adsorption r_0 would be proportional to $C_{O_2}^{1/2}$ (see footnote p. 361).

‡ P. Mars and D. W. van Krevelan, *Chem. Eng. Sci. Spec. Suppl.* 3, 41 (1949) were amongst the first to quantify the redox mechanism. They developed more general equations than (9-32).

§ Janez Levec and J. M. Smith, *AIChE J.*, 22, 159 (1976).

The effect of acetic acid concentration on the global rate was measured at three temperatures and for a constant, feed concentration of oxygen of 10.4×10^{-7} g mol/cm³. The data for particle size $d_p = 0.054$ cm are:

$1/C_{HA}$ cm ³ /g mol	$(C_{O_2}^{1/2}/r_{\text{CO}_2})$, (g)(s)/(mol) ^{1/2} (cm) ^{1.5}		
	260°C	270°C	280°C
1.21×10^5	3.48×10^3	2.47×10^3	1.90×10^3
3.10×10^5	4.70×10^3	3.30×10^3	2.55×10^3
6.30×10^5	6.00×10^3	4.05×10^3	3.00×10^3
13.0×10^5	10.2×10^3	5.75×10^3	4.40×10^3

The liquid-phase concentrations in the two preceding tables are for average values in the differential reactor.

Finally, global rates were measured for the three particle sizes over a temperature range at constant feed concentrations of acetic acid and oxygen of 33.3×10^{-7} g mol/cm³ and 10.4×10^{-7} g mol/cm³, respectively. The data are as follows:

$1000/T$ (K) ⁻¹	$r_{\text{CO}_2} \times 10^7$, g mol/(g)(s)		
	$d_p = 0.038$ cm	$d_p = 0.054$ cm	$d_p = 0.18$ cm
1.807	3.50	3.55	2.10
.....	3.45
1.842	2.50	2.60	1.70
1.876	2.00	1.40
1.912	1.42	1.13

Preliminary runs at constant temperature (280°C) and feed concentrations demonstrated that the liquid flow rate through the reactor did not affect the reaction rate, r_{CO_2} . The porosity of the catalyst particles was 0.55. For all the runs the reactor operated isothermally. Derive an equation for the intrinsic rate (i.e., the rate with no diffusion resistance) of the oxidation reaction. Obtain numerical values for the constants in the equation for each temperature.

SOLUTION The experimental rates are global values. Before we can develop an equation for the intrinsic rate at a catalyst site, the potential significance of external and internal (intraparticle) diffusion effects must be considered. The statement that the liquid flow rate did not influence the results tells us that external mass transfer is not affecting the reaction rate. This is because the liquid rate affects the mass transfer coefficient from fluid to particle and changes the concentration of reactants at the external surface of the catalyst particle (see Chap. 10). The data in the third table of the problem statement show that the rate is independent of particle size for $d_p = 0.054$ cm or less, but decreases for larger particles. This means that intraparticle diffusion does not affect the

rate for $d_p = 0.54$ cm. Particle size is a pertinent variable to use in analyzing intraparticle diffusion effects since the diffusion path length is determined by d_p (see Example 11-10). Accordingly, the global rates for $d_p = 0.054$ cm may be considered to be intrinsic rates corresponding to the bulk-fluid values of the concentrations.†

The next step is to propose various rate equations to see if they correctly represent the effects of oxygen and acetic acid concentrations, as given by the data in the first two tables. The reaction order with respect to oxygen is about one-half, as noted by plotting r_{CO_2} vs. $C_{O_2}^{1/2}$ using the values given in the first table (which are for a constant acetic acid concentration). The one-half order plot is shown in Fig. 9-2. At constant oxygen concentration, there is a linear relationship between $(C_{O_2})^{1/2}/r_{CO_2}$ and $1/C_{HA}$. This is evident by the straight line obtained when the data in the second table are plotted with these coordinates, as shown in Fig. 9-3. The equation for the straight lines in Fig. 9-3 is of the form

$$\frac{(C_{O_2})^{1/2}}{r_{CO_2}} = a \left(\frac{1}{C_{HA}} \right) + b \quad (A)$$

† Intraparticle transport effects are treated in detail in chap. 11.

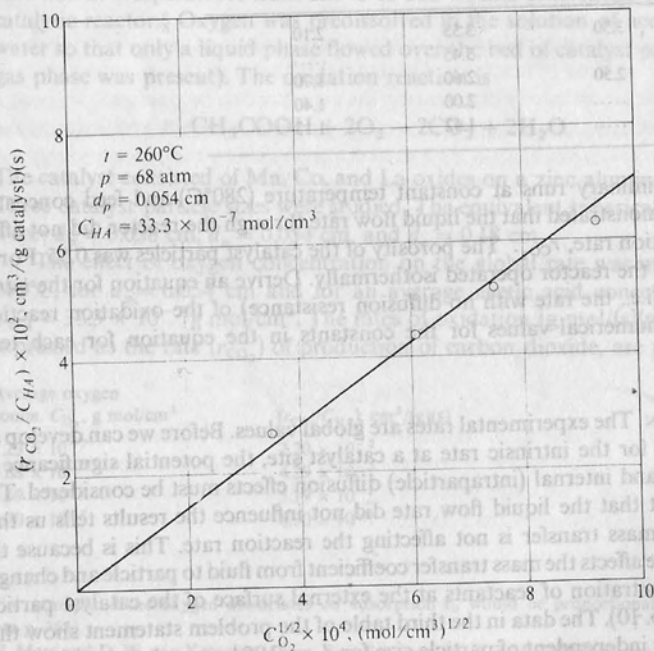


Figure 9-2 Effect of oxygen concentration on catalytic oxidation rate of aqueous acetic acid.

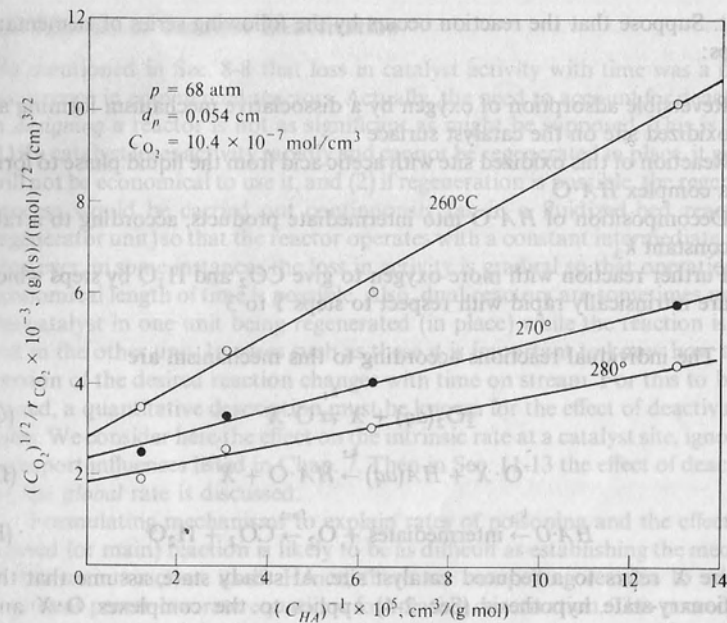


Figure 9-3 Effect of acetic acid concentration on catalytic oxidation rate of aqueous acetic acid.

which may be solved for the rate to give

$$r_{CO_2} = \frac{(1/a)C_{O_2}^{1/2}C_{HA}}{1 + (b/a)C_{HA}} = \frac{k_A C_{O_2}^{1/2} C_{HA}}{1 + k_B C_{HA}} \quad (B)$$

where k_A and k_B are functions of temperature. The values of k_A and k_B can be found from the slope ($a = 1/k_A$) and intercept ($b = ak_B$) of the lines in Fig. 9-3. The results for each temperature are:

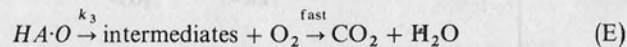
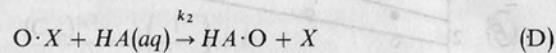
t °C	k_A cm ^{4.5} /(mol) ^{1/2} (g)(s)	k_B cm ³ /(g mol)
260	1.9×10^2	5.2×10^5
270	3.2×10^2	7.1×10^5
280	5.4×10^2	9.8×10^5

So far we have drawn no conclusions about the reaction mechanism and actually very little can be said from the rate data alone. What has been done is to find that Eq. (B) correctly correlates the experimental data. If we wish to speculate, we can choose a mechanism (probably several) which leads to Eq. (B). As an illustration of the redox mechanism for oxidation, let's do just

that. Suppose that the reaction occurs by the following series of elementary steps:

1. Reversible adsorption of oxygen by a dissociative mechanism forming an oxidized site on the catalyst surface
2. Reaction of this oxidized site with acetic acid from the liquid phase to form a complex $HA \cdot O$
3. Decomposition of $HA \cdot O$ into intermediate products, according to a rate constant k_3
4. Further reaction with more oxygen to give CO_2 and H_2O by steps which are intrinsically rapid with respect to steps 1 to 3

The individual reactions according to this mechanism are



where X refers to a reduced catalyst site. At steady state, assume that the stationary-state hypothesis (Sec. 2-4) applies to the complexes $O \cdot X$ and $HA \cdot O$. Then

$$\frac{d\bar{C}_{O \cdot X}}{dt} = 0 = k_1 C_{O_2}^{1/2} \bar{C}_X - k'_1 \bar{C}_{O \cdot X} - k_2 \bar{C}_{O \cdot X} C_{HA} \quad (F)$$

and

$$\frac{d\bar{C}_{HA \cdot O}}{dt} = 0 = k_2 \bar{C}_{O \cdot X} C_{HA} - k_3 \bar{C}_{HA \cdot O} \quad (G)$$

Equations (F) and (G) may be solved for $\bar{C}_{O \cdot X}$ and $\bar{C}_{HA \cdot O}$ to yield

$$\bar{C}_{O \cdot X} = \frac{k_1 C_{O_2} \bar{C}_X}{k'_1 + k_2 C_{HA}} \quad (H)$$

$$\bar{C}_{HA \cdot O} = \frac{k_1 k_2 C_{O_2}^{1/2} C_{HA} \bar{C}_X}{k_3 (k'_1 + k_2 C_{HA})} \quad (I)$$

Then the rate of CO_2 formation is given by reaction (E)

$$\begin{aligned} r_{CO_2} &= k_3 \bar{C}_{HA \cdot O} = \frac{(k_1 k_2 \bar{C}_X) C_{HA} C_{O_2}^{1/2}}{k'_1 + k_2 C_{HA}} \\ &= \frac{(k_1 k_2 \bar{C}_X / k'_1) C_{O_2}^{1/2} C_{HA}}{1 + (k_2 / k'_1) C_{HA}} \quad (J) \end{aligned}$$

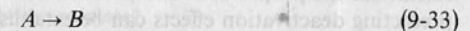
For the very low concentrations of oxygen and acetic acid in these dilute aqueous solutions, the fraction of the surface covered by the $X \cdot O$ complex could be low. Then, \bar{C}_X in Eq. (J) would be nearly constant and the result is a rate expression in agreement with the experimental data, Eq. (B).

9-6 Kinetics of Catalyst Deactivation

We mentioned in Sec. 8-8 that loss in catalyst activity with time was a frequent occurrence in commercial reactors. Actually, the need to account for deactivation in *designing* a reactor is not as significant as might be supposed. This is because (1) if a catalyst loses activity rapidly and cannot be regenerated in place, it probably will not be economical to use it, and (2) if regeneration is possible, the regeneration process would be carried out continuously (as in a fluidized-bed reactor and regenerator unit) so that the reactor operates with a constant intermediate activity. However, in some instances the loss in activity is gradual so that operation for an economical length of time is possible. Also, dual reactors are sometimes used with the catalyst in one unit being regenerated (in place) while the reaction is carried out in the other unit. In cases such as these it is important to know how the conversion of the desired reaction changes with time on stream. For this to be determined, a quantitative description must be known for the effect of deactivation on rates. We consider here the effect on the intrinsic rate at a catalyst site, ignoring the transport influences listed in Chap. 7. Then in Sec. 11-13 the effect of deactivation on the *global* rate is discussed.

Formulating mechanisms to explain rates of poisoning and the effect on the desired (or main) reaction is likely to be as difficult as establishing the mechanism of the main reaction itself. Hence, there are compelling reasons to adopt the empirical power-law rate equations for treating deactivation. This procedure has been well developed by Levenspiel[†] for various types of deactivation reactions.

We illustrate how to determine the rate as a function of time for a simple case for which deactivation is assumed to occur by blocking the active sites and where the rate of the main reaction is assumed to be directly proportional to the unblocked sites.[‡] Suppose that q represents the concentration of blocked sites (or concentration of poison on the catalyst) at any time and q_0 is the maximum concentration corresponding to completely deactivated catalyst. Then, if the main reaction is



its rate will be proportional to the fraction of the sites that are not poisoned, that is, to $1 - q/q_0$:

$$r_B = kC_A \left(1 - \frac{q}{q_0}\right) = kC_A(1 - \phi) \quad (9-34)$$

where ϕ represents the fraction, q/q_0 , of poisoned sites.

The rate of the poisoning reaction determines how ϕ varies with time. If the sites are blocked by a product, C , formed by reaction of B , the process is called *series poisoning*, or *fouling*, and the deactivation reaction is written



[†] O. Levenspiel, *J. Catal.*, **25**, 265 (1972).

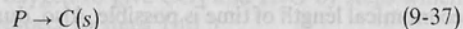
[‡] This case has been considered by S. Masamune and J. M. Smith, *AIChE J.*, **12**, 384 (1966). The Levenspiel treatment is more general in that it allows for other than first-order processes.

Its rate will be proportional to the concentration of B and the fraction of unpoisoned sites, that is,

$$r_c = \frac{dq}{dt} = \frac{q_0}{q_0} \frac{d\phi}{dt} = k_{B,p} C_B (1 - \phi) \quad (9-36)$$

Carbon deposition in hydrocarbon cracking, where some of the primary products react further to hydrogen and coke, is an example of series deactivation.

Suppose the poison is an impurity in the feed stream. The poison will deposit independently of the main reaction, according to the reaction:



If the deactivation reaction (or adsorption) occurs only on the active sites, its rate is given by

$$r_c = \frac{q_0}{q_0} \frac{d\phi}{dt} = k_p C_p (1 - \phi) \quad (9-38)$$

where C_p is the concentration of the poison. This is termed *independent* poisoning.

A third type, *parallel* deactivation, occurs when A can react in two ways: (1) to deposit poison C on the sites, and (2) to form desired product B by Eq. (9-33). The poisoning reaction and its rate are then written



$$r_c = q_0 \frac{d\phi}{dt} = k_{A,p} C_A (1 - \phi) \quad (9-40)$$

For any of these types of poisoning, the rate of production of B as a function of time is obtained by integrating Eq. (9-36), (9-38), or (9-40) and combining the result with Eq. (9-34). This is easily done if the concentration in Eqs. (9-36), (9-38), and (9-40) is constant. We conclude that if rates are measured as a function of time, with the proper concentration held constant, an appropriate expression for predicting deactivation effects can be established.

For example, if *independent* poisoning is suspected, Eq. (9-38) can be integrated, for a fixed poison concentration C_p to yield

$$\int_0^\phi \frac{d\phi}{1 - \phi} = \left(\frac{k_p}{q_0} C_p \right) \int_0^t dt$$

or

$$1 - \phi = \exp \left[- \left(\frac{k_p}{q_0} C_p \right) t \right] \quad (9-41)$$

With this result for $1 - \phi$, the rate of the main reaction, Eq. (9-34), becomes

$$r_B = k C_A \exp \left[- \left(\frac{k_p}{q_0} C_p \right) t \right] \quad (9-42)$$

Suppose that r_B was measured experimentally with the same feed (in order that C_p remain constant) but for different reactant concentrations. If the results showed a

first-order dependency on C_A and an exponential decay with time, independent poisoning could be a possibility. If the measurements were made at constant reactant concentrations, an exponential decay with time would still be expected for both independent and parallel poisoning. Thus integration of Eq. (9-40) with C_A constant, and substitution in Eq. (9-34) gives

$$r_B = k C_A \exp \left[- \left(\frac{k_{A,p}}{q_0} C_A \right) t \right] = a_1 \exp [-a_2 t] \quad (\text{for constant } C_A) \quad (9-43)$$

where a_1 and a_2 are constants. Hence, experiments at different reactant concentrations are necessary to distinguish between parallel and independent poisoning. Rate equations for all types of poisoning can be developed and compared with experimental rate data (see Prob. 9-12).

PROBLEMS

9-1 It has been proposed[†] that the gas-phase catalytic hydrochlorination of acetylene occurs by the following steps

1. Adsorption of HCl
2. Surface reaction between adsorbed HCl and acetylene in the gas phase to produce adsorbed vinyl chloride which desorbs into the gas phase.

Preliminary experimental studies indicate that both external and internal diffusional resistances are negligible. Also, the equilibrium constant for the homogeneous reaction is very large.

The rate of reaction per gram of catalyst is measured at varying total pressures, but constant composition of reactants. The results show a linear relationship between r and p , all the way down to pressures approaching zero. What conclusions may be drawn from these data concerning the controlling step in the reaction?

9-2 Two gas-solid catalytic reactions, (1) and (2), are studied in fixed-bed reactors. Rates of reaction per unit mass of catalyst, at constant composition and total pressure, indicate the variations with mass velocity and temperature shown in Figure 9-4. The interior pore surface in each case is fully effective. What do the results shown suggest about the two reactions?

[†] S. Shankar, Ph.D. Thesis, Monash University, Australia, 1976.

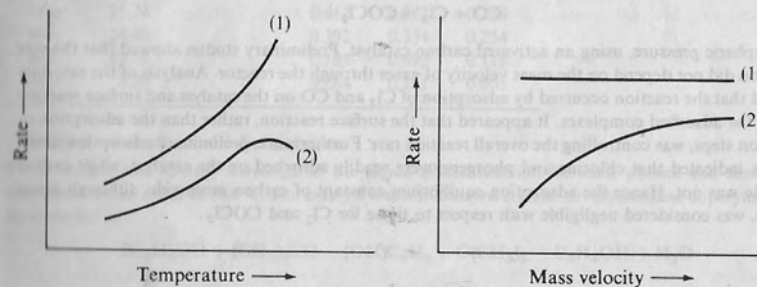


Figure 9-4 Rate vs. temperature and mass velocity.

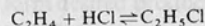
9-3 In a study of the kinetics of two different gas-solid catalytic reactions it is found that all diffusional resistances are negligible. Also, both reactions are irreversible. As an aid in establishing the mechanism of the reactions the rate is measured at a constant composition over a wide range of temperature. For the first reaction, (1), the rate increases exponentially over the complete temperature range. For the second reaction, (2), the rate first increases and then decreases as the temperature continues to rise. What does this information mean with regard to the controlling step in each of the reactions?

9-4 An isomerization reaction has the simple form $A \rightarrow B$. Assuming that the reaction is isothermal and reversible and that the external- and internal-diffusion steps have negligible concentration gradients, propose intrinsic rate equations for the following cases:

- The adsorption of A on the catalyst is controlling.
- The surface interaction between adsorbed A and an adjacent vacant center is controlling.
- The desorption of B from the surface is controlling.

In all cases the mechanism is adsorption of A , reaction on the surface to form adsorbed B , and desorption of B into the gas phase. Sketch the rate of reaction (per unit mass of catalyst) vs. total pressure (at constant composition) in each of the above three cases. Also, for comparison, include a sketch of the rate of the homogeneous reaction, assuming that it is first order. Sketches should be for constant composition.

9-5 Thodos and Stutzman[†] studied the formation of ethyl chloride, using a zirconium oxide catalyst (on silica gel) in the presence of inert methane.

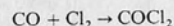


If the surface reaction between adsorbed ethylene and adsorbed HCl controls the overall kinetics, derive an expression for the rate. Neglecting external and internal transport resistances, evaluate the constants in the rate equation at 350°F from the following data:

$r \times 10^4$, lb mol/(h)(lb catalyst)	Partial pressures, atm			
	CH ₄	C ₂ H ₄	HCl	C ₂ H ₅ Cl
2.71	7.005	0.300	0.370	0.149
2.63	7.090	0.416	0.215	0.102
2.44	7.001	0.343	0.289	0.181
2.58	9.889	0.511	0.489	0.334
2.69	10.169	0.420	0.460	0.175

The equilibrium constant for the overall reaction at 350°F is 35.

9-6 Potter and Baron[‡] studied the reaction



at atmospheric pressure, using an activated carbon catalyst. Preliminary studies showed that the rate of reaction did not depend on the mass velocity of gases through the reactor. Analysis of the rate data indicated that the reaction occurred by adsorption of Cl₂ and CO on the catalyst and surface reaction between the adsorbed complexes. It appeared that the surface reaction, rather than the adsorption or desorption steps, was controlling the overall reaction rate. Furthermore, preliminary adsorption measurements indicated that chlorine and phosgene were readily adsorbed on the catalyst, while carbon monoxide was not. Hence the adsorption equilibrium constant of carbon monoxide, although it was not, was considered negligible with respect to those for Cl₂ and COCl₂.

[†] G. Thodos and L. F. Stutzman, *Ind. Eng. Chem.*, **50**, 413 (1958).

[‡] C. Potter and S. Baron, *Chem. Eng. Progr.*, **47**, 473 (1951).

(a) On the basis of this information, develop an expression for the intrinsic rate of reaction in terms of the bulk partial pressures in the gas phase. The reaction is irreversible. (b) Determine the best values for the adsorption equilibrium constants for Cl₂ and COCl₂ and the product $\bar{C}_m k_s K_{CO}$ from the following experimental data, where the temperature was 30.6°C, the catalyst size was 6 to 8 mesh, and

\bar{C}_m = total concentration of active centers, in moles per gram of catalyst
 k_s = specific reaction-rate constant for surface reaction
 K_{CO} = adsorption equilibrium constant for CO

r , g mol/(h)(g catalyst)	Partial pressure, atm		
	CO	Cl ₂	COCl ₂
0.00414	0.406	0.352	0.226
0.00440	0.396	0.363	0.231
0.00241	0.310	0.320	0.356
0.00245	0.287	0.333	0.376
0.00157	0.253	0.218	0.522
0.00390	0.610	0.113	0.231
0.00200	0.179	0.608	0.206

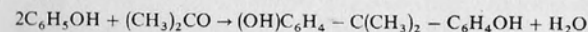
Assume that the 6- to 8-mesh catalyst particles are small enough that the pore surface was fully effective.

9-7 Potter and Baron also made rate measurements at other temperatures, and their results at 42.7, 52.5, and 64.0°C are as shown below. Assume that the adsorption equilibrium constants and the rate constant k_s follow an equation of the form $y = ae^{-b/R_s T}$, where a and b are constant and y is K_{Cl_2} , K_{COCl_2} , or $\bar{C}_m k_s K_{CO}$.

T , °C	$r \times 10^3$, g mol/(h)(g catalyst)	Partial pressure, atm		
		CO	Cl ₂	COCl ₂
42.7	4.83	0.206	0.578	0.219
42.7	10.73	0.569	0.194	0.226
42.7	1.34	0.128	0.128	0.845
42.7	9.18	0.397	0.370	0.209
42.7	9.10	0.394	0.373	0.213
52.5	14.28	0.380	0.386	0.234
52.5	15.46	0.410	0.380	0.210
52.5	6.00	0.139	0.742	0.118
52.5	3.68	0.218	0.122	0.660
64.0	25.74	0.412	0.372	0.216
64.0	24.46	0.392	0.374	0.234
64.0	13.78	0.185	0.697	0.118
64.0	8.29	0.264	0.131	0.605

Determine values of a and b for each case.

9-8 Reinicker and Gates[†] investigated the liquid phase reaction between phenol and acetone to bisphenol A and water at 364 K. The catalyst was a sulfonated styrene-divinylbenzene copolymer. The reaction is:



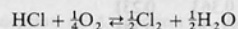
[†] *AIChE J.*, **20**, 933 (1974).

Derive a rate equation based upon the following elementary steps ($A =$ acetone, $-\text{SO}_3\text{H} =$ active group in the polymer, $P =$ phenol, $I =$ tertiary alcohol intermediate):

- reversible adsorption of acetone
- reversible reaction of adsorbed acetone and phenol (not adsorbed) to give the adsorbed tertiary alcohol intermediate
- irreversible surface reaction between adsorbed phenol and adsorbed tertiary alcohol to give adsorbed water and bisphenol A (not adsorbed).

Assume that step (c) is rate controlling. This mechanism is an approximation to the more careful development of Reinicker and Gates.

9-9 The Deacon process for production of chlorine involves the gas-phase catalytic reaction



Furusaki† studied the kinetics of this reversible reaction, with a CuCl_2 , KCl , SnCl_2 -on-silica catalyst, in differential and integral reactors. The rate of disappearance of HCl could be correlated by the equation:

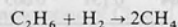
$$r = \frac{k[\text{C}_{\text{HCl}}\text{C}_{\text{O}_2}^{1/4} - (1/K)\text{C}_{\text{Cl}_2}^{1/2}\text{C}_{\text{H}_2\text{O}}^{1/2}]}{[1 + K_1\text{C}_{\text{HCl}} + K_2\text{C}_{\text{Cl}_2}]^2}$$

- Devise a series of fundamental steps of adsorption and surface reaction which will give the above rate expression.
- The rate data at 350°C , obtained in the differential reactor with a feed of HCl and air (no Cl_2 or H_2O), is as follows:

Rate $\times 10^6$ mg/(g catalyst)(s)	$\text{C}_{\text{HCl}} \times 10^6$ mg mol/cm ³
10.5	0.24
11.2	0.27
10.3	0.33
13.5	0.44
12.8	0.45
15.2	0.68
15.3	0.74
15.7	0.89

Using these data evaluate as many of the constants, k , K_1 , and K_2 , as possible.

9-10 Intrinsic rate data for the hydrogenolysis of ethane‡



over metal catalysts (such as Ni , CO) obeys the empirical equation

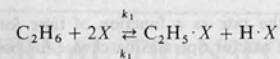
$$r = k\text{C}_{\text{C}_2\text{H}_6}^a\text{C}_{\text{H}_2}^b$$

† Shintaro Furusaki, *AIChE J.*, **19**, 1009 (1973).

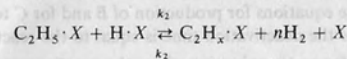
‡ J. H. Sinfelt, *Cat. Rev.*, **3**, 175 (1970).

The parameters k , a , and b depend upon the catalyst. Suppose that the mechanism is:

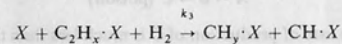
- reversible adsorption of C_2H_6 on a catalyst site



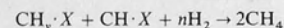
- Hydrogen extraction



- Reaction of H_2 to break the $\text{C}-\text{C}$ bond



- Further reaction with H_2 to give CH_4



A. Derive a rate equation from the postulated mechanism by assuming that the rate is controlled by step 3 (which is irreversible) and that the stationary-state hypothesis may be used to obtain the concentration of adsorbed C_2H_x .

B. Will the empirical equation be good approximation for the result derived in A?

9-11 Rates of oxidation of aqueous solutions of formic acid with dissolved oxygen over a commercial $\text{CuO}-\text{ZnO}$ catalyst at 200° to 240°C suggest† a first-order dependency for both molecular oxygen and formic acid. Preliminary data showed that the catalyst could be reduced in the presence of formic acid solutions containing no oxygen and then reoxidized when oxygen was added to the solution flowing over the catalyst bed. Hence, a redox mechanism is indicated.

A. Suggest a mechanism and note the assumptions that are necessary to explain the experimental data (that is, the first-order effects of both oxygen and formic acid).

B. At 225°C , some of the measured rate data are as follows:

$\text{C}_{\text{O}_2} \times 10^7$ g mol/cm ³	(Rate/ C_{FA}) cm ³ /(g)(min)	$\text{C}_{\text{FA}} \times 10^7$ g mol/cm ³	Rate/ C_{O_2} cm ³ /(g)(min)
2.5	3.2	12	14
6.0	6.3	18	20
7.2	7.4	20	20
10.0	10.6	23	23
		30	32
		63	74
		96	110

$\text{FA} =$ formic acid

$[\text{C}_{\text{O}_2} = 10 \times 10^{-7} \text{ g mol/cm}^3]$

For $\text{C}_{\text{O}_2} = 10.9 \times 10^{-7}$ and $\text{C}_{\text{FA}} = 28.7 \times 10^{-7}$ g mol/cm³ data for the effect of temperature on the rate are:

t , °C	240	232	225	215	208
(Rate) $\times 10^5$ cm ⁶ /(g mol)(g)(s)	5.7	3.9	1.8	0.88	0.53

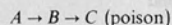
† G. Baldi, S. Goto, C.-K. Chow, and J. M. Smith, *Ind. Eng. Chem., Proc. Design Develop.*, **13**, 447 (1974).

From this information determine the constants k_0 and E in the following expression for the second-order rate constant

$$k_2 = k_0 \exp(-E/RT)$$

9-12 Derive an expression for the rate as a function of time for first-order main and poisoning reactions in a slurry reactor. The reactor operates batchwise for both solid catalyst particles and the liquid reaction mixture. Deactivation occurs by blocking of active sites with poison C , which is produced from reactant A in parallel with the production of desired product B . (The solution is simplified by dividing the rate equations for production of B and for C to eliminate time as a variable. Note that for a batch reactor the deactivation time is equal to the reaction time.)

9-13 Reconsider Prob. 9-12 for series poisoning where the reactions are:



For this case assume that the rate of production of C is much less than the rate of formation of B from A (slow poisoning). This means that the concentration of B is equal to the initial concentration of A , at any time.

EXTERNAL TRANSPORT PROCESSES IN HETEROGENEOUS REACTIONS

No matter how active a catalyst particle is, it can be effective only if the reactants can reach the catalytic surface. The transfer of reactant from the bulk fluid to the outer surface of the catalyst particle requires a driving force, the concentration difference. Whether this difference in concentration between bulk fluid and particle surface is significant or negligible depends on the velocity pattern in the fluid near the surface, on the physical properties of the fluid, and on the intrinsic rate of the chemical reactions at the catalyst; that is, it depends on the mass-transfer coefficient between fluid and surface and the rate constant for the catalytic reaction. The concentration of reactant is less at the surface than in the bulk fluid. Hence the observed rate, the *global* rate, is less than the intrinsic rate evaluated at the concentration of reactant in the *bulk* fluid.

The same reasoning suggests that there will be a temperature difference between bulk fluid and catalyst surface. Its magnitude will depend on the heat-transfer coefficient between fluid and catalyst surface, the reaction-rate constant, and the heat of reaction. If the reaction is endothermic, the temperature of the catalyst surface will be less than that in the bulk fluid (Fig. 10-1), and the observed rate will be less than that corresponding to the bulk-fluid temperature; the resistance to mass and energy transfer supplement each other. If the reaction is exothermic, the temperature of the catalyst surface will be greater than that of the bulk fluid. Now the global rate may be higher or lower than that corresponding to bulk-fluid conditions; it is increased because of the temperature rise and reduced because of the drop in reactants concentration.

In this chapter our objective is to study quantitatively how these external physical processes affect the global rate, which is the rate that we need in order to design heterogeneous reactors. Such processes are designated as *external* to signify that they are completely separated from, and in series with, the chemical reaction