Two-Step Catalytic Reactions

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SCOPE

With the advent of routine processing of kinetic data on fast computers, it is now commonplace to fit the data to rather complicated rate equations which can in turn be used in reactor design. It becomes more important than ever to assess the physical significance of these rate equations and of the rate parameters contained in them. This is particularly important in problems of control where extrapolations of the data beyond accessible process conditions may be risky unless the limitations of the rate equation are fully understood.

With heterogeneous catalytic reactions, which will be considered here exclusively, this problem has been reviewed by Froment (1970) from the viewpoint of data fitting. It is a very difficult problem. First of all, studies of elementary steps at surfaces under well-defined conditions that correspond to those of the catalytic reaction are still unavailable in spite of a very rapid advance in this field. Thus, there is practically no experimental guidance on the proper choice or behavior of the kinetic parameters that appear in rate equations in heterogeneous catalysis.

Second, with the well-documented nonideal nature of all real catalytic surfaces, it is not clear what should be the proper form of rate equations. There remains a legitimate concern about the use of rate equations based on the implausible model of ideal surfaces.

Finally, it is important to know what is the simplest rate equation that can be used with a minimum number of adjustable parameters for the case of reactions taking place through a large number of steps.

The present review considers these problems: the reliability and reproducibility of rates, the guidelines that allow one to decide whether kinetic parameters in a rate equation are physically meaningful, the available methods to take into account the nonideality of catalytic surfaces and the simplifying assumptions that cut down the number of kinetic parameters in a rate equation. To illustrate the general principles, three catalytic processes will be discussed because of their industrial importance in catalytic reforming, hydrocarbon synthesis, and nitrogen fixation.

CONCLUSIONS AND SIGNIFICANCE

A survey of the literature reveals that catalytic rates for many reactions taking place on metals under reducing conditions are amazingly reproducible from one catalyst to another. In particular, for these reactions which are conveniently called structure insensitive, there is a good agreement between rates obtained on industrial supported metals and experimental clean evaporated films. Just to recognize that a reaction belongs to the category of structure insensitive reactions is a simplification of great utility in a program of catalyst optimization. This knowledge depends only on a determination of the rate and not on the availability of the rate equation.

For the rate equation itself, it is shown that catalytic sequences taking place through a large number of steps can frequently be treated on ideal surfaces as if they took place in only two steps. This can be done when certain assumptions can be made concerning a rate determining step and a most abundant surface intermediate.

The frequent occurrence of two-step reactions is illustrated by means of the dehydrogenation of methylcyclohexane on platinum, the hydrogenolysis of ethane on Fischer-Tropsch catalysts, and the ammonia synthesis on iron. Fortunately, two-step reactions can be treated when they take place on nonuniform (real) surfaces. The rate equations that are obtained in the case of ideal surfaces and in the case of real surfaces are not very different from each other and can even be identical. In particular, the concept of a rate determining step may be preserved on a nonuniform surface.

Pending the further development of rate equations on nonuniform surfaces covering sequences with more than two steps and until data become available concerning rates of elementary steps under reaction conditions, great care must be exercised in the use of rate equations based on the assumption of ideal surfaces. Whenever possible, the parameters appearing in them should be assessed by means of a few simple arguments which provide order of magni-

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This review by Professor Boudart of the Research Committee initiates the Committee's effort in writing and obtaining reviews.

tude estimates which may help in accepting or rejecting a rate equation. With these reservations, rate equations based on a kinetic analysis of a postulated reaction sequence should be used rather than rate equations without any theoretical content. This is especially true for those reactions that can be treated as two-step reactions since a check on the physical significance of the parameters can be performed relatively readily in such cases.

DEFINITION OF RATE AND RELATED QUANTITIES

The rate r of a catalytic reaction must be expressed in a way that allows one to compare the results of different investigators. Following an old tradition it can be called the activity of the catalyst and is defined as follows:

$$r = \frac{1}{Q} \cdot \frac{dX}{dt} \qquad (1)$$

where t (in seconds) is time, X (in moles) the extent or degree of advancement of the reaction and Q the mass, volume, or surface area of the solid catalyst (Boudart, 1968). If the volume is used, it should be that of the solid particles excluding void volume. If the surface area is used, it should be, preferentially, a N_2 BET total surface area. Otherwise the area used (for example, of the metal for a metal supported catalyst) should be specified.

An alternative desirable way to express rates is by means of the turnover number N (s^{-1}) defined as in enzyme catalysis by using for Q in Equation (1) the number of moles of surface catalytic sites. The meaning of this number should be specified just as in the case of the catalyst surface. In particular, the STP volume of N_2 required to form a BET monolayer can be expressed readily in moles of surface sites. Hopefully this latter quantity may be defined in more realistic ways under favorable circumstances (for example, the moles of surface metal atoms in a supported metal catalyst). The turnover number is then the number of molecules of a specified reactant disappearing per unit time per catalytic site (properly defined) when the reaction is run at a given temperature, pressure, and reactant ratio to a specified degree of conversion. When the latter is not mentioned, it will be understood that the degree of conversion tends to zero (initial rates).

In the case of flow reactors, contact time should be avoided. Rather, space time or its inverse, space velocity, should be used. In the absence of a universal way to express space velocity it is recommended that it be defined just like the rate, as shown in Equation (1), except that dX/dt should now be the number of moles of limiting reactant fed per second to the reactor containing Q units of catalyst. In this way, the natural relation between space velocity and rate is preserved.

Selectivity S is defined most simply as the ratio of two rates: the rate r_1 of a desirable reaction and that r_2 of an undesirable reaction:

$$S = \frac{r_1}{r_2} \qquad (2)$$

In the comparison of various catalysts for a given reaction or of various reactions on a given catalyst, it may not be convenient or advisable to compare rates at a set temperature because rates are measured at the temperature at which the rate has a convenient value. Therefore, it may be preferable to compare temperatures T_r at which the rate has a set value r.

Many of the problems of reproducibility of rate measurements in heterogeneous catalysis are due to the nature of catalytic solids. These most frequently belong to the class of active solids consisting of small particles with diameters between roughly 1 and 10 nm (Boudart, 1971).* The thermodynamic and kinetic properties of these particles are strongly influenced, if not dominated, by surface states since between 10 to close to 100% of the atoms in a particle are actually at the surface. This percentage is called the dispersion of the system. The surface area of these highly dispersed powders is in the range from 50 to 500 m^2g^{-1} as measured by the BET method of nitrogen adsorption.

The problem of accessibility of reactants to the surface of active solids is a problem of considerable technological interest (Satterfield, 1970). Diffusion is not only one of the major hazards of kinetic work in heterogeneous catalysis but also the main reason why the catalytic activity of powdered solids frequently appears to be substantially less than that of enzymes or other homogeneous catalysts. The latter are accessible from all sides in the solution of reactants while, with powders, reactants must penetrate through pores of, say, $\delta = 10$ nm diam. into particles with characteristic sizes L which, in the laboratory at least, are as small as 10^{-2} cm. Now the performance of many catalysts, as measured by their turnover number N, is frequently a few powers of 10 below that of the best homogeneous catalysts. Typically, N is found to be 1 s^{-1}, in order of magnitude, for many heterogeneous catalytic systems. If reactants are gases at 1 atm, this means that the sticking probability γ of reactants is about 10^{-8}. A simple argument shows that pore diffusion will start to limit the rate of reaction when $\gamma^{1/2} > \delta/L$ (Boudart, 1968). With the above values for δ and L, the ratio δ/L is equal to 10^{-4} so that a turnover number of 1 s^{-1} corresponds to the verge of a diffusional limitation. In practice, larger turnover numbers are possible with solids, but they may then represent an underestimation of the intrinsic catalytic activity of the solid since diffusion may then influence the rate in a very serious way. In view of this limitation in our ability to measure the true activity of catalytic solids, there seems to be no sound foundation to the frequently expressed belief that enzymes are so much superior in activity to corresponding man-made inorganic catalysts. Recently, the H_2-D_2 equilibration reaction has been studied at 1 atm on powders of magnesium oxide; the reaction proceeds at 77 K with a turnover number of about 10^3 s^{-1}, that is, at a very high rate comparable to that of some enzymatic reactions operating at much higher temperatures (Boudart et al., 1972). In this case diffusional limitations with the porous catalyst could be avoided because of the very small concentration of active sites, so that the diffusion path L was only of the order of 20 nm for pore sizes δ of the order of 5 nm. Thus, even with γ as high as 10^{-5}, corresponding to $N = 10^3$ s^{-1}, the above inequality was far from being satisfied so that no diffusional limitation was to be feared.

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* 1 nm = 1 nanometer = 10A.

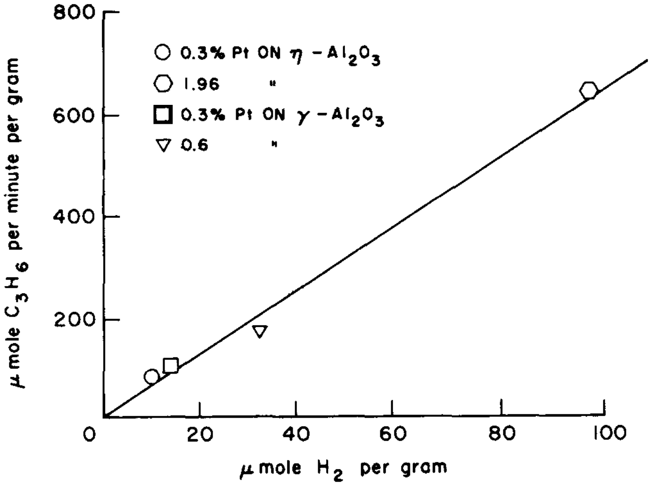


Fig. 1. Rate of reaction as a function of metal content of a supported catalyst.

MEASUREMENTS OF RATES

In the last analysis, while there exist some elaborate methods of reactor design that take into account the coupling between chemical reaction and transport phenomena (Smith, 1971), it is much preferable in a laboratory study of catalytic activity to check experimentally whether the rate is properly measured without any significant influence of diffusion of heat and mass. But even some of the commonly used diagnostic tests should be used with caution. For instance, to check the lack of importance of external diffusion it is frequently recommended that one verify the constancy of catalyst activity in a flow system when the flow rate is changed while the space velocity is kept the same. However, at the low Reynolds numbers usually attained in a laboratory reactor, the coefficients of heat and mass transfer are fairly insensitive to changes in flow velocity so that a lack of change of activity under the conditions of this test may not be a guarantee of proper behavior (Chambers and Boudart, 1966).

Similarly, in a slurry reactor the fact that increasing the rate of agitation brings catalyst activity to a plateau does not mean that the plateau corresponds to the chemical regime where diffusional limitations have been eliminated. First of all, internal (pore) diffusion may still be influencing the rate at its plateau value. Second, the increase in rate with increased agitation may be due primarily to a better suspension of the catalyst in the agitated solution with breakup of catalyst aggregates as the degree of agitation increases (Mears and Boudart, 1966).

To check that internal diffusion in catalyst pores is not influencing activity or selectivity, runs with different catalyst particle sizes indicate quite clearly such an influence if differences are found from one particle size to the next. On the other hand, if no effect of particle size is found, internal diffusion into the set of smaller pores of a bimodal pore distribution might still influence the rate, and yet no effect of change of particle size affecting only diffusion in the set of larger pores might be observed, even though diffusion in the set of smaller pores could be an important factor. As an example of this situation, synthetic zeolites consist of small crystals with an average dimension of the order of 50 nm and a set of micropores of about 1 nm in diameter. These zeolitic crystals are then packed into the particles, the size of which can be varied by pelletizing or grinding, and these particles contain another set of meso- or macropores.

Thus it appears that the usual experimental tests of diffusional limitations can be deceiving. A test that has been used by several workers, at least in an implicit way, has been described in a general way by Koros and Nowak (1967). It consists of preparing a series of catalysts differing in the fraction f of active material in them. If the activity of these catalysts, referred to unit surface area of the active material, does not depend on f, then diffusional limitations can be ruled out. Although this test can be used in principle for many types of catalysts and all types of reactors at any scale, reports of its use thus far concern supported metal catalysts and laboratory reactors. An example is shown in Figure 1 where the rate of a reaction taking place on a supported metal, referred to unit weight of catalyst, is plotted versus a measure of surface area of the metal, also referred to unit weight of catalyst. The catalysts differ chiefly by the amount of metal as the dispersion of the metal differs very little from one catalyst to the next. The straight line shown in Figure 1 is a clear indication of the absence of diffusional effects in the measurements shown. This test is so easy to use with supported metal catalysts that it should be made routinely in any catalytic study using these materials.

There are many types of laboratory reactors for gathering kinetic data in heterogeneous catalysis (Carberry, 1964). Only a few remarks concerning their characteristics will be made here. First, in spite of their great convenience and rapidity, pulse reactors should be viewed only as exploratory tools for screening new catalysts. Rates, as defined above, are not usually extractable from the data obtained from such reactors so that comparison with the work of others is rarely possible unless some doubtful assumptions are made. Pulse reactors are not generally unsuitable as kinetic tools except under special simple circumstances. The same remark applies to fluidized bed reactors. As to fixed bed reactors, they usually present problems of heat and mass transfer, channelling and back diffusion unless used in a differential mode, in which case it is very important to check the effects of products on the rate (Boudart, 1967).

A very clever way to use fixed bed quasidifferential flow reactors has been exploited by Sinfelt (1968). His method is particularly valuable when catalyst deactivation is a problem. Typically, in the study of hydrocarbon reactions in the presence of hydrogen, Sinfelt flows a mixture of hydrogen and helium over a small bed of freshly activated catalyst. At time $t = 0$, he introduces the hydrocarbon in the feedstream and runs under chosen conditions. At time t (say, $t = 180$ s), the hydrocarbon feed is interrupted, products are sent to the gas chromatograph, and the mixture of hydrogen and helium continues to sweep the catalyst bed for a rest period t' (say 600 s) during which catalyst activity, if partially lost during the previous run, can be partially or totally restored. In any event, by repeating every other run under fixed conditions chosen as standard, it is possible by reference to the rates obtained during the standard runs to correct for catalyst deactivation during the other runs and to gather kinetic data that can be extrapolated to those corresponding to a fresh catalyst.

However, in all reactor configurations except those operated in a strictly differential manner, rates are not measured directly. Rather, composition is recorded as a function of residence time or space time. The only exception is the stirred-flow reactor operating at the stationary state. Its application to heterogeneous catalysis has been pioneered by Temkin (1962), who has summarized the advantages of what he terms gradientless methods. The reactor consists of a recycle loop provided with the reactor itself and a recirculation pump. The reactor contains a very small quantity of catalyst. At the stationary state, when the rates of inflow and outflow are small as compared to the rate of recirculation, the composition is practically the same everywhere in the loop and the continuous stirred-flow condition is realized. The advantages of such reactors exceed some of their practical difficulties. Among these is the availability of a noncontaminating high flow rate recirculation pump. It must be noted that recycle reactors are also excellent for the study of gas reactions catalyzed by solids even though they are operated batchwise. This is especially true when the reaction rate is zero order and therefore does not change during a static run.

RATE EQUATIONS

The ultimate aim of a kinetic investigation is to find how the rate r depends on a certain function f of temperature T, pressure p, and composition c_i

$$r = f(T, p, c_i) \qquad (3)$$

Here c_i denotes the concentration of reactants including possibly products and inerts.

The statement of Equation (3) is commonly called the rate equation or rate law. Frequently in heterogeneous catalysis the function f is of the form of the law of mass action

$$r = k \prod_i c_i^{\alpha_i} \qquad (4)$$

where k is the rate constant, that is, a function of temperature but not of composition, and α_i (integral or fractional, positive, negative, or zero) is the order of reaction with respect to component i. The rate law (4) is traditionally called a power rate law (Weller, 1956). Alternatively, the rate equation is also written as follows:

$$r = \frac{k \prod_i c_i^{\alpha_i}}{[1 + \sum_i K_i^m c_i^m]^n} \qquad (5)$$

where the denominator expresses the competition for the sites by the components of the system and the K_i are the corresponding Langmuir adsorption equilibrium constants. Exponents m and n are often equal to unity although they may be equal to ½ or 2 respectively in the case of dissociative adsorption. A rate law of the form of Equation (5) is best called a Langmuir rate law although it was made popular by Hinshelwood, Schwab, Hougen, Watson, and others.

All that has been said above for an irreversible reaction can be generalized to the case of reversible reactions.

Normally the rate constant k appearing in Equations (4) and (5) is not that of a unique elementary process. Nevertheless, it can usually be represented by an Arrhenius expression

$$k = A \exp(-E/RT) \qquad (6)$$

with A being a pre-exponential factor (not a frequency factor) and E the apparent activation energy. Sometimes k and A exhibit compensation (Boudart, 1968), that is, change in the same direction for a reaction on various catalysts or various reactions on a given catalyst. A special case of compensation called the θ-rule occurs when, at least approximately,

$$\ln A = \text{const} + \frac{E}{R\theta} \qquad (7)$$

where θ is the isokinetic temperature, that is, the temperature at which all k's are identical as can be seen by substituting A from Equation (7) into Equation (6).

In the fifties great attention was devoted to the problem of the rate equation in heterogeneous catalysis, to the choice between power rate laws and Langmuir rate laws (Boudart, 1956), and to the determination of the kinetic parameters k, K_i, α_i, m, n, A, E and θ as they appear in Equations (4) through (7). Before again taking up these questions, it is important to note that very interesting results can be obtained by a mere consideration of rates without a knowledge of rate equations or rate parameters. Some of these results will be considered briefly in the next paragraph.

CATALYSIS BY METALS: REPRODUCIBILITY OF RATES

It is unfortunately true that reproducibility of rate measurements is frequently poor from one catalyst sample to another in a given laboratory or on a given catalyst sample from one laboratory to another. Some discrepancies are certainly due to faulty experimentation. But it is permitted to think that lack of reproducibility may be inherent to many studies on active solids because the type and concentration of active sites may depend on size and shape of catalyst particles and therefore, in a sensitive way, on methods of preparation and pretreatment.

It is therefore particularly comforting to know that, in the case of metal catalysts for certain reactions, excellent reproducibility can be obtained on catalyst samples differing in their mode of preparation, crystal size, and nature of support.

Let us consider a few examples. In the case of the liquid phase dehydrogenation of isopropyl alcohol, good agreement between turnover numbers is obtained by two groups of investigators working with nickel powders prepared in two completely different ways (Table 1). In this example, as in subsequent ones, turnover numbers are calculated on the assumption that all metal atoms at the surface are catalytic sites for the reactions considered. Whether this is true or not does not affect our conclusions since, in every example, the same assumption is made for the catalysts to be compared. Although, as pointed out in the opening section, the use of turnover numbers necessitates such assumptions, it is still a very useful quantity as it provides a readily usable measurement of rates and is expressed only in reciprocal seconds. Here we use for the average surface density of sites a value of 10^{15} cm^{-2}, which applies well to most surfaces in the absence of additional information on the nature of the crystallographic planes exposed.

A second example (Table 2) deals with two supported metal catalysts. The first one (Esso) was prepared by impregnation of η-Al$_2$O$_3$ with chloroplatinic acid; the second platinum catalyst, a commercial sample from Ketjen,

TABLE 1. $CH_3CHOHCH_{3(l)} \rightarrow CH_3COCH_{3(l)} + H_{2(g)}$

Initial turnover number at 82°C. in s^{-1}
0.10: D. E. Mears and M. Boudart, *AIChE J.*, **12**, 313 (1966) on nickel boride
0.15: S. L. Kiperman et al., *Kin. i Kat.*, 4, 605, 723 (1963) on Raney nickel
Assumption: 10^{15} sites cm^{-2}

TABLE 2. ISOMERIZATION (I) AND HYDROGENOLYSIS (H) OF NEOPENTANE

M. Boudart et al., *J. Catalysis*, **11**, 35 (1968)

Turnover numbers N at 300°C. in s^{-1} × 10^3 and selectivity S
HC: H_2 = 10: 1; 1 atm
$N_I = 3.4 \quad N_H = 2.3 \quad S = 1.5$
on 2% Pt/η-Al$_2$O$_3$ (Esso)
$N_I = 2.8 \quad N_H = 1.9 \quad S = 1.5$
on 0.6% Pt/γ-Al$_2$O$_3$ (Ketjen)
Assumption: 10^{15} sites cm^{-2}

was prepared according to an undisclosed procedure on what is probably a different form of alumina. The good agreement between turnover numbers on both catalysts for two reactions running in parallel, the isomerization and the hydrogenolysis of neopentane, is very satisfactory. Selectivities are identical within experimental error. Indeed, these data give no support whatever to the often voiced opinion that the preparation of catalysts is an art relying on poorly controlled or secret knowhow. In this example the number of platinum sites was obtained from selective hydrogen chemisorption data, as discussed elsewhere (Boudart 1969a). Let us note that, for the particle size of platinum crystallites pertaining to the example under discussion, there does not seem to be any question concerning the validity of the chemisorption technique used in the determination of platinum surface area.

However, it has become very clear in recent years that the determination of surface area (or dispersion) of particles below about 1 nm is in itself a very difficult problem. In particular, a puzzling discrepancy exists between work by Benson and Boudart (1965) on the one hand and by Mears and Hansford (1967) on the other hand. The discrepancy which deals with the relative adsorption of hydrogen and oxygen by dispersed platinum may well be resolved by newer data suggesting that, as a particle becomes small enough to reach a size of the order of 1 nm, the number of oxygen atoms adsorbed at its surface becomes smaller than the number of hydrogen atoms chemisorbed under identical conditions (Wilson and Hall, 1970). This observation, if confirmed by further work, is of great interest not only as it affects methods of determining surface area by selective chemisorption but also as a clear indication that particle size would ultimately affect catalytic activity. An indication that this is indeed the case for platinum particles in the nanometer range for oxidation reactions (but not for reactions involving hydrogen) has already been reported by Poltorak (1968). The effect of particle size on catalyst activity will be taken up again in the next section.

As there is always a possibility of surface contamination, or an effect of particle size, or an influence of the support, it appears of great interest to compare turnover numbers obtained on a practical metal catalyst in powder or supported form to those obtained on a metal evaporated film, which can legitimately serve as a reference since its surface, at least until the start of a catalytic experiment, can be considered as atomically clean. Besides, thick evaporated films of metals are not influenced by supports, and the particle size in films is in the range of 10 to 100 nm, neither too small nor too large. The last two examples (Tables 3 and 4) deal with such a comparison between a gold powder and a gold evaporated film on the one hand and between a platinum supported catalyst and a platinum evaporated film on the other hand. In each case the agreement is most satisfactory. It is hoped that many more comparisons of this type will become available, but in the meantime these examples are sufficiently varied and convincing to warrant a few conclusions.

First, although rate equations and mechanisms are still debated for all reactions on all catalysts, rates themselves, at least on metals, are reproducible even on active solids if measured properly. Second, before claims can be made on the reality of a certain effect (for example, particle size, one form or another of support interaction), it appears essential to compare one's work to that of others to check whether rates expressed in a correct way are comparable or not. Unfortunately, such comparisons are altogether too rare in the catalytic literature where rates are frequently still expressed in arbitrary units. Finally, the use of turnover numbers in heterogeneous catalysis, although based in each case on some assumed density of sites that must be carefully specified, will greatly facilitate comparison between heterogeneous and homogeneous catalysis. Such quantitative comparisons ought to become very rewarding in the near future.

TABLE 3. CYCLOHEXENE (g) + $H_2 \rightarrow$ CYCLOHEXANE (g)

Turnover number at 254°C. in s^{-1}
2 Torr HC; 20 Torr H_2

$6.0 \cdot 10^{-3}$	R. P. Chambers and M. Boudart, *J. Catalysis*, **5**, 547 (1966) on gold powder
$5.4 \cdot 10^{-3}$	C. Kemball et al., *Trans. Faraday Soc.*, **59**, 1181 (1963) on evaporated gold films

Assumption: 10^{15} sites cm^{-2}

TABLE 4. HYDROGENATION OF ETHYLENE

Temperature at which $N = 1\ s^{-1}$
23 Torr HC; 152 Torr H_2
$T = 239$ K; J. C. Schlatter and M. Boudart, *J. Catalysis*, in press on 0.5% Pt/SiO_2
$T = 236$ K; O. Beeck et al., unpublished data on Pt evaporated films

REACTIONS INSENSITIVE AND SENSITIVE TO STRUCTURE ON METALS

A comparison between rates alone can yield further information. Indeed, if it is agreed that at least under favorable conditions catalytic experiments on supported metals yield data characteristic of those expected from clean metal surfaces, a considerable amount of recent work done with supported metals receives particular significance from a theoretical standpoint. This work, carried out in the past five years in several laboratories, takes advantage of the possibility of varying the average particle size of supported metal particles between 1 and 10 nm (Boudart, 1969a). The work reported by Aben et al. (1970) and by Dautzenberg and Platteuw (1970) is particularly extensive and convincing.

These authors have studied the rate of several reactions (hydrogenation of benzene, isomerization of *n*-hexane, dehydrocyclization of *n*-hexane) over several metals (nickel, palladium, platinum) on various supports (silica, alumina, silica-alumina, silica-magnesia) with a systematic variation of the average particle size of the metal between 1 and 10 nm. For each particular reaction on a given metal, the turnover number was found to be independent of the particle size of the metal. Reactions for which this statement applies have been called facile or structure-insensitive (Boudart et al., 1966).

The importance of these findings and of similar results obtained in other laboratories and summarized elsewhere (Boudart, 1969a) is far reaching. The existence of these structure-insensitive reactions has been firmly established. It can be shown readily that when metal crystallites are grown from 1 to 10 nm, the relative proportion of surface sites in various coordination numbers will change appreciably (Poltorak, 1968). Therefore, there is an important result that can be inferred from data concerning structure-insensitive reactions. The turnover number for a given reaction on a given metal appears to be the same on a crystallite with a degree dispersion approaching 100% as on a larger crystal with properties characteristic of the bulk metal. Now, on the small crystals with almost all atoms being surface atoms, it seems natural to expect that the surface atoms act individually and retain essentially their atomic characteristics in their interaction with adsorbed molecules.

This expectation then should also extend to larger crystals, the surface atoms of which might also be considered to be isolated from the metallic community in their interaction with chemisorbed atoms and molecules. These considerations are in line with recent thinking which stresses the importance of atomic orbitals and ligand field theory of individual surface transition metal atoms (Bond, 1966; Tamm and Schmidt, 1969; Rhodin et al., 1970). Thus it appears that further work with supported metal particles, especially with very small ones approaching 100% dispersion, will contribute importantly to our understanding of the surface reactivity of bulk samples, including metallic single crystals. This statement in this form is not generally accepted although in its reverse form it is a truism.

On the other hand, one of the recurring interpretations of active centers, especially at metal surfaces, has been the belief that special sites with a certain number of metal nearest neighbors (for example, two, three, five, six) in a certain geometric pattern were required for bonding of certain adsorbates. If this is the case, the catalytic reaction ought to be structure-sensitive. Its rate per unit surface area of metal may be expected to depend on particle size, nonequilibrium shapes and perhaps certain epitaxial relations between metal and its support in the case of supported catalysts. In spite of many attempts at identification of these specialized metallic sites responsible for carrying out a given reaction, unequivocal success cannot be claimed and direct proof is still lacking in every instance.

As an example, in the investigation already discussed above in Table 2 of the hydrogenolysis of neopentane to isobutane and methane we used a platinum catalyst supported on a porous graphitized carbon (Boudart et al., 1968). A particularly favorable circumstance in this study was that over platinum neopentane was also isomerized to isopentane. Thus, it was possible to study two reactions in parallel. If then as a result of a pretreatment of the surface, it was found that the rate of isomerization did not change while that of hydrogenolysis did change, the presumption was that the pretreatment did not simply add or remove a surface contaminant. This feeling was reinforced by the fact that prior to the catalytic experiment the catalyst was submitted to repeated doses of oxygen in order to burn off any carbon contaminant at the surface of the metal. During that cleanup, the activity of the metal for both reactions increased by two orders of magnitude but the selectivity, that is, the ratio of rate of isomerization to rate of hydrogenolysis, did not change.

Now, the pretreatment during which the selectivity did change, as summarized in Table 5, was one which is likely to promote equilibrium shapes of the platinum crystallites which, however, did not change in size. Our experiments on supported catalysts then correspond very closely to those of Anderson and Avery (1966). These authors explained changes in the selectivity to isomerization when they used oriented films of platinum by the possibility of neopentane being either 1,3-diadsorbed or triadsorbed on the metal surface. In the triadsorbed state, which seems permitted geometrically only on (111) faces of the crystal or at triplet sites exhibiting the arrangement of the (111) face, neopentane does not tend to crack as rapidly as in the diadsorbed state. Thus the selectivity to isomerization ought to increase because of a reduction in the rate of cracking or hydrogenolysis. The five-fold increase in selectivity recorded in Table 5 is attributed to an increase in the surface concentration of triplet sites following high temperature pretreatment of the platinum crystallites. Because of the previous work of Anderson and Avery on oriented films and because of the uniquely favorable situation where selectivity was changed largely as a result of the change in the rate of one of the parallel reactions, this example is as convincing as any that can be found today in the catalytic literature concerning the existence of active centers on metals for a given structure-sensitive reaction.

TABLE 5. CHANGE IN SELECTIVITY FOR ISOMERIZATION OF NEOPENTANE ON A 1% PT CATALYST SUPPORTED ON CARBON (SPHERON-6)

Treatment of catalyst	Dispersion, %	Turnover number × 10^3 (s^{-1})		Selectivity N_I/N_H
		N_I to to isopentane	N_H to isobutane and methane	
Reduced in H_2 at 500°C.	35	0.86	0.34	2.5
As above followed by firing in vacuo at 900°C.	35	0.26	0.02	13

In view of this apparent sensitivity of the selectivity to structure for the reactions of neopentane on platinum, the agreement between selectivities on two different platinum catalysts as reported in Table 2 appears all the more remarkable. It can be explained by the fact that both catalyst samples were characterized by very similar values of the dispersion of platinum and were pretreated in similar fashion.

Thus, from a mere consideration of turnover numbers without further kinetic information, some rather interesting conclusions can be reached *a posteriori* concerning structure sensitive or insensitive reactions on metals. What would be even more interesting would be to predict whether reaction on a given metal will be sensitive or insensitive to structure.

As part of a systematic study of hydrogenolysis on transition metals, Sinfelt and coworkers have reported that on supported rhodium the rate of hydrogenolysis of ethane to methane, referred to unit surface area of the metal, increases by a factor of two to four as the average crystallite size increases from 1 to 4 nm (Sinfelt, 1969). Does this mean that the reaction is structure-sensitive? And if so, why? Or do we have to expect a change in the properties of the metal for very small particle sizes as a result of the formation of surface carbide, as was discussed above for the case of oxide layers on very small platinum particles? Or could it be that the stoichiometry of hydrogen chemisorbed layers, which served to determine metal surface area, changes with particle size when the latter becomes very small? These are interesting unresolved questions which can now be asked because of quantitative measurements of reaction rates.

TWO-STEP REACTIONS ON IDEAL SURFACES

By an ideal surface we mean one with sites that are identical kinetically and thermodynamically and without interaction between adsorbed species. This corresponds to the original model of Langmuir. For an overall reaction $A_1 + A_2 \rightleftarrows B_1 + B_2$ taking place in two steps involving empty sites X_1 and occupied sites X_2:

$$X_1 + A_1 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B_1 + X_2 \qquad \text{(I)}$$

$$X_2 + A_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} B_2 + X_1 \qquad \text{(II)}$$

the condition of steady state $r_I = r_{II}$ and the conservation of site density $(X_1) + (X_2) = (L)$ yield the rate law for the overall reaction

$$r = (L)\,\frac{k_1k_2(A_1)(A_2) - k_{-1}k_{-2}(B_1)(B_2)}{k_1(A_1) + k_{-2}(B_2) + k_2(A_2) + k_{-1}(B_1)} \tag{8}$$

containing the four rate constants k, the concentrations of reactants and products and the concentration of sites (L). This is readily generalized to any number of steps, provided that each one takes place with only one empty or occupied site (Boudart, 1968).

Thus, for a three-step reaction, a rate equation similar to Equation (8) would be obtained but with six rate constants, a numerator of the same form as the law of mass action and a denominator containing 6 terms. Clearly, this is far too unwieldy. Simplifications are in order. The two simplifying assumptions that are commonly made are those of a rate-determining step (*rds*) and of a most abundant surface intermediate (*masi*). A *rds* is the step, if there is one, that carries the entire free energy jump of the overall reaction, all other steps being in quasi-equilibrium (Boudart, 1968). A more general definition that is also valid when the overall reaction has reached equilibrium has been given by Wagner (1970). The notion of masi is intuitively obvious: among all adsorbed species, the masi is the intermediate the concentration of which is large enough as compared to that of all the others so that the concentration of the latter can be neglected.

Now, with these two types of simplifying assumptions, many reactions involving a large number of steps can be treated kinetically as two-step reactions and rate constants of only two steps appear in the rate law as such or in ratios, that is, as equilibrium constants. It can be said that all other steps are kinetically not significant. This is a great simplification. The price we pay is the well known ambiguity of simplified kinetics which will be illustrated for a simple isomerization reaction $A \rightleftarrows B$ taking place in three steps (Boudart, 1968).

$$* + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^*A$$

$${}^*A \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} {}^*B$$

$${}^*B \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} B + *$$

where $*$ denotes an empty surface site as usual. It is easy to show that sufficiently far away from equilibrium the same rate law

$$r = (L)\,\frac{a(A)}{1 + b(A)} \tag{9}$$

of the simplest Langmuir-Hinshelwood or Michaelis-Menten form describes the kinetics of isomerization in four different cases summarized in Table 6. But in three cases the rate parameters a and b have quite different meanings. Kinetically, these four cases are divided into two groups. In group I it is assumed that all three steps are irreversible but that ${}^*B$ is the masi; in this case $a = k_1$ and $b = k_1/k_2$. This situation is readily generalized to any number of steps. Hence a Theorem I:

In a catalytic sequence of any number of irreversible steps, if the surface intermediate involved in the last step is the *masi*, there are only two kinetically significant steps, the first one and the last one.

Let us now turn to the three cases of group II where one or more steps are reversible. The common assumption among these concerning the *masi* is now the opposite of that just made above. It is now assumed that ${}^*A$ is the *masi*.

In case IIa, the second step is *rds* and the rate parameters are now $a = K_1k_2$ and $b = K_1$ where K_1 is an adsorption equilibrium constant $K_1 = k_1/k_{-1}$. Again only two steps are kinetically significant.

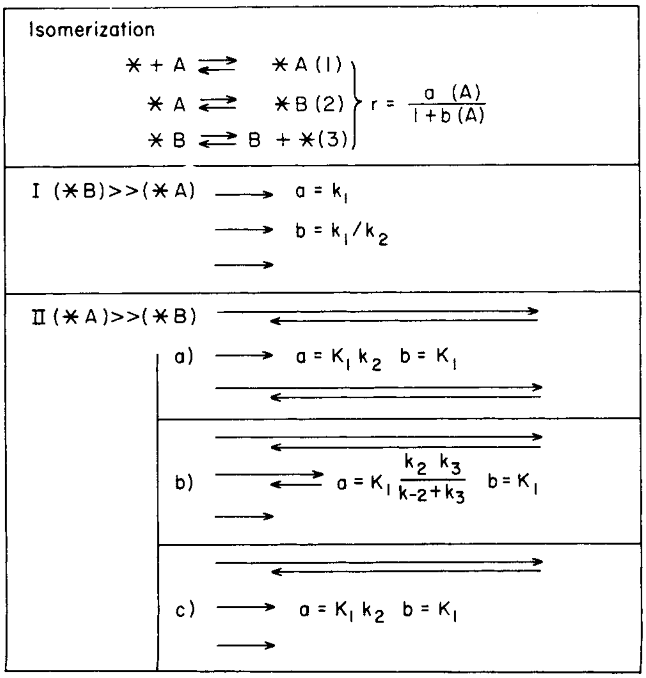
It is interesting to contrast cases I and IIa. In both cases, the rate parameter b is the ratio of two rate constants, one for adsorption and the other for desorption. But in the first case these rate constants stand for different steps: the reactant A once adsorbed will desorb only as product B. By contrast in the second case, the reactant A is in equilibrium with the surface, that is, it is adsorbed and desorbed many times before it reacts at the surface. In the first case, we do not assume adsorption equilibrium. In the second case we do. Both rate laws are formally identical. It is reasonable to expect that chemisorption of the sort leading to molecular rearrangements may frequently be irreversible so that the first case may be found actually in many cases where the rate law might lead one to believe that he is dealing with the classic case of adsorption equilibrium.

Now suppose that the first step is in quasi-equilibrium, the second reversible and the third irreversible with again the same assumption that ${}^*A$ is the *masi*. For this case IIb it is easy to show that the rate parameters in Equation (9) are $b = K_1$ as in the previous case, and

$$a = K_1\,\frac{k_2k_3}{k_{-2} + k_3} \tag{10}$$

This is the case reported by Hightower and Hall (1968) for the isomerization of cyclopropane on silica-alumina. In this instance, all three steps are kinetically significant. But, according to Hightower and Hall, in the case of isomerization of methylcyclopropane on silica-alumina, $k_3 >> k_{-2}$ so that step (2) may now also be considered as irreversible (case IIc). In that event, the rate parameters are $a = K_1k_2$ and $b = K_1$ just as in case IIa. From kinetics alone there is no possible distinction between the two-step reactions IIa and IIc. The situation is general and leads to the following Theorem II:

TABLE 6. AMBIGUITY OF CATALYTIC KINETICS



Isomerization

$$\left.\begin{array}{l} * + A \rightleftarrows\ *A\ (1) \\ *A \rightleftarrows\ *B\ (2) \\ *B \rightleftarrows B + *\ (3) \end{array}\right\} r = \frac{a\ (A)}{1 + b\ (A)}$$

I $(*B)>>(*A)$	$\longrightarrow$	$\longrightarrow$	$\longrightarrow$	$a = k_1$ $b = k_1/k_2$
II $(*A)>>(*B)$	$\rightleftarrows$			
a)	$\rightleftarrows$	$\longrightarrow$	$\rightleftarrows$	$a = K_1 k_2$ $b = K_1$
b)	$\rightleftarrows$	$\rightleftarrows$	$\longrightarrow$	$a = K_1 \frac{k_2\ k_3}{k_{-2}+k_3}$ $b = K_1$
c)	$\rightleftarrows$	$\longrightarrow$	$\longrightarrow$	$a = K_1 k_2$ $b = K_1$

In a catalytic sequence of steps, all steps that follow an irreversible step involving the *masi* as reactant are kinetically not significant.

Thus, in the cases IIa and IIc, no kinetic statement can be made about the third step, whether it is reversible or irreversible or what are its rate constants. The third step has no kinetic existence.

The cases described by Theorems I and II do not exhaust by any means the cases where a multistep reaction can be reduced to a two-step reaction. Another useful situation is described by Theorem III:

All equilibrated steps following a *rds* involving the *masi* as product can be combined in a single overall equilibrium that regulates the concentration of the *masi*. Vice versa, all equilibrated steps preceding a *rds* involving the *masi* as reactant can be combined in a similar overall equilibrium.

An example of this situation will be discussed later in connection with ammonia synthesis. In view of the ambiguity of rate equations illustrated by the simple example of isomerization, it is very important to verify not only the goodness of fit of a proposed rate equation but, much more important, the physical meaning of the rate parameters. A list of the most common parameters is shown in Table 7. At the present time these parameters must still be extracted from rate equations and are not available from work done on the elementary steps themselves under the conditions of the reaction and with a complete characterization of the surface intermediates. Although progress in this direction has been made, for instance by means of relaxation methods (Parravano, 1969), the lack of direct information about the kinetics of elementary steps in heterogeneous catalysis corresponds to a 40-year lag as compared to corresponding progress in the kinetics of free radical reactions.

At the present time only general guidance from thermodynamics and transition state theory can be offered to eliminate unlikely rate parameters. The guidelines are summarized in Tables 8 through 11. The main obstacle toward further refinements in the theoretical analysis of rate parameters in heterogeneous catalysis remains the nonuniformity of the surface. To assess the significance of rate parameters obtained from rate equations based on the assumption of surface uniformity it is essential to understand the kinetic consequences of nonuniformity.

TWO-STEP REACTIONS ON NONUNIFORM SURFACES

If we now assume that the sites are not the same thermodynamically and kinetically but keep assuming no interaction between adsorbed species, it is possible to obtain rate expressions, but only for two-step reactions. It is therefore fortunate that so many reactions can be described by only two kinetically significant steps as explained in the preceding section. A detailed derivation can be found elsewhere (Boudart, 1968). I shall just list the assumptions and discuss the results. The treatment given here is based on the general theory of Temkin as discussed by Khammouma (1972).

Consider again the two-step sequence, the rate of which is described by Equation (8) for a uniform surface. This equation remains valid for an infinitesimal number of sites per unit surface *ds′* such that their property of interest *P* varies between *P* and *P* + *dP*.

The rate on the entire surface is now

$$r = \int \frac{k_1k_2(A_1)(A_2) - k_{-1}k_{-2}(B_1)(B_2)}{k_1(A_1) + k_{-2}(B_2) + k_2(A_2) + k_{-1}(B_1)}\, ds' \tag{11}$$

with the normalization condition

$$\int ds' = (L) \tag{12}$$

or, alternatively, with $s = s'/(L)$,

$$\int_0^1 ds = 1. \tag{13}$$

We must now decide what property *P* varies over the surface and what is the analytical form of the distribution function of that property. The property *P* is chosen to be the standard affinity A^0 of the first step in the adsorption direction, that is, as written. The function is defined by the fraction of sites *ds* with a value of A^0 between $A^0 + dA^0$:

$$ds = a \exp\left(-\frac{\gamma A^0}{RT}\right) d\left(\frac{A^0}{RT}\right) \tag{14}$$

where γ is a parameter which can be shown to be equal to the exponent of the Freundlich isotherm corresponding to the exponential distribution (14)

$$\theta = \text{const} \cdot p^\gamma \tag{15}$$

where θ is the fraction of surface covered at equilibrium by a gas at pressure *p*. The factor of proportionality *a* is

TABLE 7. RATE PARAMETERS

Rate constants for		
adsorption } one site	k_a	cm^3 s^{-1}
desorption } one site	k_d	s^{-1}
surface reaction		
unimolecular	k_u	s^{-1}
bimolecular	k_b	cm^2 s^{-1}
Equilibrium constants for		
adsorption	K_a	cm^3
surface steps	K_s	—

TABLE 8. ADSORPTION EQUILIBRIUM CONSTANTS

$$K = \exp(\Delta S^0/R) \exp(-\Delta H^0/RT)$$

M. Boudart, D. E. Mears and M. A. Vannice, *Ind. Chim. Belge*, **32**, 281 (1967)

$-\Delta H^0 > 0$

$0 < -\Delta S^0 < S_g{}^0$

where $S_g{}^0$ is the standard entropy of the gas (1 atm).

See also: D. E. Mears and M. Boudart, *AIChE J.*, 12, 313 (1966).

TABLE 9. RATE CONSTANT FOR ADSORPTION

$$k_a = A_a \exp(-E_a/RT)$$

$A_a \cdot (L)$ must be less than 10^4 cm s^{-1} in order of magnitude

TABLE 10. RATE CONSTANT FOR UNIMOLECULAR SURFACE REACTION OR DESORPTION

$$k_d = A_d \exp(-E_d/RT)$$

$A_d \cdot (L)$ must be less than 10^{28} cm^{-2}s^{-1} in order of magnitude

TABLE 11. RATE CONSTANT FOR BIMOLECULAR SURFACE REACTION OR DESORPTION

$$k_b = A_b \exp(-E_b/RT)$$

A_b must be less than 10^{-4} cm^{2}s^{-1} in order of magnitude readily determined by the normalization condition (13). The next step is to relate A^0 to the reactivity of sites. This is done by means of a Brønsted relation:

$$k_1 = \text{const} \cdot K_1^{\alpha} = \text{const} \cdot \exp(\alpha A^0/RT) \qquad (16)$$

where α is the so-called "transfer coefficient," frequently found to be not too far removed from ½. If the same transfer coefficient is assumed to apply to the second step from right to left, that is, in the adsorption direction, Equation (16) and similar expressions for the other rate constants after substitution into (11), together with (13) and (14), yield

$$r = \frac{\gamma(L)}{e^{\gamma f} - 1} \frac{k_1{}^0 k_2{}^0 (A_1)(A_2) - k_{-1}{}^0 k_{-2}{}^0 (B_1)(B_2)}{[k_1{}^0(A_1) + k_{-2}{}^0(B_2)]^m \, [k_2{}^0(A_2) + k_{-1}{}^0(B_1)]^{1-m}} \int_{u_0}^{u_0 e^f} \frac{u^{-m}}{1+u} \, du \qquad (17)$$

with the following notations

$$m = \alpha - \gamma \qquad (18)$$

and

$$f = \frac{1}{RT} [A_0{}^0 - A_1{}^0] \qquad (19)$$

where subscripts 0 and 1 denote values corresponding to the upper and lower limits of the interval of variation of the affinity A^0 respectively. The auxiliary variable u is defined as the ratio of concentrations of empty to occupied sites

$$u = \frac{(X_1)}{(X_2)} \qquad (20)$$

Superscripts 0 for the rate constants of Equation (17) also refer to values corresponding to $u = u_0$.

To finish the problem it is finally assumed that, for sufficiently large values of A^0 and f, u_0 is sufficiently small (very large coverage of sites with large affinity $A_0{}^0$) and $u_0 e^f$ is sufficiently large (very small coverage of sites with small affinity $A_1{}^0$), the limits of integration in (17) become $u_0 = 0$ and $u_0 e^f = \infty$ in excellent approximation. In that case (17) becomes

$$r = \frac{\gamma(L)}{e^{\gamma f} - 1} \frac{\pi}{\sin m\pi} \frac{k_1{}^0 k_2{}^0 (A_1)(A_2) - k_{-1}{}^0 k_{-2}{}^0 (B_1)(B_2)}{[k_1{}^0(A_1) + k_{-2}{}^0(B_2)]^m \, [k_2{}^0(A_2) + k_{-1}{}^0(B_1)]^{1-m}}. \qquad (21)$$

In the limit $\gamma \rightarrow 0$, this becomes more simply

$$r = \frac{1}{f} \frac{\pi(L)}{\sin \alpha \pi} \frac{k_1{}^0 k_2{}^0 (A_1)(A_2) - k_{-1}{}^0 k_{-2}{}^0 (B_1)(B_2)}{[k_1{}^0(A_1) + k_{-2}{}^0(B_2)]^{\alpha} \, [k_2{}^0(A_2) + k_{-1}{}^0(B_1)]^{1-\alpha}}. \qquad (22)$$

The latter case corresponds to that of constant distribution as can be seen by putting $\gamma = 0$ in Equation (14). Physically this is the case corresponding to the Temkin adsorption isotherm

$$\theta = \frac{1}{f} \ln \text{const} \cdot p \qquad (23)$$

Further details are given elsewhere (Khammouma, 1972).

If now we compare the rate law (8) obtained for a two-step reaction on an ideal surface to the rate laws (21) or (22) obtained for the same two-step reaction on a nonuniform surface with a distribution of affinities corresponding to the Freundlich and Temkin isotherms respectively, it is clear that apart from numerical coefficients that can be lumped into a generally unknown density of sites (L) both rate laws for the nonuniform surface are identical in form, and besides they would be very difficult to distinguish in most cases from the rate law for an ideal surface. Indeed the numerators are the same, and the denominators contain the same terms although they are arranged differently in both cases. Furthermore, if additional assumptions are made concerning the existence of a *rds* or a *masi*, it is expected that the resemblance will be even greater. And, as will be shown in the case of ammonia synthesis, the treatment is not restricted to two-step reactions with each step involving only one surface intermediate in each direction, but it applies to other reactions as well.

This result, important as it may be, is not the only useful result of Temkin's treatment of kinetics on nonuniform surfaces. Let us note a few corollaries.

First, it can be shown that if a collection of ideal surfaces is compared as catalysts for a two-step sequence, provided that a Brønsted law (16) with $\alpha = ½$ can be assumed, the most active ideal catalyst will be that for which $(X_1) = (X_2)$, that is, that corresponding to $\theta = ½$, half-coverage of the surface by the intermediates (Boudart, 1968). This result of Temkin may be considered as a kinetic verification of Sabatier's hypothesis of the intermediate compound which must be bound to the surface with enough energy but not too strongly.

Similarly, on a nonuniform surface with a constant distribution ($\gamma = 0$), the largest contribution to the rate will come from the collection of sites with $\theta = ½$, and the entire surface will tend to operate with an overall value of θ in the vicinity of ½, provided that the parameter of nonuniformity f is large enough, for example, in the vicinity of ten, and α is close to one-half (Boudart, 1968).

Furthermore, again for a nonuniform surface with $\gamma = 0$ and $\alpha = ½$, the relative contributions of the collections of sites with highest and lowest value of the affinity are identical for a two-step isomerization reaction $A \rightarrow B$ for which adsorption of A is the *rds* and $^*B$ is the *masi* (Boudart, 1968). This paradoxical result can be understood if it is remembered that the rate of adsorption is proportional to the rate constant k and to the fraction of available sites $(1 - \theta)$. With a high value of the affinity, the rate constant will be high but the number of sites that is available is small. The opposite will be true for the sites with a low value of the affinity. It can be shown for the simple case discussed here that both products are indeed identical for the sites with the highest and the lowest value of the affinity. Hence, sites that might be expected to behave very differently, and actually do so in a chemisorption study, behave identically in the catalytic reaction. Furthermore, the ratio in the affinities of extreme sites which is equal to e^f becomes only $e^{f/2}$ for the ratio of rate constants because of the Brønsted relation and is further reduced to $e^{f/4}$ for comparing catalytic rates as a result of the product of site activity and availability (Boudart, 1969b).

For the same reason, in the case of the general two-step reaction leading to Equations (21) and (22), the concept of *rds* is preserved. This can be shown very simply by comparing rates of steps I and II in the forward direction:

$$\frac{r_I}{r_{II}} = \frac{k_1(X_1)(A_1)}{k_2(X_2)(A_2)} = u \frac{k_1}{k_2} \frac{(A_1)}{(A_2)}$$

By substitution of appropriate values of rate constants which depend on s it is verified that $u(k_1/k_2)$ does not depend on s. Hence, if r_I is much larger (or smaller) than r_{II} on one type of site, this inequality, which expresses that r_{II} (or r_I) is *rds*, will be preserved on all types of site (Madix, 1968). This result, like the preceding ones, should not be considered as general, but even if they hold only for the two-step sequence as treated in this section, the conclusions are of great interest since, as shown in the previous section, two-step reactions describe a large number of more complex ones with frequently justifiable simplifications.

In conclusion, the nonuniform surface behaves much less nonuniformly than a study of chemisorption on two different crystallographic planes would suggest at first. Rate equations are not drastically distorted by nonuniformity and sometimes are very similar. But ultimately rate parameters extracted from rate equations valid for ideal surfaces must be considered as averaged-out parameters and not rate parameters for specific events on specific sites. It is necessary to keep this in mind when the guidelines proposed in the preceding section are used in the evaluation of rate parameters.

EXAMPLE I: DEHYDROGENATION OF METHYLCYCLOHEXANE

The kinetics of dehydrogenation of methylcyclohexane M to toluene T on an alumina-supported platinum catalyst has been studied by Sinfelt et al. (1960). This work has been summarized very clearly by Thomson and Webb (1968). The rate law that was found to fit the data was the simple type of Equation (9). Small amounts of aromatics in the feed were found to exert only a slight inhibition on the rate of dehydrogenation. It was concluded that case I was better suited than case IIa. Indeed, if methylcyclohexane were reversibly adsorbed as, perhaps, 1,2-diadsorbed methylcyclohexane, aromatics would be expected to displace this surface intermediate quite readily and inhibit the rate strongly. On the other hand, if methylcyclohexane is adsorbed irreversibly and proceeds through a number of steps that are kinetically not significant to adsorbed toluene, which is the *masi* and leaves the surface irreversibly, aromatics would then compete only on equal terms with adsorbed toluene and inhibit the rate slightly.

An analysis of the rate parameters a and b yielded values for the rate constants for adsorption of M and desorption of T. From the measured activation energies pre-exponential factors were calculated by Arrhenius' equation (6). For desorption the pre-exponential factor is $3 \cdot 10^{26}$ cm^{-2} s^{-1}, which is lower than the maximum value given in Table 10, but only slightly more so, an indication that most of the platinum sites are active in the reaction. By contrast the pre-exponential factor of the rate constant for adsorption of M was found to be smaller by a factor of about 10^6 than the maximum value given in Table 9. Since most platinum sites appear to be active, the factor of 10^{-6} appears to be due to a genuinely low steric factor.

In support of the proposed interpretation of kinetic observations it is of interest to mention a study by Andreev et al. (1968) of the dehydrogenation of cyclohexane carried out on a nickel catalyst in the presence of deuterium at increasingly higher temperatures. At low temperatures at which dehydrogenation proceeds very slowly, deuterocyclohexanes are observed. The yield of the latter goes through a maximum at about 250°C., in a temperature range where the rate of dehydrogenation starts to pick up. Around 350°C. dehydrogenation proceeds rapidly, but the yield of deuterocyclohexanes is now quite small. Thus the reversible form of adsorbed cyclohexane leading to exchange (Burwell, 1969) becomes less and less important as temperature goes up, and the form that is responsible for dehydrogenation takes over and is irreversibly held since deuterated cyclohexanes tend to disappear. It must be pointed out that the apparently correct conclusion concerning the nature of the two-step reaction was arrived at on the basis of simple kinetic arguments before it found support in the more elegant work with deuterium.

EXAMPLE II: HYDROGENOLYSIS OF ETHANE

This interesting reaction—the simplest one in which carbon-carbon bonds are broken—has been used in an investigation of catalysts capable of making carbon-carbon bonds, iron catalysts promoted with potash for the Fischer-Tropsch synthesis (Cimino et al., 1954). In this investigation a kinetic explanation was proposed for the order of reaction with respect to hydrogen, negative for some catalysts and positive for some others. As this explanation has since been used systematically by Sinfelt (1969) in his work on the same reaction on many transition metals and exploited quite recently by Aika and Ozaki (1969) to explain the kinetic effects of the role of potash as a promoter in ammonia catalysis, it appears of interest to discuss this work in the light of the kinetic principles presented here and also because the early kinetic explanation of Cimino et al. has been criticized by Kemball (1966).

The power rate law for the hydrogenolysis of ethane to methane found by Cimino et al. had the form

$$r = k(C_2H_6)^p(H_2)^q\,. \tag{24}$$

The observed values of the order of reaction p and q with respect to ethane and hydrogen respectively are shown in Table 12. To explain the values of q, a two-step reaction was assumed

$$* + C_2H_6 \overset{K}{\leftrightarrow} {}^*C_2H_x + \frac{6-x}{2}H_2$$

$$ {}^*C_2H_x + H_2 \overset{k}{\rightarrow} \ldots$$

where the first step is an overall generalized adsorption equilibrium, the second step is the *rds* with participation of the *masi*, a dehydrogenated hydrocarbon fragment ${}^*C_2H_x$, and all subsequent steps leading to methane are kinetically not significant. The principles used in writing this two-step reaction are embodied in Theorems II and III above. Let us denote by (M) the ratio $(C_2H_6)/(H_2)^{(6-x)/2}$. Then the fraction of surface covered with the *masi* is

TABLE 12. HYDROGENOLYSIS OF ETHANE

$$r = k\,(C_2H_6)^p\,(H_2)^q$$

	p	x	y	q_{expt}	q_{calc}
Ni	0.7	0	4	−1.2	−1.1
Fe: no alkali	1.0	2	2	−0.7	−1.0
Fe + 0.05% K	0.9	2	2	−0.7	−0.8
Fe + 0.6% Li*	0.8	2	2	−0.4	−0.6
Fe + 0.6% K	0.7	4	0	+0.3	+0.3
Fe: impregnated with KOH	0.6	4	0	+0.1	+0.4

* Note: The Li content was erroneously reported to be 0.06% instead of 0.6% in the original paper.

$$\theta = \frac{K(M)}{1 + K(M)} \cong K'(M)^n \qquad (25)$$

where $0 < n < 1$, and a commonly used approximation to the Langmuir isotherm has been used (Boudart, 1956). The rate of the overall reaction is then

$$r = k\theta(H_2) = k'(C_2H_6)^n(H_2)^{1-n\frac{6-x}{2}} \qquad (26)$$

To compare Equations (24) and (26) it was then assumed that n was given by the experimental value of p, and the remaining question was to compare q with $1 - [n(6 - x)/2]$. To do this integral values of x were assumed. Observed and calculated value of q are given in Table 12. Clearly the proposed kinetics accounts for the shift of q from negative to positive values. More important, the necessary values of x are in three distinct categories corresponding to the very poor, poor, and good behavior of the respective catalysts in the Fischer-Tropsch reaction. It was concluded, in particular, that the role of an adequate amount of potash added to the iron catalyst was to decrease the dehydrogenating activity of the surface so as to protect hydrocarbons from too extensive dehydrogenation. Note that a rate law identical to Equation (26) can be obtained on the basis of Temkin's treatment of two-step reactions on nonuniform surfaces, with the empirical exponent n introduced in Equation (25) replaced by the physically meaningful parameter $(1 - m)$ of Equation (18).

In a discussion of the kinetic treatment of Cimino et al., Kemball (1966) has pointed out that it would be desirable to take into account the competition for the surface between ${}^*C_2H_x$ and adsorbed hydrogen. In the light of the preceding discussion of the dehydrogenation of methylcyclohexane, I believe there is another objection that might be raised against the early kinetic interpretation. I now think it is very difficult to accept the kind of reversible dissociative adsorption of ethane as postulated in the first equilibrated step of the sequence. Since kinetic schemes involving adsorption equilibria or all irreversible steps lead to similar rate equations, as explained in a preceding section, it might be possible to explain the observations of Cimino et al. without recourse to an unlikely adsorption equilibrium but with eventual explicit accounting of hydrogen adsorption as proposed by Kemball. Indeed, this can be done with the following three-step reaction:

$$2S + H_2 \overset{K}{\leftrightarrow} 2\,SH$$

$$^* + C_2H_6 + yS \xrightarrow{k_1} {}^*\,C_2H_x + ySH + \frac{6 - x - y}{2}\,H_2$$

$$^*\,C_2H_x + H_2 \xrightarrow{k_2} \ldots$$

We assume here that hydrogen is dissociatively chemisorbed in equilibrium with sites S which are not the same as the sites * on which the hydrocarbon reacts. As the hydrocarbon is adsorbed irreversibly, it loses y hydrogen atoms which are held on neighboring S sites and x hydrogen atoms that leave the surface in molecular form. As before, the *masi* on the normal sites is ${}^*C_2H_x$ so that all steps following the reaction of the *masi* are kinetically not significant. It is also assumed that the coverage θ of sites S is near saturation so that, if the collection of sites S near saturation is taken to be uniform,

$$1 - \theta = K^{-\frac{1}{2}}(H_2)^{-\frac{1}{2}}. \qquad (27)$$

This assumption is reasonable as we deal with chemisorption in the tail of the differential heat curve, with low values of the heat of adsorption. The assumption of two kinds of sites, one for hydrogen and one for the hydrocarbon, has been made very frequently in the kinetics of reactions on metals (Mears and Boudart, 1966) and is justified by the relative bulk of dissociated hydrogen and adsorbed hydrocarbon.

If it is accepted that two kinds of sites are involved, it is possible to treat the three-step reaction above as a two-step reaction on a nonuniform surface consisting of the first kind of sites. It is then assumed that the second kind of sites—for hydrocarbon—is a collection of uniform sites for the equilibrated step of hydrogen adsorption. Thus, we shall treat the two irreversible steps on the nonuniform surface by means of Equation (21) but shall treat yS as a reactant, so that the normal term $k_1(C_2H_6)$ becomes $k_1(C_2H_6)(S)^y$ or with the help of (25), $k_1'(C_2H_6)[K^{-\frac{1}{2}}(H_2)^{-\frac{1}{2}}]^y$.

In this way the rate law is simply

$$r = k(C_2H_6)^{1-m}(H_2)^{m - \frac{y}{2}(1-m)} \qquad (28)$$

Just as before, this rate law will be compared to the experimental one, Equation (24), by assuming that $1 - m$ is equal to p. Then a value for q is calculated from $m - [y/2(1 - m)]$ with values of y listed in Table 12. The calculated values of q do not require a new column in Table 12 as they are all identical to those calculated with the early scheme. It is important to note that values of y are separated into three groups corresponding, as was the case for x, to very poor, poor and good behavior in Fischer-Tropsch synthesis. Besides, y has a physical meaning related to that of x, and it can still be said that everything happens as if addition of enough potash depresses the affinity of the surface for hydrogen sufficiently so that dehydrogenation of the active intermediate is cut down.

Thus all the features of the previous scheme are preserved in the new one but there are distinct advantages in the latter. Chemisorption of the hydrocarbon is now irreversible. An uncomfortably low value of x ($x = 0$ in the case of nickel) need not be assumed. Competition for the surface by hydrogen has now been taken into account. The fractional orders of reaction are no more an approximation to the Langmuir case [Equation (25)] but appear naturally as a result of the more realistic assumption of the nonuniform surface.

Finally, it must be noted that the success of the earlier scheme in explaining the kinetics of hydrogenolysis of propane on nickel as reported by Morikawa et al. (1937) is preserved with the present interpretation. For this reaction it was found that the order with respect to propane was 0.9 and with respect to hydrogen, the strikingly negative value -2.6. With the previous scheme the latter value was also calculated from the corresponding expression for propane:

$$1 - n\frac{8 - x}{2}$$

with $n = 0.9$ and $x = 0$. In the treatment proposed here, the order with respect to hydrogen is given by the same expression as for ethane:

$$m - \frac{y}{2}(1 - m)$$

and the value of -2.6 is found with $1 - m = 0.9$ and $y = 6$. Note that the value of $y = 6$ for propane, higher than the value of $y = 4$ for ethane, was anticipated by Kemball (1966) who suggested that "the higher negative hydrogen exponent of −2.6 for the hydrogenolysis of propane on nickel compared with −1.1 for ethane could be caused by the need to free more sites from hydrogen to accommodate the larger molecule."

The present example is a vivid illustration of the similarity of kinetic results obtained with adsorption equilibrium or irreversible adsorption on the one hand and with ideal or nonuniform surfaces on the other hand. It would be unjust to conclude that this similarity weakens the merit of the kinetic analysis. Although there are of course considerable differences in these treatments, some important physical ideas remain unchanged. Thus, the important result that seems preserved is that promotion of an iron catalyst by potash subdues the affinity of the metal for hydrogen. This result should now be checked independently. As already mentioned, a similar conclusion has been reached in recent work on ammonia synthesis by Aika and Ozaki (1969).

EXAMPLE III: AMMONIA SYNTHESIS

A review of recent work on ammonia synthesis has been written by Nielsen (1970). What will be discussed here is some recent work on the kinetics of this reaction, principally on iron catalysts at relatively low temperatures (600 K) and atmospheric pressure. It has now become very clear that some of the kinetic details of the reaction are different at the higher temperatures (700 K) and high pressures used in commercial practice, although many of the principles involved are the same at both low and high temperatures.

There are four main kinetic questions in ammonia catalysis. First, which step is the *rds* and, in particular, does hydrogen participate in the *rds*? Second, which surface intermediate is the *masi*? Third, is it necessary to take into account the nonuniformity of the surface? Finally, what is the role of alkali (K_2O) and/or alkaline-earth oxides used as promoters of the iron catalyst used universally as the commercial catalyst in ammonia synthesis?

In what follows to simplify the writing without any loss of physical ideas we shall look at the kinetics of the reaction

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (29)$$

sufficiently far away from equilibrium so that the reverse net rate can be neglected as compared to the forward net rate.

Let us first assume that the surface of the catalyst is uniform, the *rds* is the chemisorption of nitrogen and the *masi* is chemisorbed nitrogen. Taking advantage of Theorem III above, we can collapse all steps into only two:

$$\begin{aligned} 2^* + N_2 &\xrightarrow{k_1} 2^*N \\ ^*N + 1.5H_2 &\overset{K_2}{\leftrightarrow} NH_3 + {}^*. \end{aligned} \qquad (A)$$

As first shown by Boudart (1956), the corresponding rate law is then

$$r = \frac{k_1(N_2)}{[1 + K_2(NH_3)/(H_2)^{1.5}]^2} \qquad (30)$$

Equation (30) has been used successfully in particular by Brill and Tauster (1963) and Aika and Ozaki (1969). If the surface is now assumed to be nonuniform, all other assumptions remaining the same, it can be shown (Ozaki et al., 1960) that, for a constant distribution ($\gamma = 0$), Equation (30) becomes

$$r = \frac{k_1{}^0(N_2)}{[1 + K_2{}^0(NH_3)/(H_2)^{1.5}]^{2\alpha}} \qquad (31)$$

which is of course indistinguishable from (30) as α tends to unity. Equation (31) is particularly useful at very low conversions. At higher conversions, when the second term in the denominator of Equation (31) becomes sufficiently larger than unity, this equation reduces to

$$r = k(N_2) \left[\frac{(H_2)^3}{(NH_3)^2} \right]^\alpha \qquad (32)$$

the celebrated equation of Temkin and Pyzhev which has dominated much of the theoretical and practical kinetics of ammonia synthesis for more than 30 years. It is very easy to obtain Equation (32) from the following two-step sequence on a nonuniform surface:

$$\begin{aligned} {}^* + N_2 &\rightarrow {}^*N_2 \\ {}^*N_2 + 3H_2 &\leftrightarrow 2NH_3 + {}^* \end{aligned} \qquad (B)$$

where the adsorption of nitrogen is the *rds* as before but the *masi* is now nitrogen chemisorbed in a molecular state. The result follows directly from application of Equation (22) by neglecting in the denominator terms containing rate constants pertaining to the *rds* which are, by definition, much smaller than terms pertaining to equilibrated steps. Therefore, on a nonuniform surface, rate equations derived on the basis of atomically or molecularly held hydrogen are indistinguishable, since the same rate law (32) can be obtained from either of the two-step sequences (A) or (B). Correlation of many kinetic data led Nielsen et al. (1964) to Equation (32) which, in their case of sufficiently high conversions, is the same as (31), with a best value of α of about 0.75.

It is important to note that in Equation (31) the rate parameters $k_1{}^0$ and $K_2{}^0$ are those of elementary steps corresponding to the collection of sites characterized by the highest affinity for nitrogen. Since they are true rate parameters and not approximations as would be the case with Langmuir kinetics, they can be used in more theoretical evaluations than is normally possible in heterogeneous catalysis.

In this light, the recent study of Aika and Ozaki (1969) acquires an almost unique significance as an isolated example of a successful check of rate parameters. In their work with unpromoted iron catalysts, a comparison was made of the rates of ammonia synthesis with mixtures of hydrogen and deuterium. It was found that values of $k_1{}^0$ did not depend on the nature of the isotopic mixture when the data were evaluated with Equation (31) with $\alpha = 1$. This absence of kinetic isotope effect is indeed expected from the assumed lack of participation of hydrogen in the *masi*. By contrast, ratios of $K_2{}^0$ obtained with pure hydrogen or with mixtures of hydrogen and deuterium should not only depend on isotopic composition but should be calculable *a priori* since these ratios represent equilibrium constants of reactions involving only gaseous H_2, D_2, HD, NH_3, NH_2D, NHD_2 and ND_3. A comparison between calculated and experimental ratios, given in Table 13, shows that the thermodynamic isotope effect is fully accounted for.

The particular significance of the agreement between ratios of experimental adsorption equilibrium constants obtained in a kinetic experiment and quantities that are calculated exactly from data on gaseous species is well illustrated by the fact that in an earlier study with iron catalysts promoted with potash such agreement was not found by Ozaki et al. (1960). To explain the observed thermodynamic isotope effect on these catalysts, it was necessary

TABLE 13. COMPARISON BETWEEN CALCULATED AND OBSERVED RATIOS OF ADSORPTION EQUILIBRIUM CONSTANTS FOR AMMONIA SYNTHESIS WITH MIXTURES OF H_2 AND D_2

Data: Private communication of A. Ozaki.
Also: K. Aika and A. Ozaki, *J. Catalysis*, 13, 232 (1969).

Atom fraction deuterium	Ratios Calc.	Ratios Expt.
0.950	0.245	0.29
0.884	0.264	0.32
0.836	0.279	0.35
0.585	0.382	0.33
0.551	0.400	0.41
0.446	0.464	0.54
0.331	0.553	0.59
0.149	0.751	0.77
0.077	0.858	0.82
0.0	1.0	1.0

to postulate that the *masi* was not $*N$ but $*NH$. The sequence of steps is then

$$\begin{aligned} 2* + H_2 &\leftrightarrow 2*H \\ 2* + N_2 &\rightarrow 2*N \\ *N + *H &\rightarrow *NH \\ *NH + H_2 &\leftrightarrow NH_3 + * \end{aligned} \qquad (C)$$

But fortunately only the second and fourth steps are kinetically significant. Thus rate laws for the two-step reaction can again be obtained readily for ideal and nonuniform surfaces. In particular, Equations (30) and (31) still apply except that the exponent of the concentration of hydrogen in these rate laws becomes unity instead of 1.5. In the study of Ozaki et al. no kinetic isotope effect could be found, as in the case of Aika and Ozaki, since k_1^0 did not depend on the isotopic composition.

The kinetic analysis of Ozaki et al. has been challenged by Logan and Philp (1968) who reanalyzed the data of Ozaki et al. on a computer and concluded that their thermodynamic isotope effect was compatible with the assumption of $*N$ as the *masi* provided that the rate constants k_1^0 were recalculated to produce a very substantial kinetic isotope effect, suggesting direct participation of hydrogen or deuterium in the *rds*. There is always a real danger in kinetics to treat data with a powerful method of analysis which may be far better than the data themselves. At any rate, the suggestion of Logan and Philp has now been invalidated by Morikawa and Ozaki (1971) who have studied the rate of nitrogen isotope equilibration:

$$^{28}N_2 + {}^{30}N_2 \rightleftarrows 2\,^{29}N_2$$

on an iron catalyst promoted with potash. Although it was found that hydrogen accelerated the nitrogen exchange by a large factor of about five, a very small isotope effect of this acceleration was found when deuterium was substituted for hydrogen. This very small kinetic isotope effect at 350°C (a factor of 1.07) is not compatible with the much larger one (a factor of 1.53) calculated from the reanalysis of Logan and Philp, also at 350°C. The finding that $*NH$ is the *masi* on iron catalysts with potash at low temperatures remains therefore an interesting possibility. This does not appear to be the case at high temperatures where the kinetics clearly show a dependence of the rate on the concentration of hydrogen to the 1.5 power and not to the first power (Nielsen et al. 1964). Neither does it seem to be the case at low temperatures on an iron catalyst which is not promoted by potash (Aika and Ozaki, 1969).

Thus Aika and Ozaki (1969) have proposed that one effect of potash on an iron catalyst is to shift the *masi* from $*N$ to $*NH$, at least at low temperatures, by decreasing the dehydrogenating ability or hydrogen affinity of the metal, just as was discussed in the previous example of the hydrogenolysis of ethane.

Another role of potash, which may be related to the acceleration exerted by hydrogen on nitrogen exchange, may be electronic. Indeed, an iron metal surface after reduction still contains oxygen in the presence of an unreduced promoter, alumina, the purpose of which is to prevent sintering of the metal ("textural promotion"). Adsorbed oxygen, by forming a double layer negative outward, would decrease the affinity of the metal for nitrogen which also forms a negative dipole layer. The role of electropositive potassium would then be to combat the effect of oxygen by forming a dipole layer positive outward. This mechanism of promotion of iron was proposed quite a while ago (Boudart, 1952). It may also apply to the acceleration exerted by hydrogen on nitrogen adsorption or exchange, as proposed by Tamaru (1963) to explain a similar effect on nitrogen adsorption; in this case hydrogen would decrease the surface potential by reacting with surface oxygen ions and converting them to OH^- groups with a smaller negative charge. Further work remains to be done to elucidate fully the promoting effect of potash and the accelerating effect of hydrogen on nitrogen adsorption and exchange.

In conclusion, it appears at the moment from most kinetic observations in ammonia synthesis at high temperatures and on iron catalysts promoted with potash that the reaction takes place on a nonuniform surface, the *rds* being the adsorption of nitrogen and the *masi* being chemisorbed nitrogen, most probably in the dissociated state (Morikawa and Ozaki, 1971). This was the conclusion already reached more than ten years ago by the school of de Boer on the basis of their extensive adsorption and kinetic work (Mars et al. 1960). Of particular importance was the study by the Dutch workers of nitrogen adsorption during ammonia synthesis. They showed that nitrogen adsorption took place at a rate equal to the synthesis rate at comparable values of the surface coverage by nitrogen. They also showed that the fraction of the surface covered varied only from 0.27 to 0.60 when the virtual pressure of nitrogen following Kemball (1966) over the catalyst changed by more than five orders of magnitude. This is perhaps the most striking demonstration of the mode of operation of a nonuniform catalytic surface operating in the optimum fashion in the region of half coverage.

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NOTATION

A = affinity, kcal mole^{-1}
pre-exponential factor of rate constant
C = constant
E = activation energy, kcal mole^{-1}
f = constant, dimensionless
k = rate constant
K = equilibrium constant
(L) = total number of surface sites per cm^2
m = constant: dimensionless
N = turnover number, s^{-1}
p = pressure

Q = mass, volume or surface area of solid catalyst
r = reaction rate
S = selectivity
s = fraction of sites
T = temperature
t = time: s
u = relative concentration of sites, dimensionless
X = extent of reaction, mole
α = transfer coefficient, dimensionless
γ = constant, dimensionless
σ = pore size, nm
θ = surface coverage

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