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Kinetics on Ideal and Real Surfaces

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The wide applicability of the Langmuir-Hinshelwood classical kinetics to surfaces which are known to depart strongly from ideal Langmuir behavior is a well-known paradox of surface catalysis. The applicability and limitations of the classical method are illustrated by means of a simple reaction. The generality of the method is demonstrated by its applicability to ammonia synthesis with and without water vapor. The limitations are often more than compensated for by the added insight into reaction mechanism which it can provide without undue complexity. A three-step approach to surface kinetics is suggested and discussed.

PARADOX OF HETEROGENEOUS KINETICS

As recalled in the preceding paper (17) in this issue, use is frequently made in catalytic studies of the model of an ideal surface with constant heat of adsorption for each chemisorbed species. Although real surfaces invariably depart from this ideal model, a systematic application of it to kinetic problems has deepened understanding of surface reactions and in practice yields rate laws which are valid over a certain useful range of the kinetic variables. This successful application of an inadequate model constitutes a well-known paradox of heterogeneous kinetics.

This paradox was first considered and resolved for a special case by Constable (5) in 1925, the same year that Taylor set forth his concept of active centers to describe the behavior of real surfaces. Constable showed that a surface with a broad distribution of active centers would act in a given reaction as if only one kind of center were operating under given conditions. In other words a real surface may be considered as a statistical collection of ideal surfaces, and for a given catalytic reaction only a limited number of members of the ensemble play an active part, forming a quasiideal surface. Thus, in spite of the known complex behavior of real surfaces, the ideal model was used extensively in subsequent years by Hinshelwood, Schwab, Hougen, Jungers, and many others to describe in considerable detail the kinetics of surface reactions. These investigators were well aware of the limitations of their model and in particular have pointed out repeatedly that the kinetic constants obtained from such rate laws did not usually agree with adsorption constants obtained in separate experiments. The nature of the problem can be illustrated by a simple example.

ANALYSIS OF A TYPICAL CASE (1)

The decomposition of stibine, SbH₃, on the walls of a vessel covered with a film of antimony is one of the first catalytic reactions studied from the kinetic standpoint. The reaction velocity was measured at 0°, 25°, 50°, and 75°C. by Stock and coworkers (13) and more recently by Tamaru (15). Stock found that the rate r could be expressed by a relation of the type

$$r = kp^n \qquad (1)$$

with $n = 0.6$. In this expression p is the partial pressure of SbH₃ and $r = -dp/dt$. The results of Tamaru are similar to those of Stock, and only the latter will be discussed. It was verified by Stock that the reaction goes to completion, solid antimony and gaseous hydrogen being the sole products, and that hydrogen had no effect on the velocity of decomposition. Stock and Bodenstein (14) proposed the following interpretation of these findings: the hydride is adsorbed on the surface and decomposes there monomolecularly. Thus the rate is proportional to the concentration of adsorbed species, i.e., to the fraction of surface θ covered with hydride molecules:

$$r = k_1\theta \qquad (2)$$

The relationship between θ and p known at the time was the empirical Freundlich adsorption isotherm:

$$\theta = k_2 p^n \qquad (3)$$

with $0 < n < 1$. If adsorption equilibrium be granted, substitution of (3) into (2) immediately gives the observed rate law (1).

Subsequently the suggestion was made to replace the empirical isotherm of Freundlich by the Langmuir isotherm:

$$\theta = \frac{bp}{1 + bp} \qquad (4)$$

where $b = b_0 \exp(q/RT)$, q being the heat of adsorption assumed to be constant over the surface. The mechanism of Stock and Bodenstein then gives by substitution of (4) into (2)

$$r = \frac{k_1 bp}{1 + bp} \qquad (5)$$

an alternative rate law that must be compared with that originally proposed. This comparison (1) shows that rate laws (1) and (5) are equally satisfactory and that there is no way of deciding which one best represents the kinetic data. More recently the Freundlich isotherm has been interpreted as being due to an exponential distribution of heats of adsorption (6). The comparison between both rate laws thus indicates that the assumption of a Freundlich isotherm corresponding to a real surface is not superior from the kinetic standpoint to the assumption of a Langmuir isotherm corresponding to an ideal surface.

It would be erroneous to conclude that the good fit of expression (5) shows that the surface of the antimony film is an ideal one. Indeed, the adsorption constants b can be examined more closely. At the four temperatures investigated they have approximately the same value. However the Langmuir constant b must decrease exponentially with temperature. Since in this case b remains practically constant within the temperature interval considered, the heat of adsorption q must be very small and practically zero. This result has no physical meaning, as a heat of adsorption at least equal to the heat of liquefaction of antimony hydride, viz., 5,700 cal./g. mole, would be anticipated. In a similar way a comparison of b_0, the preexponential factor of Langmuir's constant, with possible values for b_0 which depend on the entropy of adsorption, leads to the conclusion that experimental b_0 values are considerably larger than permissible theoretically.

Thus from the viewpoints of both apparent energy and entropy, the kinetic constants b strongly suggest that the surface cannot be ideal in spite of the good behavior of the rate law following Langmuir. If however the surface presents a distribution of heats of adsorption, the situation can be understood qualitatively by means of the following simple argument. As the temperature of the catalytic experiment is increased, the surface coverage decreases and sites with a higher adsorption energy become operative. In the first approximation it may be assumed that

$$q = q_0 + aT$$

to describe this temperature dependence of the heat of adsorption. Then

$$b = b_0 \exp(q/RT) = b_0 e^a e^{q_0/RT}$$

The constant q_0 can be small even if the true heat of adsorption q is larger and

the apparent preexponential factor $b_0 e^a$ will be larger than the true one b_0.

When the heat of adsorption varies sufficiently rapidly with coverage, relatively small variations of pressure (by one order of magnitude) as normally encountered in kinetic experiments do not change the surface coverage appreciably. As a result, the surface appears ideal kinetically at a given temperature. Variations of temperature which change the surface coverage in a more striking way, reveal the nonideality of the surface.

A practical consequence of this analysis is the well-known fact that an expression of the type $p^n (0 < n < 1)$ may always be substituted for the more cumbersome hyperbolic function $bp/(1 + bp)$, the value of the fraction n being approximately constant at a given temperature for a restricted range of pressure. Thus, practically, kinetic data that can be fitted by means of Langmuir expressions can also be fitted by means of power expressions and vice versa. This simple situation was pointed out in the preceding paper (17) and illustrated by a number of examples.

THE CASE OF THE AMMONIA SYNTHESIS (2)

It is common belief that there are a few cases where a kinetic expression fitting the data cannot be derived on the assumption of an ideal surface. The most celebrated case is that of the ammonia synthesis for which Temkin and Pyzhev (16) proposed the following rate expression:

$$r = k_s P_1 \left(\frac{P_3^3}{P_2^2}\right)^m - k_d \left(\frac{P_2^2}{P_3^3}\right)^n \qquad (6)$$

where r is the over-all rate of synthesis of ammonia (partial pressure P_2) from nitrogen (P_1) and hydrogen (P_3); k_s and k_d are rate constants for synthesis and decomposition respectively; m and n are fractions which for ease of integration are often put equal to 0.5 although other values have been reported.

The Temkin-Pyzhev rate expression was originally derived on the assumption of a uniform distribution of sites corresponding to a heat of adsorption of nitrogen decreasing linearly with coverage. Although there is abundant evidence for such a departure of surface behavior from ideality, it would appear surprising, in view of the general validity of the paradox of heterogeneous kinetics, that such an assumption be essential to the derivation of the rate expression. Indeed, De Bruyne (4) has shown that the postulation of a particular analytical distribution function was superfluous. The same rate expression can be obtained on the basis of an exponential adsorption heat curve (11). In particular, it can be obtained quite simply on the basis of ideal-surface kinetics.
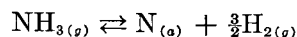
Independent evidence suggests that the slow step on a large variety of catalysts is the adsorption of nitrogen

$$N_{2(g)} \rightarrow 2N_{(a)}$$
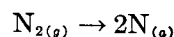
for ammonia synthesis and its desorption

$$2N_{(a)} \rightarrow N_{2(g)}$$
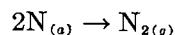
for ammonia decomposition. Adsorption equilibrium is maintained by means of the over-all fast process

$$NH_{3(g)} \rightleftarrows N_{(a)} + \tfrac{3}{2}H_{2(g)}$$

which determines the fraction of surface θ covered with adsorbed nitrogen atoms $N_{(a)}$. The surface coverage is determined directly by a Langmuir type of argument which gives the following Langmuir type of adsorption isotherm:

$$\theta = \frac{b(P_2/P_3^{1.5})}{1 + b(P_2/P_3^{1.5})} \qquad (7)$$

The rate of synthesis r_s is that of nitrogen adsorption:

$$r_s = k_1 P_1 (1 - \theta)^2 \qquad (8)$$

The rate of decomposition is that of nitrogen desorption:

$$r_d = k_2 \theta^2 \qquad (9)$$

Substitution of (7) into (8) and (9) gives a rate expression in the Langmuir form:

$$r = r_s - r_d = k_1 P_1 \left[\frac{1}{1 + b(P_2/P_3^{1.5})}\right]^2$$
$$- k_2 \left[\frac{b(P_2/P_3^{1.5})}{1 + b(P_2/P_3^{1.5})}\right]^2 \qquad (10)$$

Although this rate expression has not been tested, the remarks of the preceding paper and of the section above leave little doubt that it would satisfactorily represent the kinetic data. Indeed, because of the good approximation of power functions to represent Langmuir expressions in a limited pressure range and vice versa, Equation (10) can be written more simply:

$$r = k_s P_1 \left(\frac{P_3^{1.5}}{P_2}\right)^{2m} - k_d \left(\frac{P_2}{P_3^{1.5}}\right)^{2n} \qquad (11)$$

with $0 < m < 1$ and $0 < n < 1$. But (11) is identical with the Temkin-Pyzhev rate law (6), as was expected. When synthesis or decomposition is carried out in conditions removed from equilibrium, their rates can be described by Equation (8) or (9) respectively, the limiting cases of which are obvious.

Thus, if the surface coverage by nitrogen is small during synthesis conditions, $\theta \approx 0$, and (8) becomes simply

$$r_3 = k_1 P_1$$

a case which has been found experimentally (9).

If during decomposition the surface is nearly saturated with nitrogen, $\theta \approx 1$, and (9) gives

$$r_d = k_2$$

a zero-order decomposition which has been reported also (7).

Langmuir expressions or simplifications thereof have been shown to give correct rate expressions for ammonia synthesis in general and limiting conditions, in spite of the fact that ammonia catalysts are known to be highly nonideal (2). The practical advantage of such reasoning is even more apparent in more complex situations.

For example, a rate expression for ammonia synthesis in the presence of water vapor (partial pressure P_4) can be derived readily by taking into account the additional adsorption equilibrium:

$$H_2O_{(g)} \rightleftarrows O_{(a)} + H_{2(g)}$$
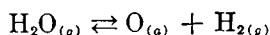
Taking into account both adsorption equilibria, a straightforward Langmuir type of reasoning gives for the fraction of surface θ covered with nitrogen atoms:

$$\theta = \frac{b(P_2/P_3^{1.5})}{1 + b(P_2/P_3^{1.5}) + b'(P_4/P_3)} \quad (12)$$

and for the fraction of surface θ' covered with oxygen atoms:

$$\theta' = \frac{b'(P_4/P_3)}{1 + b(P_2/P_3^{1.5}) + b'(P_4/P_3)} \quad (13)$$

The rate of ammonia synthesis becomes

$$r_s = k_1 P_1 (1 - \theta - \theta')^2 \quad (14)$$

The rate of decomposition is given by

$$r_d = k_2 \theta^2 \quad (15)$$

Substitution of (12) and (13) into (14) and (15) would give a rate expression of the Langmuir type that would be quite cumbersome. Again simplifications are indicated; thus

$$1 - \theta - \theta'$$

$$= \frac{1}{1 + b(P_2/P_3^{1.5}) + b'(P_4/P_3)}$$

$$\approx \frac{1}{b(P_2/P_3^{1.5})} \cdot \frac{1}{b'(P_4/P_3)}$$

$$\approx k \left(\frac{P_3^{1.5}}{P_2}\right)^m \left(\frac{P_3}{P_4}\right)^n$$

$$\theta \approx k' \left(\frac{P_2}{P_3^{1.5}}\right)^{1-m} \left(\frac{P_3}{P_4}\right)^n$$

where m and n are fractions. Then the rate expression becomes

$$r = k_s P_1 \left(\frac{P_3^{1.5}}{P_2}\right)^{2m} \left(\frac{P_3}{P_4}\right)^{2n}$$

$$- k_d \left(\frac{P_2}{P_3^{1.5}}\right)^{2-2m} \left(\frac{P_3}{P_4}\right)^{2n}$$

Following the suggestion of the preceding paper (17) to limit the choice of exponents to integers or half integers, it may be assumed that $m = n = \frac{1}{2}$, as was done

above for the case of pure ammonia; such a choice facilitates integrations. Then, finally,

$$r = k_s P_1 \frac{P_3^{2.5}}{P_2 \cdot P_4} - k_d \frac{P_2}{P_3^{0.5} \cdot P_4} \quad (16)$$

The rate law (16) has been used recently by Kiperman (10) to correlate the data of Brunauer and Emmett (3) as well as those of Larson and Tour (12) on ammonia synthesis at atmospheric and elevated pressures in the presence of water vapor. The fit of the data is very satisfactory. However, to derive (16), Kiperman used the statistical Temkin-Pyzhev approach. The latter may be more satisfactory from the theoretical viewpoint but is again shown to be superfluous if the main objective is to find an adequate rate law representing the kinetic data.

SUGGESTED PROCEDURE IN KINETIC STUDIES

In the case of the ammonia synthesis, the reaction mechanism was suggested by independent experiments, and from this mechanism it was possible to obtain rate laws following the procedure of ideal kinetics. Generally, if the mechanism of a reaction is not known, the following procedure is suggested:

The first step is to write down a kinetic expression of the type

$$r = k P_A{}^a P_B{}^b P_C{}^c \cdots$$

where A, B, C, etc., are reactants and products, and to find the values of the exponents a, b, and c. Depending on the accuracy of the data and the ambition of the investigator, these exponents may or may not be restricted to integral or half-integral values.

The second step is to find a possible mechanism which gives, after suitable simplifications of the type indicated above, the rate law found empirically in the first step. In view of the paradox of surface kinetics, this part of the search may be conducted on the assumption of classical ideal kinetics, following the systematic approach to be found in text books. Depending on the nature of the problem, kinetic adsorption constants may or may not be determined at this stage.

The third step is to confirm the assumed mechanism by a rigid analysis of the kinetic constants previously determined. The nonideality of the surface process, including heterogeneity and interactions, must then be taken into account either by postulating a surface distribution of energy sites or by introducing real adsorption isotherms determined separately.

While the third step, which must ultimately lead to an absolute rate calculation, is hardly feasible in the vast majority of cases, there are a number of

reasons for going beyond the first step whenever possible.

First of all, by virtue of the paradox of surface kinetics, there is no theoretical reason against the use of classical ideal kinetics provided its limitations are kept in mind.

Second, an assumed reaction mechanism, even without adequate and independent substantiation, may and often does lead to some understanding and control of reaction conditions and catalyst behavior. It may in particular suggest novel experiments, as any theoretical framework should do. *It would appear regrettable if investigators confined themselves to the first step of the procedure, because they believed that any higher approximation, short of considering in detail all the complexities of real surface kinetics, is illegitimate and objectionable.*

Third, a set of kinetic adsorption constants determined according to the rules of classical kinetics for a variety of reactants on a given catalyst or a given reactant on a series of catalysts, may lead to useful predictions as to the behavior of new systems. The usefulness of such a systematic approach is clearly demonstrated by the work of Jungers and his collaborators (8). Such a systematization is impossible with empirical rate laws as used in the first step. Adsorption kinetic constants may lead to practical correlations and as such are of interest to the practical worker in the field of applied catalysis, whatever may be the ultimate theoretical interpretation.

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