

Analysis of Kinetic Data for Heterogeneous Reactions

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The chemical engineer frequently has to correlate kinetic data for heterogeneous reactions simply and accurately in order to make useful predictions of reaction rates over a range of conditions. The Langmuir-Hinshelwood approach, which is frequently used for this purpose, does not have the theoretical validity commonly attributed to it, and its use leads to unnecessary mathematical complexity. A simpler method of analysis is suggested which is based on power dependencies of the rate on concentrations, the powers being restricted to integral or half-integral values. The data for several reactions are shown to be adequately correlated by the suggested procedure, which is simple and convenient.

During the last decade it has become increasingly popular for chemical engineers to analyze the kinetic data for complicated solid-catalyzed gas reactions in terms of the extended Langmuir-Hinshelwood theory (8, 21). This approach may be illustrated by a sample case:

The gas reaction $A + B \rightarrow C$ is catalyzed by a solid, and the reaction is not limited by mass or heat transfer. If it is assumed that a bimolecular surface reaction of A and B is rate controlling and that A , B , and C are adsorbed on the catalyst without dissociation, then the reaction rate is written

$$\text{rate} = \frac{kp_A p_B}{(1 + K_A p_A + K_B p_B + K_C p_C)^2} \quad (1)$$

the K 's being (unknown) adsorption coefficients characteristic of the individual gas. Other assumed mechanisms result in different equations, and the occurrence of a better fit of the data to one equation than to another is frequently employed as a sufficient criterion of the reaction mechanism.

A large body of evidence exists which indicates that the use of these equations is unjustified, both theoretically and experimentally. Furthermore, their use has two unfortunate consequences: (1) because of the mathematical complexity of the differential rate expression, it is often very inconvenient to obtain the integral rate equation and to evaluate the numerous adjustable parameters, and (2) the unwary investigator is often led to believe that he has uniquely deduced the mechanism of the reaction.

The validity of the Langmuir adsorption isotherm has been considered in detail elsewhere, and only a few of the difficulties will be mentioned here. One of the primary assumptions underlying the theory is that no interaction occurs between adsorbed molecules, which implies that the heat of adsorption should be a constant, independent of the amount of gas adsorbed. Even for physical

adsorption, this condition is satisfied in practice only in extremely rare instances (14); in general, the heat of adsorption is observed to be a sensitive function of the amount adsorbed. With regard to chemisorption, which presumably is involved in heterogeneous reactions, the author knows of no reported case for which the heat has been shown to be independent of the amount adsorbed.

Another serious difficulty arises in the practical application of the Langmuir isotherm to the adsorption of a mixture of gases. The Langmuir equation predicts that the addition to one gas of a second gas will always decrease the amount of the first gas adsorbed. Numerous cases of physical adsorption are known in which exactly the opposite behavior obtains, i.e., where the second gas increases the adsorption of the first gas (3). Very few data are available on chemisorption from gas mixtures, but recently Sastri and his coworkers have reported some excellent studies of chemisorption of hydrogen-nitrogen mixtures on iron synthetic ammonia catalysts and of hydrogen-carbon monoxide mixtures on cobalt Fischer-Tropsch catalysts (17 and 6). In both systems marked enhancement of adsorption of a gas from mixtures, over that of the pure gas at the same partial pressure was observed under certain conditions. Presumably this behavior arises from an attractive interaction between adsorbed molecules of the two constituents, an effect disregarded in the simple Langmuir theory. Adsorption of this sort corresponds mathematically to having a negative adsorption coefficient in the denominator of the extended Langmuir equation; for example, when the adsorption of A is increased in the presence of B , the amount of A adsorbed is given by an expression of the form

$$A_{ads} = \frac{kp_A}{1 + K_A p_A - K_B p_B} \quad (2)$$

In the usual application of the Langmuir-Hinshelwood approach this (experimental) result is considered to be physically impossible, and any reaction mechanism which leads to a negative adsorption coefficient is automatically discarded.

Because of difficulties of this sort, there appears to be no theoretical justification for applying the extended Langmuir equation to the kinetics of complex heterogeneous reactions. For real reactions, equations similar to (1) can be considered only as empirical relations which may or may not be useful for correlating data. Great danger exists that the form of such an empirical rate equation is accepted so literally that absolute conclusions about mechanism are deduced from what is really empirical data fitting. When one considers that the foremost investigators in the field of reaction kinetics still completely disagree on the mechanism of so simple a reaction as the ortho-parahydrogen conversion over evaporated metal films (16 and 4), it is naive to think that one can prove the mechanism of a complex reaction by, for example, obtaining a better fit to rate data with a square, rather than a first-power, term in the denominator of an expression such as Equation (1).

The principal utility of the Langmuir-Hinshelwood approach for real reactions is qualitative rather than quantitative. Most, if not all, gas-solid and solid-catalyzed gas reactions do involve reaction by chemisorbed gas species, and the limiting cases of the Langmuir isotherm are most helpful in furnishing a qualitative picture of the surface coverage. For a single reactant, for example, when the rate depends only on the first power of the reactant gas pressure, it is a reasonable conclusion that the reactant is only slightly adsorbed; when the rate is almost independent of reactant gas pressure, it is probable that adsorption is almost complete and that most available adsorption sites are occupied. Similarly, in the

TABLE 1. OXIDATION OF SULFUR DIOXIDE

Run	Eq. (4) Ref. 20		Eq. (5)	
	<i>k</i> rel.	% Dev.	<i>k</i> rel.	% Dev.
3	25.00	24.8	0.191	37.0
4	15.46	22.8	0.250	17.5
5	16.31	18.6	0.280	7.6
6	18.30	8.7	0.304	0.3
7	16.52	17.6	0.302	0.3
8	20.61	2.8	0.347	14.5
9	24.63	22.9	0.334	10.2
10	15.83	21.0	0.285	5.9
11	19.30	3.7	0.321	5.9
12	20.68	3.2	0.270	10.9
13	23.87	19.1	0.339	11.9
14	23.95	19.5	0.417	37.6
Average	20.04	15.4	0.303	13.3

case of two reactants if the rate is directly proportional to the pressure of one and inversely proportional to the pressure of the second, the reasonable qualitative conclusion is that the second reactant is very strongly adsorbed, to the detriment of the first reactant. All these results may be deduced from the limiting forms of the isotherms (7).

Unfortunately, the use of the extended Langmuir-Hinshelwood expressions to obtain this sort of qualitative information is frequently a costly procedure for the chemical engineer from the standpoint of unnecessary complication. The principal job confronting the chemical engineer who has to handle kinetic data is to correlate the data in such a way that useful predictions about reaction rates may be made for a range of conditions. Incidental information which can be deduced about reaction mechanism may be useful, but it is of secondary importance. As the earlier discussion has shown, there is no real justification for using the Langmuir-Hinshelwood expressions as the correlating rate equations. It would seem reasonable, rather, for the engineer to employ the simplest possible rate equation which will adequately fit the experimental data. The following expression for rate equations is suggested as being among the simplest forms having sufficient generality:

$$\text{rate} = k(P_A)^m(P_B)^n(P_C)^o \cdots \quad (3)$$

where *A* and *B* might be reactants, *C* a product or a foreign gas, etc., and the exponents *m*, *n*, *o* are parameters having either integral or half-integral values. In practice, one or more of the exponents will frequently be found to be zero.

The exponents in Equation (3) are simply the apparent orders of the reaction with respect to the individual components. Not only does this feature furnish easy comprehension of the pressure dependencies to the nonspecialist in kinetics; it also permits the exponents to be determined by the conventional schemes for finding reaction orders (e.g., by changing the pressure of one reactant at a time). The restriction to integral or half-integral values is made for simplicity,

but unless the experimental data cover an unusually wide range of conditions or are of unusual precision, this restriction does not prevent adequate correlation of the data. Furthermore, it appears that over a reasonable temperature range the values of the exponents are *independent of temperature*, and so only the temperature dependence of the specific rate constant need be considered. This is a real convenience in treating nonisothermal reactors, as it reduces the number of parameters which have to be determined as a function of temperature.

The utility of this approach is perhaps best illustrated by consideration of a few examples. The platinum-catalyzed oxidation of sulfur dioxide may be considered first. Lewis and Ries (10) studied this reaction in a flow system under conditions that kept the volume change during the reaction negligible. The Lewis-Ries data have been analyzed by Ueyehara and Watson according to the Langmuir-Hinshelwood procedure (20), and the differential rate equation that they deduced is of the form

$$\text{rate} = \frac{k}{(1 + \sqrt{p_{O_2}K_{O_2}} + p_{SO_2}K_{SO_2})^2} \cdot \left(p_{SO_2}\sqrt{p_{O_2}} - \frac{p_{SO_2}}{K} \right) \quad (4)$$

The square roots arise because the limiting surface reaction is assumed to be between an adsorbed sulfur dioxide molecule and an adsorbed oxygen atom; the term p_{SO_2}/K arises from consideration of the reverse reaction, *K* being the equilibrium constant. The critical series of experiments carried out by Lewis and Ries (series C) was a group made at constant temperature, pressure, space velocity, and (approximately) oxygen pressure, but at varying inlet sulfur dioxide and sulfur trioxide concentrations. Columns 2 and 3 in Table 1 show the relative values of the rate constant, *k*, and of the percentage of deviation calculated by Ueyehara and Watson from Equation (4) for each of the last twelve experiments in this series.

An alternate analysis has been made of the same data along the lines suggested by Equation (3). The differential rate expression used is

$$\text{rate} = k \left(\frac{p_{SO_2}}{\sqrt{p_{SO_2}}} - \frac{1}{K} \frac{\sqrt{p_{SO_2}}}{\sqrt{p_{O_2}}} \right) \quad (5)$$

The form of Equation (5) was suggested by data available in the literature; it was the first equation tested in this work, and in view of its successful application other possible equations were not investigated. The first term represents the rate of the forward reaction. It is identical with the equation found applicable to the forward reaction in the classical work of Bodenstein and Fink (2). The absence of oxygen pressure from this term is indicated both by Bodenstein and Fink and by Lewis and Ries. The second term, relating to the reverse reaction, was chosen as the simplest form which, in view of the choice of forward rate expression, would give the correct equilibrium relationship. [This is not the most general function which satisfies the equilibrium relation (11).]

In these experiments p_{O_2} was essentially constant (17.5 to 20.9%). If p_{O_2} is assumed constant, as was done also by Ueyehara and Watson, Equation (5) may be integrated in a straightforward way, and a value of *k* for each of the experiments may be determined from the integral expression*. A value of 194 was used for the equilibrium constant at 425°C. (9).

Columns 4 and 5 of Table 1 contain the values of the rate constant, in arbitrary units, and of the percentage of deviation calculated in this way. It is clear that the data are fitted by Equation (5) at least as well as by Equation (4); the average deviations are 13.3 and 15.4%, respectively. On the other hand, Equation (5) is clearly simpler and more tractable than Equation (4).

As a second example, the data of Tschernitz, Bornstein, Beckmann, and Hougen (19) on the hydrogenation of codimer may be considered. Three series of experiments, at 200°, 275°, and 325°C., were carried out with a differential reactor. The data were fitted by an equation of the form

$$\text{rate} = \frac{k}{(1 + K_H p_H + K_U p_U + K_S p_S)^2} p_H p_U \quad (6)$$

where p_H , p_U , and p_S are the partial pressures of hydrogen, codimer, and hydrogenated codimer, respectively, and *k*, K_H , K_U , and K_S are temperature-dependent parameters. From the rates calculated by Tschernitz, et al., it is possible to compute the average percent-

*Ueyehara and Watson treated the reactor as a differential reactor. This procedure is not valid for several of the experiments in which large fractional changes occurred in the concentrations of sulfur dioxide and sulfur trioxide.

age deviation of the specific rate constant k for each series of experiments; these values are shown in column 2 of Table 2.

TABLE 2. HYDROGENATION OF CODIMER

Temp., °C.	Eq. (6), avg. % dev.	Eq. (9), k	Eq. (9), avg. % dev.
200	20.9	0.0201	19.6
275	19.6	0.0270	32.9
325	19.4	0.0207	21.4

An alternate treatment of the same experimental data was carried out on the basis of the following equation [cf. Equation (3)]:

$$\text{rate} = kp_U^m p_H^n p_S^o \quad (7)$$

A plot of rate/ $p_U p_H$ (taken as a first approximation to the rate constant) vs. p_S showed that no systematic variation occurred as a function of p_S . This suggested a zero-order dependence on p_S —not a surprising conclusion in view of the known fact that hydrogen and olefins are much more strongly adsorbed by metals than are paraffins. Accordingly, Equation (7) was simplified to

$$\text{rate} = kp_U^m p_H^n \quad (8)$$

Least-squares treatment of the data at each temperature gave the following "best values" for k , m , and n :

Temp., °C.	k	m	n
200	0.0208	0.546	0.583
275	0.0282	0.544	0.730
325	0.0230	0.510	0.772

As m and n are to be restricted to integral or half-integral values (see above), m and n were both taken as $\frac{1}{2}$, independent of temperature. Equation (8) then became

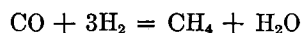
$$\text{rate} = kp_U^{1/2} p_H^{1/2} \quad (9)$$

Average values of k and the average percentage of deviation of k were computed for each temperature (columns 3 and 4 of Table 2). Although the fit of the data by Equation (9) is slightly poorer than by Equation (6), the adequacy of the former is sufficient for engineering purposes. The simplicity of Equation (9) in comparison with Equation (6) is apparent.

The maximum at 275° in the computed values of k (Table 2) is not an artifact. It occurs also in the experimental values of the rate constant of Tschernitz, et al. (their $E_k = 0.580, 0.910$, and 0.895 at 200°, 275°, and 325°, respectively), and it is suppressed only when the data are artificially smoothed to fit an assumed Arrhenius dependence. The occurrence of such a maximum as a function of temperature has been reported by both Rideal (15) and zur Strassen (22) for

the hydrogenation of ethylene over nickel and by Maxted and Moon (12) for the liquid-phase hydrogenation of crotonic and maleic acids over platinum.

Akers and White (1) studied the kinetics of the reaction



over a nickel-kieselguhr catalyst; their results may be considered as a third example. On the basis of the assumption that the rate-controlling step in methane formation is the surface reaction between three adsorbed hydrogen molecules and one adsorbed carbon monoxide molecule, they correlated the rate data by the equation

$$\text{rate} = \frac{p_{\text{CO}} p_{\text{H}_2}^3}{(A + B p_{\text{CO}} + D p_{\text{CO}_2} + E p_{\text{CH}_4})^4} \quad (10)$$

(Carbon dioxide, formed as a by-product, was assumed to be appreciably adsorbed, and carbon dioxide pressure therefore enters into the "adsorption denominator.")

Inspection of the initial reaction rates (Table 7 of Akers and White) makes it clear that, when the partial pressures of the products are zero, the rates are consistent with an expression of the form

$$\text{rate} = kp_{\text{CO}} p_{\text{H}_2}^{1/2} \quad (11)$$

It further appears that this same rate expression is capable of correlating all the rate data, including those in the presence of water, methane, and carbon dioxide, with about the same accuracy as Equation (10). For example, for series 100 of Akers and White (seven values at each of the temperatures 310°, 325°, and 340°C.), the rates may be computed from Equation (11) with an average deviation of 13 to 14%, values of k of 0.299, 0.431, and 0.444 being used at 310°, 325°, and 340°C., respectively. These data cover a fivefold range in carbon monoxide pressure and a tenfold range in hydrogen pressure, with corresponding variations in the pressures of the product gases. It thus appears that in this work the rate is substantially independent of the pressures of methane, water, and carbon dioxide and that a rate expression containing four adjustable constants at each temperature may be adequately replaced by one having only a single constant.

As a final example, one may consider the formation of phosgene from carbon monoxide and chlorine over charcoal, which was studied by Potter and Baron (13). It was concluded in this work that the controlling mechanism was a surface reaction between adsorbed carbon monoxide and chlorine, and that the data were correlated by the rate expression

$$\text{rate} = \frac{k K_{\text{CO}} K_{\text{Cl}_2} p_{\text{CO}} p_{\text{Cl}_2}}{[1 + K_{\text{Cl}_2} p_{\text{Cl}_2} + K_{\text{COCl}_2} p_{\text{COCl}_2}]^2} \quad (12)$$

The second column of Table 3, which contains the average percentage of deviations of the calculated rates at each of the four temperatures studied, shows the excellent fit of the data obtained by this method.

TABLE 3. PHOSGENE SYNTHESIS FROM CARBON MONOXIDE AND CHLORINE

Temp., °C.	Eq. (12), avg. % dev.	Eq. (13), k	Eq. (13), avg. % dev.
30.6	3.4	15.8	13.0
42.7	5.6	37.5	9.1
52.5	2.6	64.8	13.9
64.0	7.0	104.4	3.0

It again became clear from a preliminary inspection of the data that a reasonable fit could also be obtained at all temperatures by the following expression, of the same general form as Equation (3):

$$\text{rate} = kp_{\text{CO}} p_{\text{Cl}_2}^{1/2} \quad (13)$$

Columns 3 and 4 of Table 3 show the average values and the average percentage of deviations of the rate constants computed with the use of Equation (13). Although the average percentage of deviation with Equation (13) is about double that with Equation (12), it is still within acceptable limits; moreover, this is accomplished with the use of one adjustable constant (k) at each temperature, as compared with three adjustable constants ($k K_{\text{CO}}$, K_{Cl_2} , and K_{COCl_2}) for Equation (13).

It is relevant to note that Potter and Baron found that the addition of nitrogen to the reaction mixture increased the apparent adsorption of chlorine and phosgene. As they also point out, this behavior is incompatible with the Langmuir assumptions. (See above.)

Additional examples can be adduced from the literature in support of rate equations of the form of Equation (3). One well-known case is that of ammonia synthesis (5), for which the rate can be expressed as

$$\text{rate} = k_f \frac{P_{\text{N}_2} P_{\text{H}_2}^{1.5}}{P_{\text{NH}_3}} - k_b \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{1.5}} \quad (14)$$

It is significant that the deduction, now generally accepted, of the rate equation for this reaction by Temkin and Pyzhev (18) does not follow from any elementary application of the Langmuir-Hinshelwood approach.

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R. W. Houston has pointed out to the author that the data of Wan [Ind. Eng. Chem., 45, 234 (1953)] on ethylene oxidation are much better fitted by Wan's empirical rate equation, which employs simple power dependencies, than by any formulation based on a Langmuir-Hinshelwood mechanism.

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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 quasideal 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, SbH_3 , 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

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

with $n = 0.6$. In this expression p is the partial pressure of SbH_3 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:

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

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

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

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:

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