Homogeneous versus Heterogeneous Rate Equations for Catalytic Reactions

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For the correlation of heterogeneous catalytic reaction rate data two types of rate equations are commonly used: heterogeneous, obtained by the Langmuir-Hinshelwood model, and homogeneous, which regularly occur in single phase reaction systems. This communication considers the preferability of one form of rate equation to the other for a specific solid catalyzed vapor phase reaction.

Kabel and Johanson (*1*) studied the dehydration of ethanol to diethyl ether, as catalyzed by cation exchange resin in the acid form:

$$2C_2H_5OH = H_2O + C_2H_5OC_2H_5 \qquad (1)$$

Initial reaction rate data, determined from the integral kinetic data obtained experimentally, allowed selection of the most suitable rate equation from several plausible equations derived in accordance with the Langmuir-Hinshelwood model. The selected rate equation corresponded to a dual site mechanism with the surface reaction as the rate controlling step.

Lapidus and Peterson (*2*) selected the data of Kabel and Johanson to illustrate their nonlinear estimation method for the analysis of heterogeneous catalytic reactions. They reached two main conclusions with regard to that reaction system: (1) a homogeneous type rate model is as probable for describing the reaction as are the heterogeneous models, and (2) when only heterogeneous models are used, it is still impossible to conclude that any one model is more suitable than another unless external information is also considered. Kittrell, Mezaki, and Watson (*3*) provide excellent perspective on the various methods for parameter estimation, including the nonlinear estimation technique of Lapidus and Peterson (*2*) and the familiar method of model linearization which was used by Kabel and Johanson (*1*). More recently Peterson and Lapidus (*4*) have reiterated these conclusions with the additional speculation that the lack of discrimination among models in this case might be attributed to the absence of data at a variety of total pressures. It is true that such data should enhance discrimination. However, it is the contention here that the first conclusion was reached as a result of inadequate analysis of the available data rather than inadequate data available for analysis. The second conclusion will not be considered since it is a subject of current study in a number of laboratories and will probably be reported on later in a definitive treatment.

In interpreting the data analysis presented by Lapidus and Peterson (*2*) it is helpful to study the preprint of their original work (*5*). It is clear that they analyzed more data than are presented in the published article, and a more through explanation of their method of selection is found in the earlier version. In carrying out statistical tests for internal consistency of the data, they observed that the data obtained with pure ethanol feed were more reliable than data for mixed feeds, and that the last two pure ethanol runs were more reliable than the first two. Also they concluded that the runs with large amounts of ethyl ether present were less reliable than the two runs in which ether was present in the smallest amount. There is no explanation given as to why data from only one of the four runs with ethanol-water feed mixtures were considered. Possibly the remaining runs were also ruled out by the internal consistency criterion. In any case the authors emphasized the more reliable data in their subsequent statistical analyses. It should be noted that the above statisical observations of degree of data reliability are consistent with the experimental facts.

The first two pure alcohol runs were less reliable than later runs because the experimental technique was not fully refined. Large amounts of ethyl ether in the feed made reproducibility in sampling more difficult. Moderate amounts of water in the feed suppressed the reaction so that accurate product analysis became more difficult. Although Lapidus and Peterson arrived at the correct interpretation regarding the reliability of the data, it appears that they did not use certain less reliable data, which might have been quite effective in model discrimination. Still their approach might well have succeeded had they not been sabotaged by the degeneracy condition to be discussed later.

From the notation of Lapidus and Peterson the reaction in symbolic form is

$$2A = B + C \qquad (2)$$

The rate equations for the surface-reaction–controlling models may be written

$$r = \frac{k[A^2 - (BC/K_{\text{equil}})]}{[1 + K_A A + K_B B]^{\beta}} \qquad (3)$$

and the homogeneous form of Equation (3) would be

$$r = k[A^2 - (BC/K_{\text{equil}})] \qquad (4)$$

An additive term, $K_C C$, has been omitted from the denominator of Equation (3) since K_C was taken to be zero (*1*). Other homogeneous forms with different exponents on the concentration terms would be possible, but Equation (4) is the simplest form and the one selected by Lapidus and Peterson for analysis. Inspection of Equation (4) suggests that variations in the concentrations of ethyl ether and water should both affect the rate of reaction in the same way. On the contrary for $\beta > 0$ Equation (3) suggests that water B will suppress the rate of reaction more strongly than ethyl ether. To investigate the relative effects of ether and water, the most direct approach is to independently vary the concentrations of each. This was done by Kabel and Johanson and the results are shown in Figure 4 of their paper (*1*). For a 60 mole % ether–40 mole % alcohol mixture the initial rate of reaction was seven times higher than for a 60-40 mole % mixture of water and alcohol. With only 25% ether in the feed the initial rate is still double that for a feed containing 25% water. The same effect is seen by comparing the integral conversion data obtained at a given flow rate for ether-alcohol and water-alcohol feeds of the same concentration. The homogeneous rate equation can not account for this and therefore is inadequate for the description of this reaction system. By contrast, Equation (3) with $\beta = 2$ is quite successful in accounting for this effect.

Since Lapidus and Peterson were working with integral data, they too had varying water, ether, and alcohol concentrations by virtue of the effect of flow rate on extent of reaction. For any given feed mixture, however, these concentrations are not independent, and knowledge of any one enables the calculation of the others. Were it not for the freakish degeneracy of the denominator of Equation (3), integral data for pure alcohol feed should have allowed discrimination between Equations (3) and (4). This degeneracy, first noted by Lapidus and Peterson, occurs if $K_B = 2K_A$. Closely approximating this condition were $K_A = 3.4$ and $K_B = 7.0$, Kabel and Johanson's values for the ethanol dehydration reaction. For a pure alcohol feed a material balance combined with the stoichiometry of the reaction gives $B = (1 - A)/2$. The evolution of the degeneracy is illustrated by Equation (5), in which the denominator of Equation (3) becomes

$$[1 + K_A A + K_B B]^\beta$$

$$= \left[1 + K_A A + 2K_A \left(\frac{1-A}{2}\right)\right]^\beta = [1 + K_A]^\beta \quad (5)$$

Thus the denominator of Equation (3) becomes a constant, and the heterogeneous equation becomes indistinguishable from the homogeneous form on the basis of this single experiment. If a feed equimolar in alcohol A and water B with no ether is chosen, the material balance becomes $B = (1.5 - A)/2$. In this case the denominator of Equation (3) becomes $[1 + 1.5\,K_A]^\beta$. For an equimolar feed of ether and alcohol, with no water present, the material balance is $B = (0.5 - A)/2$ and the denominator of Equation (3) is $[1 + 0.5\,K_A]^\beta$. Thus for any given feed mixture the denominator of the heterogeneous rate equation becomes constant and a homogeneous form may be used. Nevertheless, the coefficient of the homogeneous equation (the apparent reaction velocity constant) will be a function of feed composition. If this coefficient is to be a function of temperature only, or if the equation is to be applied to systems with feeds different from that for which the coefficient was determined, the heterogeneous form of rate equation must be used.

Analysis of Data Set G in Table 3-IV of Lapidus and Peterson's paper (*2*) should have exposed this circumstance since water-alcohol and ether-alcohol feed mixtures were considered. There appears to be an inadequacy in the computation or the logic since the standard deviation of residuals is higher for Equation (3) fitted to the data than for Equation (4). If k, K_A, K_B of Equation (3) are determined from Data Set G, Equation (3) should do no worse than Equation (4) since for the special case of $K_A = K_B = 0$ the two equations are identical.

In the context of disciplined use of the Langmuir-Hinshelwood model, one more comment on the Lapidus and Peterson paper should be made. If the model is to have any theoretical significance the thermodynamic equilibrium constant, K_{equil}, should not have been treated as a parameter to be estimated. For the reaction of interest here its value is accurately known (*6*, *7*). Even at the highest conversions, the kinetic data available are too far removed from the reaction equilibrium position to allow a meaningful estimate of the equilibrium constant. That is, the rate of the reverse reaction is less than 3% of the forward rate even at a 30% conversion of a pure alcohol feed. To use any value other than 25.2 for K_{equil} at 120°C. would result in a thermodynamically inconsistent rate equation. Such an equation would have little promise for predicting rates beyond the range of its data, and would not be expected to predict the rate of reaction between water and ethyl ether in the absence of ethanol.

CONCLUSIONS

Lapidus and Peterson have put forth a nonlinear estimation technique which should be of real value in analyzing kinetic data. In the case of ethanol dehydration their statistical analysis failed to discriminate between models for which discrimination can be made by inspection. Peterson and Lapidus (*4*) have also applied their method to another reaction system, the catalytic dehydrogenation of ethanol, where they found Langmuir-Hinshelwood kinetics to be superior to homogeneous kinetics. They attributed their success in this latter case to the availability of data at varying total pressures, as well as feed compositions and space velocities. In the former case data were available at one pressure only. Nevertheless, on the basis of the arguments presented earlier in this article, it is believed that adequate kinetic data were available for discrimination between homogeneous and heterogeneous rate equations, and that somehow full use of them was not made in the statistical analysis.

Boudart (*8*) has shown that certain approximations make possible the mathematical reduction of a heterogeneous form of a rate equation to a homogeneous form. He has illustrated this by deriving a rate equation according to Langmuir-Hinshelwood kinetics for the catalytic synthesis of ammonia; then reducing it to the well known Temkin and Pyzhev equation, which is of homogeneous form. Lapidus and Peterson (*2*) have brought out the denominator degeneracy condition which also enables a heterogeneous rate equation to be reduced to a homogeneous form. Alertness to this possibility could enable reactor designers to significantly reduce the mathematical complexity of their calculations in certain circumstances. Similar benefits could occur in control applications. The possibility of a degeneracy condition might also be contemplated by investigators who arrive at an apparently adequate homogeneous rate equation. Before being accepted and extrapolated, such an equation should be validated by experimental data which are adequate in number and kind.

NOTATION

A, B, C = partial pressures of ethanol, water, and ethyl ether, respectively, atm. (total pressure = 1 atm.)
k = grouped constants in the kinetic term of the heterogeneous rate equation; apparent reaction velocity constant in homogeneous rate equation
K_A, K_B, K_C = Langmuir equilibrium adsorption constants, atm.$^{-1}$
K_{equil} = thermodynamic equilibrium constant
r = rate of reaction of ethanol
β = exponent on denominator of heterogeneous rate equation

LITERATURE CITED

1. Kabel, R. L., and L. N. Johanson, *AIChE J.*, **8**, 621 (1962).
2. Lapidus, Leon, and T. I. Peterson, *ibid.*, **11**, 891 (1965).
3. Kittrell, J. R., Reiji Mezaki, and C. C. Watson, *Ind. Eng. Chem.*, **57**, 18 (1965).
4. Peterson, T. I., and Leon Lapidus, *Chem. Eng. Sci.*, **21**, 655 (1966).
5. ———, *Preprint 18c*, 57th Annual AIChE Meeting, Boston, Mass. (1964).
6. Kabel, R. L., and L. N. Johanson, *J. Chem. Eng. Data*, **6**, 496 (1961).
7. Hawes, R. W., and R. L. Kabel, *AIChE J.*, to be published.
8. Boudart, Michel, *ibid.*, **2**, 62 (1956).