temperature at which a specified per cent is distilled, blends linearly; and the solid line was calculated by Equation 1, where $a_{1i} \neq 0$ and $a_{ki} = 0$ for $k > 1$. A second result, typical of the ternary system, is shown in Figure 2, where the open circles are experimental data, the dotted curve is the linear approximation, the broken curve was obtained by Equation 1 where $a_{1i} \neq 0$ and $a_{ki} = 0$ for $k > 1$, and the solid curve was calculated also by Equation 1, where $a_{1i} \neq 0$, $a_{2i} \neq 0$, and $a_{ki} = 0$ for $k > 2$. The results illustrate not only the ability of Equation 1 to predict the distillation curves accurately, but also the unrealistic behavior of the curves based on the assumption of linear additivity. Similar results were obtained for 15 ternary and 20 ten-component blends. The procedure was found fully satisfactory for the octane rating of gasoline blends and the viscosity of multicomponent oil blends.

In the programming of blending problems, when y is prescribed and x_i's are unknown, Equation 1 represents the linear approximation of the nonlinear constraint, $y = f(x_i)$, where f denotes some unknown nonlinear function.

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SCREENING OF PRODUCT INHIBITION EFFECTS BY TRANSIENT RESPONSE TECHNIQUES

The shapes of response curves to step perturbation of feed concentration provide a rapid method for screening adsorption behavior in surface reaction. Relative magnitudes of adsorption equilibrium constants and, in some instances, adsorption rate constants, for reaction products can be identified from the measurement of such responses. The method is demonstrated for an example based on published data for the dehydration of ethanol on Dowex-50.

CHEMISORPTION is an intrinsic part of catalysis, and sorption rates and equilibria for reactants and products are invaluable for gaining insight into details of reaction mechanisms. It is important to recognize that the pertinent rates and equilibria are those which exist under conditions of reaction, a complication of considerable magnitude as far as their experimental determination is concerned. The great amount of literature on adsorption and reaction on solid surfaces provides only rare examples in which both have been studied on the same catalyst, and even rarer examples of combined studies under reaction conditions.

Even simplest theory tells us that adsorption-desorption rates and equilibria for a given material are strongly affected by total surface coverage and the presence and nature of other species chemisorbed. In one of the earliest studies of adsorption rates during the course of reaction, Tamaru (1958) found that for ammonia synthesis with an iron catalyst, the rate of nitrogen adsorption was substantially accelerated by the presence of hydrogen. Thus, independent adsorption studies of reaction components

carried out with separate measurement of reaction kinetics can be very misleading; the proper experiment is conducted under conditions of surface reaction (Tamaru, 1961, 1962, 1964, 1965).

One means of doing such experimentation is making measurements under unsteady or transient conditions. If a steady-state experiment gives enough information to determine one constant appropriate to a postulated reaction model, the combination of the unsteady experiment will allow either determining two constants of the reaction model, or determining one constant plus testing the consistency of the model. The use of transient or unsteady-state techniques in catalysis research, at least qualitatively, is not new. The microcatalytic technique was first reported by Emmett and coworkers (Kokes et al., 1955), and Hall and coworkers (Hall and Emmett, 1957; Hall et al., 1960) subsequently applied this method extensively, developing a number of useful modifications. Considerable effort also has been devoted to the quantitative analysis of microcatalytic results (Bassett and Habgood, 1960; Gaziev et al., 1963; Magee, 1963; Saito et al., 1965), but the utility of these methods is generally limited to simple reaction systems.

Other types of response experiments—frequency response to a periodic imput or transient response to a step function input—are also potential unsteady-state

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methods but have been considered in detail only recently. Frequency response data appear to be as formidable in analysis as the microcatalytic pulse response data (Crider and Foss, 1966; Leder and Butt, 1966) and the experimental technique required is not simple; on the other hand, step function response appears to have real promise for detailed study of complex catalytic reactions. Lehr et al. (1968) report a recent study of ethanol dehydration catalyzed by a cation exchange resin in which the system response (reactant concentration and product distribution) to step changes in total flow rate through the reactor was determined. While this is an interesting approach, we feel the experiment using flow rate changes is ultimately limited in application, since with fast reactions or reactions with significant heat generation one could easily become involved with changing boundary layer effects which would obscure the reaction kinetics. Feed concentration forcing, however, is relatively simple experimentally and avoids such problems; accordingly, this study presents some idea of what can be learned through concentration forcing. Particular attention is given to what information can be determined concerning the adsorption and desorption behavior of reactants and products on the catalytic surface.

System for Simulation

In the absence of direct experimental results on response to concentration forcing, it is desirable to simulate a system for which kinetic parameters are available. The obvious choice in this case is the dehydration of ethanol on Dowex-50, used by Lehr et al. in their flow response studies. The reaction is selective for ether formation:

$$2C_2H_5OH \rightleftarrows C_2H_5OC_2H_5 + H_2O \qquad (1)$$
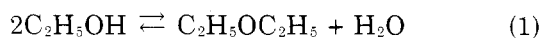
and the best-fit steady-state rate equation is reported to be a Langmuir-Hinshelwood form for reaction between two adjacently adsorbed ethanol molecules. Ether is weakly and water relatively strongly adsorbed by the resin.

We have pointed out above how an extraneous effect, changing boundary layer resistance, might foul up the interpretation of one type of response experiment. Accordingly, in the reactor simulation all such confounding effects must be included in the calculation or (much preferable, if possible) excluded from the experimentation. In the experiments which prompted this study, Lehr et al. demonstrated the absence of all such factors as mass or energy transport limits, nonideal flows, etc., with which the reaction analyst is familiar, so that experimental analysis could be carried out in terms of an isothermal, one-dimensional plug-flow reactor simulation. The following, then, may be written for the unsteady-state material balances of reaction components on the catalyst:

$$L \frac{\partial \theta_A}{\partial t} = (\kappa_A P_A \theta_V - \kappa_{-A} \theta_A) - r_A \qquad (2)$$

$$L \frac{\partial \theta_W}{\partial t} = (\kappa_W P_W \theta_V - \kappa_{-W} \theta_W) + \tfrac{1}{2} r_A \qquad (3)$$

$$L \frac{\partial \theta_E}{\partial t} = (\kappa_E P_E \theta_V - K_{-E} \theta_E) + \tfrac{1}{2} r_A \qquad (4)$$

and

$$r_A = k_A \theta_A{}^2 - k_{-A} \theta_W \theta_E \qquad (5)$$

$$\theta_A + \theta_E + \theta_W + \theta_V = 1 \qquad (6)$$

For the gas phase, the material balance equations are:

$$\frac{1}{\rho_c RT} \frac{\partial P_A}{\partial t}\bigg|_Z = - \frac{U}{\epsilon RT} \frac{\partial P_A}{\partial Z}\bigg|_t - \frac{1}{\epsilon}$$
$$(\kappa_A P_A \theta_V - \kappa_{-A} \theta_A) \qquad (7)$$

$$\frac{1}{\rho_c RT} \frac{\partial P_W}{\partial t}\bigg|_Z = - \frac{U}{\epsilon RT} \frac{\partial P_W}{\partial Z}\bigg|_t - \frac{1}{\epsilon}$$
$$(\kappa_W P_W \theta_V - \kappa_{-W} \theta_W) \qquad (8)$$

$$\frac{1}{\rho_c RT} \frac{\partial P_E}{\partial t}\bigg|_Z = - \frac{U}{\epsilon RT} \frac{\partial P_E}{\partial Z}\bigg|_t - \frac{1}{\epsilon}$$
$$(\kappa_E P_E \theta_V - \kappa_{-E} \theta_E) \qquad (9)$$

No assumptions regarding adsorption equilibrium are contained in these equations.

In the simulation of response to concentration forcing, a pure ethanol feed is initially introduced into the reactor under isothermal conditions. The appropriate initial and boundary conditions are

$$\theta_V = 1.0 \text{ at } t = 0 \text{ for all } Z$$

$$P_A = 1.0, \ P_E = 0, \ P_W = 0 \text{ at } Z = 0 \text{ for all } t$$

When steady-state conditions are established, the feed concentration is changed in a step from pure ethanol to some specified mixture; the calculations illustrated here set $P_A = 0.5$ atm., $P_E = 0.25$ atm., and $P_W = 0.25$ atm. for $t > 0$. The equations are solved by the method of characteristics to obtain the concentration-time behavior of ether and water at the reactor outlet. The results reported in this paper are computed using the experimental conditions and parameters reported by Lehr et al., as listed in Table I, and the response curves depicted in Figure 1 are thus representative of the real world. In the computations it has been assumed that pertinent constants for the reactant are known, but no data regarding product adsorption or reaction are available. The series of plots in Figure 1 illustrates responses for a number of cases in which the ratios of adsorption equilibrium and adsorption rate constants of the two products have been varied.

The purpose of these numerical experiments is to see if such response data can be used to obtain qualitative or quantitative information on product inhibition if

Table I. Parameters

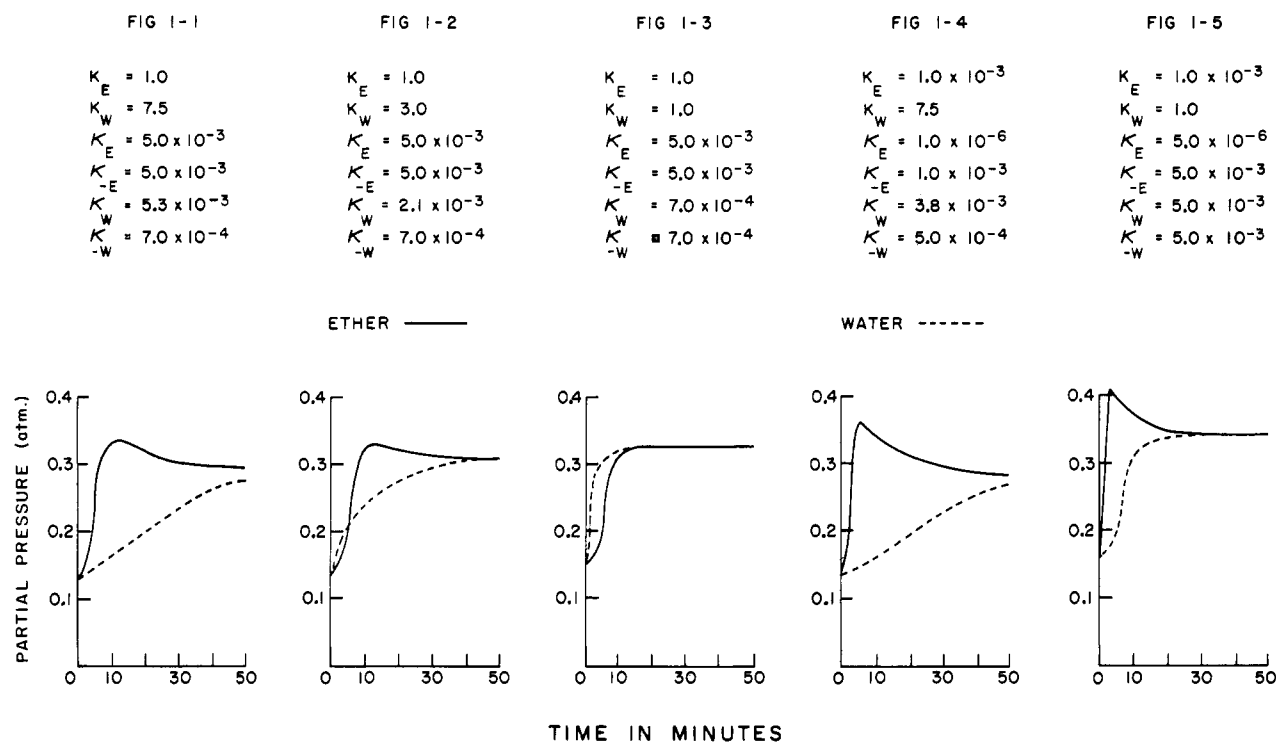|		
K_{eq}	(dimensionless)	25.2
K_A	(atm.$^{-1}$)	4.19
k_A	(moles/min. g. cat.)	2.10×10^{-4}
κ_A	(moles/min. g. cat. atm.)	1.17×10^{-3}
L	(moles/g. cat.)	0.0054
P	(atm.)	1.0
T	(° K.)	393
U	(cm./min.)	30
Z	(cm.)	20
ρ_c	(g. cat./cm.^{3})	0.184
ϵ		0.5

Figure 1. Typical curves of ether and water response to step forcing of reactor inlet concentration

appropriate parameters for the reactant are known—that is, in a rate expression of the form:

$$r_a = \frac{k_A K_A^2 [P_A^2 - (P_W P_E / K_{eq})]}{(1 + K_A P_A + K_W P_W + K_E P_E)^2}$$

can one determine K_W and K_E or their relative magnitudes from such data and might individual rate constants for adsorption and desorption (since $K_W = \kappa_W / \kappa_{-W}$, etc.) be determined in some manner? Either result would be welcome, since one could then determine product inhibition effects from a series of simple initial rate experiments.

The results given in the various parts of Figure 1, representative of typical experiments of this sort, provide definite though qualitative information regarding product adsorption. First, the relative magnitudes of the adsorption equilibrium constants are defined by the nature of the concentration response curves. Those transients involving a sharp change normally exhibiting a maximum point, such as for ether in this simulation, are indicative of a relatively small adsorption equilibrium constant with respect to others in the system. The shorter transit time of these waves through the bed is also an indicator of relatively small adsorption equilibrium constant. The gradual change of water concentration, in many cases resembling a damped second-order response, indicates a longer transit time and relatively large equilibrium constant. The general shapes of concentration responses, which can be related to bed transit times, thus provide reliable means of identifying the relative magnitude of adsorption equilibria under reaction conditions, but do not define quantitative values. Adsorption equilibria of the same or nearly the same magnitude can be clearly identified; here the shapes of the curves are similar, although they may still be displaced in time from each other, as shown in Figure 1-3. The sensitivity of the distinction is a func-

tion of experimental conditions; in the present example when the equilibrium constants differ by a factor of 3, distinct differences are recognized in the responses, while difference by a factor of 1.5 to 2.0 yields responses which would probably be only marginally distinguishable, given the precision of most conversion data. Sensitivity of the method for distinguishing relative magnitudes of adsorption equilibria can be increased by running a number of experiments with larger step changes in feed composition, though such an increase in effort extends the spirit of a simple screening precedure.

This general interpretation of response curves in terms of adsorption equilibria is not limited by the rate law—that is, similar response behavior is found in systems obeying various forms and orders of surface rate equations, so that qualitative interpretation of experimental response data requires no specialized information on kinetics. On the other hand, the method is correspondingly restricted in application to discrimination between mechanistic models.

The results of Figure 1 also indicate an interpretation in terms of sorption rate constants. When the concentration responses to the two components intersect, a system with equilibrium constants of the same order of magnitude (but unequal), is indicated, in which the ratio of adsorption rate constants is in the opposite direction to that of the equilibrium constants (Figure 1-2). This is a result of the dependence of the dispersion of the response curve on adsorption rates; the interpretation suggested cannot be employed when the equilibrium constants differ by more than an order of magnitude, since intersection would be noted only if the rate constant ratio were very large (with reference to an equilibrium constant ratio less than unity). In addition, one must be careful to eliminate effects due to the concentration dependence of adsorption rate by working with equal step changes for both products.

Conclusions

It is possible from the shapes of response curves to step-feed concentration forcing to identify relative magnitudes of adsorption equilibrium constants and, in some instances, adsorption rate constants for product species in complex catalytic reactions. The analysis put forward here is readily extended to multicomponent systems by examining sets of pairs. If independent information is available concerning the values of equilibrium constants, rate constants may be determined from such experiments by fitting computed response curves to the data. The major point, however, is the utility of such response measurements in rapid screening of adsorption behavior under reaction conditions with experiments which can easily be carried out within the framework of normal initial rate studies. The use of this technique clearly can lead to considerable simplification of more detailed studies aimed at quantitative measurement of sorption rates and equilibria.

Acknowledgment

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Nomenclature

k_A = forward surface reaction rate constant, moles/min. g. cat.
k_{-A} = backward surface reaction rate constant, moles/min. g. cat.
K_A, K_E, K_W = adsorption equilibrium constants for ethanol, ether, and water, respectively, atm^{-1}.
K_{eq} = thermodynamic equilibrium constant for dehydration reaction
L = amount of adsorbate adsorbed in a monomolecular layer on catalyst surface, moles/g. cat.
P = total pressure, atm.
P_A, P_E, P_W = partial pressure of ethanol, ether, and water, respectively, atm.
r_A = surface reaction rate of consumption of ethanol, moles/min. g. cat.
R = gas constant, atm.-cc/g.-mole, °K.
t = time, min.
T = reaction temperature, °K.
U = superficial gas velocity, cm./min.
Z = distance along the packed bed reactor, cm.

GREEK LETTERS

ϵ = void fraction of packed bed reactor, dimensionless
$\theta_A, \theta_E, \theta_W$ = fraction of catalyst surface covered by ethanol, ether, and water, dimensionless
θ_V = fraction of vacant catalyst sites, dimensionless
$\kappa_A, \kappa_E, \kappa_W$ = adsorption rate constants for ethanol, ether, and water, respectively, moles, min. g. cat. atm.
$\kappa_{-A}, \kappa_{-E}, \kappa_{-W}$ = desorption rate constants for ethanol, ether, and water, respectively, moles/min. g. cat.
ρ_c = bulk density of catalyst, g. cat./$cm.^3$

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Correction

PREDICTION AND CORRELATION OF PHASE EQUILIBRIA AND THERMAL PROPERTIES WITH THE BWR EQUATION OF STATE

In this article by R. V. Orye [IND. ENG. CHEM. PROCESS DESIGN DEVELOP. **8**, 579 (1969)], the following corrections should be made

Table II. n-C_6, $Q_2 = 0.1985950 + 06$
   CO_2, DCDT $= -17.13000$

Table III. n-C_6, F20 $= 0.308900 - 01$
   N_2, H20 $= -1.73520$
   CO_2, H20 $= 174.89500$

These values differ from those in the article by only one unit in either the least significant or next to least significant digit. The difference between computed values of C_v and $H°$ using these coefficients and those in the article is essentially negligible.