Reaction Kinetics and Adsorption Equilibria in the Vapor-Phase Dehydration of Ethanol

ROBERT L. KABEL and LENNART N. JOHANSON
University of Washington, Seattle, Washington

This work is an experimental assessment of the Langmuir-Hinshelwood model of heterogeneous catalysis. The vapor-phase dehydration of ethanol to diethyl ether, as catalyzed by cation exchange resin in the acid form, was the reaction chosen for study.

Initial reaction rate data, determined from the integral kinetic data obtained experimentally, allowed selection of the most suitable rate equation from among several plausible equations derived in accordance with the above model. The Langmuir equilibrium adsorption constants in the rate equation were compared with the corresponding constants determined directly from pure component studies in a static adsorption system. The adsorption constants determined for the three reacting components by these independent methods showed definite order-of-magnitude agreement. The adsorption studies also provided significant information about the nature of the catalytic site.

The extent of agreement in the constants determined by these two independent approaches is considered to be evidence of the theoretical validity of this model. Additional interpretation of the adsorption and kinetic data via this model suggests that the ethanol dehydration reaction proceeds through the reaction of adjacently adsorbed ethanol molecules.

The Langmuir-Hinshelwood model of heterogeneous catalysis has been widely used by chemical engineers in the correlation of experimental reaction rate data. The model stems directly from the Langmuir theory of activated adsorption (*14*) and the application by Hinshelwood (*8*) of that theory to a large number of reactions. Hougen and Watson (*10*) extended and popularized this theory for chemical engineering use. Rate equations, derived for many situations, were systematized and put into a generalized form by Yang and Hougen (*23*). Although the model has been used quite successfully in the correlation of kinetic data, its theoretical significance has been questioned. This argument has been put into focus in back-to-back articles by Weller (*22*) and Boudart (*1*). Weller suggests that the Langmuir-Hinshelwood approach does not have the theoretical validity commonly attributed to it and that, lacking theoretical validity, it is unnecessarily complex for use as an empirical equation when compared for simplicity to the common power function type of equation. Boudart has supported the rational use of the Langmuir-Hinshelwood approach with his discussion of the limitations and strengths of that theory. Because this model of heterogeneous catalysis has not been adequately tested the direct experimental evaluation presented in this paper has been carried out.

The general approach utilized in this work was to correlate reaction rate data with an equation of the Langmuir-Hinshelwood model, obtaining values of the Langmuir equilibrium adsorption constants for the components of the reaction; and to correlate pure component, static adsorption data by means of the Langmuir isotherm, obtaining independently determined values for the adsorption constants. The equilibrium adsorption constants obtained indirectly from the kinetic studies could then be compared with the corresponding constants obtained directly from the adsorption measurements. This comparison would make possible a partial evaluation of the significance of the Langmuir-Hinshelwood model of heterogeneous catalysis.

The reaction system selected for study was the vapor phase dehydration of ethanol to give diethyl ether and water:

$$2\,C_2H_5OH = C_2H_5OC_2H_5 + H_2O \quad (1)$$

A sulfonated copolymer of styrene and divinylbenzene in the acid form was used as a catalyst. It was believed that the simple form of this catalyst might allow additional insight into the nature of the catalytic site and into the mechanism of the catalytic reaction.

REACTION RATE STUDIES

Catalytic dehydration of ethanol has been the subject of much study in the last half century, although there appears to be no previous work on the vapor-phase reaction in the presence of ion exchange resin. Much of the significant work reviewed by Winfield (*5*) has been with metal oxide catalysts. On alumina above 300°C. ethanol has been found to dehydrate almost exclusively to ethylene, while below 260°C. the dehydration product is almost entirely ether. The recent application of the carbonium ion theory of acid catalyzed reactions to heterogeneous catalysis has led most investigators to agree that an intermediate, the carbonium ion or conjugate acid, exists which is common to all three compounds. Winfield has pointed out that kinetic results of sufficient detail have not been available to determine whether ether is formed by the reaction of two adsorbed alcohol molecules or by the reaction of one adsorbed molecule with one from the vapor phase. One goal of the current work was to obtain information which would contribute to a solution of this problem. The work of R. W. Taft and associates with sulfuric acid (*2*) is pertinent to the extent of similarity of the acid with the sulfonic acid group of the exchange resin.

The use of ion exchange resins as catalysts has been reported in two studies of vapor-phase reactions, as well as in many studies of liquid-phase reactions. Herrman (*7*) carried out the esterification of acetic acid with ethanol on ion exchange resin in the acid form. He found the reaction rate to be considerably higher than that obtained by other investigators who used silica gel or zirconium oxide as catalyst for the esterification. The results of his study are limited in significance since he, like many other investigators of esterification and other reactions of ethanol, failed to recognize the importance of the side reaction of ethanol to ethyl ether. Detailed discussions of such instances are found elsewhere (*11, 4*). Nevertheless Herrman's work demonstrated the excellent characteristics of hydrogen ion exchange resin as a vapor-phase catalyst. Metzner and Ehrreich (*17*) studied the vapor-phase hydration of ethylene oxide to ethylene glycol and higher glycols. The ion exchange resin used by them was similar chemically to the authors' but differed in physical properties. Thus while their work exhibited some rather unusual effects which would not be expected in this study, it is of interest that the rate of reaction was found to be proportional to the partial pressure of the ethylene oxide in the vapor phase and to the amount of water adsorbed by the resin.

It will be shown later that experiments can be conducted in the flow system in such a manner that diffu-

---

Robert L. Kabel is with the United States Air Force Space Systems Division, Los Angeles, California.

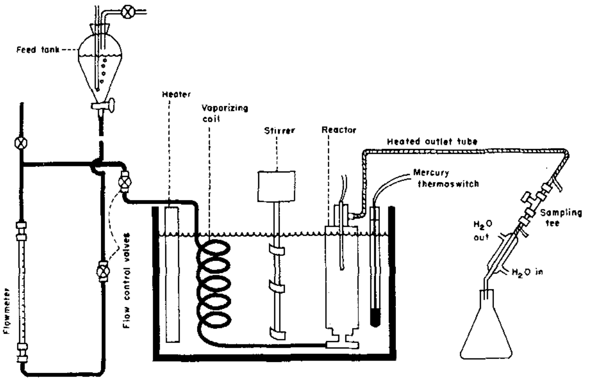

Fig. 1. Schematic diagram of reaction system.

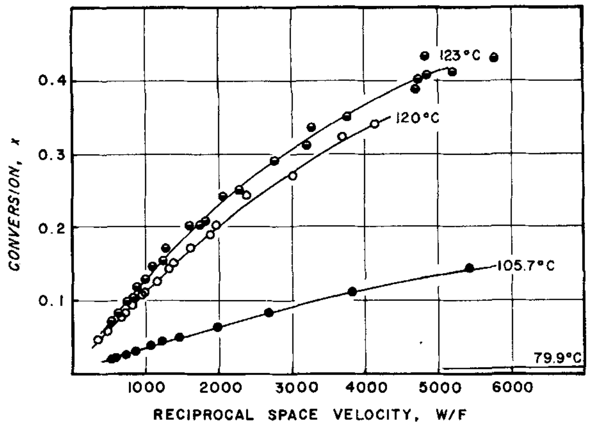

Fig. 2. Integral reaction rate data for pure alcohol feed at 1.0 atm.

sional gradients will be negligible, both at the catalyst particle surface and the particle interior. The rate of reaction will then be governed by a combination of rates of adsorption, reaction at the catalyst, and desorption. Relatively simple equations for the rate of reaction may be developed in a standard, systematic manner (9, 23) in accordance with the Langmuir-Hinshelwood approach. Such equations assume only one of the sequence steps of adsorption, reaction, or desorption to be slow enough to require consideration. The justification for such an assumption is not always trivial, especially for reactions for which the rate controlling step changes with temperature (20). Ordinarily however one step in the reaction sequence (usually the surface reaction) is slow compared with all other steps.

With this limiting-step assumption, and others implicit in the Langmuir isotherm model, three equations (of a number possible) resulted from a preliminary analysis of the reaction system. These represent the two mechanisms in some dispute, that is the reaction between adjacently adsorbed ethanol molecules [Equation (2)] and between an adsorbed ethanol molecule and a gaseous ethanol molecule [Equation (3)]. The reverse reaction in Equation (2) is assumed to take place between adjacently adsorbed water and ether molecules (or between gaseous ether and a water molecule adsorbed adjacent to a vacant site) and in Equation (3) between a gaseous ether molecule and a water molecule adsorbed on a single site. The third example is perhaps the most probable of the adsorption-controlled mechanisms, for the adsorption of ethanol rate-limiting [Equation (4)]:

$$r = [k_s sLK_A^2/2]\,[P_A^2 - (P_E P_W/K_{eq})]/ [1 + K_A P_A + K_W P_W + K_E P_E]^2 \quad (2)$$

$$r = [k_s LK_A]\,[P_A^2 - (P_W P_E/K_{eq})]/ [1 + K_A P_A + K_W P_W] \quad (3)$$

$$r = k_A L[P_A - \sqrt{P_E P_W/K_{eq}}]/ [1 + \sqrt{P_E P_W K_A^2/K_{eq}} + K_E P_E + K_W P_W] \quad (4)$$

The equations are written in terms of partial pressure rather than activity, the maximum pressure being 1 atm. in this study. The constants K_A, K_W, and K_E are those which are to be evaluated both by means of reaction rate data, and adsorption data.

Experimental

Reaction rate data were obtained in the form of integral conversion as a function of reciprocal space velocity, although much of the data could be classed as differential in nature. Product components, water and ethyl ether, were included in the feed streams to allow analysis based on variations in partial pressure under initial reaction rate conditions.

The apparatus used in the kinetics experiments is shown schematically in Figure 1. The 3.4 cm. I.D. cylindrical, stainless steel reactor was packed with a mixture of glass beads and ion exchange resin catalyst to bed depths of 5 to 10 cm. A thermocouple well extended from the top of the reactor midway into the catalyst bed, giving an indication of the bed temperature. The thermocouple readings, oil bath temperatures, and an approximate analysis of the thermal gradients within the bed allowed specification of the mean reaction temperature within ± 0.5°C. of the desired constant value.

The sampling chamber in the reactor exit line consisted of a heated T, the stem leg of which was fitted with a silicone rubber disk. A 10 μ liter syringe was inserted through the disk and the plunger slowly drawn. The hot vapors would condense within the relatively cool syringe, giving a measurable liquid sample. This method of sampling, believed to be original with this work, avoided the problems arising from immiscibility and widely differing volatilities of the reaction products.

The reaction product was analyzed chromatographically at 102°C., with polyethylene glycol on a diatomaceous earth used as a column packing. The instrument was calibrated with accurately proportioned liquid mixtures of alcohol, ether, and water in order to determine the alcohol to ether peak height ratio as a function of the corresponding mole ratio in the sample. This along with the initial reactor feed composition, and the stoichiometry of the reaction, determined the complete product analysis.

Reagent grade anhydrous ethyl ether, absolute ethanol, and laboratory distilled water were used without further purification throughout this work. The Dowex 50, X-8, 20- to 50-mesh cation exchange resin was a medium porosity resin with a total exchange capacity of 0.0054 ± 0.0003 equivalents per bone dry gram of catalyst.

The resin to be placed in the reactor was weighed in the air dried state and its weight corrected to a bone dry basis. Care was taken to avoid undue swelling and/or deactivation of the catalyst. The reaction system was operated continuously with flow rate, feed composition, temperature, and pressure being varied as desired. A run consisted of product analyses at each of a series of flow rates with other conditions constant.

Experimental equipment and techniques, as well as further information on other phases of this research, are treated in more detail elsewhere (*11*).

Results

Complete integral conversion results of the reaction rate studies are available as Table C-1 of reference *11*. They include studies at three temperature levels, 80°, 106°, and 120°C., with major emphasis at 120°C. Feed compositions include pure alcohol feeds, alcohol-water feed mixtures, and alcohol-ether feed mixtures. One run included all three components in the feed stream. Total pressure was 1 atm. except for one run. It was demonstrated that ethanol, when passed through the reaction system without catalyst, emerged unreacted. In no case throughout the study did the chromatographic analysis give evidence of catalyzed or uncatalyzed side reactions. Since it was shown that ethylene added to the feed could reliably be detected by the analysis scheme, it is concluded that no ethylene was formed at these reaction conditions. Periodic studies showed deactivation of the catalyst over a month of continuous operation to be negligible.

Typical data is shown in graphical form in Figures 2 and 3. Figure 2 il-

TABLE 1. INITIAL REACTION RATE DATA

		P_{A_0},	P_{E_0},	P_{W_0},		$r_0 \times 10^4$		
Run	W, g.	atm.	atm.	atm.	T_R, °C.	exp.	calc.	% dev.
1-1	36.9	1.000	0.000	0.000	105.7	0.326		
1-2	36.9	1.000	0.000	0.000	79.9	0.0368		
1-4	36.9	0.381	0.000	0.619	120.0	0.0866	0.0876	12.0
1-5	36.9	0.381	0.000	0.619	105.7	0.0142		
3-1	14.3*	1.000	0.000	0.000	120.0	1.347	1.367	1.5
3-2	14.3*	0.947	0.053	0.000	120.0	1.335	1.334	0.08
3-3	14.3*	0.877	0.123	0.000	120.0	1.288	1.284	0.3
3-4	14.3*	0.781	0.219	0.000	120.0	1.360	1.208	11.2
3-6	14.3*	0.471	0.529	0.000	120.0	0.868	0.868	0.0
3-7	14.3*	0.572	0.428	0.000	120.0	1.003	1.002	0.1
3-8	14.3*	0.704	0.296	0.000	120.0	1.035	1.138	10.0
3-9	14.3*	0.641	0.359	0.000	120.0	1.068	1.077	0.84
4-1	22.6*	1.000	0.000	0.000	120.0	1.220	1.367	12.1
4-2	22.6*	0.755	0.000	0.245	120.0	0.571	0.541	5.2
4-3	22.6*	0.552	0.000	0.448	120.0	0.241	0.223	7.2
4-4	22.6*	0.622	0.175	0.203	120.0	0.535		
4-6	22.6*	0.641	0.359	0.000	105.7	0.291		
4-7	22.6*	0.689	0.000	0.000	120.0	1.162		

* Catalyst blended with three times its mass of glass beads.

lustrates the influence of temperature and space velocity upon conversion of pure alcohol. The solid lines represent empirical computer fits of individual run data. Figure 3 illustrates the influence of water-alcohol feed composition upon conversion, for runs at 120°C. and 1 atm. total pressure. The broken lines represent the data as calculated with the integrated form of Equation (2). Data (not shown here) similar to those in Figure 3 were obtained for ether-alcohol feed mixtures. In this case the effect of feed composition on conversion was less pronounced than in Figure 3.

It was considered desirable to determine constants of suitable rate equations by means of initial rate data only. Evaluation of the resulting equations could then be made by integration and comparison with the integral data. This is a more sensitive and more severe test of the equations than simply curve fitting the integrated form of equations to integral data would be. It was felt that the most accurate and impartial method of determining this initial rate would be to empirically fit the available integral data with an equation whose form, while arbitrary, would reasonably describe the data over the range under consideration and would allow analytical differentiation at the origin. This was done with a cubic polynomial to increase the accuracy of the extrapolation and to avoid prejudice or bias in curve fitting and slope taking by eye. With such a technique it is necessary to show that the inflection points in the cubic curve occur beyond the high range of the data and that the extrapolation tends to pass through the origin. The origin could then be used as a valid datum point in the least squares computer fit.

Results of this extrapolation to obtain initial rates r_o are summarized in Table 1. More complete tabulations are available in reference *11*.

Not all of the data of Table 1 are of equal reliability. Improvements in temperature control of reactor, flowmeter, and chromatography column were made following runs on reactor packings 1 and 2. Runs in which large amounts of ether or water were included in the feed gave less reliable results than runs with pure alcohol feed. This was because of the low total conversion attained, difficulties owing to the high volatility of ether, and lower analytical precision for samples containing large amounts of ether or water.

Mass Transfer Considerations

Before considering the reaction rate data from the standpoint of adsorption and kinetics, one should consider the possibility of mass transfer gradients influencing the results. Possible influence may be one of the three types: diffusional resistance of the internal catalyst pores, transfer gradients at the external surface of the resin particles, and packed bed gradients such as backmixing. These will be considered in turn.

Herrman (*7*), in previous work with the same catalyst in this laboratory, found the ethanol esterification rate at 118°C. to be independent of particle size for three catalyst sizes of 16 to 20, 24 to 28, and 35 to 42 mesh. Since the measured reaction rate in the present work was less than that of Herrman, and diffusing species similar, pore diffusion would also not be expected to be of importance in the present work. In addition Figure 2 and Table 1 indicate a very marked temperature coefficient of the reaction. If the initial rate values of Table 1 are utilized to evaluate a temperature coefficient of the reaction, it is found that the reaction rate varies approximately as the thirty first power of absolute temperature. A temperature exponent of only 0.5 to 1.0 would be expected if diffusional gradients, either within or surrounding the catalyst particle, were of controlling importance.

This large temperature coefficient of reaction also gives assurance that mass transfer gradients at the particle surface are also not of major importance. An additional test is a comparison of conversion obtained at equal space velocity but at varying mass velocity. Such a comparison can be made between runs of different catalyst packings, with other conditions the same. Table 2 makes such a comparison for three pairs of runs. Conversion results were interpolated from the original data (Table C-1, reference *11*). It is evident from these comparisons that results are essentially independent of linear velocity, and of the presence or absence of glass beads blended with the catalyst.

Mass transfer effects in addition to those at or within the catalyst particle may be of importance. In an integral reactor packed bed these may be radial and axial mixing brought about as a result of thermal or concentration gradients. Table 2 is at least partial confirmation that such gradients are of minor influence in this work. Conversion at a given space velocity would not be reproducible with change in shape of the catalyst bed (or with dilution of catalyst with glass beads) if gradients or backmixing were extensive. The method of Levenspiel and Bischoff (*15*) along with the study of axial mixing of gases in packed beds, by McHenry and Wilhelm (*16*), was used to estimate quantitatively the extent of backmixing. The calculations indicated that the maximum possible backmixing effect would reduce the experimentally obtained conversions by 1 to 2% below the level predicted on the basis of pure plug flow.

Reaction Kinetics

The influence of reactor feed composition upon initial reaction rate is shown in Figure 4. It is evident from this plot that water vapor depresses the dehydration rate of ethanol far more than does an equivalent partial pressure of ethyl ether. The possibility that the desorption of a product might be the rate controlling step can be discounted on the basis of the strong effect of composition upon the rate of reaction. Since the data represent the derivatives of integral rate curves extrapolated to zero W/F, the consistency is believed very good except for the four initial rate points indicated by open symbols. In addition there is a 10% disagreement for pure alcohol feed for the two sets of runs. The reliability of the initial rate values for the open points is considered in detail in reference *11*. It was concluded that these values were of lower reliability than other runs for reasons associated with reduced analytical accuracy at low conversions and difficulties in obtaining good extrapolations to zero W/F. Examination of the ether alcohol integral data (not shown here) shows that these abnormalities are not present in the position of the integral data, which fall properly in sequence of lower curves for lower initial partial pressures of ethanol. The two initial rate results for pure alcohol feed are derived from data of runs 3-1 and 4-1. Some of these data are shown in Table 2. On the basis of this table and the superimposed integral curves of these runs the data appear to be in good agreement. However slightly differing trends within the data affect the extrapolation from which the rates are obtained.

Equations (2), (3), (4), and others similar may be written for initial rate conditions, at zero values of W/F. Only partial pressure terms for substances present in the feed will appear. For ethanol-ether binary feed mixtures the equations may be reduced to terms involving only alcohol partial pressure:

$$\sqrt{r_o}/P_{A_o} = \sqrt{k}/(1 + K_E) - \sqrt{r_o}\,[(K_A - K_E)/(1 + K_E)] \qquad (2a)$$

$$r_o/P_{A_o}{}^2 = k - (r_o/P_{A_o})K_A \qquad (3a)$$

$$r_o/P_{A_o} = k/(1 + K_E) + r_o[K_E/(1 + K_E)] \qquad (4a)$$

Therefore if one plots $\sqrt{r_o}/P_{A_o}$ vs. $\sqrt{r_o}$, $r_o/P_{A_o}{}^2$ vs. r_o/P_{A_o}, and r_o/P_{A_o} vs. r_o, the equation which applies should result in a straight line and others should result in curved lines. It should be remarked that all equations of such linearizing parameters suffer from the disadvantage of a tendency to plot a variable against a function of itself. Other forms of the equations may be obtained by multiplying both sides of Equations (2*a*), (3*a*), and (4*a*) by combinations of r_o and P_{A_o}. One consistent set would require plotting $1/P_{A_o}$ vs. $1\sqrt{r_o}$, $1/r_o$, and P_{A_o}/r_o. The linearity test should apply in each case, and it was found to do so for each set of the three equations discussed above. Only the degree of curvature was altered for plots representing Equations (2), (3), and (4). Figure 5 shows such plots for Equations (2*a*), (3*a*), and (4*a*). Since only the consistent points of Figure 4 will fall on smooth curves in Figure 5, and hence aid in the determination of linearity, the errant points have been omitted. It is evident that Equation (2*a*) gives a more nearly linear plot, and therefore Equation (2) gives the more satisfactory representation of the data. To place this conclusion on a somewhat more quantitative basis unsophisticated calculations of the correlation coefficients in accordance with Equations (2*a*), (3*a*), and (4*a*) were performed. The six data points at highest P_{A_o} of Figure 5, that is the most reliable points, were considered in these calculations. The difference between the normalizing *z* transformations of the two highest coefficients, those of Equations (2*a*) and (4*a*), was found to exceed the calculated standard error. In other words by this test Equation (2*a*) is preferable to Equations (3*a*) and (4*a*), but only at the 70% confidence level. It may be seen that inclusion in this treatment of the point at lowest P_{A_o} in Figure 5, as representative of the smooth initial rate curve of Figure 4 near the origin, would appreciably increase the confidence level. Further experimentation could do much to make this situation definitive. Theoretically it should be possible to check the suitability of Equation (2) by a similar series of curves employing the data obtained from the water-alcohol runs. However inconsistencies in the limited amount of these data, particularly for the two runs at low ethanol partial pressure, preclude the drawing of any conclusions about the superiority of one form of rate equation over another. The solid triangles of Figure 5 show the water-ethanol data in the supposedly linear form of Equation (2*b*):

$$\sqrt{r_o}/P_{A_o} = \sqrt{k}/(1 + K_W) - \sqrt{r_o}[(K_A - K_W)/(1 + K_W)] \qquad (2b)$$

Table 2. Comparison Tests for Mass Transfer Influence

Run no.	Mass of catalyst, g.	Interpolated x at: $W/F =$ 1,000	$W/F =$ 3,000
1-3	36.9	0.135	0.309
2-1	31.2	0.131	0.309
3-1	14.3*	0.118	0.270
4-1	22.6*	0.112	0.281
1-4	36.9	0.010	0.025
4-5	22.6*	0.011	0.025

* Catalyst blended with three times its mass of glass beads.

With the conclusion that Equation (2) best describes the reaction rate data, the opportunity for overgeneralization and misinterpretation arrives. It may be said with some confidence that the rate of reaction at the surface of the catalyst is the rate controlling step and that the various adsorption steps proceed at a relatively rapid rate. It is also reasonable to conclude that two adjacent sites are required for the reaction to take place. Unfortunately a number of postulated overall mechanisms might result in these same two conclusions and hence further interpretation would be on unstable ground. In particular the question of whether the reaction proceeds via an adsorbed molecule of ethanol and one from the vapor phase or between adjacently adsorbed molecules remains unanswered. The adsorption data illuminate this problem further, as will be indicated.

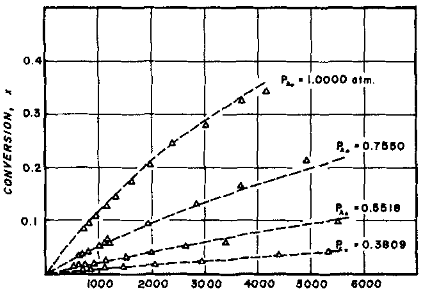

Fig. 3. Water-alcohol integral data at 120°C.

Equation (2) is seen to contain seven constants. For a given reaction K_A, K_W, K_E, and k_s are functions of temperature and catalyst, whereas K_{eq} is a function of temperature only and *s* and *L* are functions of the catalyst only. It is impossible to determine the individual values of k_s, *s*, and *L* from a kinetics study alone, although *L* might be estimated from the exchange capacity of the resin used in this work. For this reason k_s, *s*, *L*, and the factor (1/2) are lumped into a single constant $k_s{}^*$, thereby reducing the number of constants to be determined to five. Values of the thermodynamic equilibrium constant as a function of temperature are available elsewhere (*12*). The remaining four constants are to be determined from the kinetic data.

Figure 5 allows evaluation of the slope and intercept terms of Equations (2*a*) and (2*b*). It would appear that the slopes and intercepts for the two lines should provide four equations for the determination of four unknown constants. However only three of the four equations are independent because of the restriction that both curves must intersect at the point corresponding to pure alcohol feed. Therefore a statistical best fit of all of the ether-alcohol and water-alcohol data points was carried out with the restriction that the resulting two lines must intersect somewhere along the line of equal ordinates. The slopes and intercepts resulting from this treatment yielded the following equations which show the interrelations between the magnitudes of the adsorption constants:

$$K_A = 3.413 + 4.413K_E \qquad (5)$$

$$K_W = 0.816 + 1.816K_A \qquad (6)$$

A third equation yields the value of the kinetic constant k_s^* in terms of K_E. From Equations (5) and (6) it is seen that K_W is larger than K_A, which is considerably larger than K_E, regardless of the value of K_E. Some independent means of evaluating K_E is therefore required. Run 4-7, shown as x on Figure 4 serves this purpose. In this run the feed was pure ethanol, and the total pressure was 0.689 atm., not 1 atm. as in other runs. This subatmospheric pressure operation involved some sampling difficulties, and the precision may not be as high as in other runs. It is evident from Figure 4 however that the point corresponds closely with the ether-alcohol data. This indicates that ether suppresses the reaction mainly by reducing the partial pressure of the reactant, ethanol, and only slightly if at all by occupying active sites, thereby suggesting that K_E is essentially zero. From the deviation of the point from the smooth curve in Figure 4 K_E may be calculated to be 0.176. Thus the value of K_E, if not zero, is certainly very small. On the basis of this evidence the ether adsorption constant is taken to be zero and the remaining constants are calculated to give the values shown in Table 3 for 120°C.

Two criteria are important in assessing the quality of the correlation of these data. Table 1 shows the ability of Equation (2) to predict initial rates for the conditions of the runs used in determining the constants of the rate equation. The average deviation for the twelve points was 5.1%. Similarly the ability of the integrated rate equation based upon the plug flow model to predict integral data may be evaluated with existing data by examination of the agreement of the data points and the curves as in Figure 3. Computed values of W/F required for given values of conversion were compared with the experimental (W/F)'s for the same conversions. The average percentage deviation of the experimental points upon which the original correlation was based from the predicted curves was 6.4%. It is also of interest that there was an excess negative percentage deviation in the prediction of W/F of about 2.5% per data point. Thus the predicted W/F's were smaller than their corresponding experimental values by an amount which corresponds closely to the degree which might be expected to result from backmixing effects.

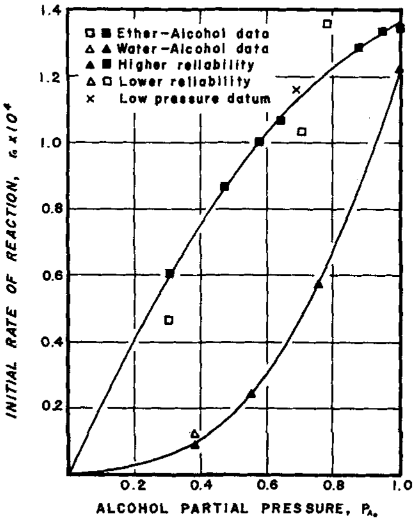

Fig. 4. Initial reaction rate data at 120°C.

In addition to the 120°C. constants Table 3 also includes estimates of the equation constants at 105.8° and 79.9°C. These are based on considerably fewer data than the constants at 120.0°C. The strong effect of temperature is seen in Figure 2. From initial rate data at 105.8°C. given in Table 1 it was possible to prepare a graph similar to Figure 5. The very similar slopes of the straight lines of this graph and those of Figure 5 suggest that the form of the rate equation remains unchanged over this temperature range. If K_E also remains essentially zero the constants at 105.8°C. may be calculated. This approach is somewhat hazardous as illustrated by the work of Thaller and Thodos (20) which demonstrates that the rate controlling step of a reaction may change with temperature. However no other assumption than the one made is justifiable on the basis of the data available. The values of K_A and K_W at 79.9°C. have been estimated by linear extrapolation of an Arrhenius type of plot from the corresponding values at the higher temperatures. This assumption, together with the previous ones, makes possible an approximate evaluation of the reaction rate constant k_s^* at 79.9°C. Values in parentheses indicate uncertainties as discussed above. The three values for log k_s^*, when plotted against the reciprocal of the absolute temperature, fall reasonably close to a straight line. From this line the activation energy of the catalyzed reaction was estimated to be 30,500 cal./g. mole of alcohol reacted.

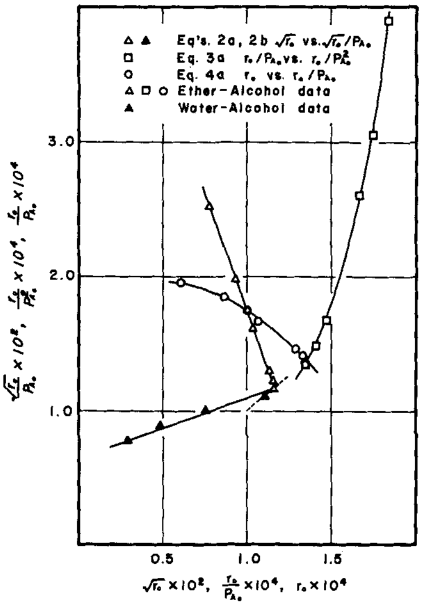

Fig. 5. Ether-alcohol and water-alcohol initial rate data in linearized form.

ADSORPTION STUDIES

The objectives of the adsorption studies are to determine for each of the components of Equation (1) the applicability of the Langmuir isotherm in correlating pure component adsorption data, the equilibrium adsorption constants as a function of temperature, the quantity of vapor adsorbed in a monolayer, and the differential heat of adsorption. This information in conjunction with the results of the reaction rate studies should allow conclusions to be drawn about the nature of the catalytic site, the validity and utility of the Langmuir-Hinshelwood approach, and the mechanism of the catalytic reaction.

The Langmuir isotherm (13)

$$y = y_m K_A P_A / (1 + K_A P_A) \qquad (7)$$

is most often applied to chemisorption systems where adsorption is limited to essentially a monolayer. On the other hand the BET isotherm (3)

$$y = y_m c P_A / [P_{A}, \text{sat} - P_A]$$
$$[1 + (c - 1)(P_A / P_{A}, \text{sat})] \qquad (8)$$

represents an extension of the Langmuir theory to allow for multilayer adsorption. Because the constant c is generally large compared with unity the BET isotherm reduces to the Langmuir isotherm when the adsorbate partial pressure is small compared with the saturation pressure. Equations (7) and (8) are both quite useful in the monolayer region, and each may be put into linear form to test its applicability to a particular set of data. When a successful correlation is obtained it is possible with either equation to estimate y_m.

Herrman (7) studied the adsorption of ethyl alcohol, water, ethyl acetate, and acetic acid vapors on the same catalyst as that used here. Qualitatively his results indicated appreciable adsorption of ethanol and water. By comparison acetic acid was adsorbed to a lesser degree, and ethyl acetate was adsorbed only very slightly.

Further information on the adsorption of water vapor on acid ion exchange resins and their salts is available in two papers by Waxman, Sundheim, and Gregor (21, 19). The curves resulting in all cases were of the sigmoid shape which is characteristic of multilayer adsorption. Slight but definite hysteresis effects were observed in these studies. Glueckauf and Kitt (6) carried out experimental studies similar to those of Waxman et al. and emphasized the low water activity region in order to allow a more extensive theoretical treatment of the cationic hydration.

Experimental

The adsorption experiments were carried out in a static adsorption system (Figure 6) which allowed independent control of temperature of adsorption and partial pressure of adsorbate vapor. The magnitude of adsorption was determined by observation of the elongation of a fused silica spring to which an aluminum foil bucket, containing adsorbent, was attached. Elongation of the spring (spring constant 9.28 cm./g.) was accurately measured by a universal type of cathetometer. The vapor lines of the system were heated with nichrome ribbon to prevent condensation. Mercury seals were improvised at the ground glass joints to prevent leakage.

The detailed procedure used in these studies differed from run to run depending upon the nature of the run and the type of information desired. Generally, after the spring position with the empty bucket in place was determined, a resin sample was placed in the bucket and the system was evacuated at the temperature of the run until the bucket ceased to rise. This allowed calculation of the weight of the resin in its base condition or bone dry state. The feed was introduced into the previously evacuated adsorbate reservoir. When a constant vapor pressure had been attained, the high vacuum valve was opened and adsorption was allowed to proceed to equilibrium. The pressure was then changed and the spring allowed to reach a new equilibrium position. Equilibration at the pressure level immediately following evacuation usually required a half day, while at following levels only about 2 hr. were required.

The chemicals used in the adsorption studies were identical to those in the reaction rate studies. The resin, supplied by the manufacturer in the sodium form, was converted in the laboratory to the hydrogen form. Thereafter it was desiccated over anhydrous calcium chloride until use. Although the resin used in the kinetics experiments was supplied in the acid form and charged in an air-dried state, it is not believed that there was any essential difference between the two batches of resin. Evidence for this is indicated later.

Water Adsorption

The adsorption of water vapor as shown in Figure 7 was found to be reversible with the exception of a temporary hysteresis effect such as was observed by Waxman et al., that is step-by-step desorption carried out following determination of an adsorption isotherm resulted in a curve slightly above the curve for adsorption at comparable pressures. Evacuation however returned the resin sample to its original base condition. Theoretical interpretation of such hysteresis effects is difficult if not impossible. Where hysteresis is present, neither adsorption nor desorption data has been clearly demonstrated to have greater significance. The adsorption data obtained in this study were of greater number, range, and precision that the desorption data. For these reasons only the adsorption curves will be treated here. Similar treatment of the desorption data yielded results consistent with, although less precise than, the adsorption results. It should also be noted that a water adsorption run carried out on a sample of the same batch of resin as used in the kinetic studies showed substantial agreement with the remainder of the data. This is taken to be validation of the comparison of the results of the two studies.

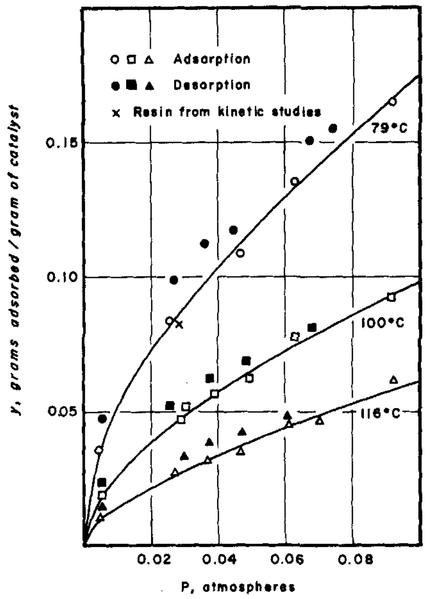

Fig. 7. Adsorption and desorption data for water vapor.

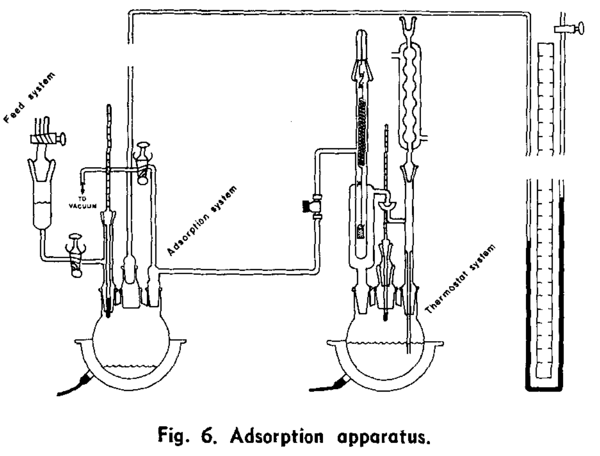

Fig. 6. Adsorption apparatus.

The range of relative pressure P/P_{sat} for the 100° and 116°C. data was low enough to make the Langmuir and BET isotherms indistinguishable. The BET equation satisfactorily correlated the 79°C. data, allowing estimation of y_m and hence the number of adsorption sites L_W. This value is given in Table 3. Although the linearized Langmuir isotherm was not entirely satisfactory in correlating the water adsorption data, all points beyond the point at lowest pressure for each temperature were sufficiently linear to permit estimates of the adsorption constants. Omission of the single point from each least squares computer fit seems reasonable since the fitted points were for pressures nearest the range of primary interest in the kinetics studies. The constants thus obtained are indicated in Table 3.

The differential heat of adsorption as a function of fractional surface coverage was determined from all of the adsorption data as a function of temperature by the use of the Van't Hoff equation. Contrary to the Langmuir assumption of constancy the heat of adsorption was found to decrease exponentially with surface coverage. At monolayer coverage it was greater than 13,500 cal./mole. This is considerably larger than the latent heat of vaporization of water, which at 100°C. is 9,700 cal./mole.

Ethanol Adsorption

The degree of adsorption obtained with ethanol feed was found to change slowly with time, possibly because of reaction on the catalyst surface. With longer exposure times it became increasingly difficult to approach the resin base condition, even with continuous evacuation. In an effort to avoid obtaining misleading data the adsorption was carried out in accordance with two procedures. The first was similar to the water studies, with equilibrations at each of several increasing pressure levels on the same sample of resin. In the second procedure a new sample of resin was used for each measurement at a new pressure, resulting in a greatly shortened contact time between the resin and the adsorbate. There appeared to be no distinction between the results of the two methods. Figure 8 presents the satisfactory correlation of the resulting ethanol adsorption data by the Langmuir isotherm. The values of K_A determined from these correlating lines are given in Table 3. The values of y_m at 79°, 100°, and 116°C. were also calculated and are given as the number of sites per gram of resin L_A in Table 3.

The determination of the differential heat of adsorption for ethanol gave somewhat more erratic results than those for water. Nevertheless the heat of adsorption was indicated to be roughly constant over the range of coverage at a value of 16,000 ± 2,000 cal./mole. Comparison with the ethanol heat of vaporization of 9,400 cal./mole at its normal boiling point is evidence that alcohol is also adsorbed by a chemisorption process.

Ethyl Ether Adsorption

Measurements of ether adsorption were carried out at various temperatures and pressures. At an ether pressure of 0.275 atm. only 0.013 g. of weight increase was observed per gram of catalyst after five days of operation at 79°C. Even on the assumption that only ether was adsorbed (when it is more likely that only a constituent of stopcock grease was adsorbed), this amount of adsorbate is of the magnitude of the smallest amounts obtained at 116°C. in the alcohol and water studies. This corresponds to a value of K_E of less than 0.15. Thus it is concluded that ethyl ether is adsorbed only very slightly, if at all.

Discussion

Ethanol and water are strongly adsorbed, while ethyl ether is not adsorbed or only very slightly adsorbed. Qualitatively these results for ethanol and water are in agreement with those of Herrman. Although it has not been demonstrated in this paper, these data for water vapor adsorption at 79°, 100°, and 116°C. are quite consistent on a quantitative basis with those of Waxman, Gregor, and Sundheim at 25° and 50°C. The hysteresis effects found in this study were also found by them to exist at the same relative pressure.

By the use of the most satisfactory correlating equations for water and ethanol it was shown in Table 3 that the amount of vapor adsorbed in a monolayer corresponded closely with the amount L_{H^+} predicted on the basis of the resin exchange capacity, on the assumption that each acid equivalent represents a molar adsorption site. This close correspondence is rather convincing evidence that the acid groups on the resin do indeed constitute the active sites for adsorption and perhaps even for catalysis. Heat of adsorption studies also support this conclusion in that the heats for both ethanol and water were well into the chemisorption range.

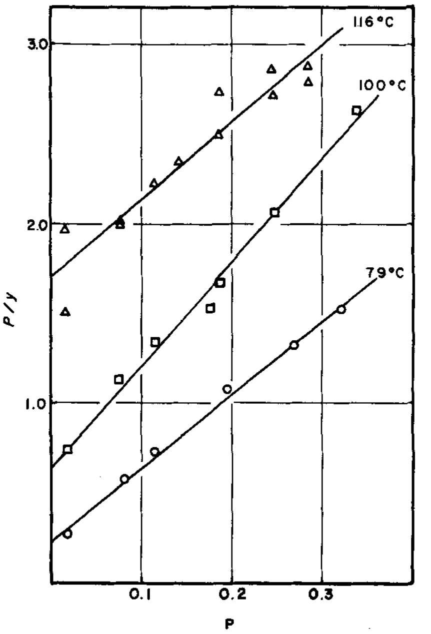

Fig. 8 Ethanol adsorption data in Langmuir isotherm form.

INTERPRETATION

Comparison of Constants from Reaction Rate and Adsorption Studies

The Langmuir equilibrium adsorption constants for the components of Equation (1) have been determined by direct measurement in a static adsorption system and by correlation of catalytic rate data in accordance with the Langmuir-Hinshelwood model of heterogeneous catalysis. The constants thus determined are summarized for comparison in Table 3. The temperatures at which the independent experiments were performed were not identical, but they were close enough to permit these comparisons. Values of K_A and K_W from the independent measurements at the two higher temperatures show definite order of magnitude agreement. The trend toward higher values of the constants with decreasing temperature is consistently displayed, with the exception of the value of K_W at 79°C. This low value is believed to have resulted from the use of the Langmuir isotherm in the correlation of BET isotherm type of data beyond the range where the two isotherms are identical. The values of the constants from the adsorption data show that the adsorption constants cannot reasonably be extrapolated to different temperatures by the Arrhenius equation. It should also be noted that both kinetics and adsorption studies indicated ethyl ether to be only very slightly adsorbed, if at all. It may be seen from Equation (7) that for y/y_m ranging from 0 to 1.0 the value of K_A may range from 0 to ∞. Therefore the extent of correspondence shown between K_A, K_W, and K_E values is believed to be well beyond that expected by chance. It suggests the Langmuir-Hinshelwood model of catalysis is a descriptive model at least for this ion exchange resin catalyst.

The Nature of the Catalytic Site and Apparent Mechanism of the Catalytic Reaction

The studies of Glueckauf and Kitt indicated that the first water molecule adsorbed on sulfonic acid ion exchange resin was taken up in hydration of the hydrogen ion. Experiments of the present work indicate that each molecule of water or alcohol is adsorbed upon an individual acid site. By application of the postulate of Glueckauf and Kitt to ethanol it is seen that the carbonium ion (conjugate acid) required for the reaction to proceed may be supplied upon the adsorption of the ethanol molecule.

This conclusion allows further speculation into the mechanism of the catalytic reaction with emphasis on the distinction between the reaction of two adsorbed ethanol molecules and the reaction of an adsorbed molecule with one from the vapor. Two possibilities for the need of adjacent sites in the reaction between an adsorbed molecule

TABLE 3. SUMMARY OF CONSTANTS FROM KINETICS AND ADSORPTION MEASUREMENTS

Kinetics

T,°C.	K_A	K_W	K_E	$k_s^* \times 10^6$	K_{eq}
120.0	3.4	7.0	(0)	229	25.2
105.8	8.9	22	(0)	40	30.2
79.9	(63)	(230)	(0)	(3.8)	44.5

	Adsorption			Molar sites/g. resin		
T, °C.	K_A	K_W	K_E	L_A	L_W	L_{H^+}
116	2.5	7.6	(0)	0.0052	—	0.0054
100	8.9	13.6	(0)	0.0039	—	0.0054
79	17	(13)	(0)	0.0053	0.0052	0.0054

of alcohol and one from the vapor phase were the adsorption of alcohol on a dual site and the requirement that adjacent sites be available for ether and water in the reverse reaction. The first possibility becomes rather unlikely in view of the above argument. Secondly both kinetics and adsorption studies indicated the adsorption of ethyl ether to be slight or negligible. Thus it is probable that the reverse reaction proceeds via the impact of an ether molecule from the vapor phase with an adsorbed molecule of water. It appears that the reaction on ion exchange resin catalyst does take place between two adjacently adsorbed molecules of ethanol. It is believed that such a mechanism is reasonable in view of the extensive adsorption of ethanol.

Validity and Utility of Langmuir-Hinshelwood Model

The success of the Langmuir-Hinshelwood model of heterogeneous catalysis, in spite of the limitations of the Langmuir adsorption isotherm in describing real systems, has been noted here and by others. It is of interest to consider at this time possible explanations for this success.

The adsorption studies have shown the assumptions of monolayer coverage and constant heat of adsorption with coverage to be inapplicable to the water-ion exchange resin system. Boudart (*1*) has analyzed the effect of variation of heat of adsorption and has pointed out that "a real surface may be considered as a statistical collection of ideal surfaces, and for a given catalytic reaction only a limited number of the ensemble play an active part, forming a quasideal surface."

With regard to the assumption of monolayer coverage the fact that a given material, for example water, may be adsorbed in excess of a monolayer does not require the excess material to play an active part in the catalytic reaction. On the contrary only chemisorption, characterized by large heats of adsorption, is believed to sufficiently activate the adsorbed molecules to bring about chemical reaction. Since adsorbed layers beyond the first are characterized by heats of adsorption nearer to the heat of vaporization of the adsorbate, these layers would not be expected to participate in the reaction except perhaps in some secondary fashion. Thus the use of the Langmuir isotherm in the development of rate equations might be viewed as considering only the significant adsorption. Furthermore the partial pressures of reacting substances in vapor phase reactions will quite often result in adsorption equilibria below monolayer coverage. As a result the Langmuir isotherm may find more appropriate use in describing reaction rate data than in describing pure component adsorption data.

A third assumption in the Langmuir isotherm, not evaluated in this work, is that multicomponent mixtures are adsorbed without interactions between components. This assumption may be the most seriously limiting of the three. Reeds and Kammermeyer (*18*), in a study on the vapor-solid system methanol-benzene-porous glass, have demonstrated the existence of an adsorption azeotrope analogous to azeotropes in vapor-liquid equilibrium systems. The difficulty of predicting the adsorption characteristics in such a binary system from pure component adsorption data is apparent. Nevertheless it may be that over the range of investigation of many studies these interactions will be small. The present study may be an example of such a situation.

Further investigation may indicate the extent to which these conclusions are applicable to other reacting systems, other operating conditions, and other forms of catalyst. Meanwhile the use of such a reaction model, supplemented if possible by adsorption data, is believed to give more insight into the nature of a surface reaction than would a mechanical application by curve fitting of empirical equations which have no theoretical foundations.

ACKNOWLEDGMENT

The authors wish to express thanks for financial support in part of this investigation, to the Office of Ordnance Research, U.S. Army, and the Richfield Oil Corporation.

NOTATION

A, E, W = subscripts referring to alcohol, ether, and water
H^+ = subscript referring to acid exchange capacity of catalyst
k = grouped constants in the kinetic term of rate equation
k_A = forward adsorption velocity constant for alcohol, atm.$^{-1}$ min.$^{-1}$
k_s = forward specific (surface) reaction velocity constant, min.$^{-1}$
k_s^* = $k_s sL/2$
K_A, K_E, K_W = Langmuir equilibrium adsorption constants, atm.$^{-1}$
K_{eq} = thermodynamic equilibrium constant, dimensionless
L = total adsorption sites on catalyst, g.-moles of sites/g. of catalyst
o = subscript indicating initial value, bed entrance value, or feed value
P_A, P_E, P_W = partial pressures, atm.
P_{sat} = saturation pressure of vapor, atm.
r = rate of reaction, g.-moles of alcohol reacted/g. of catalyst min.
s = number of catalyst sites adjacent to a given site, dimensionless
T_R = temperature in reactor, °C.
W = mass of catalyst, in bone dry state, g.
W/F = reciprocal space velocity, g. of catalyst min./g. mole of feed
x = conversion, g.-moles of alcohol reacted/g.-mole of feed
y = g. adsorbed/g. of catalyst
y_m = g. adsorbed in a monolayer/g. of catalyst

LITERATURE CITED

1. Boudart, Michel, *A.I.Ch.E. Journal*, **2**, 62 (1956).
2. Boyd, R. H., R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, *J. Am. Chem. Soc.*, **82**, 4729 (1960).
3. Brunauer, Stephen, P. H. Emmett, and Edward Teller, *ibid.*, **60**, 309 (1938).
4. Cope, C. S., and B. F. Dodge, *A.I.Ch.E. Journal*, **5**, 10 (1959).
5. Emmett, P. H., ed., "Catalysis," Vol. 7, pp. 93-182, Reinhold, New York (1960).
6. Glueckauf, E., and G. P. Kitt, *Proc. Roy. Soc.*, **228A**, 322 (1955).
7. Herrman, A. J., Ph.D. thesis, Univ. Wash., Seattle, Washington (1955). Available from University Microfilms, Ann Arbor, Michigan.
8. Hinshelwood, C. N., "The Kinetics of Chemical Change," Oxford Univ. Press, New York (1940).
9. Hougen, O. A., and K. M. Watson, "Chemical Process Principles," Part 3, Wiley, New York (1947).
10. ———, *Ind. Eng. Chem.*, **35**, 529 (1943).
11. Kabel, Robert L., Ph.D. thesis, Univ. Wash., Seattle, Washington (1961). Available from University Microfilms, Ann Arbor, Michigan.
12. ———, and L. N. Johanson, *J. Chem. Eng. Data*, **6**, 496 (1961).
13. Langmuir, Irving, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
14. ———, *Trans. Faraday Soc.*, **17**, 621 (1922).
15. Levenspiel, Octave, and K. B. Bischoff, *Ind. Eng. Chem.*, **51**, 1431 (1959).
16. McHenry, K. W., Jr., and R. H. Wilhelm, *A.I.Ch.E. Journal*, **3**, 83 (1957).
17. Metzner, A. B., and J. E. Ehrreich, *ibid.*, **5**, 496 (1959).
18. Reeds, J. N., and Karl Kammermeyer, *Ind. Eng. Chem.*, **51**, 707 (1959).
19. Sundheim, B. R., M. H. Waxman, and H. P. Gregor, *J. Phys. Chem.*, **57**, 974 (1953).
20. Thaller, L. H., and George Thodos, *A.I.Ch.E. Journal*, 6 369 (1960).
21. Waxman, M. H., B. R. Sundheim, and H. P. Gregor, *J. Phys. Chem.*, **57**, 969 (1953).
22. Weller, Sol, *A.I.Ch.E. Journal*, **2**, 59 (1956).
23. Yang, K. H., and O. A. Hougen, *Chem. Eng. Progr.*, **46**, 146 (1950).

Manuscript received September 12, 1961; revision received March 19, 1962; paper accepted April 5, 1962. Paper presented at A.I.Ch.E. New York meeting.