The Dual Nature of a Catalytic Reaction: The Dehydrogenation of *sec*-Butyl Alcohol to Methyl Ethyl Ketone at Elevated Pressures

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A detailed analysis of initial rate data obtained for the catalytic dehydrogenation of *sec*-butyl alcohol to methyl ethyl ketone in the presence of brass reveals that the controlling step of the reaction changes and depends on the operating conditions. To take advantage of the unique characteristics of initial rate equations, the experimental phase of this work has been carried out with a differential reactor and covered the temperature range 550° to 700°F. for pressures up to 15 atm. Feed compositions containing *sec*-butyl alcohol and mixtures with methyl ethyl ketone and hydrogen were used.

These studies show that the desorption of molecularly adsorbed hydrogen ceases to be the controlling step in favor of a dual-site surface reaction depending on the operating variables. In view of these observations it now becomes necessary to calculate reaction rates with both over-all rate equations and to select the lower rate as representative of the controlling step of the reaction.

Previous dehydrogenation studies for the production of methyl ethyl ketone from *sec*-butyl alcohol by means of a brass catalyst (3) were limited to atmospheric pressure and temperatures ranging from 650° to 750°F. These initial studies involved the dehydrogenation of *sec*-butyl alcohol in an integral reactor and necessitated extrapolation of conversion data into the region where the resistance to mass transfer became negligible. The resulting data were then subjected to a least-squares analysis involving a number of hyperplanes (*1*). The hyperplane represented only by positive coefficients was selected as representative of the most probable over-all rate equation. In this connection it was concluded that the desorption of hydrogen involving a single-site surface reaction was the controlling step.

The present investigation has been undertaken to extend the study of this reaction. To avoid the potential source of error associated in the extrapolation of data in the earlier studies (3), it was decided that a differential reactor would produce initial rate data directly without recourse to extrapolation. The use of initial reaction rates offers definite advantages in processing data and planning future experimental studies that would assist in the selection of a suitable rate equation. For over-all reaction rates representing a single controlling step the rate equation can be reduced to a hyperplane of the following general form:

$$y = a + bx_b + cx_c + dx_d + \dots \quad (1)$$

where $y, x_b, x_c, x_d, \dots$ are quantities that can be obtained from the experimental data, and $a, b, c, d, \dots$ are constants to be established by the method of least squares. For the selection of a proper controlling step all these constants must be positive. Equation (1) is uniquely adaptable to initial rate data and permits the study of the effect of a single variable when the other variables are held constant. Through this approach it becomes possible to trace the effect of each variable on the over-all rate equation.

RESTRICTIONS OF REACTION RATES TO INITIAL CONDITIONS

For the dehydrogenation of *sec*-butyl alcohol to methyl ethyl ketone

$$\overset{A}{sec\text{-}C_4H_9OH} \longrightarrow \overset{K}{CH_3COC_2H_5} + \overset{H}{H_2}$$

the following controlling steps give rise to the associated initial rate equations: (*a*) desorption of a product from the catalyst surface

$$r_{A_0} = A \quad (2)$$

(*b*) adsorption of a reactant on the catalyst surface

$$r_{A_0} = B\pi \quad (3)$$

(*c*) surface reaction (single sites)

$$r_{A_0} = \frac{C\pi}{1 + K_A\pi} \quad (4)$$

(*d*) surface reaction (dual sites)

$$r_{A_0} = \frac{D\pi}{[1 + K_A\pi]^2} \quad (5)$$

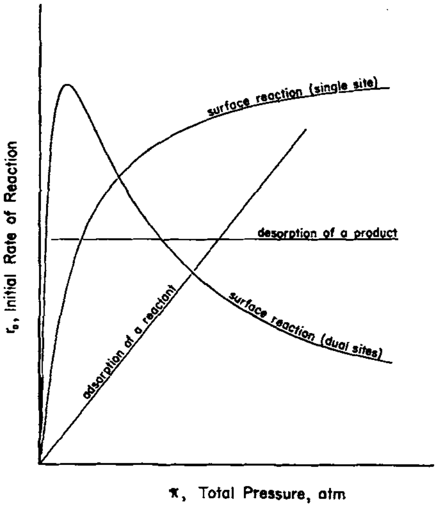

Fig. 1. Variation of initial rates with pressure for typical controlling steps.

Equations (2) through (5) result from the over-all rate equations for the controlling steps when no products are present in the feed. This condition is realized at the top differential thickness of a catalyst bed. With these equations it is possible to interpret experimental data directly. They may provide a method for substantiating the assumption that a single step controls the over-all rate of reaction.

With pressure as the operating variable the initial reaction rates can be represented for Equations (2) through (5) as indicated in Figure 1. The horizontal line representing Equation (2) shows the independence of pressure of the initial rate of reaction, and Equation (3) indicates a direct linear dependence on pressure. On the other hand the equations representative of the surface-reaction equations produce relations that are not linear. The one involving single sites gives rise to a continuous curve approaching an upper limit; the one involving dual sites reaches a maximum and then asymptotically approaches zero.

The straight-line relationships resulting from Equations (2) and (3) permit the direct establishment of the constants for these equations. The constants of Equations (4) and (5) can be obtained directly by rearranging these equations into the following linear expressions:

$$\frac{\pi}{r_{A_0}} = \frac{K_A}{C}\pi + \frac{1}{C} \qquad (6)$$

$$\sqrt{\frac{\pi}{r_{A_0}}} = \frac{K_A}{\sqrt{D}} + \frac{1}{\sqrt{D}} \qquad (7)$$

When the quantities π/r_{A_0} or $\sqrt{\pi/r_{A_0}}$ are related to the pressure, a straight line will result, the slope and intercept of which enable the calculation of the constants of Equation (4) or (5).

Initial reaction-rate data and the use of Equations (2) through (5) give information regarding the rate equation but do not completely describe the state of the reactants and products occupying the active centers of the catalyst. In order to establish specifically which components are adsorbed and what state they exist in on the active centers, it becomes necessary to obtain additional information. In this connection initial rates resulting from mixed feeds give information that should completely describe the general behavior of reactants and products on a catalyst surface and thus enable the establishment of over-all reaction rates.

EXPERIMENTAL PROCEDURE

The experimental equipment with which the data were obtained is described elsewhere (3). In order to conduct this investigation at elevated pressures, a back-pressure valve was installed between the condenser and the gas separator. With this arrangement the pressure of the reaction in the course of a run was adequately controlled and varied a maximum of ± 2 lb./sq. in. at the highest pressure of 14.6 atm. Aside from this modification the steps utilized in operating this equipment were identical with those of the earlier work presented by Perona and Thodos (3).

To obtain initial rate data, a differential reactor was utilized. The catalyst was prepared from a brass stock having a composition of 65% copper and 35% zinc, by weight. In order to produce uniformity in size and shape of the catalyst to be used, coarse brass filings were dropped through a three-phase carbon arc, where these particles melted, assumed a spherical shape, and solidified soon after leaving the arc. These raw spherical particles were then screened, and only reasonably round particles which would roll off a smooth surface were used in these studies. Only those spheres which passed through a 50-mesh screen and were retained on a 60-mesh screen were used as the catalyst for this investigation.

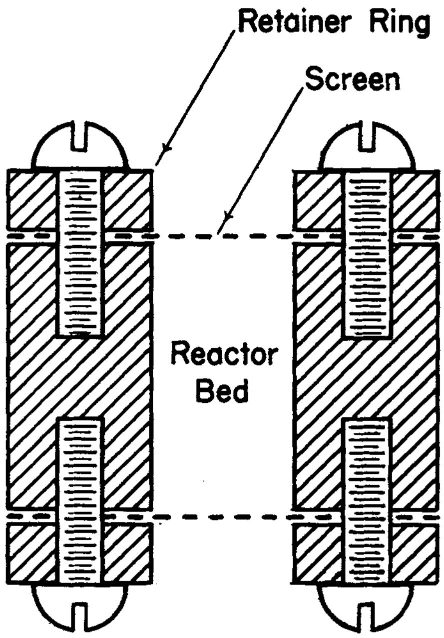

Fig. 2. Diagrammatic sketch of the cartridge type of differential bed reactor.

The use of thin differential beds approximately 1/16 in. in depth raised questions regarding bed uniformity and possible channeling effects. To eliminate these possible sources of error, the brass spheres were thoroughly mixed with glass spheres of the same size in the approximate ratio of one volume of catalyst to twenty volumes of glass spheres.

The differential reactor was confined in a hollow stainless steel cylinder, provided with stainless steel screens on the top and bottom. These screens were held securely in place with bolted-down retainer rings and confined the reactor bed within the cylindrical volume of the cartridge, which fitted snugly inside the reactor tube. A diagrammatic sketch of the reactor cartridge is presented in Figure 2. The catalyst charge was loaded into the reactor cartridge, which was then placed within the reactor tube.

Liquid samples resulting from this study were analyzed with an infrared spectrophotometer. Methyl ethyl ketone concentrations in *sec*-butyl alcohol were analyzed and ranged from 0.001 to 0.04 mole fraction.

QUALITATIVE INTERPRETATION OF RESULTS

Initial reaction rates were calculated from a material balance and the extent of conversion in the differential reactor. The initial reaction rates resulting from the experimental runs of this investigation were used to establish the rate equation for this dehydrogenation reaction. The majority of runs were conducted with pure *sec*-butyl alcohol as feed. To clarify certain aspects of the rate equation, it also became necessary to use mixed feeds. The operating temperature ranged from 550° to 700°F. and the pressure from subatmospheric conditions to 14.6 atm.

To obtain a preliminary background on the response of this reaction to pressure, five runs were conducted at 700°F. with the same catalyst charge

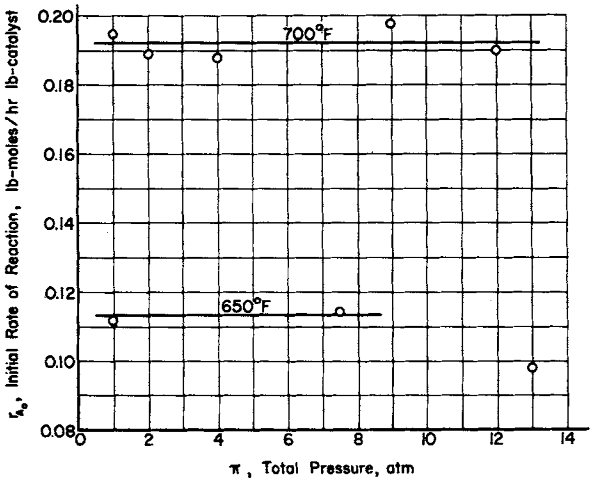

Fig. 3. Initial rates of reaction vs. total pressure for a feed of sec-butyl alcohol.

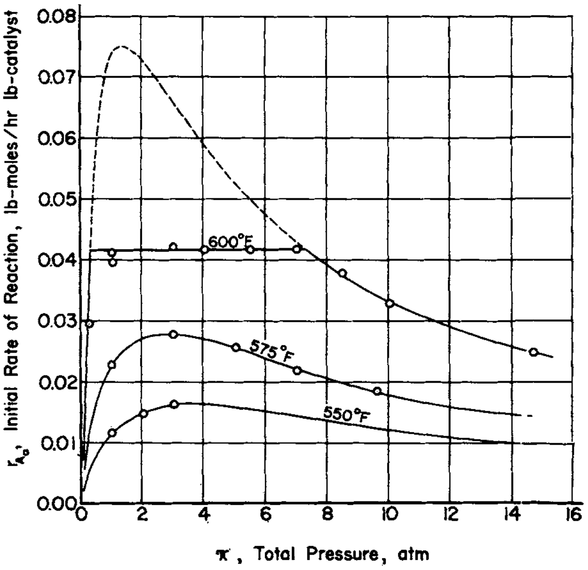

Fig. 4. Initial rate of reaction vs. pressure for a feed of sec-butyl alcohol.

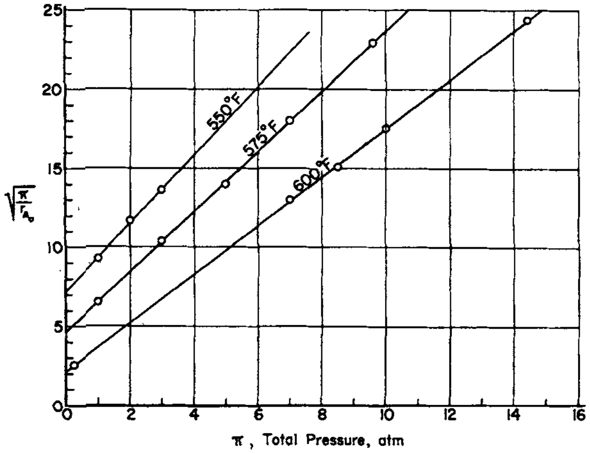

Fig. 5. Correlation of initial rate data with total pressure.

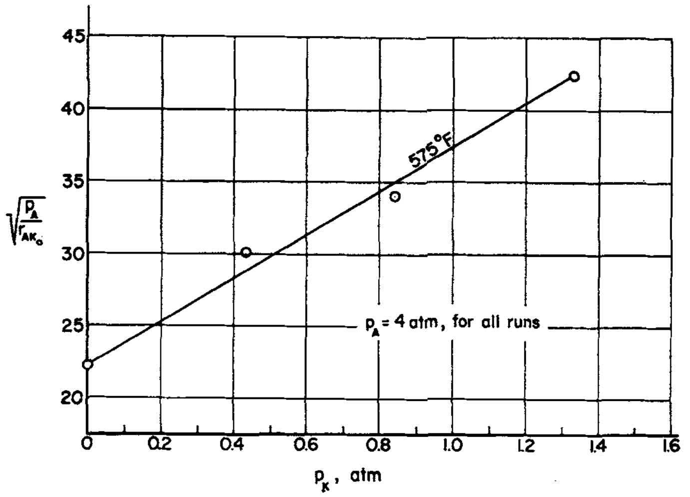

Fig. 7. Correlation of initial rate data for a mixed feed of alcohol and ketone.

of 1 g. and a feed rate of 0.0072 lb.-moles of alcohol/hr. For these runs the pressure was varied from 1 to 12 atm. The resulting initial rates presented in Figure 3 were found to be independent of pressure. This behavior suggests the possible existence of a controlling desorption step.

To take full advantage of the data obtained from a differential reactor, it is essential that the resistance to mass transfer be minimized. An exploratory set of runs was conducted to establish the existence of diffusional effects. The variation of the initial rate of reaction with feed rate was investigated at 600° and 650°F. and at several pressures. It was found that the initial rate of reaction increased to a leveling-off point beyond which the resistance to mass transfer became insignificant. Therefore in order to minimize the concentration gradients across the gas film and to relate the interfacial composition directly to the composition of the main gas stream, it became necessary to conduct the remaining runs of this study at high feed rates.

With this in mind and with a new batch of catalyst used the pressure dependence of this reaction was again investigated for three runs at 650°F. The resulting rates of reaction are presented in Figure 3. They were also found to be independent of pressure, except for the value at 13 atm., which happens to fall below the other two points. This decrease cannot be properly accounted for by means of experimental error. As was the case with the series of runs at 700°F., the first two points suggest a continuation of the probable desorption step exhibited at the higher temperature level. However the lower initial rate value at 13 atm. gives rise to the possibility of the existence of a controlling step other than the desorption of a product.

In order to investigate the possible cause for this lower initial rate, a series of runs was conducted to account for possible deviations from a desorption-controlling step. Since this rate decrease was completely absent at 700°F., it was assumed that this effect would become more pronounced with lower temperatures. Table 1 presents the experimental results obtained at 600°, 575°, and 550°F. from catalyst beds having the same level of activity. For these runs, feed rates of approximately 0.0139 lb.-moles of alcohol/hr. were used in the presence of a brass catalyst. This catalyst was diluted by glass spheres of the same size (50 to 60 mesh) in the proportions of twenty parts of glass to one part of catalyst in order to realize uniformity of flow throughout the differential reactor. These results have been plotted in Figure 4 and indicate that a definite plateau exists at the 600°F. temperature level, which completely disappears at 575° and 550°F.

The results presented at 600°F. are not only unusual but also unique in being able to account properly for the full length of the horizontal portion of the curve. The horizontal portion suggests the existence of a desorption-controlling step, whereas the remaining portions give a strong implication as to the existence of a possible dual-site surface-reaction rate equation.

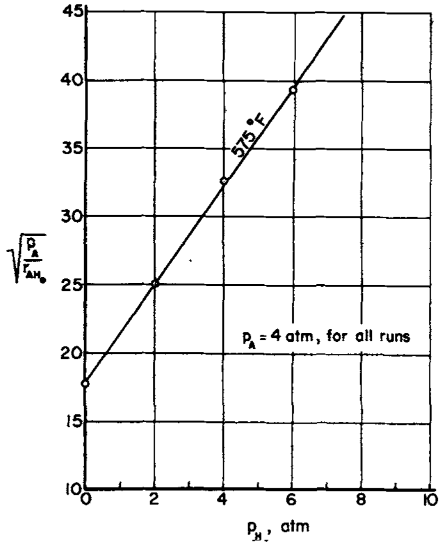

Fig. 6. Correlation of initial rate data for a mixed feed of alcohol and hydrogen.

ESTABLISHMENT OF REACTION RATES AND CONTROLLING STEPS

Surface Reaction

The general shape of the curves in Figure 4 at 575° and 550°F. and the nonhorizontal portions of the curve at 600°F. strongly suggest the existence of a dual-site surface-reaction controlling step. In view of this supposition these experimental data were fitted to Equation (7) by plotting $\sqrt{\pi/r_{A_0}}$ against π, as indicated in Figure 5. The resulting straight lines confirm this speculation and allow the calculation of $K_A/\sqrt{D}$ as the slope and $1/\sqrt{D}$ as the intercept. The rate constants resulting from Figure 5 are as follows:

t, °F.	D	K_A
550	0.0192	0.30
575	0.0430	0.412
600	0.202	0.689

and permit the calculation of the initial reaction rate for this temperature interval as

$$r_{A_0} = \frac{Dp_A}{[1 + K_A p_A]^2} \tag{5}$$

Equation (5) is applicable for the dual-site surface reaction when it is the controlling step. These results establish the existence of a dual-site reaction that should continue to prevail when the surface-reaction step is no longer controlling.

The results obtained thus far establish the presence of a dual-site reaction in which alcohol is adsorbed on a single site and is involved with an adjacent vacant site to produce the products ketone and hydrogen. Ketone should exist only in its molecular state. If hydrogen is assumed to exist on the surface in its molecular state, the following over-all rate equation applies

$$r=\frac{D\left[p_A-\frac{p_K p_H}{K}\right]}{[1+K_A p_A+K_K p_K+K_H p_H]^2} \quad (8)$$

For a mixed feed containing only hydrogen and alcohol, with the partial pressure of the alcohol held constant, Equation (8) can be rearranged to give

$$\sqrt{\frac{p_A}{r_{AH_0}}}=M+\frac{K_H}{\sqrt{D}}p_H \quad (9)$$

Experimental data obtained for a mixed feed of alcohol and hydrogen at 575°F. have been interpreted with the aid of Equation (9), and the results have been plotted in Figure 6. The linearity verifies the fact that the hydrogen on the catalyst surface exists in its molecular form. The slope $K_H/\sqrt{D}$ resulting from Equation (9) enables the establishment of the adsorption equilibrium constant for hydrogen once the value of D becomes known for the prevailing catalyst activity. This investigation was continued at 575°F. with a feed of alcohol and ketone in which the partial pressure of alcohol was held constant. As a result of these restrictions a relation comparable to Equation (9) was developed:

$$\sqrt{\frac{p_A}{r_{AK_0}}}=M+\frac{K_K}{\sqrt{D}}p_K \quad (10)$$

The resulting data, correlated with Equation (10), again produce a straight-line relationship when $\sqrt{p_A/r_{AK_0}}$ is plotted against p_K as shown in Figure 7. As for the case of hydrogen, the adsorption equilibrium constant can be calculated from the slope $K_K/\sqrt{D}$ once the constant D is determined for the prevailing catalyst activity.

A series of runs was made at a constant activity level that permitted the calculation of all the kinetic constants for Equation (8) at 575°F. The thermodynamic equilibrium constant was calculated from equilibrium studies (2) on this system. As a result the reaction rate at 575°F. becomes

$$r=\frac{0.0369\left[p_A-\frac{p_K p_H}{1.62}\right]}{[1+0.831p_A+2.91p_K+0.436p_H]^2} \quad (11)$$

TABLE 1. INITIAL REACTION RATES RESULTING FROM THE DEHYDROGENATION OF *sec*-BUTYL ALCOHOL

(feed: 100% *sec*-butyl alcohol)
Catalyst: 1 g. of brass spheres (50 to 60 mesh) mixed with glass spheres of the same size in the proportion of twenty parts of glass to one of catalyst.

Run	Temperature, °F.	Pressure, atm.	Feed rate, lb.-moles/hr.	r_{A_0}, initial rate lb.-moles of alcohol/(hr.)(lb.-catalyst)
5-30	600	1.0	0.01359	0.0392
6-1	600	7.0	0.01366	0.0416
6-2	600	4.0	0.01394	0.0416
6-3	600	10.0	0.01367	0.0326
6-4	600	14.6	0.01398	0.0247
6-6	600	5.5	0.01389	0.0415
6-7	600	8.5	0.01384	0.0376
6-9	600	3.0	0.01392	0.0420
6-11	600	0.22	0.01362	0.0295
7-14	600	1.0	0.01390	0.0410
7-16	550	1.0	0.01396	0.0115
7-17	550	3.0	0.01392	0.0161
7-18	575	1.0	0.01411	0.0227
7-19	575	3.0	0.01400	0.0277
7-20	575	5.0	0.01401	0.0255
7-21	575	7.0	0.01374	0.0217
7-23	575	9.6	0.01342	0.0183
7-26	550	2.0	0.01386	0.0146

Desorption of Hydrogen

The horizontal line of Figure 4 suggests the presence of a desorption-controlling step. For a constant alcohol-ketone composition the resulting initial rates were not independent of pressure, and on this premise the desorption step does not involve ketone. On the other hand it was found that for an alcohol-hydrogen feed the resulting initial rates remained constant and were independent of pressure. Since the addition of hydrogen in the feed gives rise to constant initial rates, it is reasonable to assume that the desorption of molecular hydrogen is the other controlling step. Therefore the following rate equation for hydrogen desorption control applies:

$$r=\frac{k_H KL\left[p_A-\frac{p_K p_H}{K}\right]}{p_K\left[1+K_A p_A+K_K p_K+KK_H\frac{p_A}{p_K}\right]} \quad (12)$$

The initial rate equation for the desorption of hydrogen follows from Equation (12) and is

$$r_{A_0}=r_{AH_0}=\frac{k_H KLp_A}{KK_H p_A}=\frac{k_H L}{K_H}$$
$$=k'_H L=\text{constant}$$

GENERAL COMMENTS

The logarithmic values of the constants D and K_A established at 550°, 575°, and 600°F. were correlated against the reciprocal absolute temperature and failed to produce to conventional linear relationships commonly associated with kinetic studies. Instead the two resulting relationships exhibited curvatures, and both possessed positive temperature coefficients. From a thermodynamic consideration K_A should exhibit a negative temperature coefficient provided that the number of active sites on the catalyst surface remains constant. The deviations found to be present in these studies may be explained on the premise of an increasing number of active sites with increasing temperature. For metallic catalyst surfaces it is reasonable to expect that increasing temperatures will produce additional active sites. As a result of activation phenomena, inactive sites which could not participate in the reaction at lower temperatures became sufficiently energized to participate in the over-all reaction.

The existence of a model which exhibits different controlling steps at different reaction conditions poses a new concept in kinetic studies. For these dehydrogenation studies the dual-site surface reaction involving an adsorbed alcohol molecule and an adjacent vacant site changes to a surface-controlling step in which the adsorbed molecule and a vacant adjacent site react to produce adsorbed ketone and molecularly adsorbed hydrogen. The surface-controlling step is favored at the lower temperatures and is independent of pressure. With increasing temperature the rate of the dual-site surface reaction increases more rapidly than the rate of the desorption step, which becomes the controlling step in the over-all reaction. This behavior is apparent from the results of Figure 3, in which the data at 700°F. indicate that the desorption step controls throughout the entire pressure range investigated. With decreasing temperature the controlling desorption step continues to control over a limited pressure interval. Outside this interval the surface reaction controls, as shown in Figure 4, at 600°F. With continued temperature decrease the controlling desorption step disappears completely in favor of a surface-reaction controlling step. In view of these findings, it becomes necessary to consider the rate of reaction with two possibilities involving both steps and to select as limiting that step which produces the lower reaction rate.

NOTATION

a,b,c,d = constants for Equation (1)
A,B,C,D = over-all rate constants, Equations (2), (3), (4), and (5)
k_H = forward-reaction velocity constant for the adsorption of hydrogen
k'_H = reverse-reaction velocity constant for the adsorption of hydrogen
K = over-all thermodynamic equilibrium constant

K_A = adsorption equilibrium constant for alcohol
K_H = adsorption equilibrium constant for hydrogen
K_K = adsorption equilibrium constant for ketone
L = total molal adsorption sites per unit mass
M = parameter, $(1+K_Ap_A)/\sqrt{D}$
p_A = partial pressure of alcohol, atm.
p_K = partial pressure of ketone, atm.
p_H = partial pressure of hydrogen, atm.
r = rate of reaction, lb.-moles/(hr.)(lb. of catalyst)
r_{A_0} = initial rate of reaction from a feed containing only alcohol
r_{AH_0} = initial rate of reaction from a feed containing alcohol and hydrogen
r_{AK_0} = initial rate of reaction from a feed containing alcohol and ketone
x_b, x_c, x_d = independent variables for Equation (1)
y = dependent variable for Equation (1)
π = total pressure, atm.

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A Study of Sieve-Tray Efficiencies

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The performance of sieve trays in the rectification of the methanol-water system without entrainment or leakage from the perforations was studied in an 8-in.–diameter five-tray column. The trays had a 2-in. weir height and 4-in. length of liquid path. Three tray geometries were studied: 1/4-in. diameter holes on 3/4-in. triangular spacing, 1/8-in. holes on 3/8-in. triangular spacing, and 3/16-in. on 7/16-in. triangular spacing. The superficial vapor velocity was varied from 2.2 ft./sec. to the limit of stable operation, which for this apparatus was 4.4 ft./sec. The ratio L_M/V_M within the column was varied from 1 to 0.5. The Murphree plate efficiency varied greatly from 105% at low concentration to 82% at high concentrations of methanol. Variations of 10 or 12 efficiency % were noted owing to changing velocities and tray geometries. Measurements of concentration gradients, foam heights, and gas pressure drops are also reported. This paper proposes a method of calculating the point efficiency and the number of individual-phase mass transfer units independent of the actual concentration gradient on the tray.

The method is applied to the methanol-water data, and calculated point efficiencies range from 50 to 65%. The value of $1/N_L$ for the methanol-water system is found to be small. The values of N_G and the effect of the velocity on N_G are believed to be the first in the literature for a tray in distillation operation. The effect of velocity is shown to be in agreement with the theory proposed by Gerster and co-workers. It is shown that $k_G' a_G$ decreases for increasing free area and increasing hole size. Finally variation in L_M/V_M is shown to have little effect on E_{MV}.

Fractionation in tray type of distillation columns is perhaps the most widely used means of separating the components of a liquid mixture. The calculation of the number of trays required for such a separation can be made readily (*31*) even for the most complicated separations. However only in recent years has much effort been directed toward analyzing the efficiency of operation of such trays in view of modern mass transfer theory (*1, 5, 6, 9, 14, 16, 17, 23, 27*). Any such analysis is complicated by the large number of variables involved in the properties of the gas and liquid phases, the conditions of operation, and the geometry of the system.

This paper reports efficiency data obtained by operating an 8-in. sieve-tray column at total reflux on the system methanol-water and discusses the data in the light of recent theory. A special study is made of the number of gas-phase transfer units.

The definitions of the transfer unit terms, appearing in the notation, will be assumed known to the reader. The usual assumptions made in using them are that the driving forces are concentration difference for liquids and partial-pressure difference for vapors and that equilibrium exists at phase interfaces. In addition in this paper it will be assumed that the vapor composition below a tray is uniform, that there is no back mixing of the vapor in the vertical direction, and that there are no unusual end effects at either bubble formation or break.

THE ADDITION OF RESISTANCES

The basic equation for obtaining the individual gas-phase value depends on the well-known (*32*) equation describing the additivity of resistances:

$$\frac{1}{N_{OG}} = \frac{1}{N_G} + \frac{m_G V_M}{L_M}\frac{1}{N_L} \tag{1}$$

Normally in using this equation one assumes N_G and N_L to be constant and plots $1/N_{OG}$ against $(m_GV_M)/L_M$ to obtain N_G from an intercept on such a plot. Using total-reflux sieve-tray plate-efficiency data, one must modify this direct approach in two ways.

First with total reflux data V_M/L_M has a value of unity, and $(m_GV_M/L_M$

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