Kinetics of the Liquid-phase Oxidation of Ethanol

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A study was made of the rate of liquid-phase oxidation of ethanol to acetic acid. An aqueous, basic solution of ethanol was allowed to trickle over a palladium-on-alumina catalyst in a packed tower while oxygen-containing gas was blown upward. The observed rates are described by an equation including a kinetic term and a mass transfer term for the diffusion of oxygen. Kinetic rate constants and gas- and liquid-film mass transfer coefficients are reported.

This paper reports the results obtained in a rate study of a reaction system in which both diffusion and kinetic effects are important. The object of the experiment was to determine the magnitude of both effects and to evaluate kinetic rate and mass transfer coefficients for the system. A solution of ethanol and sodium carbonate was allowed to trickle through a tower packed with palladium-on-alumina catalyst while oxygen-containing gas was blown upward through the tower. The ethanol was oxidized to acetic acid, which then reacted with the sodium carbonate to form sodium acetate. The reaction studied is as follows:

$$C_2H_5OH + O_2 + Na_2CO_3 \xrightarrow[Pd\,-Al_2O_3]{} NaOOCCH_3 + H_2O + NaHCO_3$$

In most cases the liquid rate to the tower was just sufficient to maintain a film of liquid on the catalyst. Liquid and gas flow rates; partial pressure of O_2; and concentration of ethanol, sodium carbonate, and sodium acetate were all varied to produce sufficient data from which the rate constants could be evaluated.

The oxidation of ethanol was chosen for investigation because it was known that the reaction proceeds smoothly at room temperature. Chemical analysis of the system would also be relatively accurate and simple. Furthermore it was hoped that the results of this work might be extended to the roughly analogous process of a trickling filter. From this viewpoint it was especially desirable to choose a reaction which can also be accomplished bacteriologically. The liquid rates were in the range used for trickling filters.

The choice of palladium as the catalyst was based on work of Mueller and Schwabe(*6*), who oxidized ethanol in a batch reactor using various platinum-group metals as catalysts. Their work indicated that any of these metals could be used as catalysts but all catalysts with the exception of palladium required an incubation period. As it was found that alumina would not interfere by catalyzing the reaction, a palladium-on-alumina catalyst containing 5% palladium was obtained. The alumina carrier was in the form of irregularly shaped particles, ⅛ to ¼ in. in size.

Mueller and Schwabe also tried acid, alkaline, and neutral reaction media. They found that in a neutral solution no reaction occurred; in acid solution, the ethanol was oxidized to acetaldehyde; and in basic solution, acetic acid was formed. It was desirable to produce acetic acid as the product of the reaction because of the simplicity of analysis. Thus it appeared necessary to use a basic solution for the experiments. Preliminary work showed that even dilute sodium hydroxide solutions attacked the alumina carrier. Ammonia inhibited the reaction completely. Various lower amines were tried, and while these did not inhibit the reaction they proved so volatile that extra precautions had to be taken to prevent substantial loss and consequent errors in analysis. Sodium carbonate was then tried and proved to be successful. Concentrations usually of the order of 0.1 molar were used. No attack on the carrier was noticed and the ethanol oxidized was completely converted to the acid. Infrared analysis and aldehyde tests showed that little or no acetaldehyde was being formed.

The equations used to correlate the data are derived in the following sections. First the kinetic rate equation, in terms of activities of the components at the catalyst surface, will be introduced. Then the mass transfer equations will be developed, relating the activity of oxygen at the catalyst surface to the oxygen concentration of the gas stream. It will be shown that the diffusion effects of the ethanol, sodium carbonate, and sodium acetate may be neglected.

DEVELOPMENT OF RATE EQUATIONS

This system involves the consideration of mass transfer across the gas and liquid films, a catalytic reaction on the surface of the catalyst, and diffusion of the products away from the catalyst. This is shown pictorially in Figure 1. Oxygen is transferred from the gas phase through the gas film and two liquid films to the catalyst surface. The ethanol and $CO_3^{=}$ ion diffuse through one liquid film to the catalyst; the HCO_3^{-} and AcO^{-} ions diffuse away from the catalyst.

There are many plausible rate equations for the catalytic reaction, but it is impossible to do more than select a most likely equation by inspection. The rate equations were developed by the methods suggested by Hougen and Watson(*4*).

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The equation which best fits the data is

$$r = \frac{\mathbf{k}_t\, a_{ei}\, a_{bi}\, a_{oi}}{(1 + K_1 a_{oi} + K_2 a_{ai})^2} \qquad (1)$$

where

r = rate of reaction, lb. moles/(hr.) (lb. of catalyst)

$\mathbf{k}_t$ = over-all kinetic rate constant

a_{ei}, a_{bi}, a_{oi} = activity at the catalyst surface of ethanol, carbonate ion, and oxygen, respectively

K_1 = adsorption equilibrium constant for oxygen

K_2 = adsorption equilibrium constant for acetate ion

This equation may be developed on the assumption that the reaction takes place by the following steps:

1. Adsorption of O_2 on a catalyst site

$$O_2 + l \rightarrow O_2\cdot l$$

2. Reaction of ethanol with the adsorbed O_2, an active site, and carbonate ion to yield adsorbed acetate ion and water and free bicarbonate ion

$$l + \mathrm{EtOH} + O_2\cdot l + CO_3^{=} \rightarrow$$

$$l\cdot \mathrm{AcO}^{-} + l\cdot H_2O + HCO_3^{-}$$

3. Desorption of the adsorbed acetate ion and water

$$l\cdot \mathrm{AcO}^{-} \rightarrow l + \mathrm{AcO}^{-}$$

$$l\cdot H_2O \rightarrow l + H_2O$$

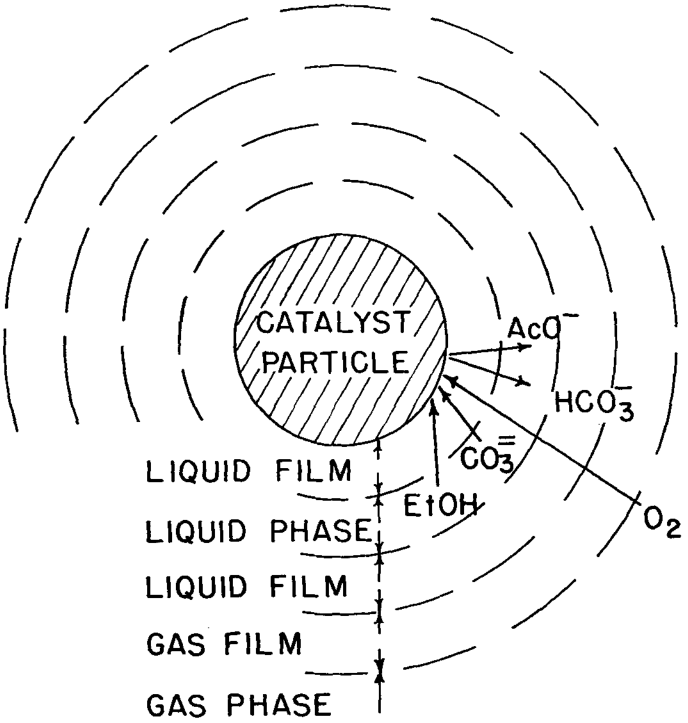

Fig. 1. Diagram of reactor mechanism.

Step 2 is a summation of several second-order reactions. Intermediates, including acetaldehyde and its hydroxylated form, are produced during reaction (*3*). For lack of information concerning the actual course of the reaction, the intermediate steps have been summarized in step 2.

The kinetic steps postulated above and their result, Equation (1), can be justified by the following information. When all variables except the partial pressure of oxygen were held constant, the rate of reaction increased with increasing O_2 partial pressure. The plot of these data suggested that the oxygen was adsorbed on the catalyst. It was also found that the rate was influenced by the concentration of the carbonate ion; this would indicate that step 2 above is the rate-controlling step. Equation (1) is based on step 2 being rate controlling. The thermodynamic data (*7*) for the reaction

$\mathrm{EtOh}(aq.) + O_2(g) + Na_2CO_3(aq.) \rightarrow \mathrm{NaAcO}(aq.) + NaHCO_3(aq.) + H_2O(l)$ shows that $\Delta G^o = -118.7$ kcal./g.mole. The equilibrium constant has a value of 1×10^{87}; consequently the reverse reaction may be neglected.

Equation (1) does not contain a water adsorption term because the water was present in large excess; its activity would be constant and the resulting rate equation would reduce to Equation (1).

Correlation of the data indicated that ethanol was not adsorbed on the catalyst, and thus no term for ethanol adsorption appears in Equation (1).

When standard states of unit molarity are assigned for the ethanol, acetate ion, and sodium carbonate; 1 atm. pressure is assigned for the O_2; and ideal behavior is assumed, Equation (1) becomes

$$r = \frac{\mathbf{k}_t\, N_{ei}\, N_{bi}\, p_{oi}}{(1 + K_1\, p_{oi} + K_2\, N_{ai})^2} \qquad (2)$$

where

N_{ei}, N_{bi}, N_{ai} = molarity at the interface of ethanol, sodium carbonate, and acetate/ion

p_{oi} = partial pressure of O_2 at the interface, atm.

Equation (2) is the basic equation used to correlate the data; however, the interfacial concentrations must be related to measurable quantities if this equation is to be useful.

MASS TRANSFER OF NONGASEOUS COMPONENTS

The concentrations of ethanol and carbonate were greater than 0.02 molar. The acetate concentration was either greater than 0.02 molar (when acetic acid was added to the feed) or so close to zero that the term K_2N_{ai} in Equation (2) was negligible. The oxygen was the limiting reactant, the maximum concentration, corresponding to a saturated solution, being 0.0003 molar. Thus if all the oxygen in a saturated solution reacted, the maximum concentration difference of the other components across the liquid film surrounding the catalyst would be 0.0003 molar. The interfacial composition would then be about (0.02 — 0.0003), or approximately 0.02. As complete reaction does not occur, the concentration difference is even smaller; consequently the interfacial compositions of ethanol, carbonate, and acetate may be taken as the main stream compositions without introduction of serious error.

DIFFUSION OF OXYGEN

The sites of the major resistance to diffusion of the oxygen are the gas and liquid films at the gas-liquid interface and the liquid film at the catalyst surface. The following equation for gas-film transfer coefficients has been proposed(*5*):

$$k_G a = B L^m G^n \qquad (3)$$

where

$k_G a$ = gas-phase mass transfer coefficient, lb. moles/(hr.)(cu. ft. of packing)(atm.)
L = liquid mass velocity, lb./(hr.)(sq.ft.)
G = gas mass velocity, lb./(hr.)(sq.ft.)
B, m, n = empirical constants

A value of 0.8 is usually assigned to n. If Equation (3) is divided by the bulk density of the catalyst to convert to a basis of 1 lb. of packing

$$\mathbf{k}_G = B L^m G^{0.8} \qquad (4)$$

where

$\mathbf{k}_G$ = gas-phase mass transfer coefficient, lb.moles/(hr.)(lb. of catalyst)(atm.)

For liquid-film coefficients at a gas-liquid interface, the following equation is suggested(*5*)

$$\frac{k_L a}{D} = \alpha \left(\frac{L}{\mu}\right)^p \left(\frac{\mu}{\rho D}\right)^{0.5} \qquad (5)$$

where

$k_L a$ = liquid-phase mass transfer coefficient, lb. moles/(hr.)(cu.ft. of packing)(lb. moles/cu.ft.)
D = diffusion coefficient, sq.ft./hr.
μ = viscosity of liquid, lb./(ft.)(hr.)
ρ = density of liquid, lb./cu.ft.
α = constant
p = constant with a value of 0.5 to 0.7 for various packings

Van Krevelen and Krekels(*9*) studied mass transfer through a liquid film to a solid at low flow rates. They propose the following equation for the liquid-film mass transfer coefficient:

$$\frac{k_{Li} a}{D} = 1.8 \left(\frac{L}{a\mu}\right)^{0.5} \left(\frac{\mu}{\rho D}\right)^{1/3} \qquad (6)$$

where

$k_{Li} a$ = liquid mass transfer coefficient at the liquid-solid interface, lb.moles/(hr.)(cu.ft.)(lb.moles/cu.ft.)

For the system under investigation the diffusion coefficients and viscosity and density of the solutions remained approximately constant because the concentration of the solutions was not changed substantially. Equations (5) and (6) may be rewritten as

$$k_L a = Q_1 L^p \qquad k_{Li} a = Q_2 L^{0.5}$$

where Q_1 and Q_2 are empirical constants.

It is likely that it would be difficult to determine separate values for the exponent of L. Assuming that the two exponents have the same value, p, the two coefficients may be combined to give an over-all liquid-phase coefficient:

$$k_{Lt} a = Q L^p \qquad (7)$$

where

$k_{Lt} a$ = combined mass transfer coefficient for diffusion in the liquid phase, lb. moles/(hr.)(cu.ft.)(lb.moles/cu.ft.)

Equation (7) may be divided by the bulk density of the packing to convert to a basis of 1 lb. of packing, and by Henry's constant for O_2 to convert the driving force from concentration units to partial-pressure units (atm.). The result is

$$\mathbf{k}_L = S L^p \qquad (8)$$

where

$\mathbf{k}_L$ = combined liquid-phase mass transfer coefficient, lb. moles/(hr.)(lb. of packing)(atm.)
S = a constant

Equations (4) and (5) may be combined to give an over-all mass transfer coefficient, $\mathbf{K}_o$,

$$\frac{1}{\mathbf{K}_o} = \frac{1}{\mathbf{k}_G} + \frac{1}{\mathbf{k}_L} \qquad (9)$$

The rate of reaction is equal to the rate of diffusion of O_2 from the gas phase to the catalyst surface, or

$$r = \mathbf{K}_o (p_o - p_{oi}) \qquad (10)$$

where

r = rate of reaction, lb. moles/(hr.)(lb. of catalyst)
$\mathbf{K}_o$ = over-all mass transfer coefficient, lb.moles/(hr.)(lb. of catalyst)(atm.)
p_o = partial pressure of oxygen in the gas phase, atm.
p_{oi} = partial pressure of oxygen at the catalyst surface, atm.

For purposes of correlation it is convenient to combine Equations (2) and (10) to give

$$p_o/r = \frac{(1 + \mathbf{K}_1 p_{oi} + K_2 N_a)^2}{\mathbf{k}_t N_b N_e} + \frac{1}{\mathbf{K}_o} \qquad (11)$$

Or, if the equivalent of $\mathbf{K}_o$ is substituted from Equations (4), (8), and (9),

$$p_o/r = \frac{(1 + K_1 p_{oi} + K_2 N_a)^2}{\mathbf{k}_t N_b N_e} + \frac{1}{SL^p} + \frac{1}{BL^m G^{0.8}} \qquad (12)$$

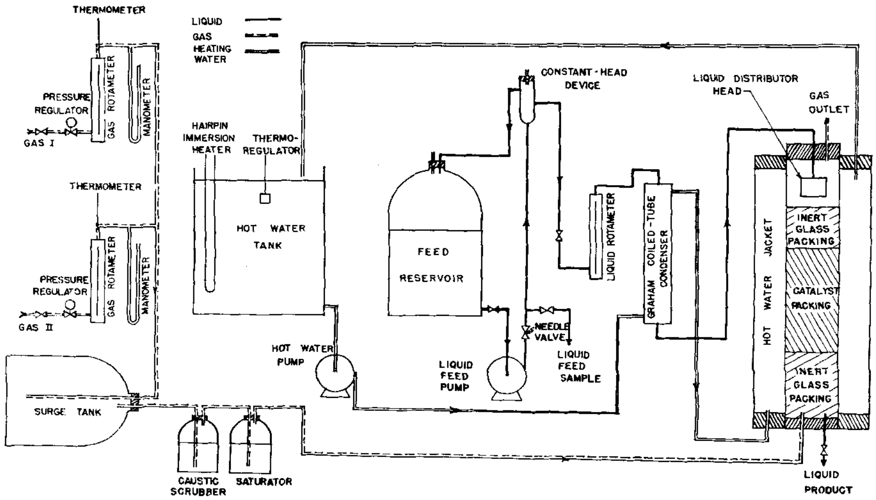

Fig. 2. Diagram of apparatus.

TABLE 1.—RANGE OF VARIABLES INVESTIGATED

Variable	Notation	Range
Gas flow rate	G	1-10 lb./(hr.)(sq. ft.)
Liquid flow rate	L	50-235 lb./(hr.)(sq. ft.)
Oxygen partial pressure in gas	p_o	0-1 atm.
Ethanol concentration	N_e	0.05-1.0 molar
Sodium carbonate concentration	N_b	0.1-0.3 molar
Acetate concentration	N_a	0-0.15 molar
Temperature	t	23° and 45° C.

where

N_a, N_b, N_e = molarity of acetate ion, sodium carbonate, and ethanol, respectively, in the main stream

Equations (11) and (12) are the completely developed forms of the rate equation (2), involving all the variables. The methods used to determine the constants in these equations are discussed in the following sections.

EQUIPMENT

A flow sheet of the equipment is shown in Figure 2.

The reactor consisted of a 20-in. length of 64-mm. glass tubing surrounded by a water jacket. The catalyst was palladium supported on alumina (5% palladium by weight); the particle size ranged from ⅛ to ¼ in. A bed depth of 7 in. was used (about 1 lb. of catalyst). A 7.5-in. layer of 4-mm. glass beads was placed above the bed and a similar 4-in. layer below the bed to ensure uniform gas and liquid flow patterns.

The liquid feed to the reactor entered at the top through a distributor equipped with four fine nozzles (orifice diameter = 0.0135 in.). The distributor was fed from a constant-head device to which liquid feed was pumped from the supply tank. Flow rates were measured with a rotameter. A Graham condenser was used as the feed preheater, warm water being the heating medium. A 1-in. depth of liquid was maintained at the bottom of the reactor to act as a gas seal.

Mixtures of air, oxygen, and nitrogen were used to produce various partial pressures of oxygen in the gas fed to the reactor. The air was taken from the laboratory service lines, the oxygen and nitrogen from cylinders. The gases passed through pressure-regulating valves to rotameters. The pressure was measured with a water manometer, temperature by thermometers. The gases after leaving the meters were combined and piped to a surge tank, from which they passed through a caustic scrubber to remove carbon dioxide and then to a saturator where the gases were bubbled through some of the liquid feed to minimize evaporation in the reactor. It was not necessary to adjust the temperature of the gas before it entered the reactor. The reactor temperature was controlled by pumping warm water from a thermostatted water bath through the various water jackets and condensers. Spun-glass insulation with an aluminum foil cover was used to insulate the jackets and water lines. All tanks and containers in the system were glass bottles. The piping, except for a few fittings on the pumps, was glass and Tygon tubing.

PROCEDURE

Three gallons of feed were made up for each run. First the warm water was circulated to the preheater and reactor jacket. Then the tanks, piping, and reactor were thoroughly flushed out with some of the feed solution to be used. The gas flow rates were adjusted to the desired values and then the gas was allowed to flow into the reactor to purge it. The liquid-feed tank was charged and the liquid admitted to the reactor at the desired rate, thus starting the run.

All runs were conducted for a period of 2 hr. when it was shown that after 2 hr. operation, steady-state conditions were reached. At the end of the 2 hr. samples of the feed and product solutions were withdrawn. The gas and liquid rates and temperatures were maintained constant throughout the run.

Less than 0.4°C. difference in temperature was found between the reactor bed at inlet and outlet and the water jacket surrounding the reactor. Thus the reactor temperature was measured by taking the jacket temperature. This procedure was justified for all gas and liquid flow rates and gas temperatures.

TABLE 2.—SAMPLE DATA—RUN 120

$G = 10.72$ lb./(hr.) (sq. ft.) $p_o = 0.205$ atm.
$L = 145$ lb./(hr.) (sq. ft.) $t = 32.0$ °C.
$r = 1.943 \times 10^{-5}$ lb. moles acetate formed/(hr.) (lb. of catalyst)

	Concentrations (molarity)		
	Inlet	Outlet	Average
N_e	0.200	0.196	0.198
N_b	0.0984	0.0940	0.0962
N_a	0.0466	0.0510	0.0488

Experiments proved that no homogeneous reaction was occurring and that the alumina carrier was not dissolving.

CHEMICAL ANALYSIS OF FEED AND PRODUCT

The analytical procedure was based on the conversion of ethanol to acetic acid. Aldehyde and ketone tests gave negative results; analytical tests by the Chemistry Department at the University of Wisconsin confirmed the presence of acetate ions. Thus it could be safely assumed that all the ethanol converted was oxidized to acetic acid.

The conversion for any given run was determined from the difference of acetic acid content of the feed and product. The analysis for acetic acid involved the back titration of the alkaline sodium carbonate solutions with acetic acid by use of a glass-electrode pH meter to locate the end point of the titration. It was difficult to locate precisely the end point for each titration, but the titration curves for feed and product samples were parallel in the region of the end points. Thus the change in acetic acid concentration could be measured by taking the difference between the titration curves without a knowledge of the exact end points.

The total sodium carbonate concentration of the feed was determined by titration with hydrochloric acid to the methyl orange end point.

RESULTS

Table 1 shows the variables and their ranges, which were investigated.

Calculation Procedures

In the evaluation of the constants of Equation (12), mean values of the concentration terms were used as the reaction caused a change in concentration. This change was of the order of 4%; because it was so small, the arithmetic average of inlet and outlet concentrations was used as the mean. Table 2 contains the data from a sample run, run 120.

Temperature corrections were introduced in the correlation of data from those runs which could not be maintained at the desired temperature. The values of the constants at the lower temperature are reported *for the average of the*

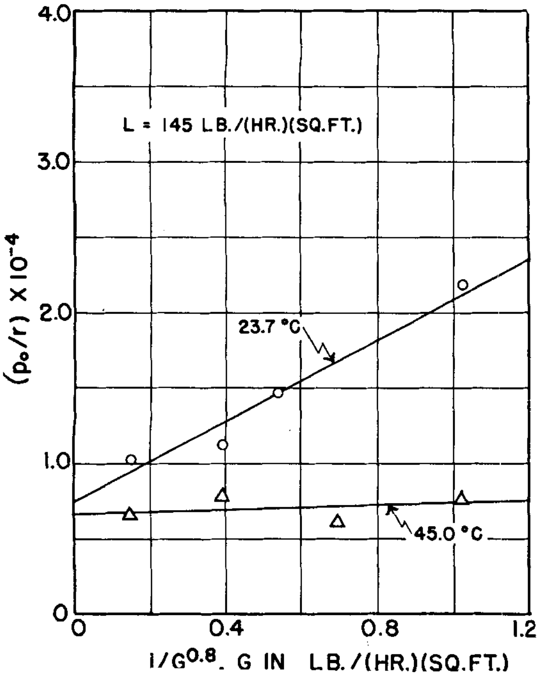

Fig. 3. Correlation of reaction rate with gas mass velocity.

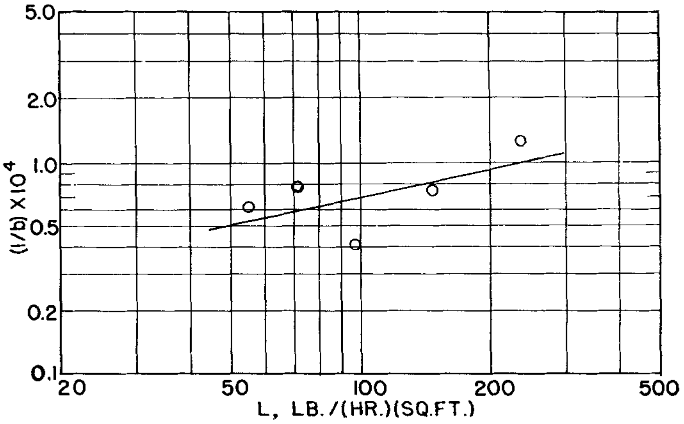

Fig. 4. Effect of liquid mass velocity on gas-phase mass transfer coefficients.

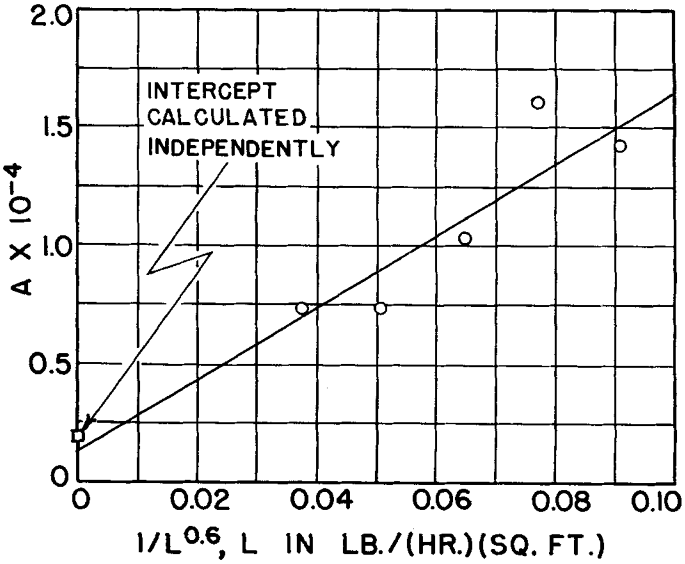

Fig. 5. Correlation of liquid phase mass transfer coefficients at 23.7°C.

TABLE 3.—CONSTANTS OF EQUATION (14) AT 23.7°C.

Liquid flow rate, lb./(hr.) (sq. ft.)	$A \times 10^{-4}$	$b \times 10^{-4}$
234	0.733	0.807
145	.734	1.359
96.2	1.033	2.415
71.6	1.602	1.304
54.6	1.419	1.621

temperatures of the runs used in a particular correlation.

The actual mathematical evaluation of the constants was done by the method of least squares.

Gas-phase Mass Transfer Coefficients

For a given liquid rate, if the concentrations of the reactants and products are held constant, Equation (12) reduces to

$$p_o/r = A + \frac{b}{G^{0.8}} \qquad (13)$$

where A and b are constants.

This incorrectly presumes that p_{oi} will remain constant. Variations in gas rate will affect the rate of transfer of oxygen, and thus p_{oi}. It is extremely difficult to evaluate the constants in Equation (12) without making this assumption. The later correlations show that R, the resistance to reaction of the chemical terms $[R = A - (1/SL^p)]$ is about 0.13×10^4; whereas the total resistance (p_o/r) varies between 0.8×10^4 and 3.5×10^4. Thus the assumption of constant p_{oi} in this correlation does not introduce a large error.

Then by varying only the gas flow rate, the constants A and b of Equation (13) may be evaluated. Table 3 reports the values obtained for various constant liquid rates. Figure 3 illustrates the data for a liquid mass velocity of 145 and temperatures of 23.7 and 45.8°C.

From Equation (12) the parameter b is related to the liquid rate by $1/b = BL^m$.

The values of the constants B and m may be determined from the data of Table 3 by plotting log $(1/b)$ vs. log L. This is shown in Figure 4. At 23.7°C. these values are

$B = 0.098 \times 10^{-4}$
$m = 0.4$

Similarly at 45°C. $m = 0.4$ and $B = 0.055 \times 10^{-4}$

Liquid-phase Mass Transfer Coefficients

The term A of Equation (13) may be written as $A = R + 1/SL^p$ where R represents the chemical reaction terms. Again assuming R constant, R, S, and p were evaluated from the data of Table 3. Values of p from 0.4 to 0.8 were assumed and R and S were evaluated. The best fit was obtained for $p = 0.6$, although the other values correlated reasonably well. Figure 5 illustrates the data for 23.7°C. The term R initially was found to be zero; subsequently it was found that $R = 0.136 \times 10^4$. Using this value of R and recalculating give the constants at 23.7°C. as

$R = 0.136 \times 10^4$
$p = 0.6$
$S = 6.63 \times 10^{-6}$

Similarly at 45°C.

$R = 0.136 \times 10^4$
$p = 0.6$
$S = 9.18 \times 10^{-6}$

Oxygen Adsorption Equilibrium Constant K_1

The most convenient form of Equation (1) for determining the oxygen adsorption equilibrium constant K_1 is

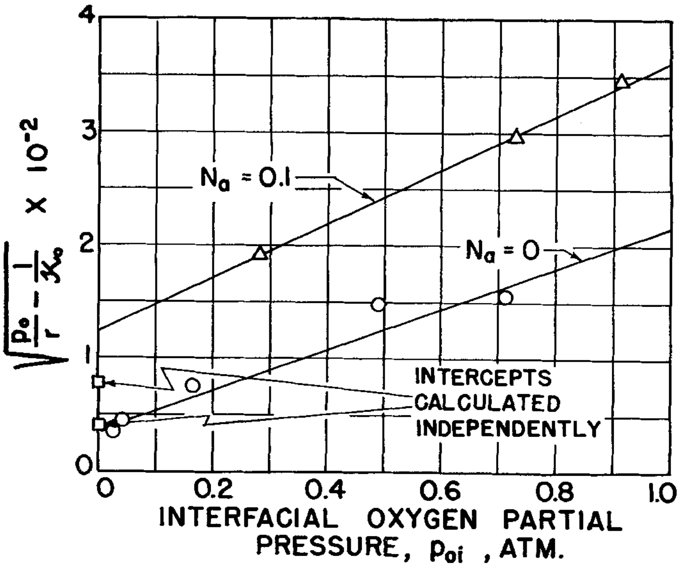

Fig. 6. Correlation of reaction rate with oxygen partial pressure at 28.6°C.

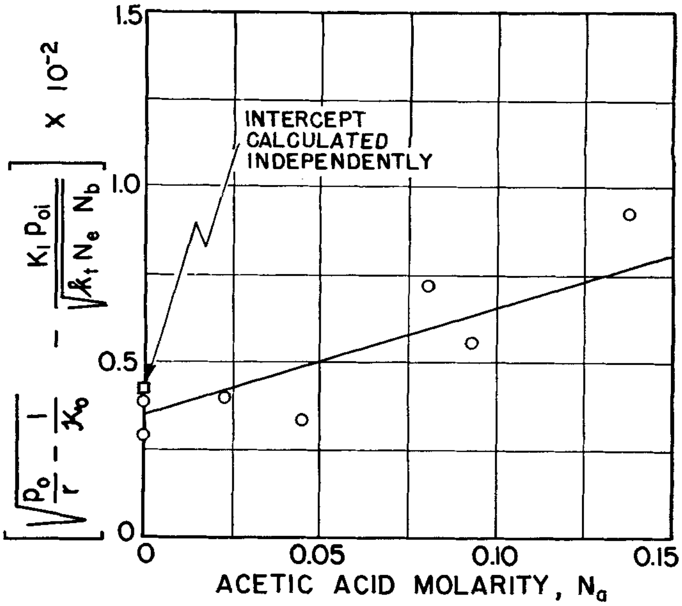

Fig. 7. Correlation of reaction rate with acetic acid concentration at 29.3°C.

$$\sqrt{\frac{p_o}{r}-\frac{1}{\mathbf{K}_o}} = \frac{1+K_2 N_a}{\sqrt{\mathbf{k}_t N_e N_b}} + \frac{K_1 p_{oi}}{\sqrt{\mathbf{k}_t N_e N_b}} \qquad (14)$$

and

$$p_{oi} = p_o - r/\mathbf{K}_o$$

Values of $\mathbf{K}_o$, the over-all mass transfer coefficient, may be calculated from the previously determined quantities by the equation

$$\frac{1}{\mathbf{K}_o} = \frac{1}{SL^{0.6}} + \frac{1}{BL^{0.4}G^{0.8}} \qquad (15)$$

The lower temperature of 23.7°C. could not be maintained at this time. The average temperature rose to 28.6°C. Interpolating for the proper values of B and S, gave $1/\mathbf{K}_o = 0.925 \times 10^4$ at 28.6°C. and $1/\mathbf{K}_o = 0.590 \times 10^4$ at 45°C.

The operating variables, except p_o were held constant; under these circumstances Equation (14) reduced to a linear equation. If $\sqrt{p_o/r - 1/\mathbf{K}_o}$ is plotted vs. p_{oi}, a straight line should be obtained with a slope of $K_1/\sqrt{\mathbf{k}_e N_c N_b}$ and an intercept of $(1 + K_2 N_a)/\sqrt{\mathbf{k}_t N_e N_b}$. This is shown in Figure 6. The value of K_1 is obtained by dividing the slope by the intercept of the curve when $N_a = 0$. From the average of the slopes of the two curves of Figure 6, at 28.6°C. $K_1 = 5.3$. Similarly at 45°C. $K_1 = 4.3$.

Acetic Acid Adsorption Equilibrium Constant, K_2

If Equation (11) is written in the form

$$\sqrt{\frac{p_o}{r}-\frac{1}{\mathbf{K}_o}} - \frac{K_1 p_{oi}}{\sqrt{\mathbf{k}_t N_e N_b}} = \frac{1}{\sqrt{\mathbf{k}_t N_e N_b}} + \frac{K_2 N_a}{\sqrt{\mathbf{k}_t N_e N_b}}$$

it will be seen that the equation is linear with respect to N_a provided the value of $\sqrt{\mathbf{k}_t N_c N_b}$ is constant. The operating conditions were such that the value of $\sqrt{\mathbf{k}_t N_e N_b}$ would be the same as in the previous section.

Figure 7 is the graph of Equation (16) at 29.3°C. The value of K_2 is obtained by dividing the slope of the line by the intercept.

The results of this correlation are
$K_2 = 9.05$ at 29.3°C.
$= 25.9$ at 45.0°C.

TABLE 4.—SUMMARY OF RESULTS

$$r = \frac{\mathbf{k}_t N_e N_b p_{oi}}{(1 + K_1 p_{oi} \times K_2 N_a)^2}$$

$$p_{oi} = p_o - r/\mathbf{K}_o$$

$$\frac{1}{\mathbf{K}_o} = \frac{1}{\mathbf{k}_G} + \frac{1}{\mathbf{k}_L}$$

$$\ln k_t = \frac{-17{,}000}{RT} + \frac{49.3}{R}$$

$$\ln K_1 = \frac{-2.375}{RT} + \frac{4.35}{R}$$

$$\ln K_2 = \frac{-12{,}750}{RT} + \frac{46.0}{R}$$

Temperature range of 23.7° to 45.0° C

Temperature = 23.7° C.
$\mathbf{k}_G = 0.098 \times 10^{-4}\ L^{0.4}G^{0.8}$
$k_G a = 4.46 \times 10^{-4}\ L^{0.4}G^{0.8}$
$\mathbf{k}_L = 6.63 \times 10^{-6}\ L^{0.6}$
$k_{J,t}a = 3.62L^{0.6}$

Temperature = 45.0° C.
$\mathbf{k}_G = 0.055 \times 10^{-4}\ L^{0.4}G^{0.8}$
$k_G a = 2.50 \times 10^{-4}\ L^{0\ 4}G^{0.8}$
$\mathbf{k}_L = 9.18 \times 10^{-6} L^{0.6}$
$k_{Lt}a = 6.85L^{0.6}$

Kinetic Rate Constant, $\mathbf{k}_t$

The value of the rate constant $\mathbf{k}_t$ is obtained directly from Equation (11):

$$p_o/r = \frac{1}{\mathbf{K}_o} + \frac{1}{\mathbf{k}_t}\left[\frac{(1 + K_1 p_{oi} + K_2 N_a)^2}{N_e N_b}\right] \qquad (11)$$

All the constants but $\mathbf{k}_t$ have been determined so that all the terms in the equation may be calculated. Then if p_o/r is plotted vs. $(1 + K_1\ p_{oi} + K_2 N_a)^2/N_e N_b$ a straight line should result with a slope of $1/\mathbf{k}_t$ and an intercept of $1/\mathbf{K}_o$. The plot of the data at 29.5°C. is shown in Figure 8. Five points falling within the labeled square were omitted from the correlation, with the result that
$\mathbf{k}_t = 0.032$ at 29.5°C.
$= 0.128$ at 45.0°C.

Temperature Effects

The constants K_1, K_2 and $\mathbf{k}_t$ may be related to the temperature

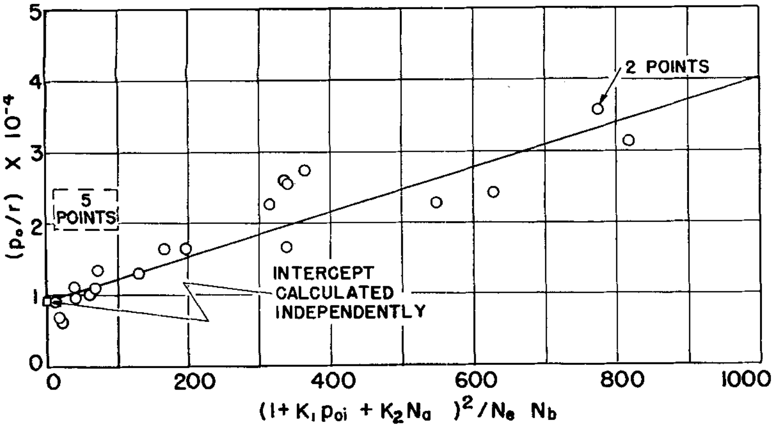

Fig. 8. Correlation of reaction rate with ethanol and sodium carbonate concentrations at 29.5°C.

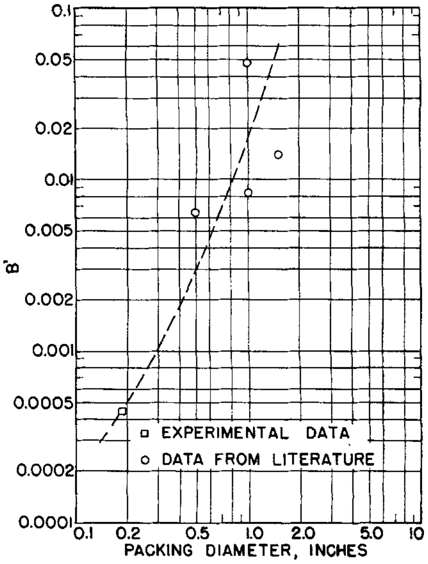

Fig. 9. Comparison of gas mass transfer correlations.

change by the equation

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

where

ΔH = enthalpy change of reaction or activation
ΔS = entropy change of reaction or activation

The appropriate equations are reported in the summary, Table 4.

DISCUSSION OF RESULTS

Independent Calculation of Intercepts

The intercepts of Figure 4 through 7 may be calculated from the known values of the constants. This serves as a check on the calculations. The calculated and graphically determined values are listed in Table 5.

Comparison of Calculated and Experimental Rates of Reaction

The rate of reaction for any run may be calculated by a trial-and-error procedure by use of the determined values of the constants. The average percentage of error between calculated and experimental values is 27.2. A total of sixty-seven runs was used in the calculations; of these, two runs had errors in excess of 100%.

The differences between calculated and experimental rates of reaction may be ascribed to temperature variations, the chemical nature of the system, and the method of analysis.

The correlations show that the constants change appreciably with temperature. Better results could be obtained by maintaining constant temperature; the agreement between calculated and experimental rates is much better for the 45°C. runs than for the lower temperature runs, where the temperature varied. Inspection of the data indicates that large variations in the feed concentrations (as is necessary to evaluate the constants) frequently caused unusual rates of reaction. It is felt that the buffering action of the acetate-carbonate system obscured rate changes caused by changes in the feed composition. A more positive means of analysis would also be desirable, as duplicate runs had as much as 15% difference in conversion.

Within the limits of analysis, the catalyst showed constant activity during the period of experimentation.

Comparison of Results with Published Data

Most data on gas-phase mass transfer coefficients have been obtained from the study of the ammonia-air-water system. Sherwood and Holloway (*8*) showed that different solutes affect the coefficients only in proportion to the 0.17 power of the diffusivities. Thus the results reported in this paper for oxygen absorption may be compared directly with the ammonia results.

Gas-film mass transfer coefficients have been correlated with the following equation (*2, 5*):

$$k_Ga = B'\,L^mG^{0.8} \tag{3}$$

B' is a constant dependent on the size of the packing. The value of m reported is about 0.4, the same value determined in this paper.

It is interesting to compare a plot of B' vs. the nominal diameter of the packing, as shown in Figure 9. The value of B' for the packing used in this experiment is 0.00045, and the diameter is assumed to be the average of the particle-size range (⅛ to ¼ in.), or 0.188 in.

Liquid-phase mass transfer coefficients have been correlated by the equation (*5*):

TABLE 5.—COMPARISON OF GRAPHICAL AND CALCULATED INTERCEPTS

				Intercept	
Figure	Temp.°C.	N_a	Formula	Calculated value	Graphical value
4	23.7	–	$\frac{(1+K_1p_{oi})^2}{k_tN_eN_b}$	0.2×10^4	0.136×10^4
	45.0	–		0.066×10^4	0.136×10^4
5	28.6	0	$\frac{1+K_2N_a}{\sqrt{k_tN_eN_b}}$	41.3	39.8
		0.0974		77.1	120
	45.0	0		21.4	31.4
6	29.3	–	$\frac{1}{\sqrt{k_tN_eN_b}}$	40.5	34.8
	45.0	—		20.4	26.8
7	28.6	—	$\frac{1}{K}$	0.925×10^4	0.924×10^4
	45.0	—		0.590×10^4	0.631×10^4

$$\frac{k_L a}{D} = \alpha\left(\frac{L}{\mu}\right)^p\left(\frac{\mu}{\rho D}\right)^{0.5} \quad (5)$$

where α is a constant dependent on packing size and p is a constant of value 0.5 to 0.8

The value of $p = 0.6$ reported here for oxygen absorption seems reasonable when compared with the foregoing values. Figure 10 shows a plot of α vs. packing diameter. From the data given in Perry(*7*) for D and N_{Sc}, α for this packing is calculated to be 3,190.

It is difficult to estimate the individual liquid-film coefficients at the gas-liquid and liquid-solid interfaces, but the apparent agreement between the results and Molstad's correlations would indicate that the major resistance to mass transfer in the liquid phase is at the gas-liquid interface. This may be corroborated by estimating a coefficient for the other liquid film from Equation (6). Brown(*1*) indicates that the surface area per volume of packing is approximately six times the area of a sphere of the same diameter as the packing (0.188 in.). Coefficients calculated on this basis are about four times as large as the experimental values, an indication that the liquid film at the gas-liquid interface offers more resistance to mass transfer than does the liquid film at the catalyst surface.

CONCLUSIONS

It may be concluded that the equations presented in Table 3 correlate the data reasonably well. The various parameters in the mass transfer equations agree with previously published work(*2, 5*). Figures 9 and 10 indicate that packing size may have a considerable effect on mass transfer coefficients.

It has been shown that for this system—oxidation of dilute alcohol solutions trickling over a palladium catalyst countercurrent to a flow of oxygen-containing gas—appreciable resistance to reaction is encountered in both gas and liquid films. Increased rates of reaction may be obtained by increasing the gas or liquid flow rates and also by increasing the oxygen content of the gas.

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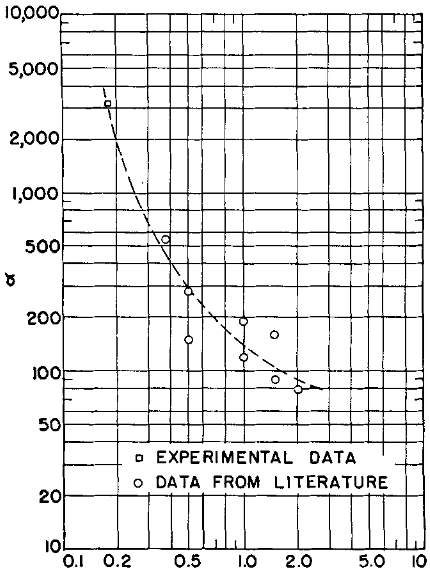

Fig. 10 Comparison of liquid mass transfer correlations.

NOTATION

$A = (1 + K_1 p_{oi} + K_2 N_a)^2 / \mathbf{k}_t N_e N_b + 1/SL^p$

a = interfacial packing area, sq. ft./cu.ft.

$a_{ai}, a_{bi}, a_{ei}, a_{oi}$ = activity of acetate ion, carbonate ion, ethanol and oxygen, respectively, at the catalyst surface

B = empirical constant

b = empirical constant

D = liquid diffusion coefficient, sq. ft./hr.

G = gas mass velocity, lb./(hr.)(sq.ft.)

H = Henry's law constant, atm./(lb. moles/cu.ft.); for oxygen, $H = 1.20 \times 10^4$

ΔH = enthalpy change of reaction or activation, cal./g. mole

$\mathbf{K}_o$ = over-all mass transfer coefficient, lb. moles/(hr.)(lb. of catalyst)(atm.)

K_1 = adsorption equilibrium constant for oxygen

K_2 = adsorption equilibrium constant for acetate ion

k_G = gas-film mass transfer coefficient, lb. moles/(hr.)(sq.ft.)(atm.)

$\mathbf{k}_G$ = gas-film mass transfer coefficient, lb. moles/(hr.)(lb. of catalyst)(atm.)

k_L = liquid-film mass transfer coefficient, lb. moles/(hr.)(sq. ft.)(lb. moles/cu.ft.)

k_{Li} = liquid-film mass transfer coefficient at a solid-liquid interface, lb. moles/(hr.)(sq. ft.)(lb. moles/cu.ft.)

K_{Lt} = effective mass transfer coefficient for all diffusion in the liquid phase, lb. moles/(hr.)(sq.ft)(lb. moles/cu.ft.)

$\mathbf{k}_L$ = effective mass transfer coefficient for all diffusion in the liquid phase, lb. moles/(hr.)(lb. of packing)(atm.)

$\mathbf{k}_t$ = over-all kinetic rate constant

l = symbol for a single active site on the catalyst

m = empirical constant

N_a, N_b, N_e = average molarity in the main liquid stream of acetate ion, carbonate ion, and ethanol, respectively

N_{ai}, N_{bi}, N_{ei} = average molarity at the catalyst surface of acetate ion, carbonate ion, and ethanol, respectively

p = empirical constant

p_o = partial pressure of oxygen in the main gas stream, atm.

p_{oi} = partial pressure of oxygen at the catalyst surface, atm.

Q = empirical constant

$R = (1 + K_1 p_{oi} + K_2 N_a)^2 / \mathbf{k}_t N_e N_b$

R = gas constant = 1.987 cal./g. mole)(°K.)

r = rate of reaction, lb. moles/(hr.)(lb. of catalyst)

S = empirical constant

ΔS = entropy change of reaction or activation, cal./(g.mole)(°K.)

T = absolute temperature, °K.

t = temperature, °C.

α = empirical constant

μ = liquid viscosity, lb./(ft.)(hr.)

ρ = liquid density, lb./cu.ft.

ρ_B = bulk density of catalyst, lb./cu.ft. = 45.5

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