Esterification of Butanol and Acetic Acid

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Knowledge of the kinetics of the reaction of butanol and acetic acid catalyzed by sulfuric acid, coupled with vaporliquid equilibrium data, should allow the calculation and design of the distillation unit for the combined steps of reaction and separation. The densities of butanol, acetic acid, and butyl acetate at temperatures from 20° C. to their respective boiling points were determined to allow estimations of the volumes at reaction temperatures. The esterification reaction was more complex than that given by the customary equation. The reaction of butanol and sulfuric acid is probably the controlling factor at room temperature, but at the temperatures used in con-

WELVE years ago Keyes (14) pointed out the desirability of carrying out esterification reactions continuously inside ordinary fractionating columns, but no theoretical considerations of such processes have been published. The patents in this field (1, 4, 16) have been based on general principles rather than on specific design data.

By applying kinetics to an esterification process and then combining these results with distillation, it should be possible to estimate what occurs in a continuous esterification system after steady-state conditions are attained. From the initial studies, it was evident that the following data were needed: (a) variation of density of the various components with temperature; (b) knowledge of the kinetics of the esterification reaction—i.e., the order and mechanism of the reaction; (c) variation of the rate constant of esterification with temperature, catalyst concentration, and proportions of reactants, and a general correlation of these factors; (d) equilibrium constant for the esterification; (e) vapor-liquid equilibria data for the system.

The first four items were studied for the system butanolacetic acid-sulfuric acid, chosen as a typical medium-boiling ester for continuous esterification. The experimental work on this system involved catalyst concentrations of 0.03 to 0.13%sulfuric acid and five moles of butanol per mole of acetic acid feed, with a total contact time of 24.4 to 46.7 minutes (15).

VARIATION OF DENSITY WITH TEMPERATURE

To correct for volume at elevated temperatures, the variation of density of butanol, acetic acid, and butyl acetate with temperature up to their normal boiling points was determined with a thin-walled Cassia flask, which had a bulb of about 100 ml. capacity and a long, thin, graduated neek of 10 ml. capacity. The Cassia flask was equipped with a tight-fitting cork, which bore a short air-cooled reflux tube, and was immersed in a rapidly stirred oil bath. The bath temperature was held to within $\pm 0.1^{\circ}$ C. of the desired temperature until the volume in the neck of the flask was constant to ± 0.01 ml. over a 3-minute period. About 30 minutes were required for each temperature reading.

Since the variation of density of water is known (11), the flask was calibrated with water to correct for the thermal expansion of glass. A relation was obtained to allow for the expansion of the tinuous processing (100-120° C.), the esterification reaction was the controlling factor. With an excess of butanol as solvent, the reaction rate was proportional to the square of the acetic acid concentration, up to 75-85% conversion. The theoretical aspects of the mechanism are discussed and compared with the generally accepted Goldschmidt equation for catalytic esterifications. The effect of catalyst concentration, proportions of reactants, and temperature on the reaction rate constant were also studied. The results correlated into a single empirical equation for predicting the rate constant from these three quantities within an accuracy of about 8% in the range studied.

flask, using the best straight-line relation calculated by the method of least squares between a plot of true and determined values:

$$d = (1.000073 - 0.0000287 T)d'$$
(1)

where T = temperature, ° C. d = corrected density d' = apparent density



MATERIALS USED. Acetic acid was recrystallized three times from commercial C.P. glacial acid; it was 99.66% pure by titration and had a melting point of 16.6° C. The butanol used was 99.92% pure, and had a water content of 0.080% and a boiling range of 116.6–117.7° C. Butyl acetate was prepared from commercial ester by treatment with acetyl chloride, followed by distillation and phosphorus pentoxide purification (3) and redistillation; its boiling point was 125.5° C. and its ester content was 99.80% by saponification in the cold with aqueous alkali.

1	Fable I.	VARIATION	OF DENSI	гу wітн Т	EMPERAT	URE
Temp T, °C	Indi- cated Expan- sion, Ml.	Indi- cated Volume, Ml.	Apparent Density, d'	Corrected Density, d	Litera- ture Value ^a , dc	Differ- ence, $(d - d_{e})$
	Acetic	Acid, 99.604	2 Grams at 2	20° C., 99.6	8% Pure	
20 80 40 50 60 70 80 90	0.00 0.98 1.98 2.97 4.10 5.25 6.32 7.51	94.86 95.84 96.84 97.83 98.96 100.11 101.18 102.37	$\begin{array}{c} 1.0500\\ 1.0393\\ 1.0285\\ 1.0181\\ 1.0065\\ 0.9949\\ 0.9844\\ 0.9730 \end{array}$	$1.0495 \\ 1.0385 \\ 1.0274 \\ 1.0167 \\ 1.0048 \\ 0.9929 \\ 0.9822 \\ 0.9705 \\ 0$	1.0498 1.0387 1.0274 1.0160 1.0046 0.9931 0.9816 0.9699	$\begin{array}{r} -0.0003 \\ -0.0002 \\ 0.0000 \\ +0.0007 \\ +0.0002 \\ -0.0002 \\ +0.0006 \\ +0.0006 \end{array}$
100 110 115	8.78 10.00 10.7	$103.64 \\ 104.86 \\ 105.56$	$0.9611 \\ 0.9499 \\ 0.9436$	$0.9584 \\ 0.9470 \\ 0.9405$	0.9582	+0.0002
						±0.0003
	Buts	anol, 76.7361	Grams at 20	° C., 99.929	% Pure	
20 30 40 50 60 70	0.00 0.76 1.60 2.61 3.63 4.70 5.98	94.86 95.62 96.46 97.47 98.49 99.56 100.84	0.8089 0.8025 0.7955 0.7873 0.7791 0.7707 0.7610	0.8085 0.8019 0.7946 0.7862 0.7778 0.7692 0.7593	0.8086 0.8000 0.7908 0.7810	-0.0001 + 0.0019 + 0.0038 + 0.0052
90 100 110 115	7.05 8.20 9.69 10.2	101.91 103.06 104.55 105.06	0.7530 0.7446 0.7339 0.7304	0.7511 0.7425 0.7316 0.7280	 	•••
20	Dutyl A	04 96	A 0011	20° Ci, 99.0	50% Fure	
20 30 50 60 70 80 90	$\begin{array}{c} 0.00\\ 1.00\\ 2.13\\ 3.28\\ 4.43\\ 5.78\\ 7.02\\ 8.41\\ 9.80\end{array}$	94.80 95.86 96.99 98.14 99.29 100.64 101.88 103.27 104.66	0.8811 0.8719 0.8617 0.8516 0.8418 0.8305 0.8204 0.8093 0.7986	0.8807 0.8712 0.8608 0.8504 0.8404 0.8289 0.8186 0.8186 0.8073 0.7964	•••	
110 120 • C	11.2 12.67 alculated fro	106.06 107.53 om density-ter	0.7880 0.7773 nperature eq	0.7856 0.7747 uations (18)	• • •	•••

Table I and Figure 1 summarize the data. Those for acetic acid are in good accord with the literature, but the values for butanol are considerably higher.

RATE OF REACTION

The mechanism of esterification depends on such variables as the concentration of reactants, concentration of catalyst, and temperature. To study these variables, batches of 50 to 135 grams total were weighed out in the order sulfuric acid, acetic acid, butanol, and were cooled in ice water. Approximately 5-ml. samples were pipetted into drawn-down soft glass test tubes (13 \times 100 mm.), which were sealed and inserted into a constant-temperature bath. Tubes were removed at various times, cooled, and dried. Then the tips were broken off, and 2 to 5 ml. of the contents were weighed out into a tared 250-ml. Erlenmeyer flask. Each sample was diluted with 50 ml. of distilled water and titrated immediately with 0.1 N sodium hydroxide, using phenolphthalein to determine the free acidity. The time was measured from insertion in the bath (the maximum elapsed time from the addition of butanol to insertion in the sealed tube in the bath



Figure 2. Reaction of Butanol and Sulfuric Acid at Various Temperatures

was 8 to 10 minutes). Some reaction undoubtedly occurs in this treatment, but it is insignificant compared with the amount of reaction at the elevated temperatures (for example, see Figure 9).

MATERIALS USED. Acetic acid for runs B through R was commercial c.p. glacial acid, 99.51% pure by titration, with a melting point of 15.5° C. For runs S through Z, the acid was recrystallized three times; 99.66% by titration and a melting point of 16.6° C. were obtained. Commercial butanol was used throughout; it had no acidity, a water content of 0.080%, and a boiling range of 116.6-117.7° C. The sulfuric acid was reagent grade, titrated 97.19 to 97.45% as sulfuric acid using phenolphthalein, and gave 97.42% when assayed as barium sulfate. The average value of 97.38% was taken.

REACTION OF BUTANOL AND SULFURIC ACID

To obtain the acetic acid present, the free acidity must be corrected for the presence of the catalyst. There is, however, a reaction between the alcohol and sulfuric acid (19, 20). The butyl monosulfate formed has a different equivalent weight from that of sulfuric acid in titration (154.18 compared to 49.04). Since the total number of moles of sulfate radical in the system is constant, the amount of butyl sulfuric acid formed can be determined from a single titration value, and the known amount of sulfuric acid:

grams butyl sulfuric acid formed = (154.18/1000) (2M - ml. N)

grams sulfuric acid remaining = $\frac{98.08}{1000}$ (ml. N - M)

where M = millimoles sulfuric acid originally present ml. N = titration equivalents used (ml. base \times normality)

Table II and Figure 2 give the results of tests with approximately 2% sulfuric acid in butanol. The reaction of butanol and sulfuric acid varies greatly with temperature. At 0° and 13° C. the rate is scarcely measurable up to 8 hours, at 25° to 30° C. the reaction proceeds over a period of days, and at 100° and 115° C. the reaction is so rapid (95 to 96% complete in 15 to 30 minutes) that the rate cannot be followed accurately. After 4 hours at 100° C. the amount of butyl sulfuric acid present decreases con-

	Тав	le II.	REACTION (F BUTA	NOL AND S	ULFURIC	Acid
Tir H	ne, ir.	Sample, Grams	Titration, Ml. N	Millim	oles H2SO4 Remaining	% of HaSO: Combined	Apparent Milli- equiv- alent, <i>B</i>
			0° C.,	1.9230%	H2SO4		
1 2 3 5 8		3.2860 3.7144 3.2866 3.9314 3.7262	1.27991.45431.29021.53121.4543	0.6443 0.7283 0.6444 0.7708 0.7306	0.6356 0.7260 0.6458 0.7604 0.7237	1.350.31-0.221.350.94	49.37 49.12 48.99 49.37 49.27
			18° C.,	1.9230%	H2SO4		
0 1 2 3 5 8 168		3.9902 3.9472 3.9720 3.9243 3.9989 4.0511 3.5623	1.5640 1.5466 1.5487 1.5292 1.5569 1.5702 1.3107	0.7823 0.7739 0.7788 0.7694 0.7840 0.7943 0.6984	$\begin{array}{c} 0.7817 \\ 0.7727 \\ 0.7699 \\ 0.7598 \\ 0.7729 \\ 0.7759 \\ 0.6123 \end{array}$	$\begin{array}{r} 0.08 \\ 0.15 \\ 1.14 \\ 1.25 \\ 1.42 \\ 2.31 \\ 12.34 \end{array}$	49.06 49.08 49.32 49.35 49.39 49.61 52.26
			25 to 30°.	C., 1.9440	% H2SO4		
16 16 40 88 768		4.0012 3.9720 3.9631 4.2303 4.0962 4.0646	1.4248 1.3439 1.0923 1.1616 0.9128 0.8477	0.7931 0.7873 0.7855 0.8386 0.8119 0.8056	$\begin{array}{c} 0.6817 \\ 0.5566 \\ 0.3068 \\ 0.3230 \\ 0.1009 \\ 0.0421 \end{array}$	20.34 29.31 60.94 61.48 87.57 94.77	54.59 57.46 70.53 70.80 87.24 93.21
			100° C.	, 1.9230%	H ₂ SO ₄		
0. 1 2 4 8 16 30	. 25 . 5 . 5	4.1889 4.3815 4.2160 4.1123 4.5070 4.7260 4.6386 4.1962 3.8925	0.8554 0.9005 0.8625 0.8410 0.9210 0.9825 0.9630 0.8772 0.8174 115° C.	0.8213 0.8590 0.8266 0.8063 0.9266 0.9095 0.8227 0.7632 ., 1.9230%	0.0341 0.0415 0.0359 0.0347 0.0373 0.0559 0.0535 0.0545 0.0545 0.0542	95.85 95.17 95.66 95.70 95.78 93.97 94.12 93.37 92.89	94.17 98.57 94.00 94.03 94.10 92.50 92.63 91.99 91.57
0	. 5	3.8350	0.7805	0.7519	0.0286	96.20	94.49



Figure 3. Determination of Order of Reaction for Catalyst Series at 100° C. and Approximately 5 Moles Butanol per Mole Acetic Acid

-	
Run	Wt. % H2SO
K	0.000
S	0.0147
H	0.0316
U	0.0679
v	0.1032
H.	0.1373

Reaction for Temperature Series with 0.03% Catalyst and Approximately 5 Moles Butanol per Mole Acetic Acid

Run

L M N O R

Temp., ° C.

30 30

100 110 120



Moles Butanol/ Mole Acetic Acid

2.991 4.992 10.03 19.62

siderably. A similar change in acidity has been reported in the reaction of ethanol and sulfuric acid (5, 19). This complication has no bearing upon this research, however, since after 4 hours at 100° C. most of the esterification rate curves deviate from straight lines. Furthermore, the amount of catalyst used in such esterifications is in the order of 0.03 to 0.13% by weight, as compared with 2% in these experiments. Thus for samples kept at room temperature or below, all of the catalyst can be assumed to be present as sulfuric acid; for samples heated to 100° C. or above, all of the catalyst can be assumed to be present as a mixture of butyl sulfuric and sulfuric acids, having a titration equivalent of 94.0. It was impossible to study the reaction of sulfuric acid and butanol in the presence of the other components; in any case it seems unlikely that there would be any important change if the other components were present.

ORDER OF ESTERIFICATION REACTION

The order of the esterification reaction can be most readily determined graphically (6). Log c vs. time gives a straight line for a first-order reaction; 1/c vs. time gives a straight line for a second-order reaction; and $1/c^2$ vs. time gives a straight line for a third-order reaction. Figures 3, 4, and 5 are qualitative plots for a few of the runs, based on the concentration of acetic acid in moles per 100 grams.

Figure 3 shows the effect of catalyst concentration at 100° C. With no catalyst (run K) straight-line plots are obtained for all three cases. With low catalyst concentrations (0.0147%, run S), a second- or third-order reaction is indicated. With catalyst concentrations above 0.015%, well defined straight lines are obtained for the second-order plot up to about 70-80% conversion, after which the curves flatten out.

Figure 4 shows that at low temperatures (runs L and M) with only limited reaction, the order is not ascertainable. At 100° C. or higher the reaction is bimolecular up to about 80 to 85% completion, as shown by the straight-line relation between 1/c and time.

Figure 5 indicates that the runs at 100 $^\circ$ C. and constant catalyst concentration are not first- or third-order reactions. With molar ratios of 3 to 1 and 5 to 1, the curves are sensibly

straight lines for the plot of 1/c vs. time. With a 10 to 1 ratio (run Y) a straight-line relation is also obtained up to 2-hour reaction time. In the case of a 20 to 1 ratio (run Z) the points for 0.5, 1, and 2 hours fall on a straight line which does not pass through the point for zero time; possibly this indicates an induction period.

Run

X U Y Z

It is apparent that the reaction between butanol and acetic acid in the presence of excess butanol and sulfuric acid as a catalyst, at temperatures above 100° C., follows a second-order (quadratic) equation up to a conversion of about 75 to 85% of the acetic acid present.

REACTION RATE EQUATION

The actual equation which governs the rate of esterification may be determined by trial and error; those generally given for esterification reactions were tested first. Assuming a nonreversible reaction,

$$dX/dt = k(A - X)(B - X)$$
⁽²⁾

which integrates into

$$kt = \frac{1}{A-B} \ln \frac{B(A-X)}{A(B-X)}$$
(3)

Assuming a reversible reaction,

$$dX/dt = k_1(A - X)(B - X) - k_2X(W + X)$$
(4)

which can be reduced to the form,

$$dX/dt = k(a + bX + cX^2)$$

This integrates into

$$kt = \frac{1}{\sqrt{-q}} \ln \frac{2cX + b - \sqrt{-q}}{2cX + b + \sqrt{-q}} - \frac{1}{\sqrt{-q}} \ln \frac{b - \sqrt{-q}}{b + \sqrt{-q}}$$
(5)

where dX/dt = velocity of reaction

- = acetic acid originally present (moles, or moles per A liter) В
 - butanol originally present (same units as A) W
 - water originally present (same units as A)

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X		-	amount of acetic acid trans-
			formed in interval (same
			units as A)
k,	k_1	-	reaction rate constants
k_2		=	reverse reaction rate constant

 \vec{K} = equilibrium constant = k_1/k_2 a = AB

$$b = (A + B + W/K)$$

$$c = 1 - 1/K$$

$$q = 4ac - b^2, \text{ where } b^2 > 4ac$$

None of these equations correlated all of the experimental data, but after a number of trials it was found that the equation

$$\frac{dX}{dt} = k(A - X)^2 \tag{6}$$

1.0 .

fitted the experimental data for all of the runs very well, up to a conversion of about 75 to 85% (as in the secondorder reaction plot).

Integration of Equation 6 gives

$$\frac{1}{A-X} = kt + I$$

Evaluating I by setting X = 0 when t = 0,

$$kt = \frac{X}{A(A-X)} \tag{7}$$

The proper form of the rate equation may be determined graphically by plotting various functions against time and noting which gives a straight-line relation: For Equation 3, log (A - X)/(B - X) vs. t; for Equation 5, log $(2cX + b - \sqrt{-q})/(2cX + b + \sqrt{-q})$ vs. t; for Equation 7, X/(A - X) vs. t.

The data for run B for these tests are plotted in Figure 6. Equation 3 gives a well defined curve and hence does not apply. The last six points on the curve for Equation 5 appear to fall on a straight line; on a larger scale, however, these points show a definite curve, and the initial point (zero time) falls far off the straight-line relation. Equation 7, however, shows a straightline relation from 0 to 3 hours, with the point for 4 hours slightly low.

As a further illustration the data for run N, using Equations 5 and 7, are plotted in Figure 7. With a larger scale and a check point at 0.5 hour, it is apparent that during the early stages the rate equation does not correspond to the mechanism proposed by Equation 5, but Equation 7 does give a straight line.

At the 3-hour point run N is 84.5% completed and run B is 86.3% completed. At the 4-hour point and above, Equation 7 no longer holds; the mechanism changes apparently to one approaching Equation 5 since the reverse reaction, saponification, is beginning to have an effect. This is indicated by the straight-line portion of the log plot above 4 hours, which shows that the normal esterification equilibrium law is setting in and is obeyed. However, in the continuous column esterification studies reported elsewhere (15), it was desired to reduce the time of contact to about 30 minutes; hence Equation 7, which gives a straight-line relation for the early stages of reaction, applies in the continuous esterifications. Long times of contact and attainment of esterification mass law equilibrium on a given plate are not needed for a high over-all extent of conversion.

Table III summarizes the complete calculations for the experimental data testing Equation 7. Figure 8 shows the relation between X/(A - X) and t for the runs at 100° C. with a molar



ratio of butanol to acetic acid of approximately 5 to 1 and with varying catalyst concentration. The degree of completion of the esterification of acetic acid is indicated on the right-hand scale. Up to 2 hours at 100° C. all of the lines are straight and pass through the origin. Run C with 0.00614% catalyst appears to be slightly irregular, showing a deviation at 3 hours. With 0.03% catalyst or higher, a conversion of 85 to 90% of the acetic acid is possible before the curves deviate from Equation 7, as equilibrium sets in and Equation 5 becomes valid.

Figure 9 gives the effect of temperature on conversion. Here again, at temperatures over 100° C., straight-line relations are obtained up to about 85% conversion. It will be noted that the points determined with heating times of 20 and 30 minutes are slightly low; this is probably because of the time required to heat the samples up to the reaction temperature.

Figure 10 illustrates effect of proportions of reactants at 100 °C. At low catalyst concentrations (0.03% or less), these runs show fairly good agreement with Equation 7. With 0.07% sulfuric acid, however, the curves for run Y (10 to 1 ratio) and run Z (20 to 1 ratio) do not pass through the origin; evidently a slight induction effect occurs here. Practically all of these data deviate from straight lines after 2 hours at 100° C., but below 75% conversion, the agreement is good.

REACTION RATE CONSTANT

DETERMINATION. In a bimolecular reaction the value for k is dependent upon the numbers expressing the concentration; for uniformity, the concentrations are expressed in moles per liter and k in liters/mole-minutes. Equation 7 can be rearranged to give

$$kA_0t = X/(A - X)$$

If the units are substituted for each term,

$$\frac{(\text{liter})}{(\text{mole})(\text{min.})} \frac{(\text{moles})}{(\text{liter})} \text{ (min.)} = \text{dimensionless ratio}$$

so that if A_0 in the left-hand member is expressed in moles per liter, the quantities on the right hand, X and A - X (i.e., the amount of acid reacted and the amount of acid unreacted) can be expressed in any units, such as moles, mole fractions, or moles per liter, provided the same units are used for each.

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				TABLE I	II. REACTI	ON RATE EQUAT	ion Data				
Catalyst Correction, %	Time, Hr.	Free Acidity, %	Actual Acetic Acid, %	Acetic Acid, Converted, X	$\frac{\text{Moles/100 G.}}{\text{Ratio,}}$ $\frac{X/(A - X)}{X}$	Catalyst Correction, %	Time, Hr.	Free Acidity, %	Actual Acetic Acid, %	Acetic Acid, Converted, X	$\frac{\text{Moles/100 G.}}{\text{Ratio,}} X/(A - X)$
Run	B, 0.0309%	H₂SO4, 100°	C., $B/A =$	4.978, A =	0.2327	Run	K, 0.000%	H2SO4, 100°	C., $B/A =$	4.965, A =	0.2332
$ \begin{pmatrix} \frac{60.05}{94} \\ \times 0.0309 \\ 0.0197\% \end{pmatrix} $	0 1 2 8 4 5 6 7 8	4.673 2.730 1.912 1.584 1.452 1.388 1.327 1.378	13.97 4.652 2.710 1.892 1.564 1.432 1.368 1.307 1.358	$\begin{array}{c} 0.0000\\ 0.15521\\ 0.18756\\ 0.20118\\ 0.20665\\ 0.20885\\ 0.20991\\ 0.21093\\ 0.21008 \end{array}$	0.000 2.003 4.155 6.383 7.933 8.757 9.211 9.689 9.287	None	0 1 2 3 4 5 6 7 8	13.06 12.40 11.84 11.82 10.79 10.38 9.933 9.591	14.05 13.06 12.40 11.84 11.32 10.79 10.38 9.933 9.591	$\begin{array}{c} 0.0000\\ 0.01636\\ 0.02782\\ 0.03662\\ 0.04525\\ 0.05405\\ 0.06086\\ 0.06883\\ 0.07398 \end{array}$	$\begin{array}{c} 0.000\\ 0.07543\\ 0.1327\\ 0.1863\\ 0.2408\\ 0.3017\\ 0.3531\\ 0.4144\\ 0.4646\end{array}$
Run	C, 0.00614%	H ₂ SO ₄ , 100	°C., B/A =	• 4.984, A =	0.2325	Run	L, 0.0322%	H ₂ SO ₄ , 0°	$C_{\cdot, B/A} =$	4.972, A 🛥	0.2329
$ \begin{pmatrix} \frac{60.05}{94} \\ \times 0.00614 \\ 0.00392\% \end{pmatrix} $	0 1 2 3 4 5 6 7	$10.441 \\ 8.374 \\ 7.743 \\ 6.806 \\ 6.541 \\ 5.931 \\ 5.710 \\$	$13.96 \\ 10.437 \\ 8.370 \\ 7.739 \\ 6.802 \\ 6.537 \\ 5.927 \\ 5.706 \\ \end{array}$	$\begin{array}{c} 0.0000\\ 0.0587\\ 0.0931\\ 0.1036\\ 0.1192\\ 0.1236\\ 0.13379\\ 0.13747\end{array}$	$\begin{array}{c} 0.000\\ 0.3377\\ 0.6679\\ 0.8037\\ 1.052\\ 1.135\\ 1.355\\ 1.355\\ 1.447\end{array}$	$ \begin{pmatrix} 60.05 \\ 49.04 \end{pmatrix} \\ \times 0.0322 \\ \hline 0.0394\% $ Run	0 2 4 6 8 <i>M</i> , 0.0322%	13.62 13.53 13.41 13.35 H ₁ SO ₄ , 30°	13.99 13.58 13.49 13.37 13.31 • C., <i>B/A</i> =	$\begin{array}{l} 0.0000\\ 0.00682\\ 0.00842\\ 0.01032\\ 0.01132\\ \end{array}$	0.000 0.03017 0.03749 0.04636 0.05109 0.2329
	8 9	$5.211 \\ 5.167$	$5.207 \\ 5.163$	$0.14578 \\ 0.14651$	$1.681 \\ 1.704$	$\binom{60.05}{49.04}$	0 1	13,35	13,99 13,31	0.0000 0.01132	$0.000 \\ 0.05109$
Run	D. 0.0198%	H.SO4. 100	$C_{} B/A =$	5.029. A =	0.2307	×0.0322	2 4	13,03 12,46	$12.99 \\ 12.42$	$0.01664 \\ 0.02613$	$0.07694 \\ 0.1264$
$\left(\frac{60.05}{94}\right)$ ×0.0198 0.0127%	0 1 2 3	6,258 3,937 2,857	13.86 6.245 3.924 2.844	0.0000 0.12675 0.16539 0.18336	0.000 1.219 2.532 3.873	0.0394% Run	6 8 N, 0.0322%	11.95 11.44 H ₂ SO ₄ , 100	11.91 11.40 °C., <i>B/A</i> =	0.03462 0.04311 • 4.972, A =	0.1746 0.2271 0.2329
	5 6 8 9	$\begin{array}{c} 2.301 \\ 1.904 \\ 1.624 \\ 1.400 \\ 1.334 \end{array}$	$1.891 \\ 1.611 \\ 1.387 \\ 1.321$	0.19282 0.20388 0.20761 0.20871	6.328 7.602 8.991 9.491	$ \begin{pmatrix} \frac{60.03}{94} \\ \times 0.0322 \\ \hline 0.0206\% \end{pmatrix} $	0.5 1 2 3 4	7.695 5.151 3.035 2.221 1.777	7.674 5.130 3.014 2.200 1.756	$\begin{array}{c} 0.10514 \\ 0.14750 \\ 0.18272 \\ 0.19627 \\ 0.20367 \end{array}$	0.8229 1.727 3.641 5.358 6.968
Run	E, 0.0307%	H ₂ SO ₄ , 100	°C., B/A =	5.079, A =	0.2287		5	1.594	$1.573 \\ 1.324$	$0.20671 \\ 0.21086$	7.893 9.567
$\frac{\binom{60.05}{94}}{\times 0.0307}$	0 1 2 3 4	5.624 3.454 2.373 1.896	$\begin{array}{r} \textbf{13.73} \\ \textbf{5.604} \\ \textbf{3.434} \\ \textbf{2.353} \\ \textbf{1.876} \end{array}$	0.0000 0.13535 0.17150 0.18951 0.19745	0.000 1.450 2.998 4.836 6.318	Run $\left(\frac{60.05}{94}\right)$	0, 0.0322%	H₂SO₄, 110 ⁴ 5.943	°C., <i>B/A</i> = 13.99 5.922	• 4.972, A = 0.0000 0.13431	0.2329 0.000 1.362
	5 6 7 8	$1.624 \\ 1.484 \\ 1.409 \\ 1.380$	$1.604 \\ 1.464 \\ 1.389 \\ 1.360$	$\begin{array}{c} 0.20198 \\ 0.20431 \\ 0.20556 \\ 0.20605 \end{array}$	7.559 8.377 8.883 9.097	$\frac{20.0322}{0.0206\%}$	1 2 3 4	$\begin{array}{r} 3.502 \\ 2.422 \\ 1.915 \\ 1.493 \\ 1.319 \end{array}$	$3.481 \\ 2.401 \\ 1.894 \\ 1.472 \\ 1.298$	$\begin{array}{c} 0.17495 \\ 0.19293 \\ 0.20137 \\ 0.20839 \\ 0.21129 \end{array}$	3,019 4,827 6,387 8,502 9,777
Run	F, 0.1608%	H ₂ SO ₄ , 100	°C., B/A =	• 4.993, A =	0.2318		8	1.188	1,167	0.21347	10.89
$\frac{(-0.05)}{-04}$ $\times 0.1608$ -0.103%	U 1234567	1.5141.3581.3571.3821.3711.3431.3431.363	$\begin{array}{c} 13.92\\ 1.411\\ 1.255\\ 1.254\\ 1.279\\ 1.268\\ 1.240\\ 1.260\end{array}$	$\begin{array}{c} 0.0000\\ 0.20830\\ 0.21090\\ 0.21092\\ 0.21050\\ 0.21065\\ 0.21115\\ 0.21082 \end{array}$	8.864 10.09 10.10 9.883 9.960 10.22 10.05	Run $\left(\frac{60.05}{94}\right)$ $\times 0.0322$ 0.0206%	P, 0.0322% 0 0.33 0.67 1 1.5 2 3	H ₂ SO ₄ , 115 6.356 3.927 2.743 1.952 1.616 1.293	°C., <i>B/A</i> = 13.99 6.335 3.906 2.722 1.931 1.595 1.272	4.972, A = 0.0000 0.12744 0.16787 0.18758 0.20075 0.20635 0.21172	0.2329 0.000 1.206 2.581 4.139 6.244 7.772 9.996
Run	G. 0.0490%	H ₂ SO ₄ , 100	$^{\circ}C_{\cdot,B/A} =$	2.998, A =	0.3535	Run	R, 0.0322%	H:SO4, 120	° C., B/A =	• 4.972, A •	0.2329
$\frac{\binom{60.05}{94}}{\times 0.0490}$	012345678	6.934 4.540 3.722 3.442 3.345 3.312 3.282 3.298	21,22 6,903 4,509 3,691 3,411 3,314 3,281 3,251 3,267	$\begin{array}{c} 0.0000\\ 0.2385\\ 0.27838\\ 0.29201\\ 0.29668\\ 0.29829\\ 0.29884\\ 0.29984\\ 0.29934\\ 0.29908 \end{array}$	$\begin{array}{c} 0.000\\ 2.074\\ 3.706\\ 4.749\\ 5.221\\ 5.403\\ 5.467\\ 5.527\\ 5.496\end{array}$	$ \begin{pmatrix} \frac{60.05}{94} \\ \times 0.0322 \\ 0.0206\% \end{pmatrix} $	0 0.33 0.67 1 1.5 2 5	5.637 3.280 2.201 1.623 1.378 1.186	$13.99 \\ 5.616 \\ 3.259 \\ 2.180 \\ 1.602 \\ 1.357 \\ 1.165$	0.0000 0.13940 0.17864 0.19661 0.20623 0.21031 0.21351	0.000 1.491 3.292 5.418 7.733 9.310 11.01
Run	H, 0.0316%	H ₃ SO4, 100	° C., B/A =	- 5.087, A -	0.2284	Run	S, 0.0147%	H ₂ SO ₄ , 100	°C., B/A =	• 4.960, A ≈	0.2355
$\frac{\binom{60.05}{94}}{\times 0.0316}_{0.0202\%}$	0 1 2 3 4 5 6 7	4.637 2.663 1.765 1.491 1.353 1.299 1.256	$18.72 \\ 4.617 \\ 2.643 \\ 1.745 \\ 1.471 \\ 1.333 \\ 1.279 \\ 1.236 \\ 1.23$	$\begin{array}{c} 0.0000\\ 0.15154\\ 0.18440\\ 0.19935\\ 0.20391\\ 0.20621\\ 0.20711\\ 0.20782\end{array}$	0.000 1.972 4.191 6.862 8.326 9.293 9.728 10.10	$\left(\frac{00.00}{94}\right)$ $\times 0.0147$ 0.0094%	0.5 1 2 3 4 6 8	10.86 9.532 7.308 6.003 5.060 3.891 3.567	10.85 9.523 7.299 5.994 5.051 3.882 3.558	$\begin{array}{c} 0.05279\\ 0.07489\\ 0.11194\\ 0.13367\\ 0.14938\\ 0.16885\\ 0.17424\\ \end{array}$	0.2921 0.4722 0.9209 1.339 1.776 2.612 2.940
	8	1.245	1.225	0.20801	10.20	Run	T, 0.0418%	H ₁ SO ₄ , 100	"C., B/A =	5.001, A =	0.2318
Run $\left(\frac{60.05}{94}\right)$ $\times 0.0211$ 0.0135%	0 1 2 3 4 5 6	H ₂ SO ₄ , 100 3.682 2.117 1.267 1.053 0.797 0.781	C., B/A = 9.151 3.668 2.104 1.253 1.039 0.783 0.717	8.030, A = 0.0000 0.09131 0.11740 0.13153 0.13510 0.13936 0.14046	0.1524 0.000 1.495 3.354 6.302 7.809 10.69 11.76	$\binom{60.03}{94}}{\times 0.0418}$ 0.0267%	0.5 1 2 3 4 6 8	$\begin{array}{r} 6.402 \\ 4.045 \\ 2.297 \\ 1.614 \\ 1.454 \\ 1.264 \\ 1.221 \end{array}$	$\begin{array}{r} 13.375 \\ 4.018 \\ 2.270 \\ 1.587 \\ 1.427 \\ 1.237 \\ 1.194 \end{array}$	0.12564 0.16489 0.19400 0.20537 0.20804 0.21120 0.21192	1.183 2.464 5.132 7.770 8.756 10.25 10.66
	7 8	0.670	0.656	0.14148	12.96	Run	U, 0.0679%	H2SO4, 100	° C., B/A	= 4.992, A =	- 0.2321
P	J. 0 01700	H-80. 100	° C., R/A =	= 9.619. A =	0.1292	$\left(\frac{60.05}{04}\right)$	0.5	4,970	$13.94 \\ 4.927$	$0.0000 \\ 0.15007$	0.000 1.829
$\frac{\binom{60.05}{94}}{\times 0.0179}$	0 1 2 3 4 5	3.390 2.028 1.298 0.886 0.693	7.756 3.379 2.017 1.287 0.875 0.682	0.0000 0.07291 0.09560 0.10776 0.11482 0.11784	0.000 1.295 2.845 5.026 7.861 10.37	×0.0434%	1.5 23 4 6 8	2.724 1.896 1.452 1.239 1.234 1.212 1.212	2.681 1.853 1.409 1.196 1.191 1.169 1.174	0.18746 0.20125 0.20864 0.21219 0.21227 0.21227 0.21264 0.21255	$\begin{array}{c} \textbf{4.199} \\ \textbf{6.524} \\ \textbf{8.893} \\ \textbf{10.66} \\ \textbf{10.70} \\ \textbf{10.93} \\ \textbf{10.87} \end{array}$
	7	0.540	0.529	0.12039	13.66 14.66			(Continued	l on page 97	3)	

		TABLE III.	(Continu	ed)	
Catalyst Correction, %	Time, Hr.	Free Acidity, %	Actual Acetic Acid, %	Acetic Acid, Converted, X	$\frac{\text{Moles}/100 \text{ G}}{\text{Ratio}}, \\ X/(A - X)$
Run 1	7, 0.1032%	H2SO4, 100°	C., B/A -	= 4.925, A =	0.2347
$ \begin{pmatrix} \frac{60.05}{94} \\ \times 0.1032 \\ 0.0661\% \end{pmatrix} $	0 0.33 0.67 1 1.5 2 3 4 8	5.082 2.744 1.819 1.341 1.354 1.319 1.311 1.307	14.00 5.016 2.678 1.753 1.275 1.288 1.253 1.245 1.241	0.0000 0.15115 0.19009 0.20550 0.21346 0.21325 0.21383 0.21383 0.21396 0.21403	0.000 1.809 4.261 7.038 10.05 9.942 10.25 10.32 10.35
Run	W , 0.13739	6 H2SO4, 100°	C., B/A	= 4.975, A =	0.2326
$ \begin{pmatrix} \frac{60.05}{94} \\ \times 0.1373 \\ 0.0878\% \end{pmatrix} $	0.33 0.67 1 2 3 4 8	4,237 2,839 1,571 1,805 1,345 1,328 1,328 1,341	13,96 4,149 2,251 1,483 1,216 1,257 1,240 1,253	$\begin{array}{c} 0.\ 0000\\ 0.\ 16347\\ 0.\ 19509\\ 0.\ 20789\\ 0.\ 21234\\ 0.\ 21166\\ 0.\ 21194\\ 0.\ 21172 \end{array}$	0.000 2.365 5.201 8.413 10.48 10.11 10.26 10.14
Run .	X, 0.069 09	6 H18O4, 100°	C., B/A	= 2.991, A =	0.3542
$ \begin{pmatrix} \frac{60.05}{94} \\ \times 0.069 \\ 0.0441\% \end{pmatrix} $	0.5 1 2 3 4 6 8	7.845 5.191 3.307 2.994 2.849 2.835 2.801	21.27 7.801 5.147 3.263 2.950 2.805 2.791 2.757	0.0000 0.22429 0.26849 0.29986 0.30507 0.30749 0.30772 0.30829	$\begin{array}{c} 0.000 \\ 1.726 \\ 3.132 \\ 5.518 \\ 6.209 \\ 6.583 \\ 6.620 \\ 6.715 \end{array}$
Run	Y, 0.07119	% H2SO4, 100°	C., B/A	= 10.03, A =	0.1242
$ \begin{pmatrix} \frac{60.05}{94} \\ \times 0.0711 \\ 0.0455\% \end{pmatrix} $	0 0.5 1 2 3 4 6 8	2.104 0.8573 0.4413 0.4297 0.4131 0.4254 0.4067	7,458 2,058 0,811 0,395 0,384 0,367 0,379 0,861	$\begin{array}{c} 0.0000\\ 0.08993\\ 0.11069\\ 0.11762\\ 0.11781\\ 0.11809\\ 0.11789\\ 0.11819\end{array}$	0.000 2.624 8.195 17.88 18.44 19.33 18.68 19.67
Run 2	7. 0.0692%	H2SO4, 100°	C., B/A .	• 19.62, A =	0.06593
$ \begin{pmatrix} \frac{60.05}{94} \\ \times 0.0692 \\ 0.0442\% \end{pmatrix} $	0 0.5 1 2 3 4 6 8	$\begin{array}{c} 0.9368\\ 0.3620\\ 0.1740\\ 0.1678\\ 0.1762\\ 0.1641\\ 0.1828\end{array}$	3.959 0.893 0.318 0.130 0.124 0.182 0.120 0.120 0.139	0.0000 0.05106 0.06063 0.06877 0.06887 0.06383 0.06383 0.06383 0.06383	$\begin{array}{c} \textbf{0.000} \\ \textbf{3.434} \\ \textbf{11.44} \\ \textbf{29.52} \\ \textbf{31.00} \\ \textbf{28.97} \\ \textbf{24.36} \\ \textbf{27.54} \end{array}$

The method of least squares was used to calculate the equation for the best straight line through the indicated points, and k was determined from the least squares value for X/(A - X) at a selected value for time for all runs made with a 5 to 1 molar ratio of butanol to acetic acid. In the proportion series this method was not used because of the indicated curvature at short reaction times with high catalyst concentrations and high ratios of butanol to acetic acid (Figure 5). Here it was deemed advisable to use the actual observed data with short reaction times.

Table IV summarizes calculations for reaction rate constant k. The initial concentration of acetic acid was calculated from Figure 1. The values for X/(A - X) are the results of least squares calculations, together with the corresponding time values, except in the proportion series where the observed data have been employed with shorter time intervals. It is apparent from Table IV that the value of k varies with the amount of catalyst, the temperature, and the ratio of moles of butanol to moles of acetic acid.

EFFECT OF CATALYST CONCENTRATION. Various investigators have found that the rate of esterification with acid catalysts is proportional to the acid concentration (13, 21) or to the hydrogenion concentration (7). Figure 11 shows a linear relation between the rate constant for the runs at 100° C. with approximately 5 moles of butanol per mole of acetic acid and between 0 and 0.14% sulfuric acid as catalyst.

EFFECT OF TEMPERATURE. Figure 12 is a plot of the logarithm of 10⁵ k against the reciprocal of the absolute temperature for data of Table IV, where variables other than temperature were constant. For the range 0° to 120° C. this curve indicates that the esterification reaction is not simple but consists of at least two different consecutive reactions with different temperature coefficients (10). However, over the range 100° to 120° C., used in the continuous-column esterification runs, the relation between log k and 1/T may be regarded as a straight line; the controlling reaction is given by Equation 6.

EFFECT OF PROPORTION. According to Watson (21), the rate of esterification is proportional to the concentration of alcohol and acid as well as catalyst. A plot of the rate constants for runs X, U, Y, and Z against the molal ratio of butanol to acetic acid



indicated a distinct linear relation; but the catalyst concentrations varied about 5%. However, from the catalyst series the rate constant is directly proportional to the amount of catalyst. Hence, by dividing the rate constant by the weight per cent of catalyst and plotting this quotient against the molar ratio of reactants, the effects caused solely by the catalyst might be expected to be eliminated. Figure 13 shows a linear relation for all of the runs in the proportion series.

RATE CONSTANT EQUATION

From the relations indicated in Figures 11, 12, and 13, the following empirical equation was deduced to define the constant in terms of catalyst concentration, proportions of reactants, and temperature for application in the continuous esterification runs:

$$k = \left(a + bC + c\frac{B}{A}C\right)\left(e + \frac{f}{T}\right)$$

The first parenthesis indicates the effect, at 100° C., of catalyst concentration and proportion, with the second parenthesis taken as unity. The second parenthesis gives the temperature effect, and is evaluated from the data at constant proportions and catalyst concentration. At 100° C., a should represent the rate of the uncatalyzed esterification-i.e., the rate constant due to acetic acid alone; hence, if the value for k obtained with no catalyst (run K) is assumed equal to a, the other four constants can be evaluated from the straight-line relations.



Figure 11. Relation between Reaction Rate Constant k and Catalyst Concentration at 100° C., with **Approximately 5 Moles Butanol per** Mole of Acetic Acid

Considering first the term involving the catalyst and proportion series at 100° C., least-squares calculations for the best straight line were made by the relation:

 \mathbf{k}

$$\frac{k-a}{C} = b + c \frac{B}{A}$$

In the proportion series the two values calculated for the rate constant at 1 and 2 hours for runs G, I, and J, and 0.5 and 1 hour for run X were used independently, rather than taking the average values in order to give more equal weight to the proportion and catalyst series. Run K with zero per cent catalyst was omitted from these calculations since it was previously involved in determining constant a. The relation obtained for the leastsquares best straight line for these data is:

$$k = 0.000618 - 0.376724 C + 0.180917 C \frac{B}{A}$$
(8)

To check the validity of Equation 8, the values of k were recalculated from the molar ratio of butanol to acetic acid and the catalyst concentration, as summarized in Table V. All of the calculated values for k are in good agreement with the experimental values, with the exception of run S (96.8% too high). The average deviation between the calculated and experimentally determined rate constants is 17.65%. Discounting the runs with catalyst concentrations below 0.015% sulfuric acid (runs K, C, and S) and those with 3 moles of butanol per mole of acetic acid (runs G and X), the average deviation is 8.92%.

To tie in the results of the temperature series with the proportion-catalyst term, it is necessary to use the calculated value for the rate constant for run N (calculated value is 6.03% higher than observed). If a least-squares treatment on the straightline relation

$$\log 100 k_T = e + f/T \tag{9}$$

is applied, using the data for the runs at 100° to 120° C., the following results are obtained, using e = 9.140142 and f =-3320.0564:

			Rate	Constant-	
Run	° C.	Actual k	kT from Eq. 9	Difference	Deviation, %
N O P R	100 110 115 120	$\begin{array}{c} 0.01745^{a} \\ 0.03004 \\ 0.03775 \\ 0.04999 \end{array}$	$\begin{array}{c} 0.01744 \\ 0.02978 \\ 0.03851 \\ 0.04947 \end{array}$	$\begin{array}{c} -0.00001 \\ -0.00026 \\ +0.00076 \\ -0.00052 \end{array}$	-0.06 -0.86 +2.00 -1.04 +0.99

^a From Equation 8.

If the rate of reaction at 100° C. is taken as the basis for this series.

$$100 k_T = 10^{\left(9.140142 - \frac{3320.0564}{T}\right)}$$

Then by proportion,

$$\frac{k_T}{k_{100}} = \frac{10^{\left(9.140142 - \frac{3320.0564}{T}\right)}}{(100)(0.01745)}$$
(10)

Where $T = 100^{\circ}$ C. (373.1° K.), Equation 10 reduces to unity and thus represents the temperature factor. Multiplying Equation 8 by Equation 10, the final empirical equation for predicting the reaction rate constant is obtained:

$$r = \left(0.000618 - 0.376724 C + 0.180917 C \frac{B}{A}\right) \left(\frac{10^{\left(9.140142 - \frac{3320.0664}{T}\right)}}{1.745}\right) (11)$$

where k_T = predicted reaction rate constant

= sulfuric acid, weight % = butanol, moles C

- B
- = acetic acid, moles = temperature, °K. A T

Application of Equation 11 to the temperature series gives results identical with those listed for the least-squares equation. The average deviation for the rate constant calculated from Equation 11 compared with the observed values for all of the runs is 15.3%, and for those runs in the range encountered in the continuous esterification experiments, 7.46%.

SUMMARY OF KINETIC DATA AND THEORY

Goldschmidt (8) and Smith (18) showed that the free hydrogen ion of a mineral acid acts as a catalyst by combining with the alcoholic hydroxyl to form a complex:

$$RCOOH + R_1OH_2^+ = RCOOR_1 + H_3O^+$$

They expressed the rate of formation of ester by the equation:

$$\frac{(\text{RCOOR}_1)}{dt} = k(\text{RCOOH})(\text{R}_1\text{OH}_2^+)$$

However, as water is formed, it competes with the alcohol for the hydrogen ion, cutting down the number of alcohol complexes. By defining a quantity r as

$$r = \frac{(R_1OH_2^+)(H_2O)}{(\text{total } H^+) - (R_1OH_2^+)}$$

based on the equilibrium between the alcohol and water complexes, solving this relation for $(R_1OH_2^+)$, and substituting in the original rate equation:

$$\frac{dx}{dt} = \frac{kr(\text{catalyst})(a-x)}{r+x}$$
(12)

where a is the original concentration of organic acid, x is the concentration of ester formed after time t, and the catalyst is a strong mineral acid.

Integrating Equation 12 and setting x = 0 when t = 0 gives:

$$k = \frac{(r+a)\ln\frac{a}{a-x} - x}{(\text{catalyst}) rt}$$
(13)

Goldschmidt tested this equation for a number of esterification reactions at 25° C. and found constant values of k up to about 80 to 90% reaction; then the reverse hydrolysis reaction became appreciable, and the value of k fell off. Smith (18) confirmed the Goldschmidt equation over the temperature range 20° to 50° C., using normal aliphatic acids in methanol catalyzed by hydrochloric acid, with an initial acid concentration of 0.5 mole per liter and a catalyst concentration of 0.005 mole. Thus, although the catalyst concentration is in the range employed in these experiments, the initial concentration of acetic acid is considerably less. The molar ratio of methanol to acetic acid used by Smith was 51.22, or more than twice that of the highest ratio of butanol to acetic acid used in these studies.



Figure 12. Relation between Reaction Rate Constant k and Temperature with 0.0322% Catalyst and 4.972 Moles Butanol per Mole Acetic Acid

Dotted line is an extrapolation of the straight-line portion.

Application of the Goldschmidt equation to these experiments was unsuccessful because the value of r at the temperatures involved was unknown. However, substitution of Smith's data for the formation of methyl acetate at 50° C. with hydrochloric acid fits Equation 7 very well up to about 50% conversion, as Table VI shows.

Up to 16.75 minutes, the values of k (in liters per mole-second), calculated by Equation 7, are in excellent accord with those obtained by Smith using the Goldschmidt equation (Equation 13). With times of reaction greater than 16.75 minutes, Equation 7

		k	$=\frac{1}{Aa}$	$\cdot \frac{X}{A-X}$			
Run	Ao, Moles/ Liter	Time, Min.	$\frac{X}{A-X}$	k	Wt. % Catalyst	B Ä	Temp., °C.
			Catalys	st Series			
KCSDEBHNT	1.7880 1.7817 1.7897 1.7677 1.7520 1.7836 1.7497 1.7853 1.7766	120 120 120 120 120 120 120 120	0.1327 0.5894 0.9051 2.5326 3.1204 4.0948 4.2700 3.5275 5.1341	$\begin{array}{c} 0.0006185\\ 0.002757\\ 0.004214\\ 0.01194\\ 0.01484\\ 0.01913\\ 0.02034\\ 0.01646\\ 0.02408 \end{array}$	0.0000 0.00614 0.0147 0.0198 0.0307 0.0309 0.0316 0.0322 0.0418	4.965 4.984 4.960 5.029 5.079 4.978 5.087 4.972 5.001	100 100 100 100 100 100 100 100
U V W	1.7792 1.8002 1.7838	120 120 60	8.785 13.595 8.207	0.04115 0.06293 0.07668	0.0679 0.1032 0.1373	4.992 4.925 4.975	100 100 100
			Temperat	ure Series			
L M O P R	1.9797 1.9299 1.7853 1.7637 1.7522 1.7418	120 120 120 120 120 120	0.02119 0.06877 3.5275 6.3570 7.9374 10.4498	0.0000892 0.0002969 0.01646 0.03004 0.03775 0.04999	0.0322 0.0322 0.0322 0.0322 0.0322 0.0322 0.0322	4.972 4.972 4.972 4.972 4.972 4.972 4.972	0 30 100 110 115 120
			Proporti	on Series			
G1 G2 H J1 J2 X0.0 X1 U Y Z	$\begin{array}{c} 2.7567\\ 2.7567\\ 1.7497\\ 1.1550\\ 1.1550\\ 0.9759\\ 0.9759\\ 2.7628\\ 2.7628\\ 2.7628\\ 1.7792\\ 0.9378\\ 0.4938 \end{array}$	60 120 60 120 60 120 30 60 120 30 30 30	2.074 3.706 4.270 1.495 3.354 1.295 2.845 1.726 3.132 8.785 2.624 3.434	$\begin{array}{c} 0.01254\\ 0.01120\\ 0.02034\\ 0.02157\\ 0.02420\\ 0.02212\\ 0.02429\\ 0.02429\\ 0.02082\\ 0.02082\\ 0.04115\\ 0.09327\\ 0.2318 \end{array}$	$\begin{array}{c} 0.0490\\ 0.0490\\ 0.0316\\ 0.0211\\ 0.0211\\ 0.0179\\ 0.0179\\ 0.0690\\ 0.0690\\ 0.0690\\ 0.0679\\ 0.0711\\ 0.0692 \end{array}$	2,998 2,998 5,087 8,030 9,619 9,619 2,991 2,991 4,992 10,03 19,62	100 100 100 100 100 100 100 100 100 100
TUVW LMNOPR GGHIILJJ.X.V.YZ	$\begin{array}{c} 1.7766\\ 1.7792\\ 1.8002\\ 1.7838\\ 1.9797\\ 1.9299\\ 1.7853\\ 1.7637\\ 1.7522\\ 1.7418\\ 2.7567\\ 2.7567\\ 1.7522\\ 1.7418\\ 2.7567\\ 2.7567\\ 1.1550\\ 0.9759\\ 0.9759\\ 0.9759\\ 2.7628\\ 2.7628\\ 1.7792\\ 0.9378\\ 0.4938\\ \end{array}$	$\begin{array}{c} 120\\ 120\\ 120\\ 120\\ 120\\ 120\\ 120\\ 120\\$	5.1341 8.785 13.595 8.207 Temperat 0.02119 0.06877 3.5275 6.3570 7.9374 10.4498 Froporti 2.074 4.270 1.495 8.354 1.295 2.845 1.726 3.132 8.785 2.845 1.726 3.132 8.785 2.843 3.434	$\begin{array}{c} 0.02408\\ 0.04115\\ 0.06293\\ 0.07668\\ urre Series\\ 0.0002969\\ 0.010246\\ 0.03004\\ 0.03004\\ 0.03775\\ 0.04999\\ on Series\\ 0.01254\\ 0.02157\\ 0.02234\\ 0.02157\\ 0.02212\\ 0.02429\\ 0.02429\\ 0.02429\\ 0.02429\\ 0.02429\\ 0.02429\\ 0.02423\\ 0.02423\\ 0.02429\\ 0.02423\\ 0.024$	$\begin{array}{c} 0.0418\\ 0.0679\\ 0.1032\\ 0.1373\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0322\\ 0.0490\\ 0.0316\\ 0.0211\\ 0.0179\\ 0.0179\\ 0.0179\\ 0.0690\\ 0.0690\\ 0.0679\\ 0.07711\\ 0.0692\\ \end{array}$	$\begin{array}{c} 5.001\\ 4.902\\ 4.925\\ 4.975\\ 4.975\\ 4.972\\ 4.972\\ 4.972\\ 4.972\\ 4.972\\ 4.972\\ 4.972\\ 4.972\\ 4.972\\ 5.087\\ 8.030\\ 8.030\\ 9.619\\ 2.991\\ 4.992\\ 10.03\\ 19.62\\ \end{array}$	100 100 100 100 100 100 100 100 100 100

TABLE IV. CALCULATION OF RATE CONSTANT k, WHERE

does not apply as shown by a plot of X/(A - X) against time; an excellent straight line is obtained for the first four points with the 16.75-minute point slightly high and the longer times considerably higher.

The Goldschmidt equation was derived from purely theoretical considerations for low concentrations of acids, whereas Equation 7 was obtained empirically at higher concentrations and also higher temperatures, but both give results in substantial agreement up to about 50% complete reaction.

In accordance with the known complexity of the reaction, shown by the deviation of the plot of $\log k$ against the reciprocal of absolute temperature (Figure 12) and the peculiar temperature sensitivity of the reaction of butanol and sulfuric acid, the following series of reactions appear probable:

H₂SO4	+	C ₄ H ₆ OH	=	C ₄ H ₉ SO ₄ H	+	H₂O	(14	4)
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C4H9SO4H	+	H_2O	=	C ₄ H ₉ SO ₄ -	+	H₃O+		(15
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 $C_4H_9OH + H_8O^+ = C_4H_9OH_2^+ + H_2O$ (16)

 $C_4H_9OH_2^+ + HOOCCH_1 = C_4H_9OOCCH_2 + H_3O^+$ (17)

T_{ABLE} $k = 0$	V. Com of k 0.000618	аракізол ат 100 — 0.376	N OF Аст ° С. ву] 5724С + (ual and Equation).180917 <i>C</i>	$\begin{array}{c} \text{Calculate} \\ 8 \text{ Where} \\ \left(\frac{B}{A}\right) \frac{\text{Li}}{(\text{Moles})} \end{array}$	D VALUES ters (Min.)
	С.	B			~	Deviation.
Run	Wt. %	Ā	Calcd.	Actual	Difference	%
KCSDEBHNTUVWGIJXY	$\begin{array}{c} 0.000\\ 0.00614\\ 0.0147\\ 0.0198\\ 0.0307\\ 0.0309\\ 0.0316\\ 0.0322\\ 0.0418\\ 0.0679\\ 0.1032\\ 0.1332\\ 0.1373\\ 0.0490\\ 0.0211\\ 0.0179\\ 0.0690\\ 0.0711 \end{array}$	4.965 4.984 5.029 5.079 4.978 5.087 4.972 5.001 4.992 4.925 4.925 4.975 2.998 8.030 9.619 10.03	$\begin{array}{c} 0.000618\\ 0.003841\\ 0.008271\\ 0.01118\\ 0.01726\\ 0.01780\\ 0.01780\\ 0.01745\\ 0.02269\\ 0.03636\\ 0.05369\\ 0.07247\\ 0.008736\\ 0.02503\\ 0.01196\\ 0.10285 \end{array}$	$\begin{array}{c} 0.\ 000618\\ 0.\ 002757\\ 0.\ 004214\\ 0.\ 01194\\ 0.\ 01913\\ 0.\ 02034\\ 0.\ 01646\\ 0.\ 02408\\ 0.\ 04115\\ 0.\ 06293\\ 0.\ 01187\\ 0.\ 02288\\ 0.\ 01187\\ 0.\ 02288\\ 0.\ 01288\\ 0.\ 01986\\ 0.\ 01986\\ 0.\ 09327\\ \end{array}$	$\begin{array}{c} 0.000000\\ +0.001084\\ +0.004057\\ -0.00232\\ -0.00232\\ -0.00254\\ +0.00254\\ +0.0029\\ -0.00139\\ -0.00139\\ -0.00479\\ -0.00313\\ +0.00421\\ -0.00313\\ +0.00421\\ -0.00313\\ +0.00421\\ -0.00358\\ -0.00790\\ -0.00558\\ -0.00790\\ -0.0055\\ -0.0055\\ -0.0055\\ -0.0055\\ -0.0055\\ -0.0055\\ -0.0055\\ -0.0055\\ -0.0055\\ -0.0055\\ -0.0055\\ -0.0055\\ -0.0055\\ -0.005\\$	$\begin{array}{c} 0.0 \\ +39.32 \\ +96.28 \\ -6.36 \\ +16.31 \\ -12.13 \\ -12.49 \\ +6.03 \\ -5.77 \\ -11.64 \\ -14.68 \\ -5.49 \\ +2.636 \\ +1.94 \\ +7.87 \\ -39.78 \\ +10.27 \end{array}$

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Reaction 14 is particularly temperature sensitive, requiring days at low temperatures and only a few minutes at elevated temperatures. Reaction 15 cannot proceed until after reaction 14 has occurred but then probably takes place instantly. Reaction 16 should also occur extremely rapidly; free hydrogen ions can scarcely be expected to exist in the neighborhood of polar alcohol molecules because of their tendency to become solvated, especially since the alcohol molecules are present in large excess. Reaction 17 can now occur; this will be recognized as the Goldschmidt equation. At low temperatures, therefore, it is likely that reaction 14 controls the rate of esterification, whereas at elevated temperatures (100 ° C. or higher) reaction 17 is the controlling factor with sulfuric acid catalyst.



Figure 13. Relation between Ratio of Reaction Rate Constant to Catalyst Concentration, (k-a)/C, and Proportions of Reactants B/A, at 100° C.

However, it is well known from latent heat determinations and surface tension measurements (2) over the range of 15° to 150° C. that acetic acid exists largely as a double molecule, $(C_2H_4O_2)_2 = 2C_2H_4O_2$, independent of temperature. On this basis, reaction 17 should be represented by

$$C_{4}H_{9}OH_{2}^{+} + (CH_{3}COOH)_{3} = C_{4}H_{9}OOCCH_{3} + HOOCCH_{3} + H_{3}O^{+}$$
(18)

The rate of formation of the ester, according to this mechanism, becomes

$$\frac{d(\text{ester})}{dt} = k'(\text{CH}_{2}\text{COOH})_{2}(\text{C}_{4}\text{H}_{9}\text{OH}_{2}^{+})$$

The concentration of the alcoholic complex will remain constant because of the rapidity of reaction 16; as soon as a molecule has reacted, the liberated hydrogen ion immediately will take up another alcohol molecule. The rate of esterification will therefore be proportional only to the concentration of acetic acid. The reduction of the concentration of the alcoholic complex by the hydronium ion can probably be neglected in these considerations in view of the small water concentrations involved and of the trend indicated in the value of k shown in Smith's data with longer times of reaction.

Let us assume that only the acetic acid molecules existing in the dimeric form contain sufficient energy of activation to react with the alcoholic complex; this seems probable because resonating systems have the property of concentrating energy over a few atoms instead of having the energy scattered over the whole molecule. Then, since two molecules of acetic acid are involved per mole of activated complex, the rate must be proportional to the square of the acetic acid concentration:

$$\frac{d(\text{ester})}{dt} = k(\text{CH}_2\text{COOH})^2$$

TABLE VI.	ESTERIFICATION OF METHANOL AND ACETIC ACID AT
50° C. (18) WITH 0.005 M CONCENTRATION OF HYDROCHLORIC
•	ACID AS CATALYST

t, Min.	A - X	x	$\frac{X}{A-X}$	k from Eq. 7	k (Goldschmidt) from Eq. 13
0 1 5.5 9 16.75 24.5 38.5	0.500 0.467 0.365 0.808 0.223 0.170 0.110	0.000 0.033 0.135 0.192 0.277 0.330 0.390	0.000 0.0707 0.370 0.623 1.24 1.94 3.55	$\begin{array}{c} 0.2356\\ 0.2240\\ 0.2306\\ 0.2466\\ 0.2640\\ 0.3073 \end{array}$	0.236 0.224 0.224 0.221 0.215 0.207

where rate constant k now includes the concentration of activated alcoholic complex. Since the moles of ester formed must be exactly equal to the amount of acetic acid reacted, X, and if A is taken as the initial concentration of acetic acid, the above equation reduces to $dX/dt = k(A - X)^2$, which is Equation 6.

EQUILIBRIUM CONSTANTS

The equilibrium constant is defined as the ratio of the concentrations of products divided by the concentrations of reactants:

$$K = \frac{(\text{ester})(\text{water})}{(\text{butanol})(\text{acetic acid})}$$

To determine the equilibrium constant for the esterification, extra test tubes of the various runs used in the rate studies were heated for additional lengths of time (16, 24, and 32 hours, in general), and the free acidity was determined. After correction for the catalyst, the amount of unreacted acetic acid remaining could be calculated, which fixed the other compositions. The average values for the equilibrium for the longer time intervals are summarized in the following tables.

The concentration of catalyst has no effect on the equilibrium constant, with 5 moles of butanol per mole of acetic acid at 100 °C.: •

	Catalyst,	
Run	Wt. %	K
D	0.0198	2.38
E	0.0307	2.26
В	0.0309	2.21
H	0.0316	2.40
N	0.0322	2.38
Ť	0.0418	2.42
U	0.0679	2.48
Ŷ	0.1032	2.40
W.	0.1373	2.31
F	0.1608	2.32
	A 11070 00	~ ~

Similarly, temperature has no marked influence on the equilibrium constant at constant catalyst concentration and proportions:

Run	Temp., ° C.		K
N O P R	100 110 115 120		2.38 2.58 2.32 2.58
		Average	2.46

The equilibrium constant is markedly affected by the proportions of reactants employed, however:

Run	Molal Ratio, Butanol/Acetic Acid	K
Q	2.998	2.25
H	5.087 8.030	2.40 2.12
Ĵ	9.619	2.01
X_{U}	2.991	2.87 2.48
Ÿ	10.03	2.12
\boldsymbol{Z}	19.62	1.66

A similar decrease in the equilibrium constant for the reaction of acetic acid and ethanol was reported by Poznanski (9, 17) who

cites a variation in K from 1.0 to 6.8, depending upon the proportions of reactants used. The average value for the equilibrium constant for the esterification of butanol and acetic acid from the above summary is about 2.35, which is considerably lower than the value of 4.24 reported by Menschutkin (9) for the uncatalyzed reaction at 155°C.

CONCLUSIONS

The controlling reaction involved in the catalytic esterification of butanol and acetic acid at elevated temperatures (100° C. or higher) is of the second order kinetically and is proportional to the square of acetic acid concentration up to 75 to 85% completion. The rate constant is a linear function of the catalyst concentration and the molar ratio of butanol to acetic acid. At temperatures in the range 100° to 120° C., the logarithm of the rate constant is proportional to the reciprocal of absolute temperature.

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Viscosity of **Carbonated Aluminate Solutions**

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Viscosity data are presented for plant solutions that have been encountered in the development of an alkaline process for the production of alumina. The solutions represent aqueous mixtures of sodium carbonate, sodium aluminate, sodium hydroxide, and minor constituents. Viscosities were measured at 15°, 30°, 45°, 60°, 75°, 90° C. and at 0-30% dissolved solids. The composition of the dissolved solids was varied from about 43% carbon dioxide-0% alumina to 0% carbon dioxide-43% alumina, with the sodium oxide nearly constant at 57%. Viscosity increased as the ratio of sodium oxide to carbon dioxide increased.

N THE course of an extended investigation of a lime-soda sintering process for alumina from low-grade bauxites and clays, a need arose for viscosity data on the plant liquors. Such data were desired for calculations of heat transfer, fluid flow, etc., for purposes of engineering design. The solutions involved were aqueous mixtures of sodium hydroxide, sodium aluminate, and sodium carbonate with small amounts of impurities. For simplicity, the solutions can be considered part of the four-component system Na₂O-CO₂-Al₂O₈-H₂O. The range of compositions encountered in plant operation falls approximately along the line shown in Figure 1, which neglects the component water.

Sodium oxide is nearly constant at 56-58%; carbon dioxide and alumina vary reciprocally from 0 to about 43%. This corresponds to sodium carbonate at one extreme and a mixture of sodium aluminate and sodium hydroxide at the other end. No viscosity data on the four-component system and relatively little data on related alkaline solutions were found in the literature. Values for solutions containing sodium hydroxide and sodium carbonate together were reported by Hitchcock and McIlhenny The measurements of viscosity in the present work were (2). carried out with sufficient accuracy for design purposes. The data obtained should be useful for application to similar industrial processes.

An Ostwald-type viscometer was mounted in a water bath consisting of a 4-liter glass beaker, motor stirrer, electric immersion heater, and calibrated thermometer. The temperature was controlled within $\pm 0.1^{\circ}$ C. Time was measured to 0.1 second with a precision electric stop clock. The test solutions were prepared from plant liquors by concentrating to a point just preceding saturation at 100° C. (compare the system NaOH-Na₂CO₃-H₂O, 1) and by diluting subsequently with water in the ratios 1:1/2, 1:1, and 1:3 by weight. Five-milliliter samples were pipetted into the viscometer. Each determination was repeated three or four times. Weighed samples of the solu-