RALPH A. TROUPE and EMILY DIMILLA Northeastern University, Boston, Mass.

Kinetics of the Ethyl Alcohol–Lactic Acid Reaction

Studies with 85% lactic acid in sealed tubes have developed a rate equation useful in designing a flow reactor for esterification of lactic acid with ethyl alcohol; with 44% technical lactic acid higher temperatures and catalyst concentrations are needed to lower reaction time to a commercially attractive level

E STERIFICATION of lactic acid with ethyl alcohol is important not only as a source of the versatile solvent, ethyl lactate, but also as a step in the purification of lactic acid. Although ethyl lactate can be produced by other methods, esterification remains of primary importance, as shown by the number of patents issued on variations of the procedure (3, 6, 7, 12, 17).

The greatest handicap to increased commercial use of lactic acid is the high

Reaction with 85% Acid

THE investigation reported was undertaken to provide fundamental data for the design of a continuous flow pipe reactor, to construct such a reactor, and to study chemical engineering fundamentals involved in its operation.

Studies on Rate of Reaction

Materials Used. Analytical grade 85% lactic acid which assayed 72.75% titratable acidity and 85.85% total acidity (both reported as lactic acid) was used in the laboratory kinetic studies. It was assayed by titration and saponification with standard sodium hydroxide solution. U.S.P. grade lactic acid which assayed 72.50% titratable acidity and 85.50% total acidity was used in the pilot plant investigation.

Reagent quality U.S.P. absolute ethyl alcohol analyzing 99.9+% purity by density measurement was employed in all these experiments. Analytical reagent grade sulfuric acid analyzing 97.05% sulfuric acid was used as a catalyst in most of the tests.

Determination of Densities of Reaction Mixtures. A modification of the method of Leyes and Othmer (9, cost of processing and purification (4, 10, 11).

Needle and Aries (77) believe that a potential market of 200,000,000 pounds exists if processes can be improved—mostly for the purer grades, for use in plastics and resins. Lactic acid may be purified by esterifying with methanol or ethyl alcohol, separating out the ester, and hydrolyzing it to pure lactic acid and alcohol, which is recovered and re-used.

14, 15) was used to determine the densities of the reaction mixtures at the temperature of reaction (Figure 1).

Reaction of Ethyl Alcohol and Sulfuric Acid. Data on the rate of reaction between ethyl alcohol and sulfuric acid were necessary to correct for the amount of catalyst present in the reaction mixture at any time. The equivalents of acid change as the sulfuric acid reacts to form ethyl hydrogen sulfate.

These data were obtained, for each reaction temperature studied, by adding 0.3 to 0.5% of sulfuric acid to ethyl alcohol and sealing the mixture in soft-glass ampoules, which were then placed in a constant temperature bath. At intervals a tube was removed and chilled and its contents were weighed and titrated with 0.1N sodium hydroxide solution, using a microburet graduated in 0.01 ml.

From the per cent sulfuric acid reacted and the original per cent of sulfuric acid, the acid equivalents at time θ can be calculated.

Reaction of Lactic Acid and Ethyl Alcohol. For each run the lactic acid, ethyl alcohol, and sulfuric acid catalyst were weighed into separate flasks, then chilled in a freezer maintained at 0° F. The chilled chemicals were combined and thoroughly mixed. Samples approximately 8 ml. in volume were sealed in soft-glass ampoules and placed in a constant temperature bath.

At intervals ampoules were removed from the bath, reduced rapidly in temperature in an ice bath, and broken open. Aliquots of the contents were weighed on a single-pan automatic analytical balance which permitted the operator to obtain a weight in less than 10 seconds. Total lactic acid was then determined (13).

Effect of Variables on Rate

Figure 2 shows the effect of temperature, catalyst concentration, and mole ratio of reactants upon the rate of reaction of 85% lactic acid and ethyl alcohol. At high catalyst concentration (0.241%) some decomposition must occur as equilibrium is approached. The curve for this condition breaks off sharply and



Figure 1. Density of reaction mixtures (85% lactic acid)

Table I.	Reaction	of Ethyl	Alcohol					
(Basis 1 manual actuation)								
(Da	sis i gram	or solution)						
		H_2SO_4						
Time,	Acid,	Reacted,	%					
Hours	Meq.	Mmole	Reacted					
Temperature	25° С., Н.S	Catalyst	0.583%					
0.0	0.1190	0.0	0.0					
2.0	0.1160	0.0030	5.0					
3.0	0.1149	0.0041	6.9					
4.0	0.1137	0.0053	8.9					
0.0	0.1106	0.0084	14.1					
24.0	0.0926	0.0264	44.3					
28.0	0.0897	0.0293	49.3					
96.0	0.0843	0.0347	58.3					
Temperature	40° C.,	Catalyst	0.565%					
	H250	J ₄						
0.0	0.1152	0.0	0.0					
1.0	0.1062	0.0090	15.7					
2.0	0.0992	0.0161	27.8					
3.0	0.0925	0.0227	39.4					
4.0	0.0896	0.0257	44.6					
6.0	0.0811	0.0342	59.3					
28.0	0.0589	0.0564	97.8					
Temperature	60° C., Ca	talyst 0.382	% H2SO4					
0.0	0.0779	0.0	0.0					
0.25	0.0724	0.0056	14.3					
0.5	0.0616	0.0163	41.9					
1.0	0.0495	0.0284	73.0					
2.0	0.0417	0.0362	92.9					
6.0	0.0395	0.0384	98 .6					
Temperature	80° C., Ca	talyst 0.449	% H ₂ SO ₄					
0.0	0.0917	0.0	0.0					
0.167	0.0544	0.0373	81.3					
0.333	0.0476	0.0441	96.2					
0.5	0.0467	0.0450	98.1					
1.0	0.0474	0.0443	96.6					
4.0	0.0464	0.0453	98.8					
Temperature	100° C., Ca	talyst 0.313	% H ₂ SO ₄					
0.0	0.0638	0.0	0.0					
0.083	0.0341	0.0297	93.1					
0.5	0.0330	0.0308	96.7					
1.0	0.0325	0.0313	98.2					

irregularities were noted in samples held for longer periods of time. This condition is similar to that reported for lactic acid and methanol (14).

In the mole ratio of reactants series, curves for ratios (E/L) of 6.28 and 8.12 intersect curves for lower ratios. This situation was not encountered in the work with 85% lactic acid and methanol (14), but was found in previous work with 44% lactic acid and methanol (15).

Order of Esterification Reaction

Table II contains the data for the reaction of 85% lactic acid with ethyl alcohol. The data, when tested in the established manner (5), did not follow the pattern of a first-, second-, or thirdorder reaction. This was expected, in view of the complex nature of the reaction mixture and the behavior previously established for lactic acid and methanol (14).

Logically, an attempt was next made to correlate the data in a manner similar to that used for lactic acid and methanol. This took the mathematical form:



Figure 2. Effect of variables on rate of reaction of 85% lactic acid with ethyl alcohol

- Mole ratio approximately 4, catalyst concentration Α. approximately 0.167% sulfuric acid Mole ratio approximately 4 at 100° C.
- B.
- c. Catalyst concentration approximately 0.1% sulfuric acid at 100° C.

$$k\theta = \frac{X}{(A-b)(A-b-X)}$$
(1)

where k is the specific reaction rate constant, θ is the time of reaction, X is the amount of lactic acid converted in time θ , and A - b represents the original titratable acidity of the reaction mixture.

When X/(A - b - X) was plotted against time, using X data from the smoothed curves of per cent esterified, reasonably straight lines were obtained in nearly every case up to 90% or more of the equilibrium per cent reacted. Exceptions were runs in which the mole ratio of reactants were 6.28 and 8.12; in these runs the curves exhibit a marked rise after the first point or two, rather than a fall. This induction period has been noted in other esterifications (1, 9,



Figure 3. **Relation** between X/(A - b - X) and time

- Mole ratio approximately 4, catalyst concentration approximately 0.167%
- Mole ratio approximately 4 at 100° C. B.
- C. Catalyst concentration approximately 0.1% at 100°C.

14). The curves of per cent esterified for these two runs did not behave as expected. The data for these runs are better fitted as a straight line by plotting X/A(A - X) against time. A is the original lactic acid present (L in this case). This may indicate that the mechanism of reaction has changed above an E/Lof 4, owing to an excess of ethyl alcohol.

In Equation 1 it can be seen that the units in the ratio X/(A - b - X) are immaterial as long as they are consistent, but in order to obtain k in the units of liters per (mole) (minute), the quantity A - b should be expressed in moles per liter and θ in minutes. Values of k were obtained by dividing the slopes of the lines by values of A - b (in moles per liter), calculated from the original titratable acidity and the density values determined for the reaction mixtures.

	Acid	ity• Ml	of $0.1N$	Reach Base /Grai	m of Solut	ion		Acid	ity: Ml.	of $0.1N$	Base/Gra	m of Solut	ion
		10y, 1011.	01 0.111	Duscrana		Total			203 , 1121	01 01211	<u>, , , , , , , , , , , , , , , , , , , </u>		Total
						Lactic							Lactic
				Titra-		Acid					Titra-		Acid
				table	Polymer	Con-					table	Polymer	Con-
	Titı	ratable A	.cid	Acid	Con-	verted,		Tit	ratable A	Leid	Acid	Con-	verted,
	Lactic		-	Orig.	verted to	Mole/	-	Lactic		á	Orig.	verted to	Mole/
Time,	acid $+$	Lactic	Con-	total	Ethyl	100 G.	Time,	acid +	Lactic	Con-	total	Ethyl	100 G.
Hours	catalyst	acid	verted	acid	Lactate	Soln.	Hours	catalyst	acid	verted	acid	Lactate	Soln.
25°	C.; 0.16	7% H₂SC	$A_{4}; E/L$	= 3.96;	L = 0.3476	5	100	° C.; 0.04	05% H ₂ S	O_4 ; E/L	= 4.02;	L = 0.34	41
0.00	29.80	29.46					0.00	29.24	29.16				
1.00	29.27	28.93	0.53	0.8320	0.15	0.0068	0.25	25.09	25.05	4.11	0.729	0.605	0.0472
2.00	28.89	28.56	0.90	0.8216	0.31	0.0121	0.50	22.02	21.98	7.18	0.040	1.01	0.0819
3.00	28.37	28.04	1.42	0.8067	0.35	0.0177	1.00	17.78	17.74	11.44	0.510	2.50	0.1392
4.00	27.99	27.00	2 70	0.7957	0.42	0.0222	4.00	9.66	9.62	19.54	0.279	3.84	0.2338
10.75	25.42	25.12	4.34	0.7227	0.84	0.0518	6.00	9.09	9.05	20.11	0.262	3.98	0.2409
24.00	21.55	21.28	8.18	0.6122	1.11	0.0929	10.00	7.73	7.69	21.47	0.223	4.24	0.2571
48.00	17.47	17.21	12.25	0.4951	1.81	0.1406	. 10	0° C. : 0.08	2% H.S	$O_A: E/L$	= 3.88:	L = 0.352	2
72.00	14.76	14.51	14.95	0.4174	1.98	0.1693	0.00	30 01	20 84	0,, 13/12	0.00,		-
							0.25	22.83	22.75	7.09	0.645	0.81	0.0790
40°	°C.; 0.16	6% H₂S C	$D_4; E/L$	= 3.87;	L = 0.353	8	0.50	17.77	17.69	12.15	0.502	2.18	0.1433
0.00	30.32	29.98					1.00	13.40	13.32	16.52	0.378	3.31	0.1983
1.00	28.05	27.74	2.24	0.785	0.35	0.0259	2.00	9.64	9.56	20.28	0.271	4.37	0.2465
2.00	26.54	26.25	3.73	0.745	0.42	0.0415	4.00	8.17	8.09	21.75	0.229	4.60	0.2635
4.00	24.30	24.09	5.89	0.083	1.55	0.0744	6.00	7.88	7.80	22.04	0.221	4.69	0.2673
10.00	20.05	10.83	10.15	0.561	1.82	0.1197	24.00	7.50	7.48	22.30	0.212	4.75	0.2711
24.00	14.25	14.07	15.91	0.398	2.43	0.1834	10	0° C.; 0.24	11% H₂S	$O_4; E/L$	= 4.14;	L = 0.338	0
48.00	10.55	10.38	19.60	0.294	2.50	0.2210	0.000	29.13	28.64				
72.00	9.28	9.11	20.87	0.258	2.65	0.2352	0.167	18.70	18.45	10.19	0.545	1.00	0.1119
							0.250	15.33	15.08	13.56	0.445	1.53	0.1509
60°	°C.; 0.16	7% H ₂SC	$D_4; E/L$	= 4.30;	L = 0.329	б	0.333	13.18	12.93	15.71	0.383	1.00	0.1737
0.00	28.27	27.93					0.500	10.72	10.47	18.17	0.310	2.32	0.2049
0.25	26.82	26.50	1.43	0.804	0.46	0.0189	2.000	7.71	7.46	21.18	0.221	3.52	0.2330
0.50	25.44	25.17	2.76	0.763	0.92	0.0368	2.000		~				0,21/0
0.75	24.11	23.86	4.07	0.724	0.99	0.0506	1	00° C.; 0.1	1% H ₂ SC	$D_4; E/L =$	= 1.05; I	L = 0.6509	•
1.00	10 65	10 47	5.10 9.46	0.090	1.05	0.0021	0.000	55.36	55.16	~			A 0000
2.00	17 18	17.00	10.03	0.516	1.48	0.1241	0.167	40.81	40.71	8.45	0.718	0.77	0.0922
4.00	15.41	15.24	12.69	0.462	1.71	0.1440	0.333	38 44	28 24	14.57	0.025	2 30	0.1396
5.00	13.76	13.59	14.34	0.412	2.05	0.1639	1.000	31.75	31.65	23.51	0.486	4.87	0.2838
6.00	12.83	12.66	15.27	0.384	2.51	0.1778	2.000	28.42	28.32	26.84	0.435	7.05	0.3389
24.00	8.06	7.89	20.04	0.239	3.63	0.2367	4.000	28.73	28.63	26.53	0.440	7.43	0.3396
		-~ -					6.000	27.88	27.78	27.38	0.427	7.55	0.3493
80	°C.; 0.16	7% H ₂ SC	$J_4; E/L$	= 4.04;	L = 0.343	0	9.500	29.25	29.15	26.01	0.448	7.82	0.3383
0.00	29.46	29.12					1	00° C.; 0.1	1% H₂S C	$D_4; E/L =$	= 2.15; 1	L = 0.4908	5
0.25	25.50	25.31	3.81	0.737	0.20	0.0407	0.000	41.79	41.59				
1 00	16 36	16 10	12 03	0.015	1 51	0.0005	0.167	34.36	34.26	7.33	0.698	0.48	0.0781
2.00	12.41	12.24	16.88	0.356	2.10	0.1898	0.333	29.07	28.97	12.62	0.590	0.97	0.1359
3.00	9.99	9.82	19.30	0.286	3.12	0.2242	0.500	25.66	25.56	16.03	0.520	3.28	0.1931
4.00	9.06	8.89	20.23	0.259	3.26	0.2349	2,000	19.81	16.71	21.00	0.401	4.33	0.2043
6.00	8.10	7.93	21.19	0.231	3.47	0.2466	4.000	15.24	15.14	26.45	0.308	5.60	0.3205
24.00	7.21	7.04	22.08	0.205	3.77	0.2585	6,000	15.11	15.01	26.58	0.306	5.90	0.3248
100			• • • • • • • •		7 0 244		10	nº C • 0 00	0607 12.5		- 6 28.	T - 0.25	25
100	0.; 0.10	10% H2S	$\cup_{i} E/L$	= 4.1V;	$\mu = 0.340$	10	100	21 40	2070 H2C	J4, 14/14	- 0.20;	1 - 0,23	
0.000	29.20	28.86					0.000	21.08	21.48	2 21	0 760	0.15	0 0236
0.167	21.51	21.34	7.52	0.020	0.34	0.0786	0.167	16.68	16.58	4.90	0.654	0.30	0.0520
0.333	12.94	12.77	16.09	0.403	2 40	0.1490	0.333	12.68	12.58	8.90	0.496	1.35	0.1025
1.000	0.30	0.22	10.64	0.270	3.03	0.2267	0.500	10.25	10.15	11.33	0.401	1.79	0.1312
2.000	7.89	7.72	21.14	0.226	3.61	0.2475	1.000	6.80	6.70	14.78	0.264	2.45	0.1723
4.000	7.32	7.15	21.71	0.210	3.90	0.2561	2.000	4.91	4.81	16.67	0.190	2.80	0.1947
							4.000	4.18	4.08	17.40	0.161	3.15	0.2055
10	0° C.; 0.0	0% H₂SO	04; E/L	= 4.12; 1	5 = 0.3390)	0.000	4.05	3.95	17.53	0.150	3.30	0.2083
0.00	28.77	28.77					10	00° C.; 0.1	% H₂SO	4; $E/L =$	• 8.12; <i>l</i>	L = 0.208	5
0.25	27.24	27.24	1.53	0.805	0.68	0.0221	0.000	17.87	17.67	<u>.</u>			
0.50	26.36	26.36	2.41	0.777	1.09	0.0350	0.0833	16.24	16.14	1.53	0.775	0.12	0.0165
1.00	24.23	24.23	4.54	0.715	1.03	0.0018	0.107	14.24	14.14	3.53	0.678	0.21	0.0374
2.00	21.09	10 24	7.08	0.021	2.40	0.1252	0.333	0.20	0 10	0.50 g 49	0.552	0.53	0.0709
5.00	16.32	16.32	12.45	0.482	3.63	0.1608	1.000	6.10	6.00	11.58	0.202	1.81	0,1330
7.00	14.68	14.68	14.09	0.433	3.83	0.1792	2.000	4.28	4.18	13.49	0.2005	2.35	0.1584
24.00	9.20	9.20	19.57	0.271	4.10	0.2367	4.000	3.48	3.38	14.29	0.162	2.47	0.1676
48.00	7.75	7.75	21.02	0.228	4.58	0.2560	6.000	3.38	3.28	14.39	0.157	2.75	0.1714

Table II. Reaction Rate Data for 85% Lactic Acid and Ethyl Alcohol

Equation for Rate Constant

As can be seen from Figure 3, temperature, catalyst concentration, and mole ratio of ethyl alcohol to lactic acid affected the value of k. Therefore, it was necessary to derive an expression for k which reflected the effect of each of these variables.

The value of k was directly propor-

tional to C, the concentration of sulfuric acid catalyst, when temperature and mole ratio of reactants were held constant. The relationship for a range of catalyst composition between 0.0 and



Table III. Actual and Calculated Values of k

Temp	\mathbf{Wt}		k,	Liter/(Mole)(N	Min.)	%
° C.	Catalyst	E/L	Calcd. ^a	Actual ⁶	Difference	Deviation
25	0.167	3.96	0.000125	0.000129	-0.00004	- 3.10
40	0.166	3.87	0.000408	0.000482	-0.000074	- 15.35
60	0.167	4.3	0.001936	0.001944	-0.00008	- 0.41
80	0.167	4.03	0.006524	0.007007	-0.000483	- 6.89
100	0.166	4.10	0.020640	0.020662	-0.000022	- 0.11
100	0.0	4.12	0.001895	0.001895	0.0	0.0
100	0.0405	4.02	0.006367	0.006244	+0.000123	+ 1.97
100	0.082	3.88	0.010592	0.124560	-0.001864	14.96
100	0.241	4.14	0.029415	0.031717	-0.002302	- 7.26
100	0.10	1.05	0.003671	0.003613	+0.000058	+ 1.61
100	0.10	2.15	0.007103	0.007319	-0.000216	- 2.95
100	0.10	6.28	0.019989	0.021126	-0.001137	- 5.38
100	0.10	8.12	0.025729	0.024283	+0.001446	+ 5.95
^a From 1	Equation 9.					
^b From 2	Equation 1.					

Table IV. Equilibrium Constants for Reaction of 85% Lactic Acid with Ethyl Alcohol

E/L Approximately 4, nately 0.167 $\%$ ${ m H}_2{ m SO}_4$
Equilibrium Constant,
K
1.92
2.02
1.63
1.74
1 77
1.//
Av. 1.81
L/L Approximately 4, 100° C.
1.70
1 77

0.166		1.77	
0.082		1.85	
0.0405		1.87	
0.0		1.75	
	Av.	1.79	

Proportion Series, Temp. 100° C., Catalyst Approximately 0.1% H₂SO₄ E/L

1.05	2.92
2.15	2.69
4.10	1.77
6.28	1.65
8.12	1.33

0.241% sulfuric acid at 100° C. and a ratio of ethyl alcohol to lactic acid of approximately 4 is:

 $k = 0.117C + 0.001895 \tag{2}$

This equation and the others which follow were derived to give nearly uniform percentage deviations rather than uniform deviations from the curve (8),

In the case of E/L, the mole ratio of reactants, (k - a)/C was plotted against E/L where a is the value of k corresponding to 0% catalyst concentration. This has the effect of putting k on a catalyst-free basis, so that it will truly reflect the variation with mole ratio of reactants. A substantially linear relationship exists for the range of mole ratios chosen. At 100° C, this line may be expressed by the equation:

$$\frac{k - 0.001895}{C}$$
 =

0.03120 (E/L) - 0.0150 (3)

where 0.001895 is the value of k corresponding to 0% catalyst (obtained from Equation 2).

When log k was plotted against the reciprocal of the absolute temperature, practically no deviation from linearity could be observed. For a temperature range of 25° to 100° C., with a mole ratio of reactants of approximately 4

and a catalyst concentration of about 0.167% sulfuric acid, the relationship was:

 $\log 10^4 k = 11.086 - 3265/T \tag{4}$

where T is the temperature in degrees Kelvin. From these data the energy of activation was calculated as 14,920 calories per mole.

To assemble these three equations into a single empirical equation, the relationship involving the mole ratio of reactants and catalyst concentration (Equation 3) was taken as a base and the temperature relationship (Equation 4) was applied to it as a proportionality factor. Equation 4 may also be expressed in the form:

$$k(10^4) = 10^{(11.086 - 3265/T)}$$
(5)

The run at 100° C. in the temperature series is also common to Equation 3 and thus will serve as a basis for the proportion. At 100° C. Equation 5 becomes:

$$k_{100} (10^4) = 10^{(11,086} - 3265/373) (6)$$

while at temperature T it is:

$$k_T (10^4) = 10^{(11,086} - \frac{3265/T}{7})$$
 (7)

The ratio of temperatures is then:

$$\frac{k_T}{k_{100}} = \frac{10^{(11.086 - 3265/T)}}{215.1} \tag{8}$$

When combined with the catalystmole ratio expression for k the following relationship is obtained:

$$k = [0.03120(E/L)C - 0.0150C + 0.001895] \left[\frac{10^{(11,086 - 3265/T)}}{215.1} \right] \quad (9)$$

where k is the reaction rate constant, liters per (mole)(minute), E/L is the ratio of moles of ethyl alcohol to moles of lactic acid, C is the weight per cent sulfuric acid catalyst, and T is the temperature in degrees Kelvin.

Using Equation 9, values of k were calculated for each of the experimental run conditions. In Table III these calculated values are compared with the experimental values obtained using Equation 1. The average deviation is 5.2%.

Mechanism of Reaction

As all the lactic acid converted is not directly indicated by a drop in the value of titratable acidity, it appears likely that two reactions predominate (14).

ESTERIFICATION OF MONOMERIC LAC-TIC ACID WITH ETHYL ALCOHOL. Because of the large amount of water originally present, the reverse reaction of hydrolysis probably competes with this forward reaction.

$CH_{3}CHOHCOOH + CH_{3}CH_{2}OH \rightleftharpoons$ $CH_{3}CHOHCOOCH_{2}CH_{3} + H_{2}O$ (10)

Hydrolysis of Lactic Acid Condensation Polymers to Monomeric Lactic Acid. This probably takes place

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in several stages, but may be summed up as:

$$HO\begin{bmatrix} CH_{3} \\ | \\ CH-COO\end{bmatrix}_{n} H + (n-1) H_{2}O \longrightarrow$$

n-CH₃CHOHCOOH (11)

Apparently the reaction mechanism changes at higher ratios of alcohol to acid. This may in some way reflect the fact that in the higher ratios a larger percentage of the acid converted came from the drop in titratable acidity than in the runs at lower ratio.

Equilibrium Constants

Samples of the reaction mixture were kept in the constant temperature bath until the composition became constant. This procedure permitted calculation of equilibrium constants for the reaction

$$K = \frac{(\text{ethyl lactate}) (\text{water})}{(\text{lactic acid})(\text{ethyl alcohol})}$$

No appreciable variation in the value of the equilibrium constant with temperature or catalyst concentration can be seen in Table IV. A definite trend can be detected in the equilibrium constants when the ratio of reactants is varied. The average value of the equilibrium constants for all runs is 1.89.

Pilot Plant Investigation

A small pilot plant of the continuous flow type was constructed to test the applicability of the specific reaction rate equation to scale up the laboratory data to plant size equipment (Figure 4).

			Table V. Acidity:	Analytical Mi. of 0.1N 1	Data from R Base per Gram	eactor Runs of Solution			
		<u> </u>	11014109 ;	Titratable A	.cid	Titratable Acid	Polymer	Total Lactic Acid	
		Total	Lactic		· · · · · · · · · · · · · · · · · · ·	Orig.	Converted	Converted,	
Run		Lactic	acid +	Lactic		total	to Ethyl	Mole/100 G.	%
No.		Acid	catalyst	acid	Converted	acid	Lactate	Soln.	Converted
1	Feed Product	34.63	29.53 18.57	29.35 18.40	10.95	0.530	0.75	0.1170	33.7
2	Feed Product	34.63	29.53 16.12	29.35 15.95	13.40	0.460	1.80	0.1520	43.8
3	Feed Product	34.70	29.67 20.23	29.41 19.97	9.44	0.575	0.48	0.0992	28.6
4	Feed Product	34.70	29.67 19.67	29.41 19.41	10.00	0.559	0.52	0.1052	30.3
5	Feed Product	34.41	29.21 25.35	29.16 25.30	3.86	0.735	0.30	0.0416	12.10
6	Feed Product	34.41	29.21 25.70	29.16 25.65	3.51	0.745	0.30	0.0381	11.08
7	Feed Product	23.06	19.64 11.81	19.54 11.71	7.83	0.507	1.11	. 0.0893	38.7
8	Feed Product	23.06	19.64 14.44	$19.54 \\ 14.34$	5.20	0.625	0.51	0.0571	24.7
9	Feed Product	23.06	19.64 14.43	19.54 14.33	5.21	0.622	0.44	0.0565	24.5
10	Feed Product	41.62	35.37 31.43	35.27 31.33	3.94	0.751	0.19	0.0413	9.91
11	Feed Product	41.62	35.37 30.99	35.27 30,89	4.38	0.743	0.33	0.0471	11.3
12	Feed Product	34.27	29.21 22.08	29 .0 4 21.91	7.13	0.640	0.28	0.0741	21.6
13	Feed Product	34.27	29.21 21.10	29.04 20.93	8,11	0.610	0.37	0.0848	24.7
14	Feed Product	34.81	29.67 16.79	29.50 16.62	12.88	0.475	2.56	0.1544	44.3
15	Feed Product	34.81	29.67 22.76	29.50 22.59	6.91	0.645	0.68	0.0759	21.8
Тс	able VI. Com	parison of A	ctual Yields	of Ethyl La	ctate with Th	ose Calcula	ted Using E	quations 9 a	nd 1
Run	Tomn	Residence		C, Wt 07	k, Liter/(Mole)	(A - b),	X. Mol	e/100 Grams	07
No	° C	Min	E/I	Catalyst	(Min.)	Liter	Coled	Evntl	70 Diff
1	05 2	15 65	3.06	0 172	0 0150355	2 706	n 1103		⊥ 1 10
2	95.0	21.7	3.96	0.173	0.0157536	2.706	0.1105	0 1520	-7.25
3.	94.8	8.68	3.95	0.250	0.0218060	2.712	0.0998	0.0002	+ 0.60
4	94.8	9.30	3.95	0.250	0.0218060	2.712	0.1044	0,1052	- 0.76
5	95.6	8.65	4.05	0.0501	0.0058790	2.689	0.0351	0.0416	- 15.62
6	97.6	8.70	4.05	0.0501	0.0065674	2.689	0.0388	0,0381	+1.84
7	94.9	26.0	7.15	0.1	0.0171930	1,662	0.0833	0.0893	- 6.72
8	94.9	17.4	7.15	0.1	0.0171930	1.662	0.0649	0.0571	+13.65
9	94.9	15.0	7.15	0.1	0.0171930	1.662	0.0586	0.0565	+ 3.72
10	95.0	5.0	3.05	0.1	0.0075522	3.357	0.0397	0.0413	- 3.87
11	94.9	6.15	3.05	0.1	0.0075056	3.357	0.0473	0.0471	+ 0.42
12	97.9	6.35	4.18	0.167	0.0188963	2.677	0.0706	0.0741	- 4.72
13	97.9	8.33	4.18	0.167	0.0186994	2.677	0.0855	0.0848	+ 0.83
14	84.8	47.2	3.93	0.167	0.0084068	2.720	0.1531	0.1544	- 0.84
15	84.8	15.0	3.93	0.167	0.0084068	2.720	0.0753	0.0759	- 0.79

Construction. The reactor consisted of a coil of 3/s-inch copper tubing having an effective volume of 1000 ml. Temperature control was achieved by immersing the coil in a constant temperature bath consisting of a 55-gallon drum filled with water, whose temperature was regulated by a Sarco thermostat which actuated a valve in a steam sparge line.

Feed to the system was from a 2-liter aspirator bottle using a proportioning pump. Discharge from the reactor was through a 0.25-inch needle valve into a short coil of copper tubing immersed in an ice bath.

Operation. The reactants were weighed and stored in separate bottles, placed in a freezer kept at 0° F. The temperature of the water bath was adjusted to the desired level. Water, mixtures of ethyl alcohol and water, and some of the reaction mixture were pumped through the system while pressure and rate of flow were adjusted. The pressure was maintained at approximately 15 to 30 pounds per square inch gage to keep the system entirely in the liquid phase.

The chilled reactants were combined, sampled for analysis, and pumped through the system. When enough of this material had been pumped to displace the contents of the apparatus, samples of the chilled effluent were taken at intervals. These samples were analyzed immediately by a procedure identical with that used in the kinetic studies.

Pilot Plant Results

Because the most efficient operation of the pilot plant would call for operation at the highest practical temperature that could be reached without decomposition, the temperature for most of the runs was set at approximately 95° C. A few runs were made at a lower temperature to test the validity of the temperature factor in the rate equation.

The mole ratio of reactants, E/L, was varied from approximately 3 to approximately 7. An attempt was made to cover ratios between those studied in the laboratory tests. Catalyst concentration was varied from about 0.05% to about 0.250% sulfuric acid.

Residence times in the reactor from 5 to 47.2 minutes were produced by changing the flow rate of the reactants. Residence times were calculated by dividing 1000 ml., the reactor volume, by the flow rate in milliliters per minute at the operating temperature.

The specific reaction rate constants were calculated for each set of conditions, using Equation 9. The constants thus calculated were substituted in Equation 1 and the equation was solved for X (the amount of acid reacted).

The results of the 15 reactor runs are shown in Table VI together with the calculated values of X. Average deviation is 4.18%. From the operation of the flow reactor it can be seen that future work should include exploration of temperatures above 100° C. in an effort to determine the highest operating temperature without decomposition.



Figure 5. Density of reaction mixtures (44% technical acid)

perature in an ice bath, and broken open. Weighed aliquots were analyzed by titration to the neutral red end point, using standard sodium hydroxide solution. Only the titratable acidity was determined in this manner. No attempt was made to determine the amounts of polylactylic acids present because of the



Reaction with 44% Technical Acid

D_{ATA} on the available commercial grade of lactic acid and commercial 95% ethyl alcohol were obtained at the same time and under similar conditions as data on the purer materials.

An empirical relationship was derived to correlate the effect of the process variables—temperature, catalyst concentration, and ratio of reactants—on the specific reaction rate constant. Other data presented are variation of the density of reaction mixtures with temperature and composition, and equilibrium constants for the esterification. No pilot plant runs were made.

Rate of Reaction

Materials. Technical grade 44% lactic acid, analyzing 44.03% titratable acidity (as lactic acid), was used. No total acidity (by saponification) was determined experimentally for this material, as the presence of impurities made this determination unreliable. The correlation between total and titratable acidity as reported by Watson (16) was used to find the total acidity.

Industrial 190-proof ethyl alcohol analyzing 92.50% by weight, as determined by density measurement, was employed in all runs. Analytical reagent grade sulfuric acid analyzing 97.05% sulfuric acid was used as a catalyst in most of the tests.

Determination of Densities. Densities were determined as in the work with 85% acid. A thin-walled cassia flask, previously calibrated with water, was used (9). Data are shown in Figure 5.

Reaction of Lactic Acid and Ethyl Alcohol. For each run the lactic acid, ethyl alcohol, and sulfuric acid catalyst were weighed into separate flasks, and then chilled in a freezer maintained at 0°F. The chilled chemicals were combined and thoroughly mixed. Samples of approximately 8-ml. volume were sealed in soft-glass ampoules and placed in a constant temperature bath.

At intervals, ampoules were removed from the bath, reduced rapidly in tem-

Figure 6. Effect of variables on rate of reaction of 44% crude lactic acid with ethyl alcohol

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relatively small amounts of these substances and the difficulty of determining them. Only a negligible error is introduced by this omission (15). For the equilibrium samples, corrections for the amount of polymer present were made (13).

All titration values were corrected to compensate for the acidity of the catalyst present.

Effect of Variables on Rate

Table VII lists data on the reaction between technical 44% lactic acid and ethyl alcohol. These data are shown graphically in Figure 6 for various temperatures, catalyst concentrations, and mole ratios of reactants.

It is apparent that, at a mole ratio of reactants of approximately 4 and a temperature of 100° C., the catalytic effect

of sulfuric acid is negligible when the concentration of catalyst is below 0.3%. At 0.302% sulfuric acid a moderate increase in rate can be seen, while a definite increase in rate appears in the run with 0.503% catalyst.

In Figure 6, C, the curves for 6.45 and 8.46 mole ratios of ethyl alcohol to lactic acid intersect the curves of lower ratio. In previous work on technical grade lac-

	Ta	ble VII. I	Reaction Rate	Data for Cruc	le 44% Lacti	c Acid and E	thyl Alcoh	ol	
	Titratable A	cidity, Ml.	Lactic			Titratable .	Acidity, Ml	• Lactic	
	0.1N Base	/G. Soln.	Acid			0.1N Bas	e/G. Soln.	Acid	
	Lactic		Converted,			Lactic		Converted,	
Time,	acid +	Lactic	Mole/100 G.	Conversion,	Time,	acid +	Lactic	Mole/100 G.	Conversion,
Hours	catalyst	acid	Soin.	%	Hours	catalyst	acid	Soln.	%
25°	C.; 0.100% H	$_2$ SO ₄ ; E/L	= 4.10; $L = 0.$	2544	100°	С.; 0.302% Н	$_2$ SO4; E/L	= 4.27; L = 0	.2496
0.0	25.02	24.82	•••	•••	0.0	24.98	24.36		
2.0	24.91	24.71	0.0011	0.43	0.25	24.02	23.71	0.0065	2.60
4.0	24.80	24.61	0.0021	0.82	1.0	22.62	22.31	0.0205	8.20
6.0	24.67	24.48	0.0034	1.33	2.0	19.98	19.67	0.0469	18.80
11.0	24.70	24.52	0.0030	1.18	4.0	17.42	17.11	0.0725	29.10
48 0	24.00	24.24	0.0000	2.00	0.0	10.01	15.70	0.0800	34.70
72.0	23.50	23.09	0.0095	5.05	7.5	14.79	14.48	0.0988	39.00
,2.0		20.00	0.0147	5.77	100°	С.; 0.503% Н	$_{2}SO_{4}; E/L$	= 4.45; L = 0	.2453
40°	С.; 0.100% Н	$_{2}SO_{4}; E/L$	= 3.59; L = 0.	2702	0.0	24.95	23.93		
0.0	26.55	26.35		• • •	0.5	22.52	22.01	0.0192	7.82
1.0	26.19	26.00	0.0035	1.30	1.0	20.57	20.06	0.0387	15.80
3.0	26.11	25.94	0.0041	1.52	2.0	17.84	17.33	0.0660	26.95
4.0	25.98	25.82	0.0053	1.96	3.0	16.07	15.56	0.0837	34.10
6.0	25.92	25.77	0.0058	2.15	4.0	15.02	14.51	0.0942	38.40
10.0	25.69	25.56	0.0079	2.92	5.0	14.07	13.50	0.1037	42.25
24.0	25.00	24.95	0.0140	5.18	0.0	13.34	12.83	0.1171	45.30
48.0	23.57	23.47	0.0288	10.05	1.0	12.73	12.22	0.11/1	47.00
72.0	22.03	22.55	0.0380	14.05	100	°C.; 0.0% H ₂	$SO_4; E/L =$	= 4.15; L = 0.2	2529
60°	С.; 0.101% Н	$_{2}SO_{4}; E/L$	= 3.87; $L = 0.$	2615	0.0	24.67	24.67	•••	•••
0.0	25.72	25.51			0.5	23.47	23.47	0.0120	4.75
2.0	24.45	24.34	0.0117	4.48	1.0	22.00	22.00	0.0201	7.93
4.0	23.98	23.87	0.0164	6.28	2.0	21.03	21.03	0.0304	14.40
6.0	23.35	23.25	0.0226	8.65	4.0	10.19	18.19	0.0048	25.00
7.5	23.30	23.20	0.0231	8.85	24.0	12 70	12 70	0.0738	43 40
24.0	21.20	21.10	0.0441	16.85	48.0	11.69	11.69	0.1298	51.30
48.0	18.05	17.95	0.0756	28.90					
72.0	15.95	15.65	0.0908	37.00	100	• C.; 0.1% H ₂	SO4; E/L =	= 8.40; L = 0.1	1084
80	°C.; 0.1% H ₂	SO_4 ; $E/L =$	4.07; L = 0.2	555	0.0	10.03	16.43		
0.0	25.12	24.92			0.5	10.05	15.95	0.0048	2.85
1.0	23.78	23.68	0.0124	4.86	4.0	13 02	12 02	0.0192	20.85
2.0	23.10	23.00	0.0192	7.51	5.0	12.44	12.34	0.0331	24.25
4.0	21.76	21.66	0.0326	12.75	6.0	12.05	11.95	0.0448	26.60
6.0	20.77	20.67	0.0425	16.65	24.0	8.58	8.48	0.0795	47.20
24.0	15.87	15.77	0.0915	35.80	100	• C • A 107 T	50. m/r -	- 6 4E. T - 0	0.07
90.0	11.93	11.83	0.1309	51.10	100	C., 0.1% H ₂	504; <i>E/L</i> =	= 0.45; L = 0.1	1997
100	° C.; 0.1% H ₂	SO_4 ; E/L =	= 4.22; L = 0.2	2507	0.0	19.68	19.48		•••
0.0	24 66	24 46			1.0	18.35	18.25	0.0123	6.16
0.25	24.00	24.40	0.0047	1 88	2.0	17.00	10.90	0.0252	12.62
0.5	23.52	23.42	0.0104	4.15	4.0	13.22	12.12	0.0430	21,90
1.0	22.56	22.46	0.0200	7.98	24.0	0.72	0.62	0.0577	28.90
2.0	20.91	20.81	0.0365	14.55			2.02	0.0900	19.10
3.0	19.45	19.35	0.0511	20.40	100	$^{\circ}$ C.; 0.1% H ₂	SO_4 ; E/L =	= 2.09; L = 0.3	3322
4.0	18.55	18.45	0.0601	24.00	0.0	32.61	32.41		
5.0	17.54	17.45	0.0702	28,00	0.5	31.33	31.23	0.0118	3.55
6.0	16.85	16.75	0.0771	30.75	1.08	29.77	29.67	0.0274	8.24
7.0	16.24	16.14	0.0832	33.20	2.0	27.60	27.50	0.0491	14.80
8.0	12.85	15.75	0.0871	34.70	6.0	23.67	23.57	0.0884	26.60
271.U 48 A	12.97	12.87	0.1159	40.20	24.0	21.94	21.84	0.1057	31.75
10.0	16.66	16.16	0.1234	±9,20	100°	C.; 0.1% H₂S	$50_4; E/L =$	1.005; L = 0.	3992
100°	C.; 0.201% H	$_{2}$ SO ₄ ; E/L	= 4.30; L = 0.	.2485	0.0	39,15	38,95		• • •
0.0	24.65	24.24	••••		0.5	37.22	37.12	0.0183	4.59
0.5	23.36	23.16	0.0108	4.35	1.0	35.46	35.36	0.0359	8.99
2.0	21.57	21.37	0.0287	11.52	2.0	33.34	33.24	0.0571	14.31
4.U 6 0	16.25	17.05	0.0059	20.50	4.0	30.75	30.65	0.0830	20.80
24.0	10.25	11 00	0.0819	32.90	0.0	29.57	29.47	0.0948	23.78
#1.V	16.17	*****	V. 144J	DC. KE	23.0	28.95	28.85	0.1010	25.30



Figure 7. Relation between $X/(A^2 - b - X)$ and time

- A. Mole ratio approximately 4, catalyst concentration approximately 0.1%
- B. Mole ratio approximately 4 at 100° C.
 C. Catalyst concentration approximately 0.1%
 - at 100° C.

tic acid esterifications, this unusual behavior was attributed to interference of impurities in the mixture (15). Since then, analytical grade lactic acid and ethyl alcohol have exhibited the same behavior. It appears, therefore, that this trend is due not to the presence of impurities but to a change in mechanism at the higher proportions of alcohol.

Order of Esterification Reaction

The data for the reaction of analytical grade 85% lactic acid and absolute ethyl alcohol were best fitted by the relationship:

$$i\theta = \frac{X}{(A-b)(A-b-X)} \qquad (12)$$

where A - b is the original titratable acidity; X is the amount of lactic acid converted in time θ ; θ is the time of reaction; and k is the specific reaction rate constant. Therefore, it seemed logical to attempt to correlate the data on the reactions involving the 44% technical grade lactic acid by this equation.

X/(A - b - X) was plotted against time with X data obtained from the smoothed curves of per cent esterified, using the values of original titratable acidity for A - b (Figure 7). Although data were not correlated as well as in the work with the purer acid, reasonably straight lines were obtained in nearly every case up to about 60% of the equilibrium per cent reacted.

Considering the facts that the presence of impurities made sampling difficult, the longer reaction times caused some decomposition, and the presence of large amounts of water in the mixture made the reverse reaction of hydrolysis more important, the poorer correlation of data for the reaction mixtures containing 44% lactic acid is not surprising.

As in the case of 85% lactic acidethyl alcohol, the slopes of the curves were obtained by taking the average slope through the points in the straight-line region and the origin. Whereas in the runs with the purer lactic acid, induction periods were noted for the higher ratios of ethyl alcohol to lactic acid, none was found with 44% acid, even though the curves for the higher ratios intersected the other curves.

In order to obtain k in the units of liters per (mole) (minute), A - b must be expressed in moles per liter and θ in minutes. Since X/(A - b - X) is a ratio, the units are immaterial as long as they are consistent. Values of k in Table VIII were obtained by dividing the slopes of the lines in Figure 7 by values of A - b, in moles per liter, calculated from the original titratable acidity and the density values for the mixtures.

Equation for the Rate Constant

As can be seen from Figure 7, temperature, catalyst concentration, and mole ratio of ethyl alcohol to lactic acid affect the value of k.

When the specific reaction rate constant, k, was plotted against per cent sulfuric acid catalyst, C, two straight lines resulted instead of the usual single linear relationship found in investigations of this type. For catalyst concentrations from 0 to 0.263% sulfuric acid the value of k was essentially constant at 0.000645liter per (mole) (minute). Above 0.263% sulfuric acid it varied linearly with catalyst concentration.

It was necessary to derive two expressions: Up to 0.263% H₂SO₄ k = 0.000645 (13) Above 0.263% H₂SO₄

 $k = 0.00328C - 0.000218 \quad (14)$

where C is the concentration of sulfuric acid catalyst in per cent of the total mixture.

The point of intersection of these curves differs from that found in the reaction of 44% technical lactic acid and methanol (15). As the source of crude acid was different in each case, further evidence is added that the point of intersection is a function of the amount of impurities present in the acid.

As the amount of sulfuric acid present (0.1%) in the runs in which the mole ratio of reactants was varied exerted no catalytic effect on the reaction, it was not necessary to obtain k on a catalyst-free basis in the correlation of the effects of mole ratio on specific reaction rate constant. Accordingly k was plotted against E/L. An average of the values of k for 0, 0.1, and 0.2% catalyst was plotted for the E/L = 4 point, as it was believed that this would give greater accuracy.

The points for E/L = 6.45 and E/L = 8.46 do not line up on the curve. This is not surprising in view of the peculiar behavior of the data for these runs (Figure 7, C). In arriving at the best straight line through the data points, the two points mentioned above were not considered. At 100° C. the relationship was found to be:

$$k = 0.0001031(E/L) + 0.00024 \quad (15)$$

As there is no catalytic activity below 0.263% sulfuric acid, no term for catalyst concentration is required in the equation. To determine the effect of mole ratio and catalyst concentration for values of C above 0.263%, another equation was derived by transposing the data as follows:

From Equation 14 the theoretical value of k at 0% catalyst is -0.000218. The line sought should conform to the

general equation:

$$\frac{k-a}{C} = m(E/L) + b \tag{16}$$

where m and b are the slope and intercept, respectively.

In Equation 16 *a* is the value of *k* at 0% catalyst concentration. Therefore, the value of -0.000218 is substituted for it. As the catalyst concentration which will give *k* equal to 0.000645 is $0.263\%_0$, this value must be substituted for *C* in the equation, because the catalyst concentration in the series of mole ratio runs was in the region where the apparent effect of catalyst concentration was negligible.

Values of k and E/L were substituted in Equation 16 and the equation was solved for m and b.

The equation thus obtained for values of C of 0.263% and above is:

k = 0.000342(E/L)C + 0.000177C - 0.000218(17)

	Table V	III. Com	parison of Act	ual and Calcu	lated Values o	fk
Temn	C. Wt. %		k,	Liter/(Mole)(M	lin.)	Deviation.
° C.	Catalyst	E/L	Calculated ^a	$Actual^b$	Difference	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
25	0.100	4.10	0.0000121	0.0000113	+0.000008	+ 7.08
40	0.100	3.59	0.0000288	0.0000297	-0.0000009	- 3.03
60	0,101	3.87	0.0000943	0.0001013	-0.0000070	- 0.91
80	0.100	4.07	0.000268	0.000312	-0.000044	-14.10
100	0.100	4.22	0.000675	0.000631	+0.00044	+ 6.97
100	0.201	4.3	0.000683	0.000647	+0.00036	+ 5.56
100	0.302	4.27	0.000758°	0.000772	-0.000014	- 1.82
100	0.503	4.45	0.001438 ^c	0.001430	+0.00008	+ 0.56
100	0.0	4.15	0.000668	0.000658	+0.000010	+ 1.52
100	0.100	1.005	0.000344	0.000346	-0.000002	- 0.58
100	0.100	2.09	0.000460	0.000420	+0.000040	+ 9.51
100	0.100	6.45	0.000905	0.000705	+0.000200	+28.4
100	0.100	8,46	0.001112	0.000785	+0.000327	+41.6
^a Fro	m Equation	19.				
^b Fro	m Equation	12.				
^o Fro	m Equation	20.				

A plot of $\log k$ against the reciprocal of the absolute temperature shows almost perfect linearity over the range 25° to 100° C. for mole ratios of approximately 4, and a catalyst concentration of approximately 0.1% sulfuric acid.

The equation for this line is:

$$\log 10^5 k = -2579/T + 8.721 \quad (18)$$

where T is the temperature in ° K.

Combining Equations 15 and 17 with Equation 18 yields two expressions covering the range of variables studied.

For catalyst concentrations up to 0.263% sulfuric acid:

Table IX. Equilibrium Constants for Reaction of Crude 44% Lactic Acid with Ethyl Alcohol

Tem	p eratu re	Series.	E/L,	Approx	imately
4;	Catalyst,	Approxi	mately	0.1%	H_2SO_4

	Equilibriu	ım
Temp.,	Constan	t,
° C.	K	
25	2.35	
40	2.47	
60	2.76ª	
80	2.21	
100	2.09	
	Av. 2.28	

Catalyst	Series.	E/L	Approximately	4;
	Tempe	rature,	100° C.	
H_{2}	SO4. %			

0.503		2.01	
0.302		2.10	
0.201		2.11	
0.100		2.09	
0.0		2.68^{a}	
	Av.	2.08	

Proportion Seri Catalyst, Ap	ies. Tempe proximately	rature, 0.1%	100° C.; H2SO4
E/L			
1.005		3.42	
2.09		2.56	

2.09	2.50
4.22	2.09
6.45	1.66
8.46	1.49

^a Omitted from average of this group.

$$k = [0.0001031(E/L) + 0.00024] \left[\frac{10^{(8.721 - 2579/T)}}{64.1} \right]$$
(19)

For catalyst concentrations above 0.263% sulfuric acid:

$$k = [0.000342(E/L)C + 0.00177C - 0.000218] \left[\frac{10^{(8.781 - 2879/T)}}{64 1} \right] (20)$$

where k is the reaction rate constant in liters per (mole) (minute), E/L is the ratio of the moles of ethyl alcohol to moles of lactic acid, C is the weight per cent sulfuric acid catalyst, and T is the temperature in ° K.

The values of k predicted from Equations 19 and 20 are compared with those obtained from experimental data and Equation 12 in Table VIII. Average deviation for all runs is 9.8%.

Equilibrium Constants

Samples of the reaction mixture were allowed to remain in the constant temperature bath until their composition became constant, in order to obtain data for calculating equilibrium constants. The equilibrium constants calculated here do not take into account any solid phase present, impurities in solution, or the partial decomposition that occurs under some conditions. They are, therefore, not true equilibrium constants.

$$K = \frac{(\text{ethyl lactate}) (\text{water})}{(\text{lactic acid}) (\text{ethyl alcohol})} \quad (21)$$

Table IX shows that temperature and catalyst concentration exert little effect on the equilibrium constant in the ranges studied. It is apparent that the mole ratio of ethyl alcohol to lactic acid influences the value of the constant.

Discussion of Results

The kinetic data indicate that with 44% technical lactic acid, higher temperatures and higher catalyst concentra-

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tions are needed to lower the reaction time to a commercially attractive level. As both factors tend to increase decomposition of the lactic acid and solid impurities are precipitated from the reaction mixture, a flow-type reactor with reactants in the liquid phase will probably not be satisfactory.

Nomenclature

C

E

K

k

L

θ

- A b =original titratable acidity. moles per liter
 - = constant, corresponds to the theoretical value of k for 0%catalyst
 - = weight % catalyst based on total weight of mixture
 - = moles of ethyl alcohol per 100 grams of solution
 - = equilibrium constant
 - = specific reaction rate constant, liters per (mole)(minute)
 - = moles lactic acid per 100 grams of solution
- = temperature, ° K. TX
 - = moles lactic acid converted at time θ , per 100 grams of solution
 - = time, minutes or hours as specified

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