TABLE IV. STEADY-STATE COUNTERCURRENT EXTRACTION OF 30-GRAM SAMPLES OF ROLLER-DRIED SKIM MILK POWDER

(A = phosphoric acid–phosphate solution, 150 ml. of 0.25% sodium dihydrogen phosphate, 20 ml. of N phosphoric acid; B = sulfuric acid–sulfate solution, 150 ml. of 0.25% sodium sulfate, 20 ml. of N sulfuric acid)

	Solution, %			Solid[a], %		
Extraction	Lactose	Nitrogen	Nitrogen, % of Original	Protein (N × 6.38)	Ash	Lactose
A	10.7	0.13	12	87.3	3.19	0.8
B	10.5	0.12	11	78.5	4.57	5.3

[a] Results on moisture-free basis.

Phosphate and sulfate were next tested as anions in this process, for hydrochloric acid is more corrosive and the residual chloride ion content of the recovered protein and of the lactose solution might be undesirable in certain applications. Steady-state operation was obtained after five batches of solid had been extracted. Eight further extractions were run and the samples pooled for analysis. The results (Table IV) are in general agreement with those presented earlier. The lactose concentration was lower than in the previous experiments because a larger volume of extracting solvent was used. The ash content of the solid from extraction B was higher and the protein content lower, in part caused by the insolubility of calcium sulfate. In these experiments the recovery of protein was good. The loss of 12 and 11% of the total nitrogen in the extract indicates a loss of about 6% of protein nitrogen, or conversely a recovery of 93 to 94% of the protein nitrogen if mechanical losses are disregarded.

DISCUSSION

Recovery of whole milk protein from dried skim milk can be carried out in a batch or countercurrent extraction process; the conditions for this have been worked out on a laboratory scale. However, pilot plant study of engineering aspects will be required before operating costs can be determined. The process would appear to be relatively simple to operate on a commercial scale, and the cost of chemicals would be low. The product, the whole protein of milk, would be unique. Such a protein is not now available on the market. The lactose extract might be used directly in fermentation or in food products, or it might be crystallized by the conventional process.

The economic aspects of such a process depend on the complicated price structure of the dairy industry and on future trends, which are difficult to predict (*3*). Nonfat milk solids are stable currently at the government support level of 11 cents a pound for the roller-dried and 12.25 cents a pound for the spray-dried product. Casein is 21 cents a pound; lactose is 17 cents a pound for the crude product and 26 cents a pound for the U.S.P. grade. The recovery of lactose by crystallization from casein whey ranges from 60 to 70% to over 90%; the authors have not been able to carry out experiments on the extracts to determine what yields could be expected in large scale operation. It is evident that the commercial application of this process would depend to a large extent on the price and market for the whole milk protein.

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n-Butyl Oleate from *n*-Butyl Alcohol and Oleic Acid

DONALD F. OTHMER AND SANJEEV ANANDA RAO[1]

Polytechnic Institute of Brooklyn, Brooklyn, N. Y.

ACCURATE kinetic data on the esterification reaction are needed for the design and successful operation of industrial esterification units. Requirements are: (*a*) order and (*b*) rate of the reaction; (*c*) an over-all mathematical expression of the variation of the rate with temperature, catalyst concentration, and proportions of reactants; (*d*) equilibrium constants; and (*e*) variation of density of the various components with temperature. Previous studies have been made to show the utility of such data in application to production of butyl acetate (*7*) and dibutyl phthalate (*1*). A number of aliphatic esters of oleic acid have been investigated, and it was desired to supply data for the commercially important, *n*-butyl oleate, which is prepared from oleic acid and *n*-butyl alcohol catalyzed by sulfuric acid.

REACTION OF BUTYL ALCOHOL AND SULFURIC ACID

Earlier investigations show that the reaction of butyl alcohol and sulfuric acid gives increasing amounts of butylsulfuric acid at elevated temperatures (*1*, *7*). Two per cent sulfuric acid in butyl alcohol was used over a reaction temperature of 0° to 115° C., and had an apparent, milliequivalent value of 94, which has been used in this investigation for the catalyst concentration factor.

MATERIALS

OLEIC ACID. Crude oleic acid as received from the Nopco Chemical Company had the following analysis: acid value, 190; iodine value, 90; saponification value, 200; unsaponified, 3%. The methyl ester was prepared using sulfuric acid (0.03 mole %) as catalyst. The ester was fractionally distilled at 10 mm.; the fraction boiling at 190° C. was collected and redistilled at 10 mm. of pressure four times. The methyl ester was hydrolyzed, and the oleic acid was removed by distillation at 100 mm. of pressure. The oleic acid thus removed was purified four times by distillation at 100 mm. of pressure. The purified oleic acid was titrated with standard alkali, and the molecular weight determined to be 290.092. The molecular weight of a sample of C.P. oleic acid supplied by the Amend Drug Company was determined to be 289.802, which checked with that of pure oleic acid

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[1] Present address, The Ohio Oil Company, Robinson, Ill.

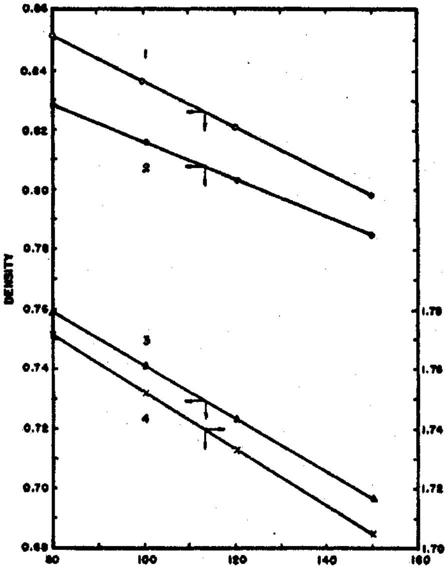

Figure 1. Variation of Density with Temperature

1. Oleic acid
2. Butyl oleate
3. *n*-Butyl alcohol
4. Sulfuric acid

as obtained from the crude within 0.1%. The purity of the oleic acid was then calculated on the basis of its molecular weight and was found to be 97.37%.

n-Butyl Alcohol. Reagent grade was used. It was distilled and the center cut, with boiling point of 117.71° C., was used, containing 0.02% water and no free acidity.

Sulfuric Acid. Reagent grade acid was used of 95.5% sulfuric acid by analysis.

EXPERIMENTAL STUDIES ON RATE OF ESTERIFICATION

The following effects were to be investigated:

Concentration of reactants—molar ratio of butyl alcohol to oleic acid (*B/A*) from 1 to 1 to 20 to 1—at a constant reaction temperature of 100° C. and a constant catalyst concentration of approximately 0.9%.

Catalyst concentration—0% to 2.85% sulfuric acid—at a constant reaction temperature of 100° C. and a constant *B/A* of approximately 5 to 1.

Reaction temperature—80° to 100° C.—at a constant *B/A* of 5 to 1 and a constant catalyst concentration of approximately 0.9%.

EXPERIMENTAL PROCEDURES

Esterification. To prevent reaction in the initial stage, the required amounts of sulfuric acid, oleic acid, and butyl alcohol were weighed into separated tared Erlenmeyer flasks which were then immersed in an ice bath. The chilled oleic acid and butyl alcohol were poured into the flask containing sulfuric acid, and the empty flasks were weighed.

Approximately 5 ml. of the cold mixture were pipetted into drawn-down test tubes (13 × 100 mm.) which were sealed by a flame with approximately 1 ml. of air space, and immersed in the ice bath. All tubes were added to a bath maintained ±0.5° between 80° and 150° C.

Sample vials were taken out at pre-set time intervals and cooled in the ice bath. The vial was then dried, the tip broken off, and a sample of approximately 2 to 3 grams was weighed carefully into a tared Erlenmeyer flask. 25 ml. of c.p. acetone were added to dissolve the sample which was then titrated against 0.1 *N* alcoholic potassium hydroxide and backtitrated with 0.1 *N* hydrochloric acid in order to obtain a double check, using phenolphthalein as indicator.

The results of these runs are summarized in Table I.

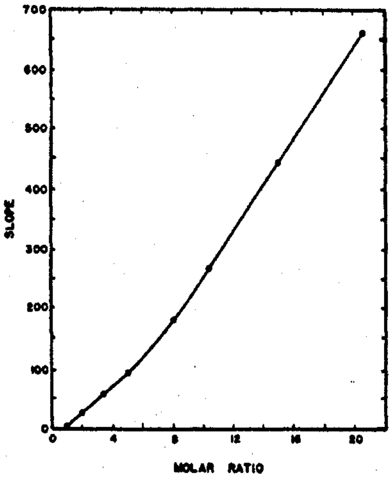

Figure 2. Slope of Second-Order Reaction *vs.* Molar Ratio

Density. For the development of the experimental data obtained it is necessary to convert the concentrations to the form of moles per liter. In order to do this, it is essential to know the density of the various reactants at the experimental temperatures. These data are available for water and butyl alcohol. Determinations were made as previously for oleic acid and *n*-butyl oleate (*1, 7*). The stem of a 100-ml. Cassia flask was replaced with a 20-ml. microburet, graduated to 0.02 ml., and readable with a lens to 0.01 ml. The density was determined from measurements of the different levels on the buret (hence total volume) reached by a known mass at different temperatures. Suitable corrections were applied for the expansion of the glass. The data are given in Table II and Figure 1.

DISCUSSION OF EXPERIMENTAL DATA

Molar Ratio Series. As *B/A* is increased, the rate increases and the yield increases to a maximum of 98.95%. (Yield in this paper refers to the per cent of butyl oleate obtained, based on theoretical 100% conversion.) After a reaction time of 3 hours, the per cent yield starts to fall, owing to the predominance of side and reverse reactions.

Temperature Series. The rate increases with temperature,

Butyl alcohol and oleic acid in the presence of sulfuric acid as a catalyst react rapidly to give a yield of 90% of *n*-butyl oleate in 30 minutes at temperatures of 100° to 150° C. After a yield of 90 to 99%, side reactions and reverse reactions predominate and the yield starts to fall. Maximum yield was obtained in 2 to 3 hours under varying conditions of temperature, catalyst concentrations, and ratio of butyl alcohol to oleic acid. The reaction was second-order up to a yield of 92 to 97% of *n*-butyl oleate. Reaction rate was proportional to catalyst concentration between 0.5 and 1.2%, to the molar ratio of butyl alcohol to oleic acid, and to the negative reciprocal of the reaction temperature from 100° to 150° C. Catalyst concentration, molar ratio of butyl alcohol to oleic acid, and temperature were correlated with rate. An empirical equation was derived which would predict the rate constant from these three variables within an accuracy of 4% for molar ratios not above 10 to 1 of butyl alcohol to oleic acid, for catalyst concentrations of 0.5 to 1.2%, and for temperatures above 100° C. The equilibrium constant was also determined, and the effects of the three variables were observed. Catalyst concentration and temperature had no marked influence, but increasing the molar ratio of butyl alcohol to oleic acid caused a decrease in yield. The heats of reaction of this system at 100° to 150° C. were evaluated graphically.

TABLE I. REACTION RATE DATA[a]

Time, Min.	$(A - X)$	X	% E	$\frac{X}{A_0(A - X)}$
Run *A*: H_2SO_4 = 0.7927%; Temp., 100° C.; B/A = 0.9996; A_0 = 2.2754				
0	0.2782	0	0	0
10	0.2499	0.0283	10.17	0.05
20	0.2105	0.0677	24.35	0.14
30	0.1999	0.0783	28.13	0.17
60	0.1515	0.1267	45.53	0.37
90	0.1250	0.1532	55.05	0.54
120	0.1087	0.1695	60.93	0.69
180	0.0831	0.1951	70.14	1.03
240	0.0755	0.2027	72.87	...
300	0.0706	0.2076	74.64	...
Run *B*: H_2SO_4 = 0.9000%; Temp., 100° C.; B/A = 1.9135; A_0 = 1.8821				
0	0.2335	0	0	0
10	0.1176	0.1159	49.63	0.52
20	0.0787	0.1548	66.30	1.05
30	0.0596	0.1739	74.46	1.55
60	0.0343	0.1992	85.30	3.08
90	0.0240	0.2095	89.69	4.63
180	0.0127	0.2208	94.55	9.22
300	0.0110	0.2225	95.30	...
360	0.0187	0.2148	92.00	...
Run *C*: H_2SO_4 = 0.9631%; Temp., 100° C.; B/A = 3.3808; A_0 = 1.4735				
0	0.1857	0	0	0
10	0.0666	0.1191	64.16	1.21
20	0.0408	0.1449	78.04	2.41
30	0.0293	0.1564	84.19	3.62
60	0.0160	0.1697	91.37	7.19
90	0.0110	0.1747	94.08	10.78
120	0.0084	0.1773	95.48	14.35
180	0.0056	0.1801	96.95	...
240	0.0209	0.1648	88.76	...
300	0.0437	0.1420	76.43	...
Run *D*: H_2SO_4 = 0.9047; Temp., 100° C.; B/A = 5.0759; A_0 = 1.1789				
0	0.1505	0	0	0
10	0.0477	0.1028	68.32	1.83
20	0.0282	0.1223	81.30	3.69
30	0.0198	0.1307	86.87	5.61
60	0.0105	0.1400	93.04	11.34
90	0.0072	0.1433	95.23	16.95
120	0.0055	0.1450	96.39	22.65
180	0.0021	0.1484	98.62	...
240	0.0112	0.1393	92.54	...
300	0.0308	0.1197	79.55	...
Run *E*: H_2SO_4 = 0.9087%; Temp., 100° C.; B/A = 8.1745; A_0 = 0.8627				
0	0.1115	0	0	0
10	0.0277	0.0838	75.14	3.51
20	0.0156	0.0959	85.96	7.10
30	0.0110	0.1005	90.14	10.59
60	0.0057	0.1058	94.85	21.40
90	0.0038	0.1077	96.59	32.87
120	0.0029	0.1086	97.38	...
180	0.0013	0.1102	98.83	...
240	0.0063	0.1052	94.40	...
300	0.0205	0.0910	81.62	...
Run *F*: H_2SO_4 = 1.0199%; Temp., 100° C.; B/A = 10.3734; A_0 = 0.7245				
0	0.0947	0	0	0
10	0.0196	0.0751	79.34	5.30
20	0.0109	0.0838	88.48	10.61
30	0.0075	0.0872	92.14	16.18
60	0.0039	0.0908	95.95	32.64
90	0.0026	0.0921	97.23	48.48
120	0.0021	0.0926	97.83	...
180	0.0013	0.0934	98.68	...
240	0.0049	0.0898	94.85	...
300	0.0169	0.0778	82.18	...
Run *G*: H_2SO_4 = 0.8876%; Temp., 100° C.; B/A 14.9653; A_0 = 0.5435				
0	0.0707	0	0	0
10	0.0117	0.0590	83.44	9.27
20	0.0064	0.0643	91.03	18.67
30	0.0044	0.0663	93.86	28.12
60	0.0022	0.0685	96.84	56.49
90	0.0015	0.0692	97.82	...
120	0.0012	0.0695	98.33	...
180	0.0008	0.0699	98.83	...
240	0.0030	0.0677	95.74	...
300	0.0118	0.0589	83.28	...
Run *H*: H_2SO_4 = 0.9230%; Temp., 100° C.; B/A = 20.6224; A_0 = 0.4154				
0	0.0547	0	0	0
10	0.0087	0.0460	84.13	15.17
20	0.0045	0.0502	91.74	26.73
30	0.0031	0.0516	94.32	39.94
60	0.0016	0.0531	97.11	80.95
120	0.0009	0.0538	98.30	...
180	0.0006	0.0541	98.95	...
240	0.0023	0.0524	95.83	...
300	0.0089	0.0458	83.75	...
Run *I*: H_2SO_4 = 0.9365%; Temp., 80° C.; B/A = 5.1424; A_0 = 1.1939				
0	0.1493	0	0	0
10	0.0910	0.0583	39.07	0.54
20	0.0641	0.0852	57.08	1.11
30	0.0498	0.0995	66.64	1.67
60	0.0295	0.1198	80.24	3.39
90	0.0213	0.1280	85.71	5.01
120	0.0165	0.1328	88.97	6.74
180	0.0115	0.1378	92.35	10.09
240	0.0135	0.1358	91.01	...
300	0.0233	0.1260	84.40	...
Run *J*: H_2SO_4 = 0.9365%; Temp., 120° C.; B/A = 5.1424; A_0 = 1.1435				
0	0.1493	0	0	0
10	0.0314	0.1179	79.00	3.29
20	0.0178	0.1315	88.10	6.47
30	0.0125	0.1368	91.67	9.61
60	0.0064	0.1429	95.71	19.52
90	0.0045	0.1448	97.00	28.26
120	0.0018	0.1475	98.77	...
180	0.0126	0.1367	91.56	...
240	0.0597	0.0896	60.00	...
Run *K*: H_2SO_4 = 0.9365%; Temp., 150° C.; B/A = 5.1424; A_0 = 1.1053				
0	0.1493	0	0	0
10	0.0187	0.1306	87.51	6.34
20	0.0104	0.1389	93.06	12.14
30	0.0072	0.1421	95.22	18.01
60	0.0038	0.1455	97.46	34.82
90	0.0015	0.1478	99.03	...
120	0.0045	0.1448	96.97	...
180	0.0501	0.0992	66.46	...
Run *L*: H_2SO_4 = 0.0000%; Temp., 100° C.; B/A = 5.1270; A_0 = 1.176				
0	0.1510	0	0	0
30	0.1474	0.0036	2.37	0.02
60	0.1436	0.0074	4.93	0.04
120	0.1375	0.0135	8.91	0.08
180	0.1317	0.0193	12.80	0.12
240	0.1260	0.0250	16.55	0.17
300	0.1212	0.0298	19.73	0.21
360	0.1165	0.0345	22.88	0.25
Run *M*: H_2SO_4 = 0.1221%; Temp., 100° C.; B/A = 4.8936; A_0 = 1.2092				
0	0.1549	0	0	0
10	0.1000	0.0549	35.47	0.45
20	0.0736	0.0813	52.48	0.91
30	0.0562	0.0987	63.73	1.45
60	0.0351	0.1198	77.37	2.83
90	0.0254	0.1295	83.59	4.21
120	0.0198	0.1351	87.21	5.64
180	0.0138	0.1411	91.09	8.46
240	0.0122	0.1427	92.15	9.70
300	0.0122	0.1427	92.15	...
360	0.0131	0.1418	91.54	...
Run *N*: H_2SO_4 = 0.1476%; Temp., 100° C.; B/A = 5.0620; A_0 = 1.1850				
0	0.1519	0	0	0
10	0.0832	0.0687	45.21	0.70
20	0.0601	0.0918	60.45	1.29
30	0.0470	0.1049	69.09	1.89
60	0.0286	0.1233	81.19	3.64
90	0.0204	0.1315	86.59	5.45
120	0.0158	0.1361	89.59	7.26
180	0.0110	0.1409	92.80	10.88
240	0.0108	0.1411	92.91	...
300	0.0112	0.1407	92.64	...
360	0.0125	0.1394	91.76	...
Run *O*: H_2SO_4 = 0.2626%; Temp., 100° C.; B/A = 5.1528; A_0 = 1.1717				
0	0.1502	0	0	0
10	0.0715	0.0787	52.37	0.94
20	0.0476	0.1026	68.31	1.84
30	0.0357	0.1145	76.21	2.73
60	0.0203	0.1299	86.51	5.47
90	0.0143	0.1359	90.51	8.14
120	0.0110	0.1392	92.70	10.84
180	0.0075	0.1427	95.01	16.26
300	0.0114	0.1388	92.43	...
Run *P*: H_2SO_4 = 0.4819%; Temp., 100° C.; B/A = 5.1471; A_0 = 1.1712				
0	0.1499	0	0	0
10	0.0512	0.0987	65.82	1.64
20	0.0318	0.1181	78.77	3.17
30	0.0232	0.1267	84.54	4.67
60	0.0127	0.1372	91.51	9.21
90	0.0088	0.1411	94.14	13.71
120	0.0067	0.1432	95.56	18.39
180	0.0039	0.1460	97.40	...
240	0.0115	0.1384	92.34	...
300	0.0418	0.1081	72.12	...
Run *Q*: H_2SO_4 = 1.9578%; Temp., 100° C.; B/A = 5.1110; A_0 = 1.1677				
0	0.1482	0	0	0
10	0.0385	0.1097	74.06	2.44
20	0.0228	0.1254	84.63	4.71
30	0.0161	0.1321	89.15	7.03
60	0.0086	0.1396	94.22	13.95
90	0.0085	0.1397	94.28	...
120	0.0134	0.1348	90.97	...
180	0.0331	0.1151	77.68	...
240	0.0535	0.0947	64.00	...
Run *R*: H_2SO_4 = 2.8523%; Temp., 100° C.; B/A = 5.1434; A_0 = 1.1580				
0	0.1462	0	0	0
10	0.0352	0.1110	75.93	2.72
20	0.0201	0.1261	86.23	5.41
30	0.0141	0.1321	90.34	8.07
60	0.0104	0.1358	92.88	11.27
90	0.0107	0.1355	92.65	...
120	0.0159	0.1303	89.13	...
180	0.0351	0.1111	76.01	...
240	0.0554	0.0908	62.10	...

[a] X = oleic acid converted, moles/100 grams; $(A - X)$ = oleic acid remaining, moles/100 grams; A_0 = oleic acid originally present, moles/liter; % E = *n*-butyl oleate.

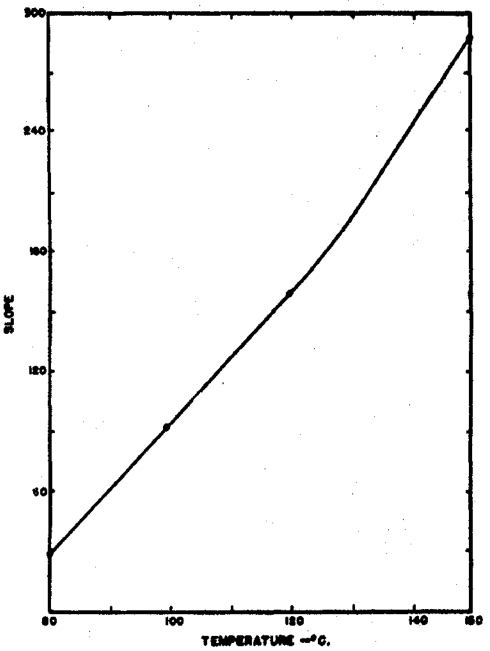

Figure 3. Slope of Second-Order Reaction *vs.* Temperature

as does the yield, up to a maximum of 99.03%; but higher temperatures increase side and reverse reactions. At 150° C. the maximum yield is obtained within 1.5 hours, after which the yield falls rapidly.

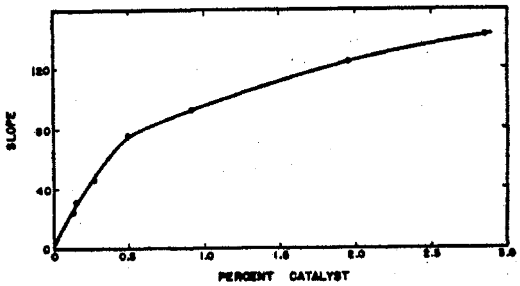

Figure 4. Slope of Second-Order Reaction *vs.* Per Cent Catalyst

Catalyst Series. With no catalyst, the yield after 6 hours is only 22.88%; and with 0.1221% catalyst, a maximum yield of 92.15% is obtained in 4 hours. Increase in catalyst up to approximately 1.2% increases the yield. Higher catalyst favors side and reverse reactions, and the yield falls from a maximum of 98.62% with approximately 0.9% to 92.88% with approximately 2.85%. Increase in catalyst, however, always increases the rate.

ORDER OF REACTION

The order of the reaction can be determined graphically by plotting different functions of the concentration, c, of the free oleic acid (in moles per 100 grams), against the time in hours.

Table II. Variation of Density with Temperature

Component	Density, Grams/Ml. at 80° C.	100° C.	120° C.	150° C.
Oleic acid	0.8511	0.8360	0.8208	0.7985
n-Butyl alcohol	0.7590	0.7419	0.7236	0.6964
n-Butyl oleate	0.8295	0.8165	0.8041	0.7850
Sulfuric acid	1.7715	1.7527	1.7332	1.7040
Water	0.9718	0.9584	0.9434	0.9173

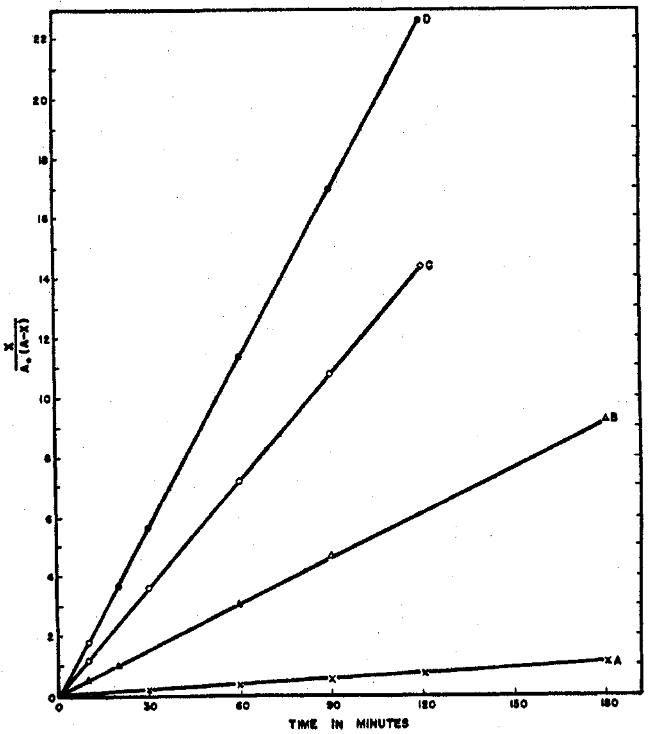

Figure 5. Determination of Rate Constant k

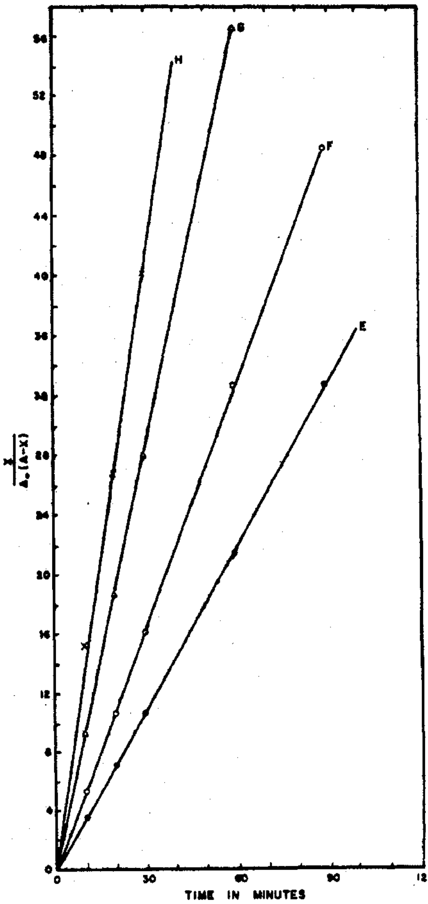

Figure 6. Determination of Rate Constant k

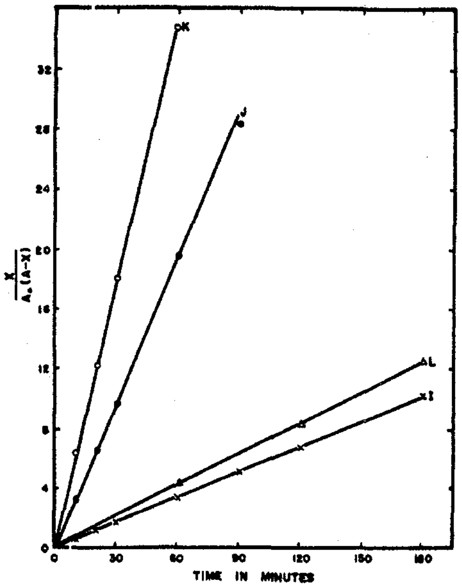

Figure 7. Determination of Rate Constant k

For run L multiply $\frac{X}{A_0\,(A-X)}$ by 0.01

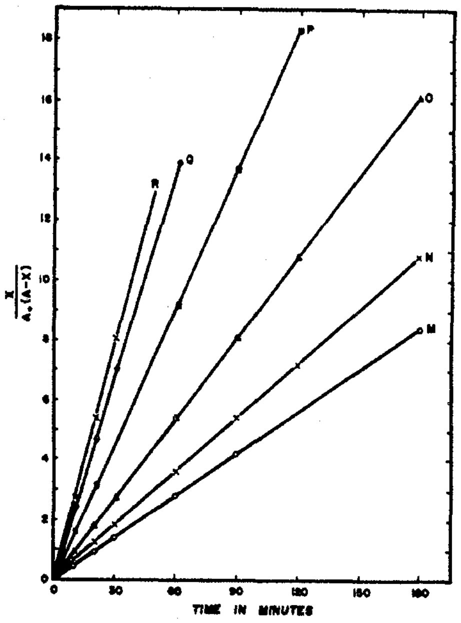

Figure 8. Determination of Rate Constant k

1. Log c versus time gives a straight line for a first-order reaction.
2. $1/c$ versus time gives a straight line for a second-order reaction.
3. $1/c^2$ versus time gives a straight line for a third-order reaction.

The data obtained in Table I were recalculated and the second-order plots ($1/c$ versus time) yielded straight lines—the molar ratio series up to approximately a yield of 97%; the temperature series to about 97%; and the catalyst series to about 92 to 97%. Those for first- and third-order did not give straight lines.

The reaction at temperatures above 80° C. follows a second-order, quadratic equation up to about a yield of 92 to 97%. The slopes of these second-order reaction lines for the various series were determined and plotted in Figures 2, 3, and 4 against the molar ratios, temperature, and weight per cent catalyst. The smooth curves obtained show that the experimental data were mutually consistent.

REACTION RATE EQUATION

Type of Equation. The equation governing the rate may be determined by trial and error. A number of equations are generally assumed as expressing second-order reactions, and these were tested in the usual graphical ways by plotting various functions against time (*1–3, 7*) to find which gives a straight line relation. The one which did, is

$$kt = \frac{X}{A_0(A-X)} \qquad (1)$$

where A_0 = oleic acid originally present, moles/liter
A = oleic acid originally present, moles or moles/100 grams
X = amount of oleic acid transformed in the time interval, t (same units as A)
k = reaction rate constant

When $\frac{X}{A_0(A-X)}$ was plotted against t, straight lines were obtained for all runs up to a yield of 96%. Hence, Equation 1 holds for this reaction.

Determination of Rate Constant. The reaction rate constant, k, of each individual run was evaluated from the slope expressed by the above relation. The data are in Table I and indicated in Figures 5 through 8.

Effect of Catalyst Concentration on Rate Constant. Previous investigators have found that the rate of esterification with acid catalyst is proportional to acid catalyst concentration or hydrogen ion concentration. The reaction rate constant for the catalyst series was plotted against the weight per cent catalyst, Figure 9, which gave a linear relation (at low catalyst concentration).

Effect of Proportions on Rate Constant. The rate is proportional to the concentration of alcohol as well as to concentration of catalyst. Hence, if the rate constant for the molar ratio series is divided by the weight per cent of the catalyst, and if this quotient is plotted against the molar ratio of butyl alcohol to oleic acid, the effects caused solely by the catalyst would be eliminated. Figure 10 shows a linear relation for the runs in the molar ratio series.

Effect of Temperature on Rate Constant. Temperature exerts a powerful influence upon rates of reactions, usually less at higher temperatures. Figure 11 shows the logarithm of the rate constant versus the reciprocal of the absolute temperature. The straight line from 100° to 150° C. indicates that the con-

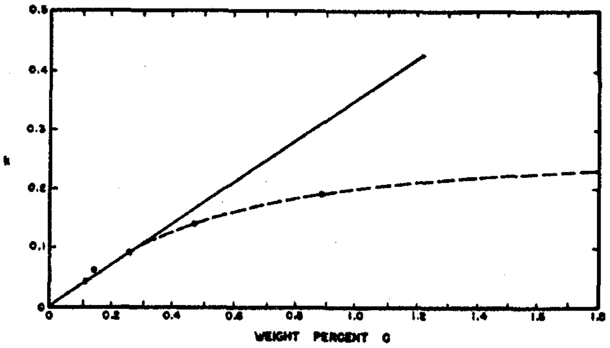

Figure 9. Relation between Reaction Rate Constant k and Catalyst Concentration at 100° C. with Approximately 5 Moles of Butyl Alcohol per Mole of Oleic Acid

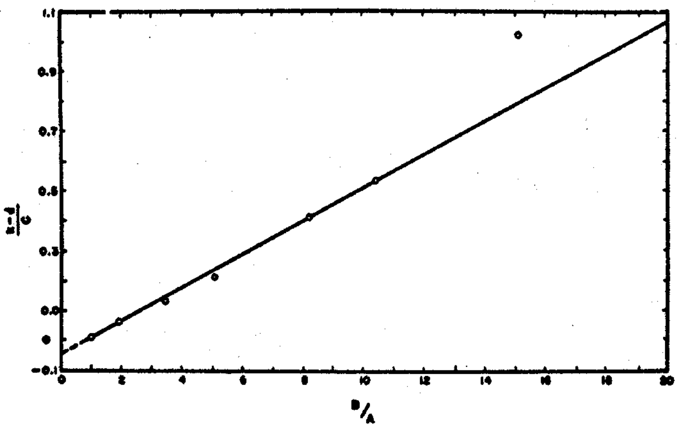

Figure 10. Relation between Ratio of Reaction Rate Constant to Catalyst Concentration, $(k - d)/C$, and Molar Ratio of Butyl Alcohol to Oleic Acid, B/A, at 100° C.

trolling reaction is expressed by the equation $k \propto 1/t$. However, for 80° C. the reaction rate is actually lower than was expected. This proves that the esterification of butyl alcohol and oleic acid in the presence of sulfuric acid as a catalyst, as expressed by this equation, is essentially a high temperature reaction, as it can be seen that there is a rapid increase in the velocity constant from 80° to 100° C.

RATE CONSTANT EQUATION. The straight line relations in Figures 9, 10, and 11 indicate that a simple empirical equation would express the rate as a function of catalyst concentration C (directly at constant molar ratio and temperature), of molar ratio B/A (directly at constant catalyst and temperature), and of reaction temperature T (inversely at constant molar ratio and catalyst).

The general equation for a straight line will apply since all relations are linear. For the catalyst series, $k = a + bC$. For the molar ratio series, $k = (a' + b' + B/A)m$, where a', b', and m are constants.

Temperature is an intensive quantity and must exert its effect as a separate factor. This is evaluated by multiplying the general equation connecting the other variables by a temperature factor. The various effects may thus be combined in the form of a general equation:

$$K = (d + eC + fB/A)(g + h/T) \quad (2)$$

where d, e, f, g, and h are constants.

The first parenthesis expresses the effect of the catalyst concentration and the molar ratio at a temperature of 100° C., while the second parenthesis gives the temperature effect, evaluated on the rate at 100° C., taken as unity.

At 100° C. the constant d should represent the rate due to oleic acid alone; hence, if the value of k obtained for run L with no catalyst is assumed equal to d, the other four constants can be evaluated from the straight-line relations obtained.

Considering the first parenthesis involving the effect of the catalyst and molar ratio, the equation can be rearranged as follows:

$$\frac{k - d}{C} = e + fB/A \quad (3)$$

If $(k - d)/C$ is plotted against B/A, a straight line plot will result, having an intercept equal to e and a slope of f. This was done in Figure 10; and the equation corresponding is

$$k = 0.0007 - 0.048C - 0.05435C(B/A) \quad (4)$$

The value of the constants (which does not include the temperature effect) checked closely when tested by the method of least squares. As a further check, the values of k were recalculated for the molar ratio series and for the catalyst series (Table III). For the molar ratio series, the calculated values of k agree very well for runs A through F, showing an average deviation of only ±3.9%; but for runs G and H there is an average deviation of −27%. This can be expected as these two runs were for extreme conditions.

TABLE III. COMPARISON OF ACTUAL AND CALCULATED VALUES OF k AT 100° C.

Run	C, Wt. %	B/A	k Calcd.[a]	k Actual	k Calcd.[b]	Difference[c]	Deviation, %
			Molar Ratio Series				
A	0.7927	0.9996	0.0057	0.0057	0.0057	0.0000	0.00
B	0.9000	1.9135	0.0513	0.0512	0.0511	−0.0001	−0.20
C	0.9631	3.3808	0.1196	0.1196	0.1314	+0.0118	+9.87
D	0.9047	5.0759	0.1888	0.1888	0.2069	+0.0181	+9.59
E	0.9087	8.1745	0.3652	0.3652	0.3608	−0.0044	−1.21
F	1.0199	10.3734	0.5387	0.5387	0.5268	−0.0119	−2.21
G	0.8876	14.9653	0.9411	0.9411	0.6800	−0.2611	−27.74
H	0.9230	20.6224	1.3492	1.3492	0.9909	−0.3583	−26.56
			Catalyst Series				
L	0.0000	5.1270	0.0007	0.0007	0.0007	0.0000	0.00
M	0.1221	4.8936	0.0404	0.0457	0.0273	−0.0184	−40.26
N	0.1476	5.0620	0.0605	0.0607	0.0342	−0.0265	−43.66
O	0.2626	5.1528	0.0903	0.0903	0.0616	−0.0287	−31.78
P	0.4819	5.1471	0.1533	0.1385	0.1124	−0.0261	−18.85
D	0.9047	5.0759	0.1888	0.1888	0.2069	+0.0181	+9.59
Q	1.9578	5.1110	0.2325	0.2357	0.4506	+0.2149	+91.17
R	2.8523	5.1434	0.1878	0.2691	0.6611	+0.3920	+145.70

[a] Calculated by the bimolecular equation $k = (1/A_0t)(X/A - X)$.
[b] Calculated by Equation 4, $k = 0.0007 - 0.048C + 0.05435C(B/A)$.
[c] Calculated by Equation 4, $-k$ actual.

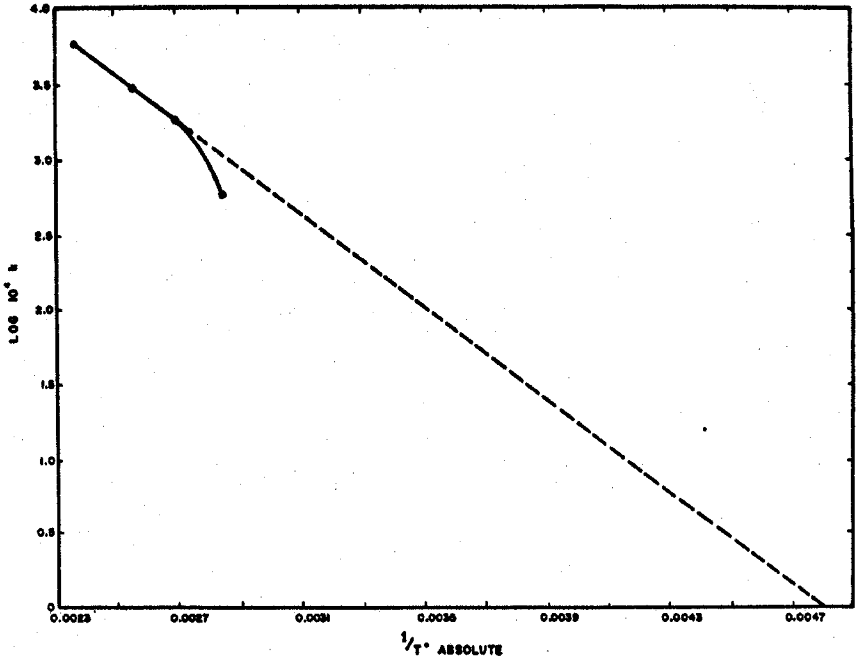

Figure 11. Relation between Reaction Rate Constant and Temperature with Approximately 0.9% Catalyst and 5 Moles of Butyl Alcohol per Mole of Oleic Acid

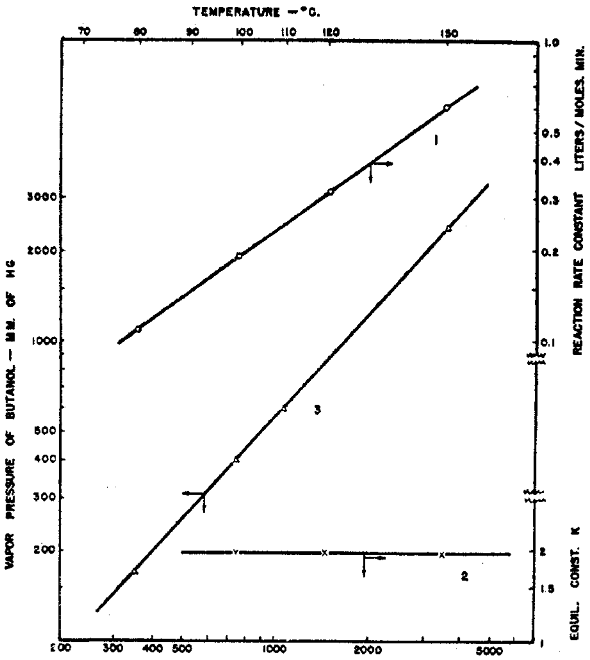

Figure 12. Correlation of Data against Vapor Pressure of Water

1. Reaction rate constant *vs.* vapor pressure of water
2. Equilibrium constant *vs.* vapor pressure of water
3. Vapor pressure of *n*-butyl alcohol *vs.* vapor pressure of water

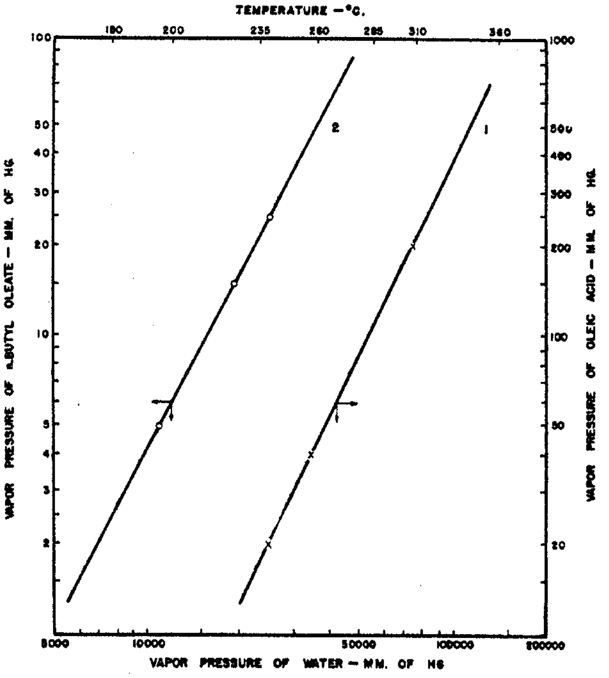

Figure 13. Correlation of Data against Vapor Pressure of Water

1. Vapor pressure of oleic acid *vs.* vapor pressure of water
2. Vapor pressure of *n*-butyl oleate *vs.* vapor pressure of water

For the catalyst series, the reaction rate increases rapidly with increasing catalyst. For low catalyst, approximately 0.1 to 0.25%, there is an average deviation of −39%. For very high catalyst concentrations of 2 to 3% there is an average deviation of +118%. This was expected as high catalyst concentrations tend to accelerate the reverse and side reactions, but for catalyst concentrations between 0.5 to 1.2% the agreement of the actual values of k to the calculated ones was good. It was not possible to derive an equation that would hold for all the catalyst concentrations, owing to the peculiar behavior of the reaction with high and low catalyst concentration.

INCLUSION OF TEMPERATURE FUNCTION. Temperature controls rate according to the relation

$$\log k = g + h/T$$

By plotting, as in Figure 11, log $10^4\,k$ versus $1/T$ for the temperature series, the constants g and h were evaluated to give

$$\log 10^4\,k = 7.522 - 1583.57/T \tag{5}$$

These values checked closely by the method of least squares.

Equation 5 was then tested with the data obtained at 80° to 150° C. for the temperature series as shown in Table IV. Close agreement of the calculated values of the reaction rate constant with the experimental values was obtained with an average deviation of ±0.43%, except for run I having a reaction temperature of 80° C. where a deviation of +94% is obtained. Hence, this equation holds for 100° C. and above. A final equation for expressing the reaction rate constant is obtained by multiplying Equations 4 and 5.

$$k_T = 0.0007 - 0.048C - 0.05435C\,(B/A)\,7.522 - 1583.57/T \tag{6}$$

where k_T = predicted reaction rate constant
C = sulfuric acid, weight %
B = butyl alcohol, moles
A = oleic acid, moles
T = temperature, ° K.

Equation 6 will predict the reaction rate within an accuracy of ±4% upon the insertion of the proper values for molar ratio, per cent catalyst, and temperature; for molar ratios not above 10 to 1 of butyl alcohol to oleic acid, for catalyst concentrations of 0.5 to 1.2%, and reaction temperature above 100° C.

EQUILIBRIUM CONSTANTS

The equilibrium constant, K, is defined as the ratio of the concentrations of products divided by the concentrations of reactants.

$$K = \frac{(\text{ester})(\text{water})}{(\text{butyl alcohol})\ (\text{oleic acid})}$$

Since all the runs were carried out until equilibrium was reached, the data obtained were used in evaluating the equilibrium constant for the various runs, except runs A and L, Table V.

The equilibrium constant is markedly affected by the proportions of the reactants employed, decreasing with increasing B/A.

The reaction temperature of 100° to 150° C. and the catalyst concentration have no marked influence on the equilibrium constant. The average value of the equilibrium constant for the temperature series is 0.194 and for the catalyst series, 0.180.

HEAT QUANTITIES INVOLVED IN ESTERIFICATION OF *n*-BUTYL OLEATE

Previous reports (*9, 10*) have shown that reaction rate constants, equilibrium constants, solubility product constants, and ionization constants give straight line plots on logarithmic paper against the vapor pressure of a reference substance at the same temperature. The slopes of these straight lines are determined by the heat quantities. This method can be used to correlate, to interpolate, or extrapolate experimental data available upon the change of the various equilibrium constants with temperature. In addition, the slopes of the lines can be used in evaluating the heat of reaction of the system at any temperature. Such plots were made in Figures 12 and 13 against the vapor pressures of water for the reaction rate constants, the equilibrium con-

TABLE IV. COMPARISON OF ACTUAL AND CALCULATED VALUES OF k AT 80° TO 100° C.

Run	Temp., ° C.	Calcd.[a]	Actual	Calcd.[b]	Difference[c]	Deviation, %
I	80	0.0560	0.0560	0.1089	+0.0529	+94.46
D	100	0.1888	0.1888	0.1895	+0.0007	+0.37
J	120	0.3140	0.3140	0.3116	−0.0024	−0.76
K	150	0.5803	0.6003	0.6013	+0.0010	+0.17

[a] Same as Table III.
[b] Calculated by Equation 5.
[c] Same as Table III.

TABLE V. EQUILIBRIUM CONSTANT K

Run	B/A	K	Run	C, Wt. %	K
	Molar Ratio Series			Catalyst Series	
B	1.9135	0.480	*M*	0.1221	0.174
C	3.3808	0.282	*N*	0.1476	0.171
D	5.0759	0.195	*O*	0.2626	0.176
E	8.1745	0.122	*P*	0.4819	0.186
F	10.3734	0.097	*D*	0.9047	0.195
G	14.9653	0.067	*Q*	1.9578	0.180
H	20.6224	0.050	*R*	2.8523	0.177
					Av. 0.180

Run	Temp., ° C.	K
	Temperature Series	
D	100	0.195
J	120	0.193
K	150	0.194
		Av. 0.194

stants, the vapor pressure of *n*-butyl alcohol (*4*), the vapor pressure of oleic acid (*11*), and the vapor pressure of *n*-butyl oleate.

The heats of reaction were evaluated from Figure 12 at different temperatures from 100° to 150° C. A summary of the heats of reaction at different temperatures is given in Table VI, and a plot of the heats of reaction versus temperature is shown in Figure 14.

The latent heats of *n*-butyl alcohol, oleic acid, and *n*-butyl oleate were evaluated from Figures 12 and 13 at different temperatures from 100° to 150° C. A summary of the latent heats of the various components at different temperatures is given in Table VII and in a plot in Figure 14.

The heat of combustion of *n*-butyl oleate was found (*5, 6*) to be 3302.3 kg.-cal. per mole at 20° C. from which the heat of formation was evaluated to be −203 kg.-cal. per mole.

CONCLUSIONS

Esterification of butyl alcohol and oleic acid above 80° C. is a second-order reaction.

TABLE VI. HEATS OF REACTION

Temp., ° C.	Heat of Reaction, Cal./Kg.
100	−26.95
110	−26.63
120	−26.30
130	−25.95
150	−25.23

TABLE VII. LATENT HEATS

Component	Temp., ° C.	Latent Heat, Cal./Kg.
n-Butyl alcohol	100	609.1
	110	601.8
	120	594.3
	130	586.5
	150	570.1
Oleic acid	100	1142.7
	110	1129.1
	120	1114.9
	130	1100.3
	150	1069.3
n-Butyl oleate	100	1056.4
	110	1044.9
	120	1030.8
	130	1017.2
	150	988.8

The rate constant is a linear function of the catalyst concentration and the molar ratio of butyl alcohol to oleic acid. At temperatures in the range of 100° to 150° C. the logarithm of the rate constant is proportional to the reciprocal of absolute temperature.

The empirical equation derived will predict the reaction rate within an accuracy of ±4% for molar ratios not above 10 to 1 of butyl alcohol to oleic acid, for catalyst concentrations of 0.5 to 1.2%, and for reaction temperatures above 100° C.

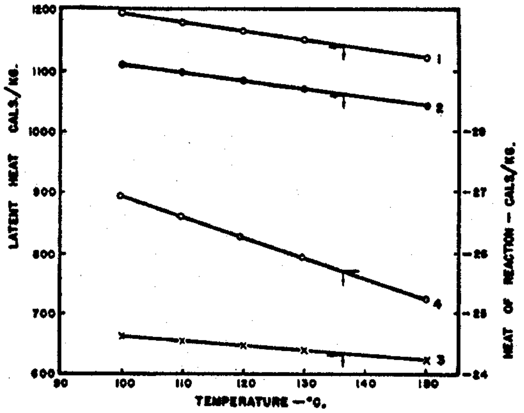

Figure 14. Correlation of Latent Heats and Heats of Reaction with Temperature

1. Latent heat of oleic acid
2. Latent heat of *n*-butyl oleate
3. Latent heat of *n*-butyl alcohol
4. Heat of reaction of system

The catalyst concentration and the reaction temperature in the range of 100° to 150° C. have no marked influence on the equilibrium constant. However, the equilibrium constant decreases with the increase in molar ratio of butyl alcohol to oleic acid.

The reaction is very slightly endothermic. The heat of reaction is a linear function of temperature in the range of 100° to 150° C.

The latent heats of *n*-butyl alcohol, oleic acid, and *n*-butyl oleate are linear functions of temperature in the range of 100° to 150° C.

The formation of *n*-butyl oleate from the elements is endothermic.

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