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Newark College of Engineering, D. Eng. Sc., 1966
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KINETICS OF THE LACTIC ACID-BUTYL ALCOHOL
ESTERIFICATION REACTION

BY
JOEL^{H.} KAPLAN

- A DISSERTATION
PRESENTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE
OF
DOCTOR OF ENGINEERING SCIENCE IN CHEMICAL ENGINEERING
AT
NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey
1966

KINETICS OF THE LACTIC ACID-BUTYL ALCOHOL
ESTERIFICATION REACTION

BY
JOEL KAPLAN
FOR
DEPARTMENT OF CHEMICAL ENGINEERING
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: _____ CHAIRMAN

NEWARK, NEW JERSEY

JUNE, 1966

ABSTRACT

Kinetic and equilibrium data for the esterification reaction of monomeric lactic acid with normal butanol were determined in a series of experiments utilizing a batch stirred tank reactor. The variables studied were temperature and catalyst concentration. The kinetic data were successfully represented by the integrated equation for a second order reversible reaction.

Rate constants were obtained at three temperature levels and four catalyst levels. The observed rate constants in the catalytic reaction were linearly correlated with catalyst concentration and also satisfied the Arrhenius criterion. The activation energy and frequency factor for the uncatalyzed reaction were determined to be 13,190 calories and 673 liter/mole second respectively. The activation energy and frequency factor for the catalyzed reaction were 13,580 calories and 547 liters²/mole-second-mmole catalyst respectively.

The equilibrium value for the esterification reaction was determined to be $3.02 \pm .13$ and was found to be independent of catalyst concentration and mole ratio of the reactants.

The conversion time-data was determined by titrametric and chromatographic methods.

Kinetic and equilibrium data were also obtained for the dimerization reaction of lactic acid to lactyllactate. It was established that the dimerization reaction had virtually no effect upon rate of the lactic acid-butanol reaction.

A $2\frac{1}{2}$ order reversible reaction equation was derived as a model for the kinetics of an uncatalyzed esterification reaction, but it did not apply to the esterification reaction studied.

ACKNOWLEDGEMENTS

There are many who expressed thoughtful interest during the course of this investigation, to them I say thank You.

To Dr. Saul I. Kreps, I wish I could say more than thank you. His patience, wisdom and understanding were the corner stones upon which this thesis is built. He has been more than a thesis advisor, he has played the roles of a father confessor, a relentless taskmaster and an endearing friend. To him I owe a debt of deep gratitude.

J. K.

VITA

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CHAPTER I

Introduction

A. SCOPE AND PURPOSE OF THE INVESTIGATION

This paper will present the kinetic determination of the order of reaction, rate constants and Arrhenius constants for the esterification of lactic acid by butyl alcohol.

The development of an economical process to convert technical grade lactic into 88 per cent lactic acid which meets U.S. Pharmacopoeia specifications, has been the motivating force behind the current study.

A typical outline of such a process is as follows:

1. The crude lactic acid from the fermentation process is esterified by n-butyl alcohol.
2. Unused alcohol, ester and water are separated from the reaction mixture.
3. Pure butyl lactate is reconverted to lactic acid and butyl alcohol by hydrolysis and butyl alcohol is recovered and recycled to the esterification step.

The choice of n-butyl alcohol as the esterifying agent is not an arbitrary one. Methyl alcohol is an industrial esterifying agent now

employed, but its use entails high alcohol-to-acid mole ratios, on the order of 10 and 25 to 1, to force the reaction to the ester side, plus costly fractionation equipment for separating the alcohol, ester and water. Methyl alcohol was rejected because of these uneconomical features. Ethyl alcohol was also rejected because its use also involved similar high molar ratios of alcohol to acid.

These high molar ratios are needed to force the reaction to an economical degree of completion. If butyl alcohol were used as the esterifying agent, the reaction could be brought to completion without need for a high alcohol to acid mole ratio. The reaction can be completed by distilling off the water of reaction as a constant minimum-boiling azeotrope with butanol, and the condensed, separated butanol can be recycled to the reaction vessel for further use as an esterifying and entraining agent. The relative immiscibility of n-butyl alcohol with water renders it preferable to the infinitely soluble ethyl and methyl alcohols for esterification when azeotropic distillation is used for completion of the reaction.

The physical properties of the acid, alcohol and ester involved in the reaction make this azeotropic distillation very favorable. The boiling point of lactic acid is in doubt, however, it can be considered nonvolatile; the boiling point of butyl lactate is $160-190^{\circ}\text{C}^5$ at 75 millimeters Hg. pressure, while the normal boiling points of n-butyl alcohol and water are 117.71°C^5 and 100.0°C^5 respectively.

Furthermore, the expected binary azeotrope of butanol and water which boils at 92.25°C ⁶ has a binary composition of 25 mole per cent butanol and 75 mole per cent water. Thus, three moles of water are distilled off for each mole of butanol vaporized and the esterification reaction can theoretically be brought to complete conversion of lactic acid.

A simple block diagram shown in Figure I illustrates the essential features of a continuous operation for manufacturing butyl lactate.

Referring to Figure I, the esterification mixture is pumped into a bubble cap or sieve plate column. The lactic acid is continuously esterified by butanol during passage through column I, and the resultant butyl lactate is purified and then continuously hydrolyzed.

In the case of a high boiling ester such as butyl lactate, the water of reaction is withdrawn overhead as an azeotrope with butanol. This distillate is condensed and then withdrawn from the condenser into a separator where it separates into two layers. The layers are continuously separated, with the top layer, mostly butyl alcohol, being returned to the column to further esterify the lactic acid.

The butyl lactate is the resultant end product at the bottom of the column. This crude butyl lactate is continuously vacuum distilled to recover pure butyl lactate. The pure ester is then continuously steam

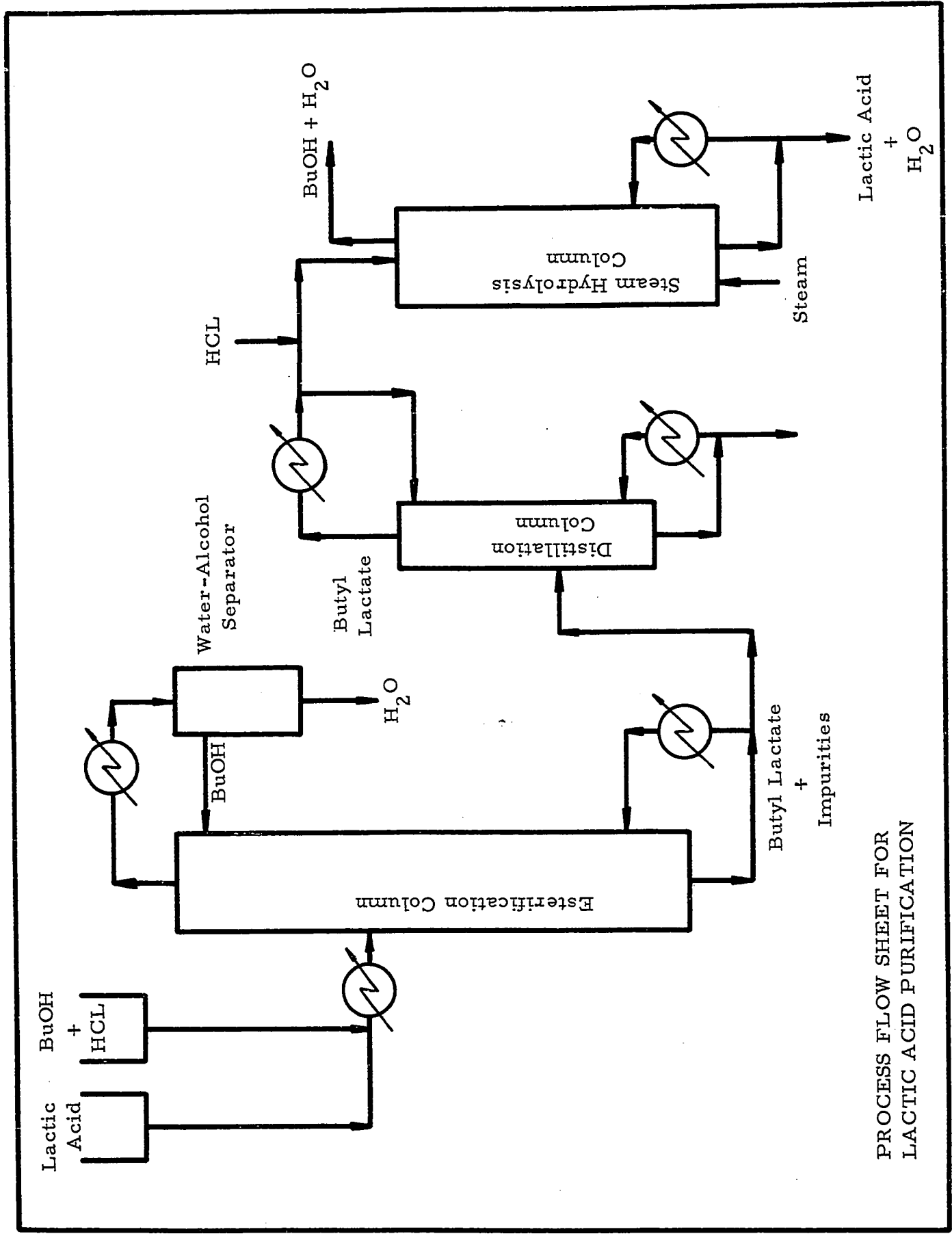
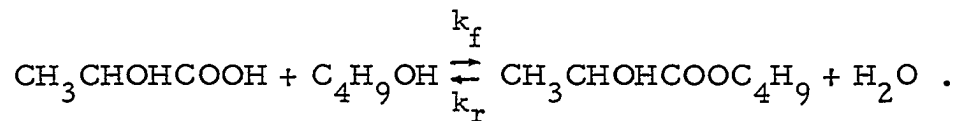


Figure I

hydrolyzed to lactic acid, which is bottoms product of column III, and butyl alcohol which is the top product. Both products contain water derived from the excess steam. The lactic acid concentration can be manipulated as a function of the operating variables of the equipment.

In order to design a continuous column reactor or a simpler batch reactor the kinetics of the reaction must be known under varying conditions of temperature, catalyst concentration, and the mole ratio of the reactants.

The present work investigates kinetic aspects of the esterification reaction:



B. HISTORICAL BACKGROUND

Lactic acid, α -hydroxypropionic acid ($\text{CH}_3\text{CHOHCOOH}$), as an unnamed constituent of sour milk, has been known since biblical times but it was not until 1780 that it was isolated and identified by Scheele. In 1881, Charles E. Avery set up the first commercial lactic acid plant at Littleton, Massachusetts. The principal use of this acid was as a deliming agent in the tanning industry.

Because of the early growing demand, prominent chemical producers undertook competitive production of lactic acid; such companies included American-Maize Products Co., Clinton Foods Inc., E. I. duPont de Nemours Co., and Sheffield Farms Co.. However, these companies have nearly all been driven out of the market by a relative newcomer in the lactic acid field, Monsanto Co.. The early producers of lactic acid depended upon a process involving the fermentation of starch, whey, molasses or corn for their crude lactic acid supply, but Monsanto utilizes a new process for producing lactic acid synthetically without recourse to an agricultural substrate, and without employing fermentation. This process, not yet made public, most probably proceeds from acetaldehyde to lactonitrile to lactic acid. Monsanto Co. does not manufacture any lactic acid to meet U.S.P. specifications. Such acid, according to Needle and Aries,¹ has an annual market potential of 200,000,000 pounds if the price is low.

Thus, a method is still being sought to produce U. S. P. lactic acid at reasonable consumer prices from a fermentable substrate.

It is the purpose of this paper to investigate the feasibility of developing such a process.

Fermentation Process for Crude Lactic Acid

The process described below is based upon an American Maize² scheme. Culture tanks are charged with 375 gallons of aqueous medium with substrate composition comprising 15 per cent corn sugar, 0.375 per cent malt sprouts, and 0.25 per cent diammonium phosphate as nutrients. Included also is 10 per cent calcium carbonate which acts as a buffer to maintain pH in the optimum range of 5.8 to 6.0. The culture, Lactobacillus delbruckii, is injected into these charged sterile tanks to produce the inoculum. The inoculum is then used to inoculate a 30,000 gallon fermentor containing the same medium described above. The 30,000-gallon fermentor contains 24,000 gallons of the medium which is held at an operating temperature of 120°F for approximately four to six days. The final product in the fermentor is not free lactic acid but the calcium salt, amounting to about 18 per cent of the total batch weight. From the fermentor, the liquor is pumped to a settling and decanting tank where the pH is first adjusted to 10.0 with hydrated lime, and the temperature is raised to 180°F. The elevated temperature and pH serve

to coagulate protein present, making settling easier. The clarified liquor from the settling tank is pumped to a first bleach tank where activated carbon is added to the calcium lactate solution at the rate of 3 pounds of carbon to 40 gallons of 14 per cent calcium lactate solution. The slurry is filtered and the filtrate is concentrated in a single effect vacuum evaporator. The concentrate from the evaporator is pumped to wooden tubs where 50°Be sulfuric acid is simultaneously added. The ensuing reaction of sulfuric acid with the calcium lactate produces insoluble calcium sulfate and a lactic acid solution. The reaction mixture from the wooden tubs is filtered and the filtrate, lactic acid, is pumped to a series of bleaching tanks for successive treatments with activated carbon and then to plate and frame filters where the filtrate of 8 per cent lactic acid solution is collected.

Two stainless steel vacuum acid evaporators are used to concentrate the 8 per cent lactic acid solution to 50 per cent lactic acid. This concentrate is treated with sodium sulfide to precipitate heavy metals such as iron, copper and lead, and it is then subjected to a third carbon bleach. The effluent lactic acid is now essentially free from sulfuric acid, heavy metals and color.

To make an 88 per cent edible acid, the 50 per cent product is concentrated in an acid evaporator to 88 per cent lactic acid and then it is treated again with carbon and sodium sulfide.

The non-edible 88 per cent and 44 per cent technical acids are produced in the same equipment, but the sodium sulfide and activated carbon treatments are eliminated.

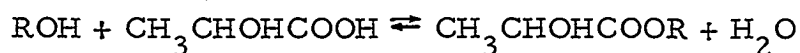
Eighty-Eight Per Cent U. S. P. Acid

The crude, technical and edible grades of lactic acids contain organic impurities which are very difficult to remove. The principle impurities are sugars (glucose or sucrose) and butyric and acetic acids. The elimination of these materials from lactic acid is the major concern of all further purifying operations. Currently, the crude acid is purified by either of the following processes.

(1) Solvent extraction with isopropyl ether. Jenemann³ patented a process whereby the filtered crude 44 per cent lactic acid solution is extracted with isopropyl ether. The acid is then re-extracted from the isopropyl ether by pure water. The resulting solution is concentrated as desired by distilling off the water from the relatively non-volatile lactic acid. The Jenemann process has been used to produce both edible and U. S. P. lactic acids.

(2) Esterification Processes. There are many different esterification procedures for purifying and concentrating lactic acid but in essence they are all similar. Alcohols react with the crude lactic acid

to yield esters which are then separated from the crude residues either by extraction or distillation. These esters are hydrolyzed to produce water white U. S. P. lactic acid. The reactions are



This process has gained commercial interest since it is thought that the esterification process is more economical and less dangerous than the isopropyl ether extraction. Methyl alcohol was being used by DuPont as the esterifying alcohol in the commercial process, and methyl lactate was fractionally distilled from the residues.

The distilled methyl lactate is subsequently hydrolyzed to lactic acid which meets the specification set forth in the United States Pharmacopia Code.

Production of U. S. P. Acid

The United States production of U. S. P. lactic acid was by the methyl alcohol esterification route. The market price for U. S. P. (88 per cent) grade lactic acid on a 100 per cent lactic acid basis was \$1.03 per pound while the technical grade (88 per cent) acid sells for \$0.28 per pound.⁴ This great divergence in the prices of the U. S. P. and technical grade acids encourages investigation and development of methods of purification which would reduce the cost of U. S. P. lactic acid and improve its

competitive position in the chemical market. Annual production of lactic acid on a 100 per cent basis has been approximately 5.5 million pounds but as stated above, Needle and Aries have predicted a market potential of 200 million pounds per year, especially as a chemical intermediate and a component of plasticizers, if the cost of the purer grades can be reduced.

Uses of Lactic Acid

Currently the largest outlet for lactic acid is in the food industry. The edible grade, 88 per cent lactic acid, is used as an acidulant in almost any kind of food or beverage. Lactic acid is used to adjust the pH in the production of beer, jellies, cheese, dried egg whites and other food products.

The properties which make lactic acid ideally suited as a food acidulant are

Lactic acid has a mildly acid taste in contrast to the sharp biting taste of other acids.

Lactic acid does not mask or overpower other flavors.

Lactic acid acts as a preservative.

Lactic acid is in a liquid state thus simplifying application problems.

The technical acid, usually sold as 44 or 88 per cent lactic acid, is principally used in the tanning industry where lactic acid converts calcium oxide used to dehair the hides to soluble calcium lactate. Other uses for the technical acid are as brighteners in textiles, fluxing agents in solders, and catalysts in the synthesis of phenolic and amine resins.

The U. S. P. acid (88 per cent lactic acid) is used primarily for medicinal and pharmaceutical purposes but its potential use as a chemical intermediate is unlimited.

Prior Investigations

There have been only three published studies on the kinetics of esterification of lactic acid, two by Troupe and Kobe^{25,26} and one by Troupe and Dimilla,²⁷ and these works deal with methyl or ethyl alcohol as the esterifying agent. On the other hand, innumerable works dealing with the commercial aspects of purifying lactic acid by esterification have appeared in the literature.

Esterification processes. Filachione and Fisher⁸ proposed a method whereby alcoholic vapors are passed through a crude lactic acid solution and the resulting exit vapors are fed into a continuous still to separate the three vapor components; alcohol, water and lactate ester. As an

example, 510 ml. of crude lactic acid containing 0.22 moles of calcium lactate, 22 grams of concentrated sulfuric acid and excess sulfuric acid for catalytic purposes was charged to a reactor and methyl alcohol vapors were passed through. The resultant vapors contained water, methyl alcohol and methyl lactate. Seventy-five per cent of the crude lactic acid was esterified.

Schopmeyer and Arnold¹³ were issued a patent on the continuous esterification of crude lactic acid by methyl alcohol and sulfuric acid. The methyl lactate was fractionally distilled to produce pure product.

Gonzalez¹⁸ showed that chlorosulfuric can be successfully used as a catalyst for the esterification of lactic acid by methyl alcohol. One mole of acid was reacted with 3.5 moles of alcohol and 0.02 moles of chlorosulfonic acid for two hours at reflux. The mixture was neutralized, washed with sodium carbonate and dried over sodium sulfate to give an ester-alcohol solution.

Arnold and Childs²⁰ were granted a British patent on the manufacture of pure lactic acid and its esters using sulfuric acid as catalyst and ethyl alcohol as the esterifying agent. The ethyl lactates were steam hydrolyzed to give a pure lactic acid solution.

Filachione and Fisher¹⁴ were issued a second patent on the production of ethyl lactate from ethyl alcohol and polylactic acid. Two and

one-half moles of ethyl alcohol and one equivalent of polylactic acid were heated in the presence of an acid catalyst for four hours at 100°C. The yield reported was 57 per cent based on ethyl alcohol. The investigators reported that increased yields were obtained by using condensation products of the hydroxy acid and polyhydric alcohols.

Jones¹⁵ reports the esterification of lactic acid by n-butyl alcohol using an alkoxide as the catalyst.

Gabriel and Bogen¹¹ were issued a patent for producing butyl lactate by the simple means of heating butyl alcohol and crude lactic acid and distilling off the ester. The ester produced was a colorless liquid with a boiling point of 186 to 189°C.

Filachione and Costello²³ devised a scheme for producing lactate esters by converting crude lactic acid into its ammonium salt. The ammonium lactate was then reacted with n-butyl alcohol to form the butyl lactate. Conversion was reported at 50 per cent after the necessary rectification procedures were followed.

Schulz and Richardson⁹ patented a continuous process for the preparation of butyl lactate from ammonium lactate. They describe an apparatus in which a solution of ammonium lactate (derived from a crude fermentation solution) is concentrated by countercurrent extraction using n-butyl alcohol and subsequently esterifying the extract to produce butyl lactate.

Smith and Claborn²² describe esterification processes for the production of methyl, ethyl, propyl and butyl lactates. Five moles of calcium lactate are reacted with an equivalent amount of sulfuric acid and 1.5 to 2.0 moles of butyl alcohol. To this solution is added benzene or toluene to form an azeotrope. The solution is stirred slowly and heated to reflux temperature. Water is taken off by use of a Betz-Holden trap and when the theoretical amount of water is removed, the esterification is complete. The time required was about 1 to 8 hours depending upon the reflux rate. The ester solution which contains some alcohol and water was rectified in a Widmer column and yields of 80 to 95 per cent were reported.

Wezowicz⁵¹ investigated the lactic acid (technical grade), butanol esterification reaction using sulfuric acid as catalyst. Conversions of 40 to 50 per cent were reported.

Swier⁵² studied the same system as Wezowicz but substituted hydrochloric acid for sulfuric acid as the catalyst. Swier's conversions were 80 to 100 per cent of initial lactic acid. Both Swier and Wezowicz drove the reaction to completion by azeotropically distilling off the water of reaction.

Wenker¹⁰ patented a process in which 70 to 85 per cent crude lactic acid was continuously esterified by an aliphatic alcohol and catalyzed by sulfuric acid. The product ester was then continuously hydrolyzed.

Weisberg and Othmer¹⁷ described a continuous esterification process for producing a pure anhydrous, water soluble lactate. Crude sodium lactate, an aliphatic alcohol and sulfuric acid were mixed to give a solution of pH 1.0 to 1.4. The mixture was refluxed for one hour, neutralized, and flash evaporated to remove excess alcohol and water. The alcohol is separated by distillation and the lactate is dried azeotropically by using butyl alcohol.

Weisberg and Stimpson¹² devised a continuous esterification process for producing alkyl lactates. The process involves flash esterification of a lactic acid solution containing less than 25 per cent water with 3 to 20 parts alcohol in the presence of sulfuric acid at a pH of 0.7 to 1.4. The mixture is preheated, fed to a flash chamber which is held at a temperature above the boiling point of the solution. The mixed vapors are then separated by known procedures.

Sly¹⁶ describes an apparatus wherein an aliphatic alcohol, strong mineral acid and crude lactic acid are heated together to form the ester. The reaction mixture is flash evaporated to separate the non-volatile and the volatile components. Water is separated by addition of a water insoluble entrainer such as ethyl butyl ether to the mixture and azeotropically distilling the water.

Mishima¹⁹ showed that the lactate ester can be produced from the nitrile. To 300 grams of nitrile, 390 grams of alcohol, 70 grams of

water, and 460 grams of sulfuric acid are added. The mixture is heated to 140°C , the alcohol and water are distilled off, and the residue is fractionated to obtain the ester.

A Belgian patent was granted to Knapsack-Greisheim²⁴ for the continuous process of the preparation, purification and isolation of lactic acid. Lactic acid is prepared by the hydrolysis of lactonitrile using sulfuric acid at a temperature of 127°C . The hydrolysis takes from 2 to 4 hours after which the products are separated from ammonium sulfate by countercurrent extraction with isopropyl ether. The extract, which contains water, is fed into an evaporator and the solvent is removed at about 80°C . A pure lactic acid solution is left.

Kinetics of Esterification

The preceding literature has dealt only with possible commercial processes for purifying lactic acid. Yet in order to design a commercial apparatus for esterification, the kinetics of the reactions should be known. However, only three articles have appeared in the literature dealing with the kinetics of esterification of lactic acid.

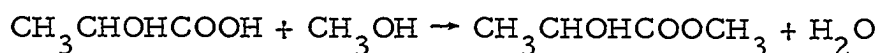
Troupe and Kobe²⁵ were the first to investigate the kinetic aspects of the esterification of lactic acid. They studied the lactic acid-methanol reaction catalyzed by sulfuric acid. The lactic acid they used was the

85 per cent U.S.P. acid which contained 15 per cent water and 85 per cent of a mixture of lactic acid (I) and lactyllactic acid (II).

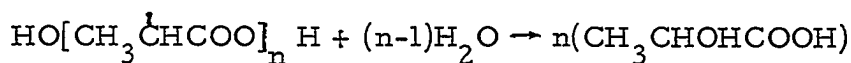
The authors were aware of this fact but assumed that the lactyllactic acid did not react with the alcohol.

They assumed the following mechanism:

1. Esterification of monomeric acid



2. Hydrolysis of lactic acid condensation polymers



In order to determine the amount of methyl lactate at any time they devised a complex analysis scheme which conformed to their assumed mechanism.

From their investigation, Troupe and Kobe arrived at the following kinetic expression

$$kt = \frac{x}{(A - b)(A - b - x)} \quad (1)$$

where A = total lactic acid originally present, moles
 b = a constant which varies with ratio of reactants
 x = lactic acid converted to ester, moles
 k = specific rate constant, liter/mole minute
 t = time, minutes

They also correlated k with temperature, catalyst concentration and mole ratio of methanol to lactic acid.

The form of this correlation was

$$k = [.08750(M/L)C - 0.08955 C + 0.00435] \times \frac{10^{(10.91369 - 3139.3/T)}}{314.3} \quad (2)$$

where (M/L) = mole ratio of alcohol to acid

C = catalyst weight per cent

T = temperature, $^{\circ}\text{K}$.

Troupe and Kobe²⁶ also conducted investigations using 44 per cent technical grade lactic acid and methanol. They arrived at the same kinetic expression given in equation (1). A correlation for k was also obtained which fitted into the general form of equation (2), the only difference being in the values of the empirical constants, viz.,

$$k = [0.000175(M/L) + 0.000580] \frac{10^{(10.364 - 3609/T)}}{136.5} \quad (3)$$

In comparing the results of the two studies by Troupe and Kobe, one notes that the specific rate constant for the 85 per cent U. S. P. acid-methanol reaction and the 44 per cent technical grade acid are vastly different; with all else being constant, the specific rate constant k , for the U. S. P. system is 40 times as great as for the technical grade reaction.

Troupe and Di Milla²⁷ investigated the kinetics of the reaction between lactic acid and ethyl alcohol using both U. S. P. acid and technical grade acids, and they also arrived at a kinetic expression identical with equation (1). This model held for both the U. S. P. system and technical acid system. The k's again were vastly different for the U. S. P. and the technical acid reactions. With all conditions constant, the rate constant for the U. S. P. system was 300 times as great as that for the technical acid system.

The following table directly compares the values of the rate constants from the preceding four investigations at common conditions.

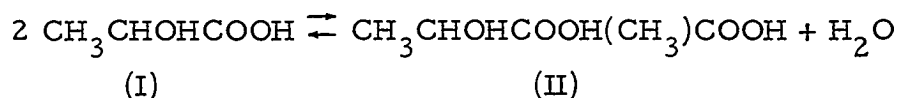
Table 1

RATE CONSTANT COMPARISONS FOR DIFFERENT
LACTIC ACID SOLUTIONS

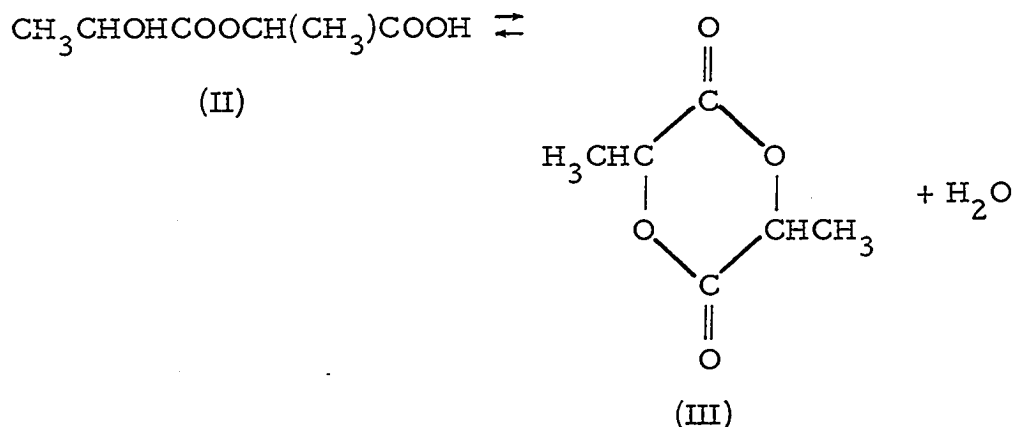
Temperature	--	100° C.	
Catalyst Concentration, Weight Per Cent	--	.10	
Mole Ratio of Alcohol to Acid		8.00	
<u>Reference</u>	<u>Alcohol</u>	<u>Specific Rate Constant liter/(mole)(min.)</u>	
		<u>U. S. P. Acid</u>	<u>44 Per Cent Technical Acid</u>
25, 26	Methanol	.0672	.00158
27	Ethanol	.0243	.000785

C. GENERAL CHEMISTRY OF LACTIC ACID

Before discussing the esterification of the butanol-lactic acid system, it would be well to consider the chemistry of lactic acid. There have been many conflicting statements concerning the composition of lactic acid. This arises because, as an hydroxy acid, lactic acid can react with itself to form many products. Watson²⁸ points out that two moles of lactic acid (I) will react to form one mole of lactyllactic acid (II):

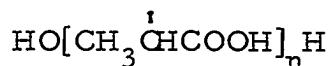


The lactyllactic acid can rearrange to form a stable six-membered ring, lactide (III), a white crystalline solid.

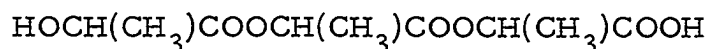


Linear polylactyllactic acid (IV) may also be formed through loss of water in successive reactions of the carboxyl and alcohol groups.

The formula for such a polymer can be represented as



A specific example would be dilactyllactic acid:



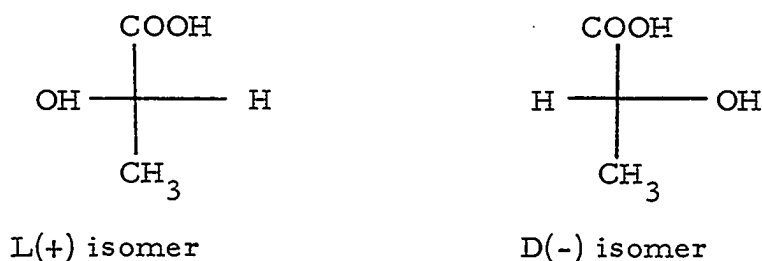
Since all these reactions are readily reversible, it is evident that the composition of a lactic acid solution is dependent upon the concentration of acid in solution, on the temperature, and the length of storage. Watson²⁸ points out that lactyllactic acid is not immediately converted into lactic acid upon dilution. At room temperature the time to achieve equilibrium is several weeks. However, equilibrium may be effected rapidly by heating the solution in the presence of an acid catalyst. No one up to the present writing has established the values of equilibrium constants for the various reactions.

Eder and Kutter²⁹ state that in solutions of 90 per cent or less lactic acid there exist only free lactic acid and lactyllactic acid. This view coincides with that of Watson and has been confirmed by the present work. However, Montgomery³⁰ in his studies of lactic acid solution by partition chromatography stated that even in dilute solutions there exist equilibria between the monomer, dimer and trimer acids. The poly lactyllactic acid could, however, have been formed during the

chromatographic procedure, and thus may be regarded as an artifact. The present work presents rigorous data showing that in 88 per cent U. S. P. acid only monomer, dimer and water are present. This data will be presented in succeeding chapters.

The physical properties of lactic acid are shown in Table 2. Viscosities and densities of aqueous acid solutions are summarized in Table 3.

One further note might be made about the optical properties of lactic acid. Since lactic acid contains an asymmetric carbon atom, it occurs as both the dextrorotatory (+) and levorotatory (-) optical isomers.



However, the fermentation acid and Monsanto's synthetic product are the racemic mixture of isomers. The Monsanto process which starts with the inactive aldehyde and inactive cyanide gives the inactive acid since equal amounts of the two possible stereoisomers are formed viz.,

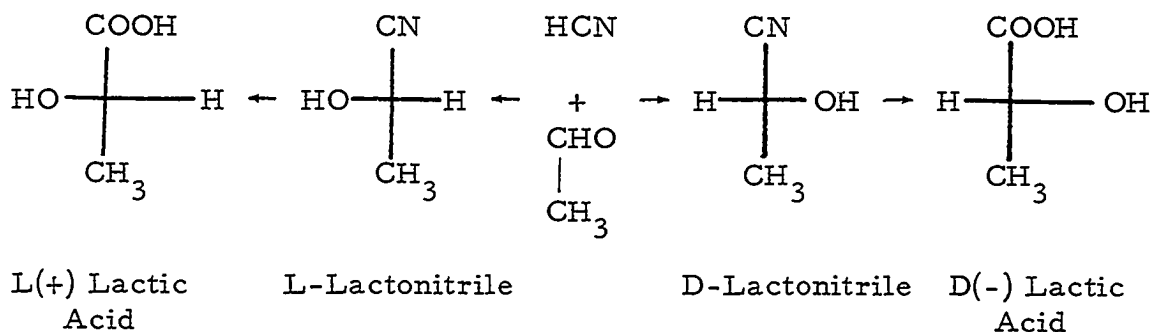


Table 2

PROPERTIES OF LACTIC ACID³¹

Structural Formula:	$\text{CH}_3\text{CHOHCOOH}$
Molecular Weight:	90.08
Melting Point:	16.8°C
Dissociation Constant:	1.374×10^{-4} at 25°C
Heat of Combustion:	3615 cal/g
Thermal Conductivity:	$0.110 \text{ BTU}/^\circ\text{F}/\text{ft}^2/\text{hr}$ at 15°C
Specific Heat:	$0.505 \text{ cal}/\text{g}/^\circ\text{C}$ at 20°C
Density, Lbs/gal (88 per cent solution):	10.0
Density, Lbs/gal (55 per cent solution):	9.4
Solubility in water:	∞
Solubility in Alcohol:	∞

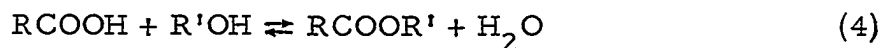
Table 3³²

VISCOSITY AND DENSITY OF AQUEOUS LACTIC
ACID SOLUTION AT 25°C

<u>Lactic Acid per cent Concentration</u>	<u>Viscosity centipoise</u>	<u>Density g/ml.</u>
9.16	1.15	1.0181
24.35	1.67	1.0545
45.48	3.09	1.1054
64.89	6.96	1.1518
75.33	13.03	1.1748
85.32	28.50	1.1948

D. MECHANISM AND KINETICS OF ESTERIFICATIONS

Esterification is defined as the reaction between an acid and an alcohol.



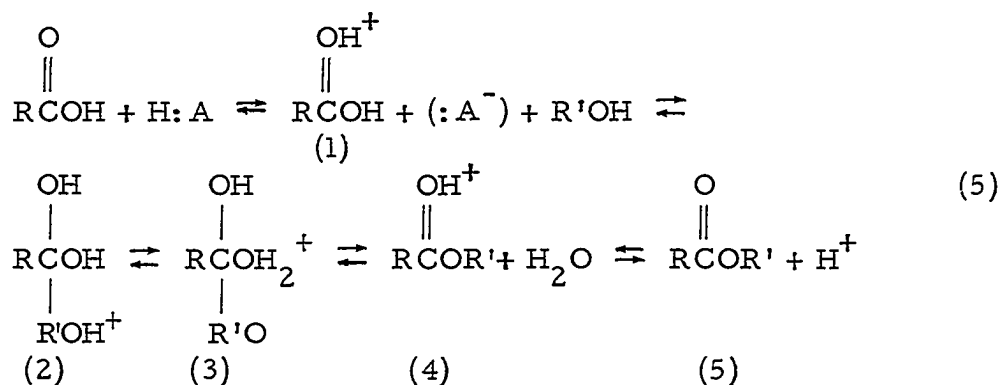
Esterification reactions are reversible and the position of equilibrium is determined by the ratio of velocities of the forward and reverse reactions. The mechanism of esterification is not as simple as that depicted in equation (4). Usually esterification reactions are acid catalyzed to increase their rate of approach to equilibrium. From previous evidence^{33,34,35} it has been found that a mechanistic model consistent for most acid catalyzed esterification must meet the following requirements:

1. All steps must be significantly reversible: the principle of microscopic reversibility must apply to each step.
2. An acyl-oxygen bond rupture must occur. This fact has come to light through the isotopic oxygen labeling work of Bender³⁵ and Roberts and Urey.³⁶ Reid³⁷ has also shown that in the reaction of acetic acid and ethyl mercaptan the acyl-oxygen bond must be broken.
3. The transition state complex in the esterification reaction must be derived from a molecule of water, ester and a proton.

4. The reaction path must proceed through an intermediate which can survive long enough to exchange oxygen with the solvent.

Consistent with these requirements, Datta, Day and Ingold³³

proposed the following mechanism for an acid catalyzed esterification:



This mechanism is commonly referred to as the A_{AC2} mechanism.

According to Gould,³⁸ in the forward direction the formation of the protonated acid is rapid but the nucleophilic attack by the alcohol is slow and all other succeeding steps are rapid. The kinetic picture of the above mechanism would be dependent on the rate determining step which is the reaction of the protonated acid with the alcohol. The kinetic equation for the forward reaction would then be:

$$r_f = k_f(\text{RCOOH}_2^+)(\text{R'OH}). \tag{6}$$

But the protonated acid is in equilibrium with the organic carboxylic acid and the inorganic acid catalyst.



The equilibrium constant is given by the equation

$$\text{Keq} = \frac{(\text{RCOOH}_2^+)}{(\text{RCOOH})(\text{H}^+)} \quad (8)$$

Concentration of the protonated acid may then be given by

$$(\text{RCOOH}_2^+) = \text{Keq}(\text{RCOOH})(\text{H}^+) \quad (9)$$

Substituting (8) into (5) we obtain

$$r_f = k_f \text{Keq}(\text{RCOOH})(\text{H}^+)(\text{ROH}) \quad (10)$$

Since k_f , Keq , and H^+ are considered constant we may rewrite (10) in the form

$$r_f = k_1(\text{RCOOH})(\text{ROH}) \quad (11)$$

where $k_1 = k_f \text{Keq}(\text{H}^+)$.

By similar reasoning, we obtain the equation for the reverse reaction as

$$r_r = k_2(\text{RCOORH}^+)(\text{HOH}) \quad (12)$$

where $k_2 = k_r(1/\text{Keq})(\text{H}^+)$.

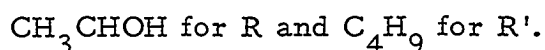
This assumes that the rate determining step in the hydrolysis reaction

is the nucleophilic attack by the water molecule on the protonated ester.

The net rate of reaction, r_{net} , would be the sum of the forward rate and the reverse rate.

$$r_{\text{net}} = k_1(\text{RCOOH})(\text{ROH}) - k_2(\text{RCOOR}')(\text{HOH}) \quad (13)$$

The preceding equations demonstrate the most probable mechanism for an acid catalyzed esterification reaction. These equations can now be made specific for the lactic acid-butanol reaction by simply substituting



Equation (13) represents the general differential equation of a second order reversible reaction which can be represented by the general reaction



Hougen and Watson³⁹ have solved this differential equation and have obtained the following integral solution

$$t = \frac{V K_{\text{eq}}}{k_f} \frac{1}{\sqrt{-q}} \ln \frac{(2cX_a + b - \sqrt{-q})(b + \sqrt{-q})}{(2cX_a + b + \sqrt{-q})(b - \sqrt{-q})} \quad (15)$$

where $q = 4ac - b^2$.

$$a = K_{eq} N_{A_0} N_{B_0} - N_{R_0} N_{S_0}$$

$$b = - K_{eq} N_{B_0} - K_{eq} N_{A_0} - N_{R_0} - N_{S_0}$$

$$c = K_{eq} - 1$$

where the terms are defined as

t = time elapsed

k = forward reaction rate constant

K_{eq} = equilibrium constant = $\frac{k_f}{k_r}$

N_{A₀}, N_{B₀}, N_{R₀}, N_{S₀} = moles of A, B, r and S initially present
per unit mass of charge.

X_a = moles of A converted to product per unit mass of charge.

V = volume of reacting system per unit mass of charge.

Equation (15) was used in this work with favorable results for the lactic acid-butyl alcohol system and also for the dimerization of lactic acid to lactyllactic acid.

Rate of the "Uncatalyzed" Reaction

Although equation (15) works extremely well as a model for the acid catalyzed lactic acid-butanol esterification, Flory⁴⁰ and Hinshelwood⁴¹ have pointed out that, in the absence of a strong mineral acid catalyst, the reaction rate equation should be represented as a third order reaction: second-order with respect to carboxylic acid concentration and first order with respect to alcohol concentration,

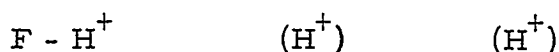
$$r_f = k_f(\text{acid})^2 (\text{alcohol}) \quad (16)$$

The present author has deduced an analytical solution of the reaction velocity expression for the lactic acid-butanol reaction which is uncatalyzed by a strong mineral acid, the development of which follows.

Although no mineral acid catalyst is present, a catalytic proton is more or less readily available in the so-called "uncatalyzed" reaction. The proton is supplied by the dissociation of lactic acid



The equilibrium concentrations are



where F = moles of lactic acid at any time

H^+ = moles of protons at any time

K_i = ionization constant

$$K_i = \frac{(H^+)^2}{(F - H^+)} \quad (18)$$

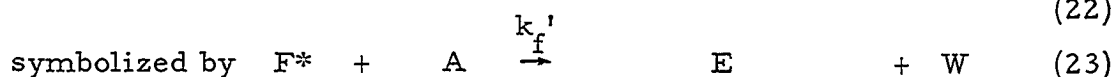
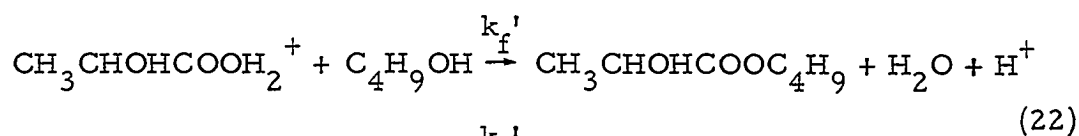
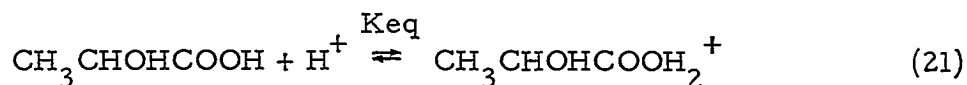
But $F \gg H^+$ for a weakly ionized acid. Thus,

$$K_i = \frac{(H^+)^2}{(F)} \quad (19)$$

The concentration of protons in the reaction mixture is given by

$$(H^+) = \sqrt{F K_i} \quad (20)$$

The protonation of free lactic acid now proceeds as usual



where A = moles of alcohol at any time

E = moles of ester at any time

W = moles of water at any time

F^* = moles of protonated acid

The reaction rate is thus

$$r_f = k_1 (F^*)(A) \quad (24)$$

but

$$F^* = K_{eq} (F)(H^+) = K_{eq} (F) \sqrt{F K_i} \quad (25)$$

Substituting in (24) we obtain

$$r_f = k_1' K_{eq} K_i (F)^{1.5} (A) \quad (26)$$

Letting $k_1' K_{eq} K_i = k_1$ (27)

and since $F = (F_o - X)$ (28)

$$A = (A_o - X) \quad (29)$$

where F_o = moles of lactic acid per unit mass of feed

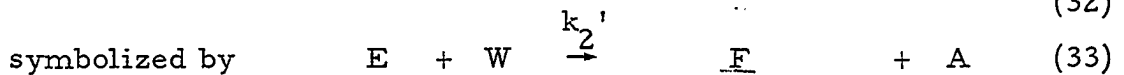
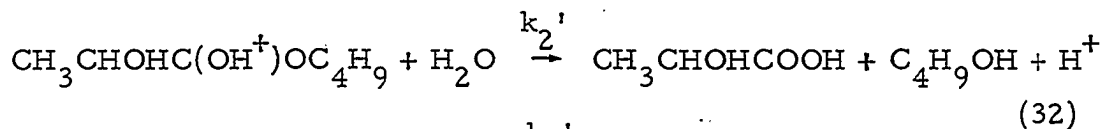
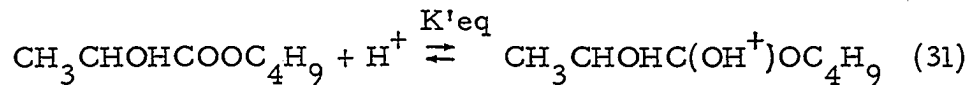
X = moles of lactic acid converted at any time per unit mass of feed

A_o = moles of butyl alcohol per unit mass of feed.

Then

$$r_f = k_1 (F_o - X)^{1.5} (A_o - X) \quad (30)$$

In the same manner for the reverse reaction,

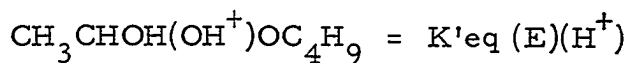


The rate of the reverse reaction is

$$r_r = k_2' (CH_3CHOHC(OH^+)OC_4H_9)(H_2O) \quad (34)$$

where r_r = rate of formation of lactic acid.

But



and from equation (17)

$$\text{H}^+ = \sqrt{(\text{F})(\text{K}_i)} .$$

Substituting the preceding two values into (34) one obtains

$$r_r = k_2' K'\text{eq} \sqrt{(\text{K}_i)(\text{F})(\text{E})(\text{W})} . \quad (35)$$

$$\text{Let } k_2' K'\text{eq} K_i = k_2 \quad (36)$$

$$\text{and since } \text{E} = (\text{E}_o + \text{X}) \quad (37)$$

$$\text{W} = (\text{W}_o + \text{X}) \quad (38)$$

where E_o = initial moles of ester

W_o = initial moles of water

$$\text{then } r_r = k_2(\text{E}_o + \text{X})(\text{W}_o + \text{X})(\text{F}_o - \text{X})^{\frac{1}{2}} . \quad (39)$$

The observed net rate of formation of ester is, as before, the forward rate of reaction minus the reverse rate,

$$r = k_1(\text{F}_o - \text{X})^{1.5}(\text{A}_o - \text{X}) - k_2(\text{E}_o + \text{X})(\text{W}_o + \text{X})(\text{F}_o - \text{X})^{\frac{1}{2}} . \quad (40)$$

or

$$V \frac{dx}{dt} = k_1(\text{F}_o - \text{X})^{1.5}(\text{A}_o - \text{X}) - k_2(\text{E}_o + \text{X})(\text{W}_o + \text{X})(\text{F}_o - \text{X})^{\frac{1}{2}} . \quad (41)$$

The solution to equation (41) is not trivial. The final integrated form of the equation is given by equation (42), and the analytical solution is given in Appendix C.

$$\begin{aligned}
 k_1 t = & -R \frac{V}{N-P} \frac{1}{\sqrt{-N}} \log \frac{N + \sqrt{(F_o - X)\sqrt{-N}}}{N - \sqrt{(F_o - X)\sqrt{-N}}} - \frac{1}{\sqrt{-P}} \log \frac{P + \sqrt{F_o - X}\sqrt{-P}}{P - \sqrt{F_o - X}\sqrt{-P}} \\
 & -R \frac{V}{N-P} \frac{1}{\sqrt{-N}} \log \frac{N + \sqrt{F_o}\sqrt{-N}}{N - \sqrt{F_o}\sqrt{-N}} - \frac{1}{\sqrt{-P}} \log \frac{P + \sqrt{F_o}\sqrt{-P}}{P - \sqrt{F_o}\sqrt{-P}}
 \end{aligned}
 \tag{42}$$

where $P = \frac{J}{2R} - M$

$N = \frac{J}{2R} + M$

$J = (-2R F_o - B)$

$R = (1 - \frac{1}{Keq})$

$B = (-A_o - F_o - \frac{E_o}{Keq} - \frac{W_o}{Keq})$

$M = \frac{L}{R} - \frac{1}{4} (\frac{J}{R})^2$

$L = (C + A F_o^2 + B F_o)$

$C = [F_o A_o - \frac{1}{Keq} (E_o W_o)]$

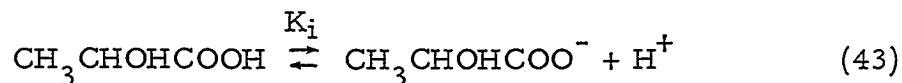
$V = \text{volume of feed}$

It is obvious that equation (42) is a long, complex function and that if equation (15) fits the data well enough for the experimenter's needs, then equation (42) should not be considered.

Mineral Acid Catalyzed Reaction

The following equations represent the catalyzed system.

Ionization of lactic acid in the presence of the strong mineral acid is represented as



Equilibrium concentrations are

$$(F - y) \qquad y \qquad y + \text{H}^+$$

where y = ions from dissociation of lactic acid

H^+ = protons from dissociation of strong mineral acid

The equilibrium ratio is the constant

$$K_i = \frac{(y)(y + \text{H}^+)}{(F - y)} \quad (44)$$

But $F \gg y$, hence

$$F K_i = (y)(y + \text{H}^+) \quad (45)$$

$$y^2 + \text{H}^+ y - F K_i = 0 \quad (46)$$

$$y = \frac{-\text{H}^+ \pm \sqrt{(\text{H}^+)^2 + 4 K_i F}}{2} \quad (47)$$

The total amount of hydrogen ion in solution is therefore total

$$\text{hydrogen ion} = (\text{H}^+) + \frac{((-\text{H}^+) \pm \sqrt{(\text{H}^+)^2 + 4 K_i F})}{2} \quad (48)$$

The forward rate of esterification can then be represented by following the form of equation (30)

$$r_f = k_1' K_{eq}(F_o - X)(A_o - X) H^+ + \frac{(-H^+) \pm \sqrt{(H^+)^2 + 4 K_i(F_o - X)}}{2} \quad (49)$$

Similarly the reverse reaction is

$$r_r = k_2' K_{eq}(E_o - X)(W_o - X) H^+ + \frac{(-H^+) \pm \sqrt{(H^+)^2 + 4 K_i(F_o - X)}}{2} \quad (50)$$

The net rate of reaction therefore is

$$r_{net} = H^+ + \frac{(-H \pm \sqrt{(H^+)^2 + 4 K_i(F_o - X)})}{2} [k_1(F_o - X)(A_o - X) - k_2(E_o - X)(W_o + X)] \quad (51)$$

and if it is reasonable to assume that the quantity $4 K_i(F_o - X)$ is very small compared to $(H^+)^2$, then equation (51) simplifies to

$$r_t = (H^+)[k_1(F_o - X)(A_o - X) - k_2(E_o + X)(W_o + X)] \quad (52)$$

Since (H^+) is a constant, equation (52) can be rewritten as

$$\frac{dX}{dt} = r_t = k_f(F_o - X)(A_o - X) - k_r(E_o + X)(W_o + X) \quad (53)$$

The solution to the equation is given by Hougen and Watson (equation (15)).

However, if the term $4 K_i(F_o - X)$ should be of the same magnitude as $(H^+)^2$, equation (51) cannot be solved for a fruitful answer unless K_i is known. Furthermore, the author sees no analytical solution to equation (51) even if K_i is known.

E. INFLUENCE OF KINETIC FACTORS

In order to completely characterize the rate of the reaction between lactic acid and butyl alcohol the following parameters should be estimated:

Order of reaction,

Value of the effective rate constant and its functional dependence upon temperature and catalyst concentration,

Equilibrium constant and its functional dependence upon temperature.

These parameters and the methods of obtaining estimates will be discussed in the following pages.

Order of reaction. Since the mechanism for the esterification reaction has been well established, the difficulty in obtaining the order of reaction is trivial. As has been pointed out in the preceding chapter, in the uncatalyzed reaction the order should be two and one half in both the forward and reverse reactions. In the catalyzed reaction, if the ionization constant of the carboxylic acid is very small, the reaction will be second order. The latter situation applies to a strong mineral acid-catalyzed esterification.

Rate Constant. It was first shown by Arrhenius that the rate constant is dependent upon the temperature of the reacting system in the following manner

$$k = A e^{-(E^*/RT)} \quad (54)$$

where k = rate constant
 A = frequency factor
 E^* = activation energy
 R = universal gas constant
 T = temperature in $^{\circ}\text{K}$.

Taking logs of equation (54)

$$\ln k = \ln A - E/RT \quad (55)$$

and after plotting $\ln k$ against $1/T$, a straight line should be observed if the reaction is elementary. The slope of this line would be equal to the activation energy divided by R .

This Arrhenius equation is the basic model for the collision state theory of reaction, however, Eyring⁵³ and his coworkers have developed a similar but different model for the temperature dependency of the specific rate constant. Their model termed the transition state model takes the following form

$$k = \frac{K^{\circ}T}{h\nu_m} e^{\left(-\frac{\Delta H^*}{RT} + \frac{\Delta S}{R}\right)} \quad (56)$$

where K° = Boltzmann Constant, $1.3805 (10^{-16})$ erg/ $^{\circ}$ K molecule

h = Planck constant, $6.624 (10^{-27})$ erg-sec/molecule

γ = Activity coefficient of the activated complex

ν_m = Average molal volume of the system

In comparing equations (54) and (56) it is seen that

$$A = \frac{K^{\circ}T}{h\nu_m} e^{\frac{\Delta S^*}{R}} \quad (57)$$

and

$$E = \Delta H^* + RT \quad (58)$$

The crucial difference between the Arrhenius equation and the Eyring equation is that the Arrhenius equation assumes the frequency factor to be temperature independent while the Eyring form assumes that the frequency factor is temperature dependent.

In working with the Eyring equation, one must know the values of the activity coefficient of the activated complex and average molal volume of the system. Generally, the activity coefficient is not known but if it can be assumed to be unity and the molal volume is known, then ΔS^* and ΔH^* can be calculated. For almost all engineering applications, the Arrhenius equation is preferred because of its relative simplicity over the Eyring equation.

However, the rate constant k depends only on the temperature if all other conditions are constant. These other conditions include

the catalyst concentration

the ionic strength of the solution

the pressure

the solvent wherein the reaction takes place

the density of the reaction mixture.

In this paper only catalyst concentration, density and temperature were fully investigated. The effect of ionic strength was also disregarded since it has been shown by Davies⁴³ that in ester hydrolysis reactions the rate constant is independent of ionic strength.

If the density of the reacting system changes during the course of reaction, the rate constant will also appear to change. However, it will be shown that the density during the course of the lactic acid-butanol reaction is essentially invariant.

The reaction velocity constant is extremely sensitive to the catalyst concentration from reaction to reaction. Bell⁴⁴ has shown that the observed rate of an acid catalyzed reaction may be written as

$$r = k_o(A) + k_{H^+}(H_3O^+)(A) \quad (59)$$

and the observed rate constant is

$$k_{obs} = k_o + k_{H^+}(H_3O^+) \quad (60)$$

where k_o = rate constant of uncatalyzed reaction

k_{H^+} = rate constant of catalyzed reaction

(H_3O^+) = concentration of hydronium ions, catalyst

(A) = substrate concentration

If k_{obs} is plotted against the catalyst concentration, a straight line with a slope equal to k_{H^+} and an intercept equal to k_o should be obtained. If the rate constant of the uncatalyzed reaction is much smaller than $k_{H^+}(H_3O^+)$ then the plot of k_{obs} versus (H_3O^+) will result in a straight line of slope equal to k_{H^+} that will pass through the origin.

Equilibrium constant. Guldberg and Waage have mathematically defined the equilibrium constant as the ratio of the forward reaction rate constant to the reverse reaction rate constant in a reversible chemical reaction, viz.,



$$K_{eq} = \frac{k_1}{k_2} \quad (62)$$

Conceptually, the equilibrium position is that position where the forward rate of reaction is equal to the reverse rate of reaction.

The equilibrium constant can also be represented for equation (61) as

$$K_{eq} = \frac{C_C C_D}{C_A C_B} \quad (63)$$

where C_C , C_D , C_A , C_B = concentrations of the reactants and products.

The functional dependence of the equilibrium constant upon temperature was first deduced by van't Hoff in 1886. Mathematically it is expressed as

$$\frac{d \ln K_{eq}}{dT} = \frac{\Delta H}{RT^2} \quad (64)$$

where $\frac{d \ln K_{eq}}{dT}$ = rate of change of the equilibrium constant with respect to temperature

ΔH = heat of reaction, calories per mole

R = universal gas constant, calories/ $^{\circ}C$ per mole

T = temperature in $^{\circ}$ Kelvin.

In almost all esterification reactions the heat of reaction is very small or zero, hence, the equilibrium constants for these reactions are practically invariant with change in temperature.

Glasstone⁴⁵ also points out that the equilibrium constant is independent of the catalyst in all reactions except for those cases

where the catalyst will affect the activities of reacting substances. Jones and Lapworth⁴⁶ found that the equilibrium constant of the ester hydrolyses of ethyl acetate was altered by the concentration of hydrochloric acid catalyst but Kendall⁴⁷ showed that this alteration was not caused by appreciable change in the activity of the reacting substances but by a complex formation between ethyl acetate and hydrochloric acid, and between ethyl alcohol and the hydrochloric acid as well.

CHAPTER II

EXPERIMENTAL PROCEDURES

I. Raw Materials

(a) U. S. P. Lactic Acid. U. S. P. lactic acid, 88 per cent, was donated by Van Dyk and Co. , Inc. The acid was analyzed for lactic acid content by a modified procedure of the method of Eder and Kutter.²⁹ The free water present was determined by Karl Fisher analysis.

Based on seven replicate samples, the analysis of the lactic acid is tabulated below:

Analysis of 88 Per Cent Lactic Acid

	<u>Per Cent</u>	
	<u>Average</u>	<u>Variance</u>
Monomeric Acid, $\text{CH}_3\text{CHOHCOOH}$	55.97	.924
Dimeric Acid, $\text{CH}_3\text{CHOHCOOCH}(\text{CH}_3)\text{COOH}$	32.24	.910
Water, H_2O	<u>11.24</u>	<u>.402</u>
Total	99.45	2.236

The 95 per cent confidence level interval statement for the total material balance is

99.45 per cent \pm 3.13 per cent

with 18 degrees of freedom.

(b) Monomeric Lactic Acid. As stated before, 88 per cent lactic acid contains both monomer and dimer in solution. To avoid complexities in the kinetic study and to be sure that the resultant data represents the reaction between monomeric acid and butyl alcohol, the U. S. P. lactic must be converted completely to monomeric form.

This conversion procedure is as follows:

Dilute a given weight of 88 per cent acid to approximately 20 per cent using water as the diluent.

Heat this solution to a gentle boil at approximately 103°C and reflux for 24-36 hours.

The diluted solution is distilled in vacuo at a pressure of 30 mm mercury in order to remove the diluent, water. The distillation should be continued until the residual solution is approximately 75 to 80 per cent monomeric lactic acid.

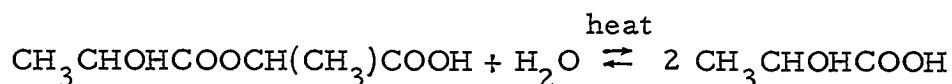
The solution is frozen in a dry ice refrigerator until ready to use; this prevents formation of the dimer.

The results of a typical hydrolytic conversion are tabulated below.

Analysis of Monomeric Lactic Acid

	<u>Per Cent</u>
Monomeric Lactic Acid	74.05
Dimeric Lactic Acid	5.48
Water	19.67
Total	100.20

The conversion of the dimer in the 88 per cent acid to monomer is presented by the following equation:



The final solution is titrated for monomeric and dimeric acid before using it for any kinetic studies.

(c) n-Butyl Alcohol. C. P. grade butanol was obtained from Union Carbide Corp. The water content obtained by Karl Fisher analysis was $.0768 \pm .002$ per cent. The boiling point at standard conditions was 117.75°C as compared to the National Bureau of Standard value of 117.71°C . A chromatographic analysis of the butanol was also made on the F and M model 810 flame ionization gas chromatograph, using an eight foot diethylene glycol succinate liquid phase on diatoport S support column. The chromatogram showed only one peak, with no impurities present.

(d) Butyl Lactate. Reagent grade butyl lactate was obtained from Baker Chemical Co. for density and chromatographic studies. The water content of butyl lactate as obtained by Karl Fisher analysis was 0.120 per cent. A chromatographic analysis of the butyl lactate showed only one peak, and no impurities were present.

(e) Catalyst, Hydrochloric Acid. Reagent grade hydrochloric acid was obtained from Baker Chemical Co. as 36 per cent aqueous hydrochloric acid. Solutions of 8 N hydrochloric acid were prepared and standardized. The standardization of the catalyst solutions was carried out by base titration using standardized 1 N sodium hydroxide solution.

II. Analytical Methods

(a) Lactic Acid Content. The method of Eder and Kutter,²⁹ which was modified by the author, was used to determine the concentrations of monolactic acid and lactyllactic acid in aqueous solutions. This method is as follows.

A weighed sample of lactic acid solution, P, equivalent to 0.4 grams of lactic acid is diluted to 20 cc with distilled water.

This solution is titrated to a neutral end point with 0.1 N NaOH (A, mls).

The titrated solution is heated in a bath at 90°C for 15 minutes with sufficient excess of 0.1 N NaOH (B, mls.) to saponify the lactyllactic acid present in solution.

The solution is cooled to room temperature and backtitrated with 0.1 N HCl (C, mls.) to a neutral end point.

The weight per cent and moles per unit weight of solution of the monomeric or free lactic acid are given by the following equations:

$$\text{Weight per cent monomeric lactic acid} = \frac{0.09008(\text{AX} + \text{CY} - \text{BX})}{\text{P}} \times 100 \quad (65)$$

$$\text{Millimoles monomeric lactic acid per gram of solution} = \frac{(\text{AX} + \text{CY})}{\text{P}} \quad (66)$$

The weight per cent and moles per unit weight of lactyllactic acid, the so-called dimer, is given by the following equations.

$$\text{Weight per cent dimeric lactic acid} = \frac{.162(\text{BX} - \text{CY})}{\text{P}} \times 100 \quad (67)$$

$$\text{Millimoles of dimeric lactic acid per gram of solution} = \frac{(\text{BX} - \text{CY})}{\text{P}} \quad (68)$$

where X and Y are the normalities of the sodium hydroxide and hydrochloric acid solutions respectively.

Automatic titrator. A Beckman automatic titrator model No. BK was used to titrate lactic acid solutions for free lactic acid, and lactyllactate or butyl lactate as the sample required. The end point of these titrations was established at pH 7.0. A check of the automatic titrator at pH 7.0 against a phenolphthalein end point showed no discrepancies. A standard glass electrode and calomel electrode were used as the electrode pair on the titrator.

(b) Butyl Lactate Determination. The analysis for butyl lactate in a reaction mixture was obtained by two independent approaches, titrametric analysis and vapor phase chromatography. The titrametric analysis will be described in this section while a separate section will be devoted to the chromatographic analysis.

The quantitative measurement of butyl lactate is represented by the following equation.



This titration was carried out using the aforementioned Beckman automatic titrator.

A reaction mixture contains butanol, monolactic acid, dilactic acid, water, butyl lactate and hydrochloric acid-catalyst. The procedure for analyzing this reaction mixture for butyl lactate is as follows.

A weighed sample of the reaction mixture, W, equivalent to 0.7 grams of lactic acid is diluted to 20 cc with distilled water.

This solution is titrated to a neutral end point with 0.1 N NaOH (A, mls.).

The titrated solution is heated in a 90°C temperature bath for 15 minutes with sufficient excess of 0.1 N NaOH (B, mls.) to saponify the lactic acid and butyl lactate present in solution.

The solution is cooled to room temperature and backtitrated with 0.1 N HCl (C, mls.) to a neutral end point.

If the concentration of catalyst, hydrochloric acid, is known as well as the concentration of lactic acid, then the concentrations

of lactic acid, monomer form, and butyl lactate can be determined by the following equations:

Monomeric Acid Concentration

$$M = \frac{[A - (W \cdot V)] X}{W} - D_o \quad (69)$$

where M = millimoles of lactic acid per gram

A = milliliters of sodium hydroxide used

W = weight of sample

V = milliliters of 100 per cent hydrochloric acid per gram of sample expressed as milliliters of sodium hydroxide per gram of sample

X = normality of sodium hydroxide

D_o = initial concentration of lactyllactic acid in millimoles per gram of sample

Butyl Lactate Concentration

$$E = \frac{[(B)(X) - (C)(Y)]}{W} - D_o \quad (70)$$

where E = millimoles of ester per gram of sample

B = milliliters of excess sodium hydroxide

C = milliliters of hydrochloric acid

Y = normality of hydrochloric acid.

(c) Water; Karl Fisher Analyses. The water content of the lactic acid was determined by Karl Fisher water analysis using a Thomas

model No. 10. Karl Fisher potentiometric apparatus. The procedure for determining the water content of lactic acid is as follows.

Standardize the Karl Fisher reagent (T, mls.) by titrating a known weight (W) of a methanol water standard (expressed as mg water/ml. standard, S) of density ρ , to an electrometric end point of a scale reading between 90 and 100. This end point must be stable for at least 30 seconds.

Compute V, the milligrams of water titrated by one milliliter of Karl Fisher reagent as follows

$$V = W \times \frac{1}{\rho} \times S \times \frac{1}{T} \tag{71}$$

where V = milligrams of water per milliliter of Karl Fisher reagent

W = weight of standard, grams

ρ = density of standard g/ml.

S = milligrams of water per milliliter of standard

T = milliliters of Karl Fisher reagent.

Take a weighed sample of lactic acid, (J, grams), approximately 0.30 grms. and titrate with Karl Fisher reagent (volume T) to an electrometric end point of between 90 and 100 of the full scale reading. The per cent water in the lactic acid (K) is

$$K = \frac{T \times V}{J} \times 100 \text{ per cent} \tag{72}$$

Vapor phase gas chromatograph. A dual column, F and M model 810 flame ionization gas chromatograph was used to detect the concentration of butyl lactate present in the reaction mixture. Calibration data for the concentration of ester, in moles per liter of solution, as a function of the area of the response peak, in count units, was developed. It was found that this calibration was highly dependent upon operating conditions of the gas chromatograph. It was therefore necessary to calibrate the apparatus every time an unknown set of samples were to be analyzed. The analytical columns were 8 feet long, 1/8 inch diameter, 10 per cent diethylene glycol succinate with one per cent phosphoric acid on diatoport S 80-100 substrate. The normal operating conditions on the chromatographic unit were

<u>flow rate</u>	3.0 scale reading
helium pressure	50.0 psi
hydrogen pressure	12.0 psi
oxygen pressure	5.0 psi
detector temperature	210°C
injection block temperature	210°C
temperature program rate	10°C/minute
temperature range	90°C to 150°C
sample injection	0.3 ml
attenuation	10 ³ x 32

The data for a sample calibration can be found in Table 4 and peak area calibration is shown in Figure II.

The results from the VPC unit are extremely sensitive to the quantity of sample injected. A Hamilton model 9001 microliter syringe was used as the injection apparatus. The author has found that in order to obtain reproducible results, much care and practice are essential for acceptable results.

The VPC analysis of a reaction mixture sample showed that only butanol and butyl lactate were sensed by the flame ionization unit in the range of temperatures studied (90°C to 150°C).

Density experiments. In order to solve the kinetic expression, equation (15), the volume of the reacting system must be known at any set of conditions. It was necessary therefore to determine the density, ρ , of the reacting system as a function of four variables in the ranges in which kinetic studies were to be made.

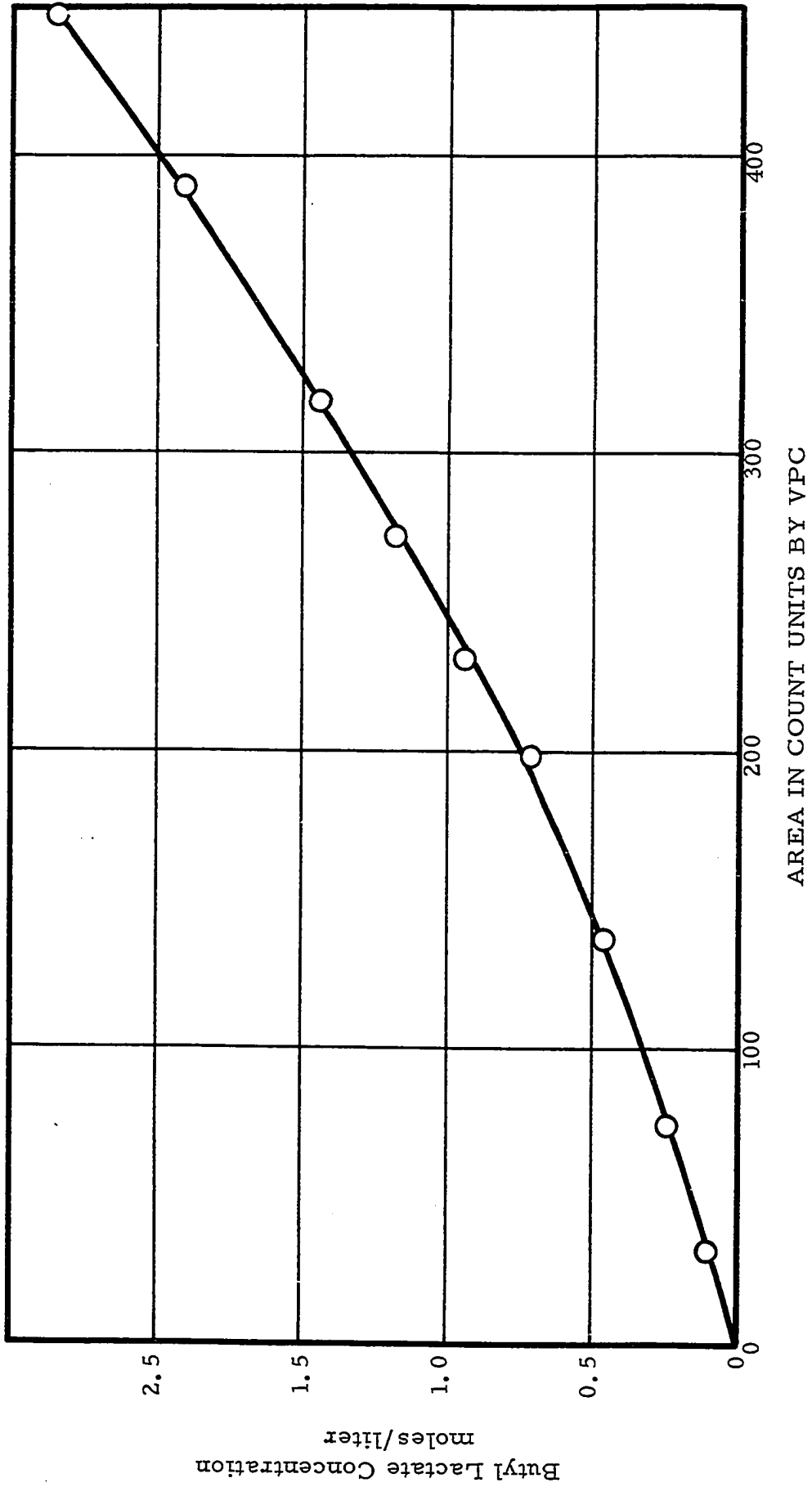
Temperature of the reacting system,

Mole ratio of monomeric lactic acid to butanol,

Initial water concentration in lactic acid,

Per cent conversion of reactants to products.

Functionally this can be represented as



TYPICAL CALIBRATION CURVE OF BUTYL LACTATE BY VPC

Figure II

Table 4TYPICAL CALIBRATION DATA FOR CHROMATOGRAPHIC
DETERMINATION OF BUTYL LACTATE

<u>Butyl Lactate</u> <u>moles/liter</u>	Peak Area Counts		
	<u>1</u>	<u>2</u>	<u>3</u>
.094	37	36	30
.235	70	67	72
.467	137	138	135
.705	196	192	198
.940	245	238	230
1.176	270	262	270
1.411	320	312	315
1.881	370	392	382
2.351	455	447	437
2.851	495	485	490

$$\rho = f(\text{temperature, mole ratio of reactants, initial water content, per cent conversion})$$

The functional relationship can be obtained through the use of a statistically designed experiment, in this case a second order rotatable central composite design as described by Box and Hunter.⁴⁸

The resultant expression which is a regression model of order two is

$$\begin{aligned} y = & b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_{11} x_1^2 + b_{22} x_2^2 \\ & + b_{33} x_3^2 + b_{44} x_4^2 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{14} x_1 x_4 \\ & + b_{23} x_2 x_3 + b_{24} x_2 x_4 + b_{34} x_3 x_4 \end{aligned} \quad (73)$$

where y = density, grams/ml.

x_1 = mole ratio of reactants

x_2 = temperature, °C

x_3 = per cent conversion

x_4 = initial water content, expressed as the weight ratio of lactic acid to water

b_i = coefficients of the variables.

The presentation of the design is given in Appendix C.

The final equation took the form

$$\begin{aligned}
y = & .869 - .026 x_1 - .010 x_2 - .0015 x_3 - .0046 x_4 \\
& + .00016 x_1 x_3 - .00062 x_1 x_3 - .00062 x_1 x_3 \\
& + .00077 x_1 x_4 + .00083 x_2 x_3 + .0083 x_2 x_4 \\
& - .00081 x_3 x_4 + .0073 x_1^2 + .0011 x_2^2 - .000063 x_3^2 \\
& + .000049 x_4^2
\end{aligned} \tag{74}$$

and when only significant terms are considered, on a 95 per cent confidence level,

$$y = .869 - .026 x_1 - .010 x_2 + .0073 x_1^2 \tag{75}$$

The correlation coefficient for this equation is 0.96. In essence, equation (75) says that density is only dependent upon the mole ratio of lactic acid to butanol and the temperature. Using equation (75), densities of the reacting mixture can be calculated at any desired temperature and mole ratio as long as the values are within the ranges of the experimental design.

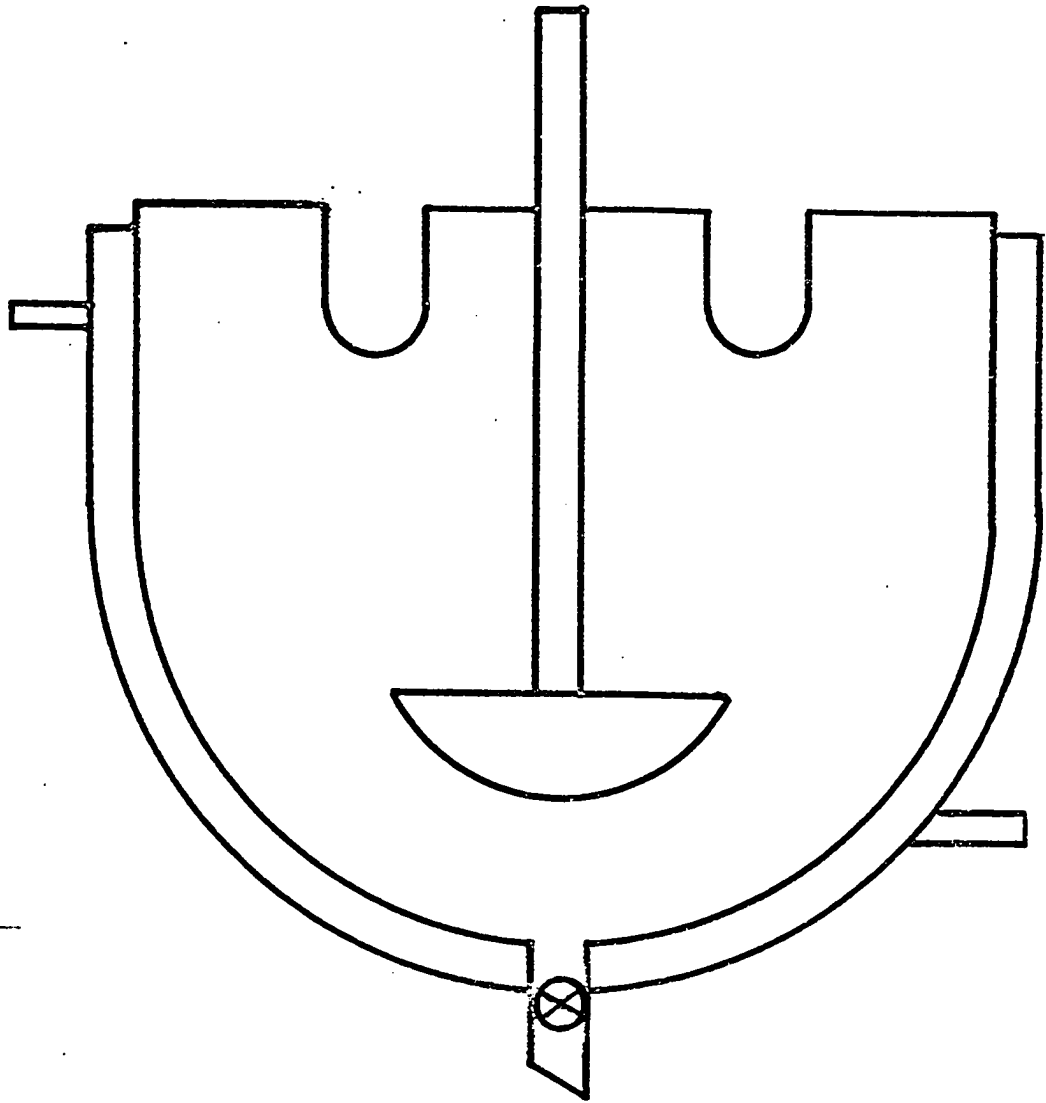
The densities at the various design points were determined by use of calibrated pycnometers. The temperatures were held constant by use of a Bronwill temperature controller to plus or minus 0.10°C. The concentrations of monomeric lactic acid and water were obtained from Eder and Kutter analysis and Karl Fisher analysis respectively. The butanol and butyl lactate concentration, on a weight basis, were known by simply weighing out known amounts of butyl lactate and butanol on a Sartorius analytical balance, to the nearest 0.0001 gram.

III. Equipment

(a) Reaction Vessel. A reaction vessel designed by the author was used throughout all of the kinetic studies. A diagram of this vessel is shown in Figure III. The vessel was a jacketed three neck 500 ml round bottom fitted with a sample takeoff valve. The reaction vessel was heated by a glycerine-water solution whose temperature was maintained by a Haake model NB combination circulating and heating apparatus. Constant checking of the temperature of the reaction mixture revealed that temperature was maintained at $\pm 0.02^{\circ}\text{C}$. Agitation was produced by use of a 3 inch wide Teflon paddle blade whose speed was controlled by a Variac variable transformer. A 10 inch reflux condenser was used as vent, and no vapors were ever seen to escape the reaction vessel.

(b) Ancillary Equipment.

Thermometers. Special thermometers which were graduated to one hundredth of a degree Centigrade were supplied by Scientific Glass Corp. These thermometers were graduated the ranges -10°C to 65°C and 50°C to 110°C . All thermometers used were calibrated against a standardized National Bureau of Standards thermometer and were accurate to $\pm 0.01^{\circ}\text{C}$.



REACTION VESSEL

Figure III

Sample Bottles. Serum bottles of 25 milliliters capacity were used as sample bottles for storing the liquid samples withdrawn from the reaction vessel. These bottles were able to withstand great thermal shock as exemplified by their resistance to cracking when a bottle at 100°C was suddenly thrust into a dry ice-acetone bath.

IV. Dimerization of Monomeric Lactic Acid

The procedure for obtaining the rate constants and equilibrium constants for the dimerization reaction is presented below, together with the details of a typical run.

Run D800. 98.30 grams of monomeric lactic acid (78.50 weight per cent monomer, 14.28 per cent water and 7.72 per cent dimer) was charged into the reaction vessel and heated to a temperature of 80.40°C . The initial mole composition of the reaction mixture per 1000 grams of charge was 8.7383 moles of monomer, 7.9430 moles of water and 0.4760 moles of dimer. When the material reached temperature, usually after five minutes under vigorous agitation, a 10.0 cc sample was taken and immediately frozen in a dry ice-acetone mixture.

The temperature was maintained at $80.4 \pm 0.05^{\circ}\text{C}$ and samples were periodically taken. These samples were also immediately frozen to stop the reaction.

Samples were titrated for free lactic acid and lactic acid dimer. The results are shown in Table 5.

The reaction was continued for 48 hours at which time essential equilibrium was achieved.

Table 5

RUN NO. D800 - DIMERIZATION OF LACTIC ACID

Sample No.	Initial Lactic Acid Initial Dimer	Time min.	Weight grams	.1020N NaOH Titrated mls	.1020N Excess NaOH Added mils.	Density .0514NHCl Backtitrated mls/liter	Temperature Catalyst Concentration 0.0 moles/liter	80.40°C 1.15 grams/liter Dilactic Acid mls/liter
1a		5	.3320	30.00	8.00	12.75	10.0429	.5564
1b		5	.3290	29.65	8.00	12.75	10.0097	.5615
2a		10	.3220	28.80	8.00	12.75	9.9176	.5737
2b		10	.3110	28.00	8.00	12.85	9.9857	.5750
3a		17	.3260	29.40	7.00	10.75	10.0090	.5695
3b		17	.3290	29.65	11.00	18.30	9.9372	.6340
4a		25	.3580	32.30	8.00	12.20	9.9763	.6068
4b		25	.4005	36.10	8.00	12.30	10.0454	.5277
5a		35	.3270	29.50	8.00	12.40	9.9538	.6282
5b		35	.3585	32.35	8.00	12.10	9.9762	.6233
6a		50	.3450	31.00	10.00	15.80	9.9470	.6929
6b		50	.3270	29.10	9.00	14.20	9.7770	.6615
7a		70	.3270	29.10	10.00	15.50	9.6533	.7835
7b		70	.3525	31.40	9.00	13.20	9.6614	.7814
8a		90	.3850	33.90	10.00	13.40	9.3390	.9894
8b		90	.3260	28.60	9.00	13.30	9.4639	.8268
9a		120	.3200	28.05	9.00	12.80	9.3474	.9346
9b		120	.3350	29.15	9.00	12.55	9.2699	.9369
10a		150	.3140	27.35	9.00	12.00	9.1139	1.1031
10b		150	.3170	27.50	10.00	13.75	9.0394	1.1363
11a		200	.3505	29.90	11.00	14.60	8.7873	1.2190
11b		200	.3680	31.70	9.00	10.70	9.2730	.8313

V. Esterification of Monomeric Lactic Acid

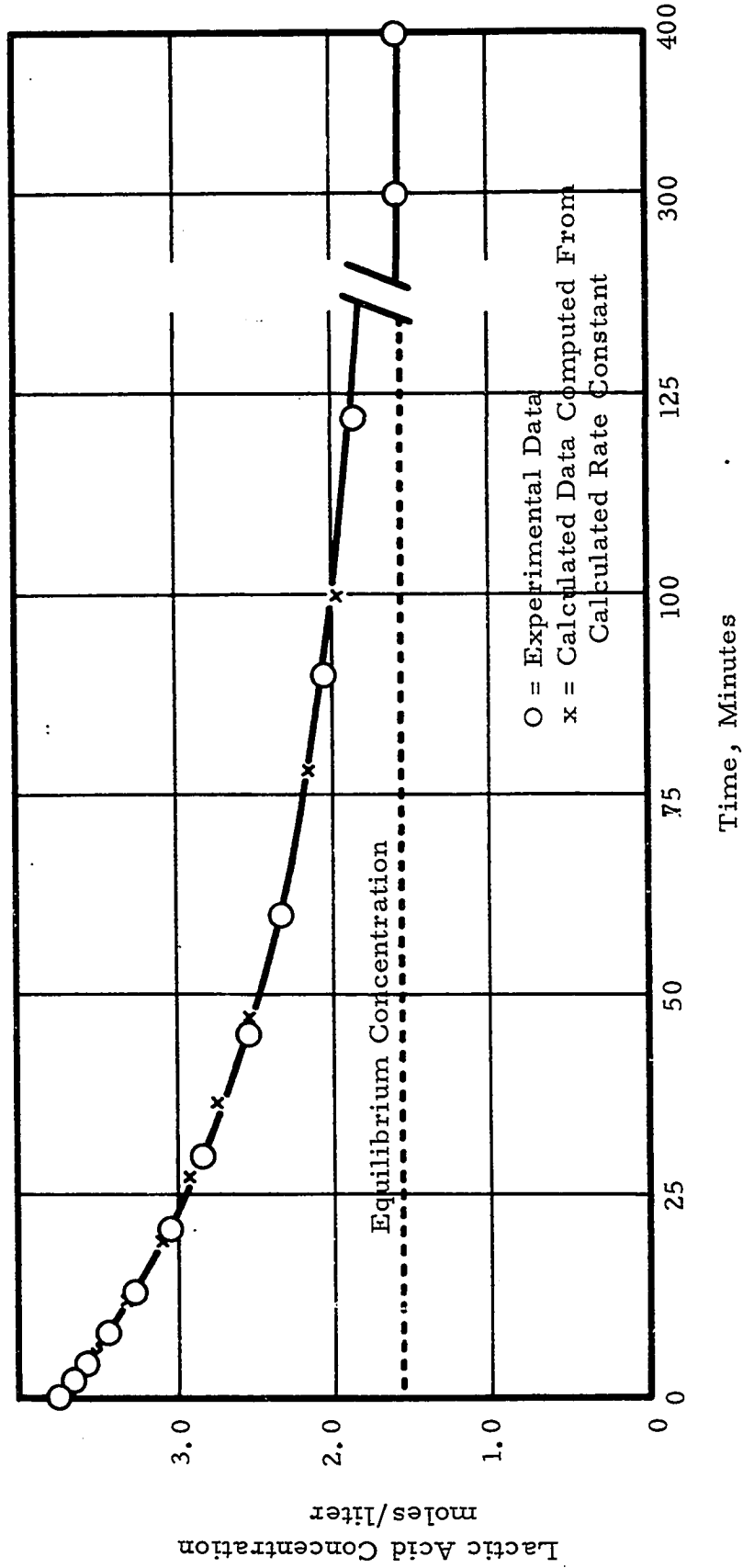
Run E802. 102.50 grams of reagent grade butanol was charged into the reaction vessel and heated to $80.40 \pm 0.05^{\circ}\text{C}$. When the butanol reached temperature, 93.15 grams of a monomeric lactic acid solution (81.08 weight per cent monolactic acid, 4.22 per cent dimer and 15.70 per cent water) was also charged into the reaction vessel. When the solution reached temperature, usually 10 minutes, an initial sample was taken and immediately frozen. Two cc's of 8.00 N hydrochloric acid solution was added by pipette. Temperature was maintained at $80.40^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$ and samples were taken at predetermined time intervals. These samples were also frozen immediately to kill the reaction. Samples were titrated for free lactic acid, dimeric lactic acid and butyl lactate. Samples also were analyzed by vapor phase gas chromatography for butyl lactate. These results are shown in Table 6. A time concentration curve is shown in Figure IV.

The reaction was continued for 48 hours at which time essential equilibrium was achieved.

Table 6

RUN NO. E802 - ESTERIFICATION OF LACTIC ACID

Sample No.	Time min.	Initial Lactic Acid grams	Initial Butyl Lactate grams	Initial Dimer grams	Weight NaOH Titrated ml.	Excess NaOH .0990N added ml.	HCl.098N Backtitrated ml.	Lactic Acid mono. moles/kg	Butyl Titration moles/kg	Lactate by VPC moles/kg	Temperature 80.40 °C	Catalyst Concentration 10.23 mmole/liter	Density .8939 grams/liter
1a	2.0	.7710	30.35	10.00	6.80	3.6869	.2197	.273					
1b	2.0	.8855	34.70	10.00	6.30	3.6720	.2210	.					
2a	4.25	.8060	31.00	10.00	5.85	3.5975	.3169	.321					
2b	4.25	.8715	33.40	11.00	6.65	3.5840	.3017						
3a	8.00	.7190	26.70	15.00	10.35	3.4662	.4546	.407					
3b	8.00	.8250	30.55	12.00	6.60	3.4558	.4560						
4a	13.00	.7540	26.60	13.00	6.70	3.2824	.6360	.675					
4b	13.00	.7740	27.30	17.00	10.60	3.2820	.6322						
5a	21.00	.8330	27.50	14.00	5.40	3.0570	.8282	.905					
5b	21.00	.7670	25.40	12.00	3.90	3.0683	.8505						
6a	30.20	.7895	24.40	14.00	4.10	2.8495	1.0466	1.080					
6b	30.20	.8850	27.60	17.00	5.70	2.8773	1.0705						
7a	45.00	.8490	23.70	17.00	3.90	2.5534	1.3321	1.240					
7b	45.00	.0560	24.00	17.00	3.85	2.5655	1.3253						
8a	60.00	.8890	23.20	19.00	3.55	2.3734	1.5245	1.510					
8b	60.00	.8720	22.60	17.00	1.90	2.3556	1.5165						
9a	90.25	.8760	20.10	20.00	2.10	2.0614	1.8253	1.820					
9b	90.25	.8740	20.00	22.00	4.00	2.0553	1.8434						
10a	122.25	.8750	18.20	22.00	2.30	1.8490	2.0315	2.03					
10b	122.25	.7235	15.00	25.00	8.60	1.8423	2.0559						
11	300.00	.8085	12.40	30.00	5.75	1.3082	2.7764	2.750					
12	400.00	.8480	13.00	30.00	4.35	1.3075	2.7996						



LACTIC ACID TIME CONCENTRATION CURVE

FOR RUN NO. E802

Figure IV

CHAPTER III

EXPERIMENTAL RESULTS

Dimerization Reaction

The dimerization reaction was studied at three temperature levels and four catalyst levels. These levels together with the equilibrium values at these values are enumerated in Table 7. Table 8 tabulates the rate constants of the dimer reaction at the different temperature and catalyst levels. The time concentration data for the reaction and the values of the rate constants for each experimental condition are tabulated in Tables 20 to 25 which are compiled in Appendix A.

The functional relationship between the rate constant k and the catalyst concentration at 80.40°C is clearly seen in Figure V. The slope of this line is numerically equal to the value of catalytic constant k_{cat} . A linear regression model was fitted to the rate constant-catalyst concentration data and the following equation resulted

$$k_{\text{o}} = 1.52 (10^{-6}) + 1.43 (10^{-6}) H \quad (76)$$

where k_{o} = observed rate constant liter/mole second

H = catalyst concentration mmoles/liter.

Table 7EQUILIBRIUM CONSTANT FOR
DIMER REACTION

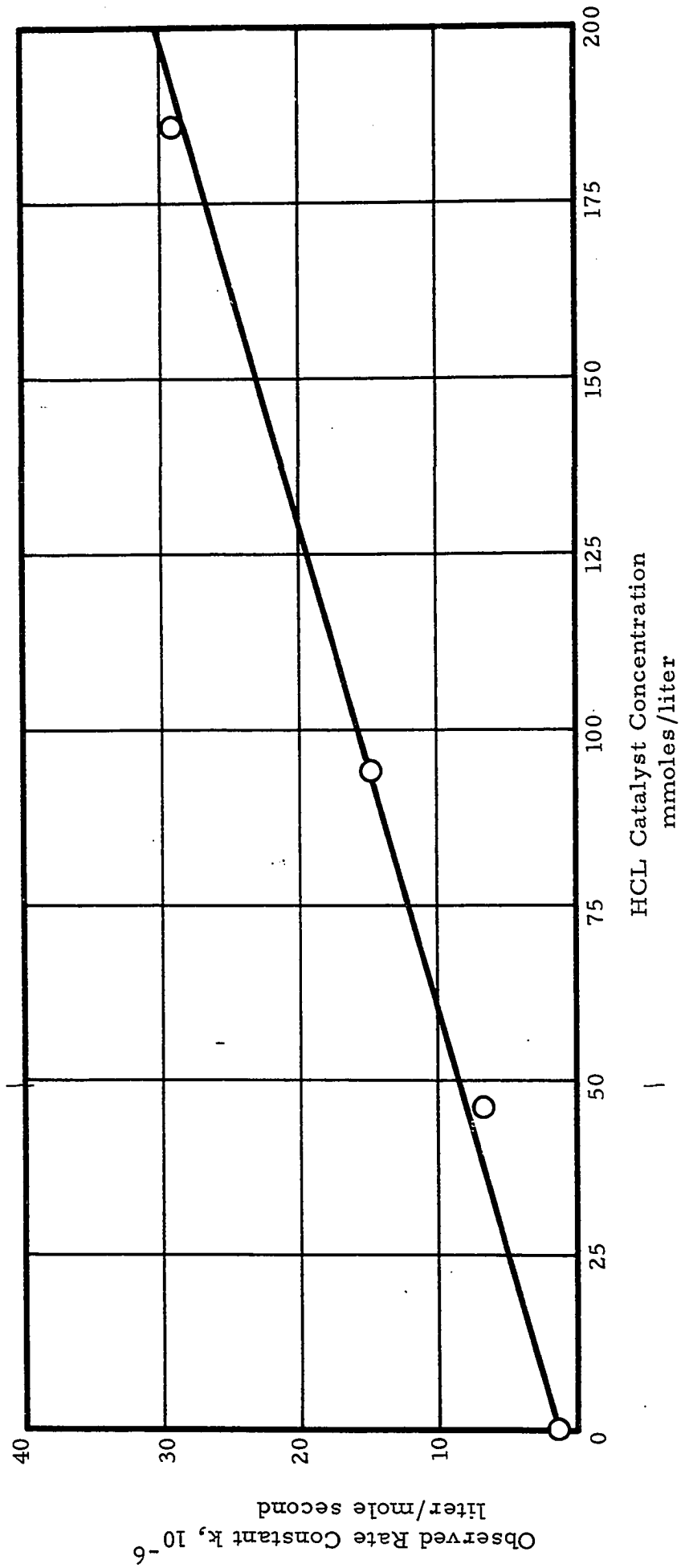
<u>Temperature °C</u>	<u>HCl Catalyst Concentration mmoles/liter</u>	<u>Equilibrium Constant K_{eq}</u>
80.40	0.0	-
80.40	9.4	0.368
80.40	4.6	0.362
80.40	18.6	0.363
65.40	18.4	0.362
95.40	9.2	0.369

Average K_{eq} = 0.362 ± 0.002

Table 8

DIMER REACTION RATE
CONSTANTS

<u>HCl Catalyst Concentration mmoles/liter</u>	<u>Temperature °C</u>	<u>Rate Constant liter/mole second 10⁶</u>
0.0	80.40	1.52 ± 0.38
4.6	80.40	6.73 ± 0.63
9.4	80.40	14.85 ± 0.20
18.6	80.40	29.23 ± 5.15
18.4	65.40	9.34 ± 0.62
9.2	95.40	38.19 ± 2.90



OBSERVED RATE CONSTANTS OF DIMER REACTION

at 80.40°C

Figure V

The catalytic constant from equation (76) is obviously

$$1.43 (10^{-6}) \frac{\text{liter}^2}{(\text{mole})(\text{second}) \text{ mmoles catalyst}}$$

The correlation coefficient for the preceding equation was 0.9972.

The apparent activation energy for the dimerization reaction was calculated by the following equation

$$E^* = \frac{(2.303) RT_1 T_2}{T_2 - T_1} \log \frac{k_2}{k_1} \quad (77)$$

where k_1 = observed rate constant liter/(mole) second at temperature T_1

k_2 = observed rate constant liter/(mole)second at temperature T_2

R = universal gas constant, calories/mole $^{\circ}\text{C}$

T_1, T_2 = temperature $^{\circ}\text{K}$.

Using the rate constant values at 80.40°C and 65.40°C at a catalyst concentration of 18.4 mmoles/liter, an activation energy of 16,200 cal. was obtained. Using the rate constant values 80.40°C and 95.40°C at a catalyst concentration of 9.2 mmoles/liter, an activation energy of 17,100 cal. was obtained. Averaging these two activation energies, an approximate activation energy for the dimerization reaction is obtained, 16,650 cal. Using this value, an approximate value for the frequency factor A is obtained, $3.12 (10^5)$ liter/mole second.

Esterification Reaction

The material balance and stoichiometry for a typical esterification are shown in Table 9. The esterification reaction was also studied at three temperature levels and at five catalyst levels. These levels are enumerated in Table 10.

The equilibrium values of the esterification reaction at the different temperature, catalyst and mole ratio levels are also tabulated in Table 10. The time concentration data as well as the specific rate constants are given in Tables 26 to 39 in Appendix B.

The calibration curve of the flame ionization vapor phase gas chromatograph was shown in Figure III. This graph was used to determine the concentration of butyl lactate ester during the course of the reaction. Table 6 shows a comparison between the ester concentration as obtained from the Eder and Kutter titration and the ester concentration obtained from the gas chromatograph. Table 11 summarizes the evidence for the conclusion that the small amount of dimer present in the reaction mixture does not change with time.

Tables 12 to 14 summarize the rate constant data as a function of catalyst concentration at the three temperatures investigated. Figure VI illustrates the functional relationship between the rate constant and concentration of mineral acid at the temperatures studied. In addition to

Table 9

MATERIAL BALANCE AND STOICHIOMETRY

RUN NO. E802

Time min.	First Titration Dimer mole/kg		Second Titration Dimer and Ester moles/kg		Δ (Monomer and Dimer) moles/kg		Δ (Dimer and Ester) moles/kg		Per Cent of Theoretical Material Balance Accounted For	
	Sample		Sample		Sample		Sample		Sample	
	A	B	A	B	A	B	A	B	A	B
0.00	4.016	4.019	0.299	0.294	-	-	-	-	100.02	99.97
2.00	3.896	3.879	0.420	0.421	0.120	0.140	0.121	0.127	100.04	99.67
4.25	3.807	3.793	0.517	0.512	0.089	0.086	0.097	0.091	100.23	99.79
8.00	3.676	3.665	0.655	0.655	0.131	0.128	0.138	0.143	100.39	100.14
13.00	3.492	3.491	0.837	0.833	0.184	0.174	0.182	0.178	100.34	100.23
21.00	3.267	3.277	1.029	1.050	0.225	0.214	0.197	0.217	99.58	100.30
30.00	3.059	3.067	1.246	1.271	0.208	0.210	0.217	0.221	99.79	100.55
45.00	2.763	2.775	1.532	1.526	0.296	0.292	0.286	0.255	99.55	99.69
60.00	2.583	2.565	1.724	1.716	0.180	0.210	0.192	0.190	99.83	99.24
90.00	2.271	2.265	2.025	2.043	0.312	0.300	0.301	0.327	99.58	99.86
122.20	2.059	2.053	2.255	2.255	0.212	0.212	0.207	0.212	99.47	99.86

Table 10

EQUILIBRIUM CONSTANTS FOR ESTERIFICATION
REACTION

Temperature °C	HCl Catalyst Concentration mmoles/liter	Mole-Ratio Alcohol to Acid	Equilibrium Constant K _{eq}
65.40	0.0	2.68	2.72
65.40	13.42	3.02	3.10
65.40	12.90	1.73	3.00
65.40	15.60	1.95	2.82
80.40	0.0	2.52	3.07
80.40	3.53	2.34	2.90
80.40	17.17	2.06	3.04
80.40	18.50	4.30	3.20
95.40	0.0	2.58	3.00
95.40	4.50	1.98	3.10
95.40	9.05	1.91	3.30

Average K_{eq} = 3.02 ± 0.13

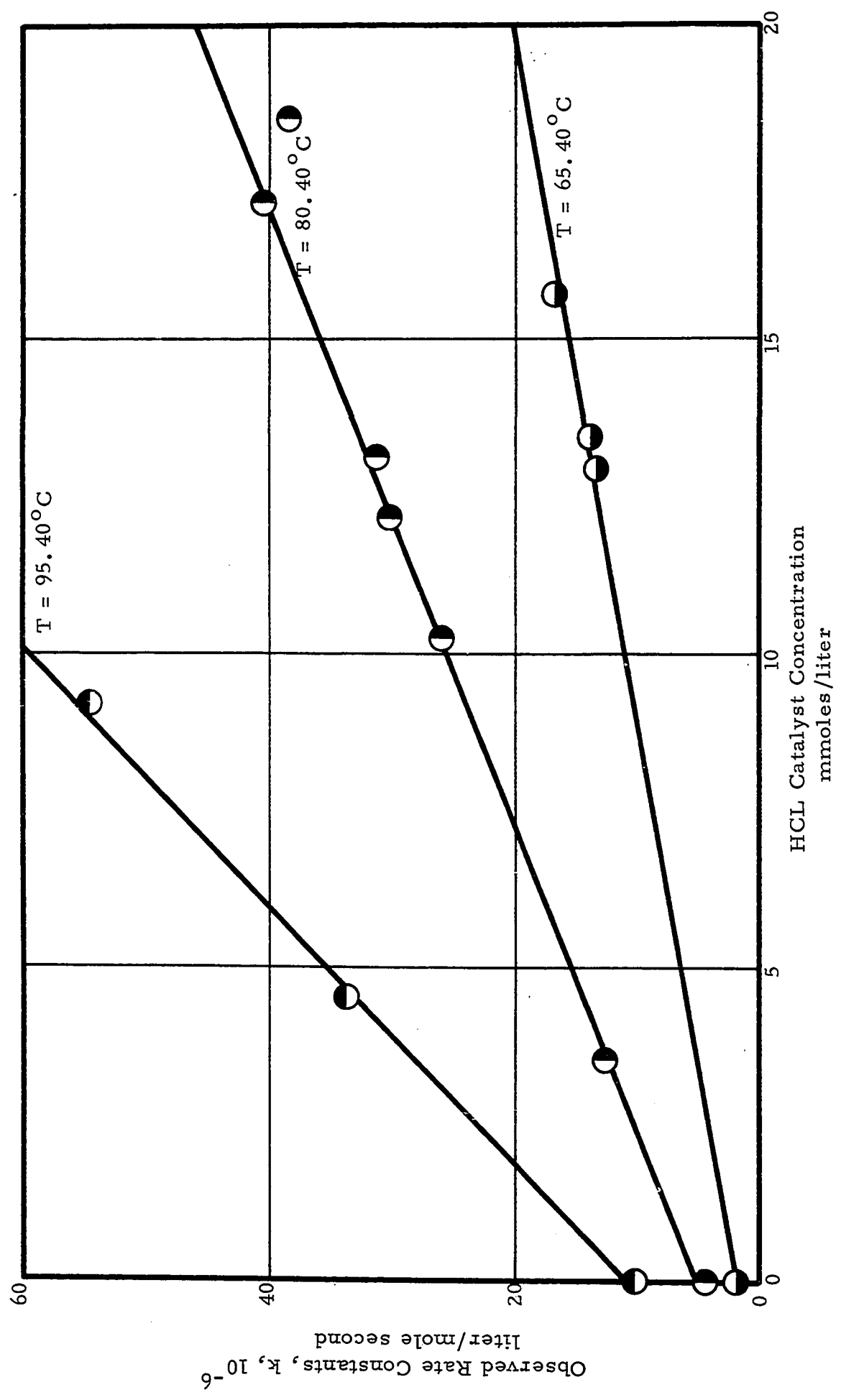
Table 11

DATA FOR ASSUMPTION THAT DIMER DOES
NOT REACT DURING ESTER REACTION

RUN NO. E802

Original Dimer Concentration 0.200 moles/kg

Time min.	Ester Concentration from VPC moles/kg I	Ester and Dimer Titration Method moles/kg II	(Ester and Dimer) Concentration from Titration Method Minus Ester by VPC
0.0	0.173	0.363	0.190
2.0	0.273	0.420	0.147
4.25	0.321	0.517	0.196
8.00	0.407	0.655	0.238
13.00	0.675	0.837	0.162
21.00	0.905	1.029	0.124
30.20	1.080	1.246	0.166
45.00	1.240	1.532	0.192
60.00	1.510	1.724	0.214
90.00	1.820	2.025	0.205
122.22	2.031	2.232	0.201



OBSERVED RATE CONSTANTS OF ESTER REACTION AT THREE TEMPERATURES

Figure VI

this graph, a linear regression model has been fitted to the data and takes the form

$$k_{\text{obs}} = k_o + k_{\text{cat}} (\text{H}^+) \quad (78)$$

where k_{obs} = observed rate constant liter/mole second

k_o = uncatalyzed rate constant liter/mole second

k_{cat} = catalyzed rate constant liter²/mole second mmole catalyst

The constants for this model at the respective temperature are depicted in Tables 12 to 14.

Table 15 summarizes the esterification rate constant data for both the catalyzed and uncatalyzed reactions at the respective temperatures. Using these values, an Arrhenius plot for the catalytic and uncatalytic reactions was developed. This plot is presented in Figure VII. Complementary to this plot, a linear regression model was also fitted to the Arrhenius equation

$$k = A e^{-E^*/RT}$$

to determine the values of A, the frequency factor and E*, the activation energy for both reactions. This model took the transformed form of

$$\ln k = A' + B X \quad (79)$$

where $A' = \ln A$

$B = -E^*/R$

$X = 1/T \text{ } ^\circ\text{K}$

Table 12

ESTERIFICATION RATE CONSTANTS

Temperature 65.40°C

<u>HCl Catalyst Concentration mmoles/liter</u>	<u>Rate Constants liter/mole second (10⁶)</u>	<u>Mole Ratio of Alcohol to Lactic Acid</u>
0.0	2.05 ± 0.25	2.68
13.42	13.75 ± 1.28	3.02
12.90	13.75 ± 1.02	1.73
15.60	17.36 ± 0.92	1.95

Regression model for $k_{\text{obs}} = k_o + k_{\text{cat}}(\text{H})$

$$k_{\text{obs}} = [1.904 + 0.937(\text{H})] (10^{-6})$$

Correlation coefficient = 0.995

Table 13

ESTERIFICATION RATE CONSTANTS

Temperature 80.40°C

<u>HCl Catalyst Concentration mmoles/liter</u>	<u>Rate Constants liter/mole second (10⁶)</u>	<u>Mole Ratio of Alcohol to Lactic Acid</u>
0.0	4.16 ± 0.221	2.52
3.53	12.75 ± 0.965	2:34
10.23	26.10 ± 2.13	1.86
12.10	30.03 ± 2.74	1.95
13.00	30.88 ± 2.39	1.07
17.17	40.53 ± 2.51	2.06
18.50	37.38 ± 4.26	4.46

Regression model for $k_{\text{obs}} = k_o + k_{\text{cat}}(\text{H})$

$$k_{\text{obs}} = [5.600 + 1.914 (\text{H})] (10^{-6})$$

Correlation coefficient = 0.989

Table 14

ESTERIFICATION RATE CONSTANTS

Temperature 95.40°C

<u>HCl Catalyst Concentration mmoles/liter</u>	<u>Rate Constants liter/mole second (10⁶)</u>	<u>Mole Ratio of Alcohol to Lactic Acid</u>
0.0	10.24 ± 1.33	2.58
4.50	33.89 ± 3.07	1.98
9.05	54.85 ± 2.34	1.91

Regression model for $k_{\text{obs}} = k_o + k_{\text{cat}}(\text{H})$

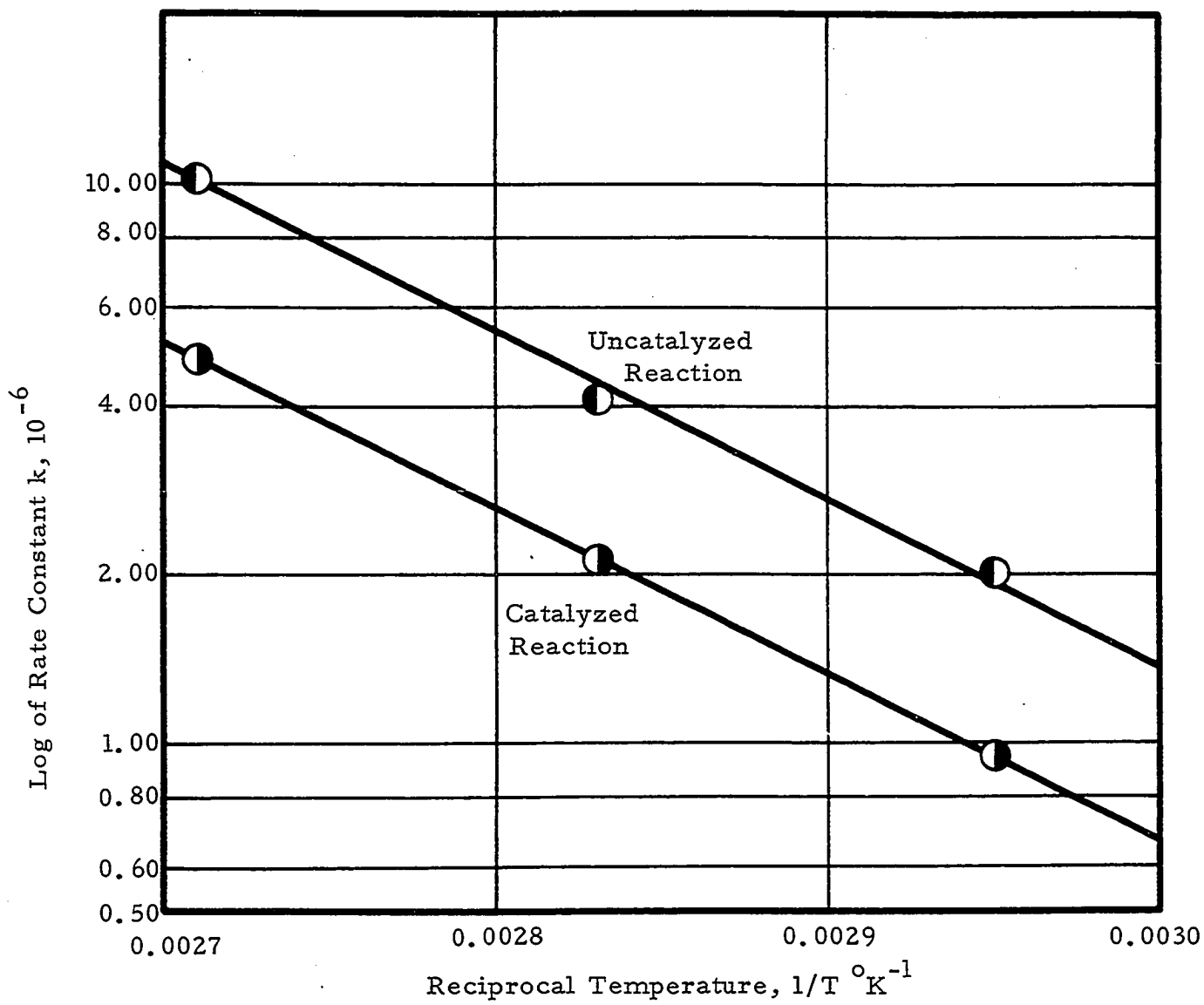
$$k_{\text{obs}} = [10.732 + 4.928 (\text{H})] (10^{-6})$$

Correlation coefficient = 0.992

Table 15

UNCATALYZED AND CATALYZED
RATE CONSTANTS

Temperature °C	Uncatalyzed Rate Constants liter/mole second (10 ⁶)	Catalyzed Rate Constants liter ² /mole mmole HCl second (10 ⁶)
65.40	2.05 ± 0.25	0.937 ± 0.22
80.40	4.16 ± 0.22	1.91 ± 0.22
95.40	10.24 ± 1.33	4.93 ± 0.22



ARRHENIUS PLOT FOR CATALYZED AND UNCATALYZED ESTERIFICATION REACTIONS

Figure VII

Upon solution of this equation and reversion to the initial equation of $k = A e^{-E^*/RT}$, the noncatalyzed rate constant was represented as

$$k_o = 673 e^{-13,190/RT} \text{ liter/mole second} \quad (80)$$

while the catalyzed rate constant was represented as

$$k_{\text{cat}} = 547 e^{-13,580/RT} \text{ liter/mole second-} \quad (81)$$

mmole catalyst

These rate constants can also be represented by the Eyring equation (see equation (56)). Using the catalytic and noncatalytic rate constants shown in Tables 12 to 14, the noncatalyzed rate constant can be represented as

$$k = \frac{K^o T}{h (.0619)} e^{-(59.8/R + \frac{10,480}{RT})} \quad (82)$$

while the catalytic rate constant can be represented as

$$k = \frac{K^o T}{h (.0619)} e^{-(60.6/R + \frac{10,590}{RT})} \quad (83)$$

The above values were calculated by assuming the activity coefficient to be 1.0 and molal volume to be 0.0619 liter/mole.

Computer Programs. The computer programs used to calculate the rate constant values of the dimerization and esterification reactions are given in Appendix D.

CHAPTER IV

DISCUSSION OF RESULTS

Influencing Factors

The major concern of this paper is the kinetics of esterification of monomeric lactic acid in normal butyl alcohol but before this reaction could be considered, it was necessary to examine any other factors that might affect the esterification rate. Two factors that could influence the ester reactions are the reaction between the dimer and alcohol and the reaction between two moles of monomer to form a mole of dimer and a mole of water.

The obvious method of preventing any influence by the dimer-alcohol reaction is to eliminate the dimer from the lactic acid solution. The total elimination of dimer from reaction solution was not possible but the dimer concentration was reduced to such an extent that the monomer-dimer mole ratio was approximately 20:1 for all reactions. It was further substantiated by vapor phase chromatography that this small amount of dimer does not react with butyl alcohol. In a chromatographic analysis of a typical reaction mixture, the only peaks that were observed were attributable to butyl alcohol and butyl lactate. No peaks were observed that would indicate the presence of butyl

lactyllactate which would be the main product of the reaction between dimer acid and butanol.

It was also found from a stoichiometric balance that the concentration of dimer at any time appeared to be constant. This stoichiometric balance was determined by means of the Eder and Kutter method and the gas chromatograph. Table 9 shows the results of the first and second titration in the Eder and Kutter method at different time intervals. The first titration determines the total amount of carboxylic acid groups present at the indicated time while the second titration determines the total amount of saponifiable groups present at the indicated time. The third column marked Δ (Monomer plus Dimer) represents the change in carboxylic acid groups from one time value to another. These differences were calculated by subtracting the carboxylic acid concentrations at one time value from that immediately preceding it. Column four marked Δ (Ester plus Dimer) was similarly calculated. On comparison between columns 3 and 4, one readily sees that for each carboxylic acid group that disappears, one saponifiable group appears; thus the stoichiometry of the reaction is established that one mole of monomeric acid gives rise to one mole of butyl lactate.

To prove that the dimer concentration is constant, the reader is referred to Table 11. The second column in Table 11 represents the ester concentration as found by the gas chromatographic analysis

while the third column represents the difference between the saponifiable material as determined by the method of Eder and Kutter and the ester concentration as determined by the gas chromatograph. If the dimer concentration is constant throughout the course of the reaction, then this difference should also be a constant. That this is so is clearly indicated in Table 11.

To ascertain the effect of the dimerization reaction upon the esterification reaction, it was necessary to study the dimerization reaction in its isolated state, that is, free from any interfering reactions. The data for the rate constants of the dimerization reaction are given in Table 8. As can be readily seen, these values are of the same magnitude as the esterification rate constants. One would naturally assume that the dimerization had a profound effect upon the esterification rate; however, this effect was not observed. If the dimerization were important, then one would see an increase in dimer concentration at the early stages of the reaction but according to gas chromatographic data, which is shown in Table 11, this is not the case. The dimer concentration appeared to be constant. This apparent paradox can be explained by the following rationale. Although the dimerization rate constants are nearly of the same magnitude as the esterification rate constants, the ester constants are still greater by a factor ranging from 2:1 to 10:1. Furthermore, the dimerization reaction at any time is never far from

its equilibrium position during the esterification runs. Thus the driving force to form more dimer is greatly diminished. Furthermore, as the esterification proceeds, lactic acid monomer is dissipated and water of reaction is formed. This in turn will inhibit the formation of dimer since the addition of water is a condition for hydrolyzing the dimer. It is apparent that since the dimer concentration is constant throughout the reaction, the monomer-dimer reaction must essentially be at its equilibrium position.

This argument is substantiated by the following quantitative facts.

At the initial or zero time of the esterification reaction (using the data of Run E802) the rate of formation of ester was calculated to be $671 (10^{-6})$ moles/liter second, while the initial rate of dimerization was $24 (10^{-6})$ moles/liter second. At 60 per cent of equilibrium conversion, the rate of formation of ester was found to be $270 (10^{-6})$ moles/liter second while the rate of dimerization was $4.4 (10^{-6})$ moles/liter second.

Second Order Model

As mentioned quite often before, the specific rate constants for both the dimerization esterification reactions were estimated by use of a second order reversible kinetic model. Goldschmidt⁴⁹ has pointed out that esterification reactions are hydrogen ion catalyzed and should follow second order rate expressions; however, Flory⁴⁰ stated that in the absence of a strong mineral acid, in an uncatalyzed reaction, a second molecule of the acid must function as a catalyst and the reaction should follow third order kinetics. But in the present work it has been shown that not only has the catalyzed reaction followed second order kinetics but the uncatalyzed reaction does so as well.

To further demonstrate that the second order model fits the catalyzed and uncatalyzed reactions better than other known models, the rate constants for the esterification reaction were calculated using six other models. These models were:

- (A) First order irreversible in lactic acid,
- (B) First order irreversible in butyl alcohol,
- (C) Second order irreversible, first order with respect to alcohol and acid,
- (D) Third order irreversible, second order in acid and first order in alcohol,

Table 16

RATE EQUATION MODELS

L = moles lactic acid per unit mass of feed

M = moles butanol per unit mass of feed

R = moles water per unit mass of feed

Keq = equilibrium constant, in proper units

<u>Model</u>	<u>Reaction</u>	<u>Rate Equation</u>
A	$L \rightarrow R + S$	$r = k L$
B	$M \rightarrow R + S$	$r = k M$
C	$L + M \rightarrow R + S$	$r = k (L)(M)$
D	$2L + M \rightarrow R + S$	$r = k (L)^2 M$
E	$L + M \rightleftharpoons R + S$	$r = k(L)(M) - \frac{k}{K_{eq}} (R)(S)$
F	$L \rightleftharpoons R + S$	$r = k(L) - \frac{k}{K_{eq}} (R)(S)$
G	$L^2 \rightleftharpoons R + S$	$r = k(L)^2 - \frac{k}{K_{eq}} (R)(S)$

Table 17

ESTERIFICATION RATE CONSTANTS

USING SEVEN DIFFERENT MODELS

Uncatalyzed Reaction
Rate Constants (10^3)

80.40°C

A	B	C	D	E	F	G	Time Seconds
.000027	.000010	.003932	337.93	.003962	.000027	.832201	1158.
.000025	.000010	.003646	337.95	.003674	.000025	.851876	1158.
.000029	.000011	.004172	217.26	.004214	.000029	.450961	1800.
.000029	.000011	.004116	217.26	.004157	.000029	.453253	1800.
.000028	.000011	.004120	132.88	.004177	.000028	.226073	2940.
.000028	.000011	.004095	132.88	.004152	.000028	.226717	2940.
.000030	.000011	.004433	106.99	.004510	.000030	.157477	3648.
.000030	.000011	.004367	107.00	.004442	.000030	.158763	3648.
.000029	.000011	.004277	81.23	.004369	.000029	.103907	4800.
.000030	.000011	.004351	81.23	.004445	.000030	.102774	4800.
.000029	.000011	.004264	64.92	.004377	.000029	.071286	6000.
.000029	.000010	.004205	64.92	.004314	.000029	.072042	6000.
.000027	.000010	.003993	54.06	.004111	.000027	.054986	7200.
.000023	.000010	.004130	54.05	.004257	.000023	.052538	7200.
.000026	.000009	.003827	46.30	.003954	.000026	.041938	8400.
.000028	.000010	.004104	46.28	.004251	.000028	.039136	8400.
.000026	.000009	.003891	34.03	.004076	.000026	.021186	11400.
.000026	.000009	.003891	34.03	.004076	.000026	.021186	11400.
.000024	.000008	.003711	25.80	.003946	.000024	.010568	15000.
.000023	.000008	.003573	25.81	.003789	.000023	.011515	15000.
.000029	.000008	.004714	12.67	.006120	.000029	.015215	30000.
.000019	.000005	.003151	8.44	.004098	.000019	.009830	45000.
.000014	.000004	.002336	6.33	.003019	.000014	.008832	60000.
.000011	.000003	.001894	5.06	.002465	.000011	.005793	75000.

A = First order irreversible in lactic acid, l/min

B = First order irreversible in butyl alcohol, l/min

C = Second order irreversible, first order in acid and alcohol, liter/mole min

D = Third order irreversible, second order in acid, first order in alcohol, liter²/mole² min

E = Second order reversible, first order in acid and alcohol, liter/mole min

F = First order reversible in lactic acid, l/min

G = Second order reversible in lactic acid, liter/mole min

Table 18

ESTERIFICATION RATE CONSTANTS
USING SEVEN DIFFERENT MODELS

HCl Catalyzed Reaction 10.23 mmoles/liter

Rate Constants (10^3)

80.40°C

A	B	C	D	E	F	G	Time Seconds
.000119	.000063	.019096	4033.04	.019353	.000119-8	.451641	120.
.000154	.000032	.024705	4032.43	.025051	.000154-7	.910636	120.
.000152	.000081	.024559	1896.21	.024977	.000152-2	.979955	255.
.000167	.000083	.026970	1895.95	.027445	.000167-2	.886455	255.
.000158	.000083	.025783	1005.99	.026382	.000158-1	.219508	480.
.000164	.000086	.026824	1005.88	.027455	.000164-1	.193293	480.
.000167	.000087	.027631	617.82	.028542	.000167	-.564679	780.
.000167	.000037	.027678	617.82	.028592	.000167	-.564096	780.
.000160	.000082	.026920	381.43	.028222	.000160	-.252526	1260.
.000157	.000080	.026400	381.49	.027653	.000157	-.256783	1260.
.000150	.000075	.025696	264.52	.027411	.000150	-.126464	1812.
.000144	.000073	.024719	264.62	.026300	.000144	-.132605	1812.
.000159	.000077	.027977	198.85	.030369	.000159	-.049792	2400.
.000141	.000069	.024368	176.76	.027439	.000141	-.044260	2700.
.000139	.000068	.024532	176.79	.027023	.000139	-.045842	2700.
.000126	.000060	.022619	132.18	.025674	.000126	-.015721	3600.
.000123	.000061	.023034	132.14	.026228	.000123	-.013999	3600.
.000110	.000050	.020357	87.36	.024351	.000110	.010517	5415.
.000110	.000051	.020473	87.35	.025039	.000110	.010963	5415.
.000096	.000043	.016210	64.20	.024120	.000096	.020597	7335.
.000096	.000043	.018313	64.19	.024342	.000096	.021063	7335.
.000053	.000023	.011887	25.76	.022728	.000053	.006300	18000.
.000043	.000017	.008921	19.32	.016994	.000043	.004709	24000.
.000034	.000014	.067091	15.46	.014063	.000034	.003910	30000.

A = First order irreversible in lactic acid, 1/min

B = First order irreversible in butyl alcohol, 1/min

C = Second order irreversible, first order in acid and alcohol,
liter/mole min

D = Third order irreversible, second order in acid, first order in
alcohol, liter²/mole² min

E = Second order reversible, first order in acid and alcohol, liter/mole min

F = First order reversible in lactic acid, 1/min

G = Second order reversible in lactic acid, liter/mole min

- (E) Second order reversible, first order in alcohol and acid,
- (F) First order reversible in acid,
- (G) Second order reversible in acid.

The rate equations are given in Table 16.

The rate constants that resulted from these different models are shown in Tables 17 and 18. For the uncatalyzed reaction it is obvious that the third order irreversible and second order reversible in lactic acid can immediately be discarded since the rate constants fall off appreciably with increasing time in one case and the rate constants are negative in the second case. The first order irreversible model in lactic acid as well as in butyl alcohol can be discarded along with the second order reversible model in lactic acid for the following reasons. The rate constants in these three models are of the magnitude of 10^{-8} which is an unlikely figure for the reaction of concern. Peng⁵⁰ has shown that the rate constants for the uncatalyzed reaction of butyl alcohol with acetic acid at temperatures of 70-80°C are of the magnitude of 10^{-6} mole/liter second. Since lactic acid can be assumed to have approximately the same reactivity as acetic acid, it would be appropriate to expect its rate constant to have a magnitude in the range of 10^{-6} . It is also interesting to note that the second order irreversible model, first order with respect to acid and alcohol, has practically the same value for the rate constants as does the second order reversible

model. This simply means that the reverse reaction of hydrolysis did not yet have a significant effect upon the reaction. However, if we look at Table 35, which outlines the different models for the catalyzed reaction, we see that in the second order irreversible model the rate constant starts to fall off as the time increases but in the reversible model, the rate constant is still steady as time increases.

Referring back to Peng,⁵⁰ it is of interest to compare his rate constant values for the esterification of acetic acid by butanol, with the author's values for the lactic acid-butanol reaction. Peng's values for the frequency factor and the activation energy were 570 liter/mole second and 13,700 calories for the uncatalyzed reaction respectively. This is in very close agreement with the author's values of 673 liter/mole second and 13,190 calories.

From this data, it can be concluded that lactic acid has relatively the same reactivity as acetic acid. In fact, comparing Peng's rate constant at 80.0°C for the acetic-butanol reaction which was $1.73 (10^{-6})$ liter/mole second and the lactic acid-butanol rate constant at 80.0°C which was $4.10 (10^{-6})$ liter/moles second, it can be concluded that lactic acid is even more reactive than acetic acid. This greater reactivity is further evidenced by the fact that lactic acid has a larger dissociation constant than acetic acid in aqueous systems, $1.38 (10^{-4})$

versus $1.75 (10^{-5})$ at 25°C . This increased reactivity of lactic acid over acetic acid is due to electron withdrawing effect of the hydroxyl group in the lactic acid molecule.

It was stated previously that Flory thought that the uncatalyzed reaction should be represented as a third order reaction. For this to be the case it would be necessary that the reaction follow a general acid catalysis. It was the writer's thought that the assumption of specific acid catalysis in the esterification reaction could still be adhered to and it was on this basis that a 2-1/2 order reversible model was derived. The underlying assumption for this model is that the hydrogen ion which catalyzes the reaction is supplied by the dissociated lactic acid in aqueous solution. This model was tested with the data from three uncatalyzed esterification reactions. The result of this test was anomalous. The calculated rate constants were all negative which is an impossibility. There are only two explanations for such a finding - the model was incorrectly derived or the model is correctly derived but does not fit the physical situation at hand. The derivation was checked several times by the writer and no errors were encountered. This then leaves us with the alternative situation that the model is not applicable in this case. The rate constant data for the 2-1/2 order reversible reaction as a function of time is given in Table 19.

Table 19

RATE CONSTANTS FOR ESTERIFICATION REACTION
CALCULATED BY 2-1/2 ORDER REVERSIBLE MODEL

Time seconds	Rate Constant, k mole ^{1.5} /liter ^{1.5} seconds (10 ³)
1158	-.258
1158	-.258
1800	-.166
1800	-.166
2940	-.103
2940	-.103
3648	-.083
3648	-.083
4800	-.063
4800	-.063
6000	-.051
6000	-.051
7200	-.043
7200	-.043
8400	-.037
8400	-.037
11400	-.028
11400	-.028
15000	-.022
15000	-.022
30000	-.014
30000	-.014
45000	-.009
45000	-.009
60000	-.007
60000	-.007
75000	-.002
75000	-.002

Comparison of Lactic Acid Reaction Data with Other Investigations

The reader will recall that earlier in this paper reference was made to Troupe and Kobe's work on the esterification of lactic acid by methanol. It would be well here to compare the findings of their investigations with those of the writer. The equation as derived by Troupe and Kobe took the differential form

$$\frac{dx}{dt} = k (A - B - X)^2 \quad (84)$$

where X = amount of lactic acid converted in time t

t = time of reaction

k = specific rate constant

A = original lactic acid present

B = a constant which varies with the mole ratio of the reactants.

This equation implies that the reaction is a second order irreversible reaction with respect to lactic acid. This is in disagreement with the model offered by the writer in which the order is first order in lactic acid and first order in alcohol. Troupe and Kobe's equation was not derived theoretically but was empirically obtained by curve fitting methods for the data of their reaction. Using this equation as their basis, Troupe and Kobe noticed that the rate constant calculated from their equation not only varied as a function of temperature and catalyst concentration, which is to be expected, but also varied with

the mole ratio of methanol to lactic acid concentration. By definition, a rate constant is independent of the concentration of the reactants unless activities are changed. Hence, the Troupe and Kobe value can be called a pseudo rate constant.

This situation of a rate constant functionally dependent upon the mole ratio of the reaction can be readily explained for the Troupe and Kobe work. It must be remembered that the lactic acid solution used in their investigation was 85 per cent lactic acid and was composed of 35 per cent dimer and 50 per cent monomer. On a mole basis, this would be approximately 2.5 moles of monomer for each mole of dimer. With this high concentration of dimer, there is a very great possibility that two other reactions will occur and subsequently affect the esterification rate. These two reactions are (1) the esterification of dimeric acid and (2) the hydrolysis of dimeric acid.

Although Troupe and Kobe seemed to recognize that these reactions were a possibility, they also neglected to compensate for them; thus it is clear why the rate constant varies as the mole ratio since increasing or decreasing the amount of butyl alcohol added to the system will have a profound effect upon the rate of reaction, of the other simultaneously occurring reactions and upon the over-all specific rate constant which is to be observed. The activation energy for the methanol-lactic acid reaction was 14,350 calories. Although this may or may not be the

energy of activation of the elementary reaction of methanol and lactic acid, it certainly falls into the range of activation energies for esterification reactions which lie between 11,000 to 15,000 calories.

Troupe and Dimilla worked with the ethyl alcohol-lactic acid system and used the same kinetic model as their basis. They also were working in a lactic acid solution whose composition was 35 per cent dimer and 50 per cent monomer. The activation energy for the ethanol-lactic acid system was 14,920 calories. The magnitudes of the rate constant calculated by Troupe and Kobe, and Troup and Dimilla for the uncatalyzed reaction at 100°C were 7×10^{-5} liter/mole seconds and 3×10^{-5} liters/mole seconds, respectively. These figures compare favorably with the author's figure of 1.02×10^{-5} liters/mole seconds for the uncatalyzed reaction at 95°C. However, it is very difficult to compare the author's results with that of the preceding cases since the reactions studied were not under the same initial conditions.

On further inspection of the 85 per cent U. S. P. data of Troupe and Kobe, one finds that very few or no data points were taken during the early stages of the esterification. In the majority of their experimental runs no data were taken in the lactic acid conversion range of 0.0 to 30.0 per cent and in several instances, data were not taken until after 50 per cent of the initial lactic acid was converted to ester. This type of data recording can lead one to erroneous conclusions, since the best estimates of kinetic data are usually observed in the conversion range of 25 to 60 per cent.

Equilibrium and Rate Constants for the Esterification Reaction

Thus far the discussion has been centered around the forward esterification rate constant, but in order to derive a value for the forward rate constant as well as the reverse rate constant it was necessary to obtain a value for the equilibrium constant. These equilibrium constants are tabulated in Table 10. Referring to this table, it is evident that the equilibrium constant is functionally independent of temperature, catalyst concentration and mole ratio of reactants. This is to be expected if the reaction is elementary and if the heat of reaction is zero. Referring to Table 13, it is also seen that the rate constant at 80.40°C in catalyst concentrations of approximately 17 - 18 millimoles of hydrochloric acid/liter is also independent of the mole ratio of reactants in a range of 2 to 1, and 4 to 1.

Dimerization Study

It must be remembered throughout this discourse that the dimer reaction was studied only to ascertain its influence upon the esterification reaction and subsequently the dimer reaction was not completely characterized for its kinetic parameters. Thus, only approximate values for the activation energy of this reaction were obtained. The

dimer reaction rate constants at the different temperature and catalyst levels are given in Table 8. It is seen that at 80.40°C the reaction rate constant is completely characterized in its catalyst dependency while at 95.40°C and 65.40°C this was not the case. Referring to equation (59)

$$k_{\text{obs}} = k_o + k_{\text{cat}} (\text{H}^+)$$

it is seen that to truly characterize the reaction, k_o and k_{cat} , at all temperatures should be known. The necessary data were not determined at either 95.40°C or 65.40°C; however, an approximate activation energy can be estimated by comparing the rate constants at 95°C and 65.40°C to the rate constants of 80.40°C at the respective catalyst concentrations. This approximation assumes that the uncatalyzed rate constant k_o is significantly smaller than the value $k_{\text{cat}} (\text{H}^+)$ term in equation (1). Using this assumption, the activation energy as calculated from the rate constant values at the 95.40°C and 80.40°C levels was 16,200 calories while the value calculated from the 65.40°C and 80.40°C levels was 17,100 calories.

Use of Kinetic Data

As stated before, the primary concern of this paper is the determination of the kinetic parameters that control the esterification reaction of butanol and lactic acid. These parameters were determined by using an 85 per cent lactic acid solution which contained the same mole ratio of lactic acid monomer/lactic acid dimer as does a 44 per cent lactic acid solution; however, the actual engineering application of this reaction would be in a continuous flow apparatus. Therefore, it would be advisable to make a preliminary check of the kinetic parameters at these conditions to make certain that they apply.

CHAPTER V

CONCLUSIONS

1. The kinetics of the esterification reaction between monomeric lactic acid in butyl alcohol can be successfully represented by a reversible second order reaction model of the form $A + B = C + D$.
2. The kinetic parameters characterizing the reaction can be represented as

$$k_f = A e^{-E/RT} + (H^+) A' e^{-E'/RT}$$

where k_f = the forward rate constant, liter/mole second

$$E = 13,190 \text{ calories}$$

$$E' = 13,580 \text{ calories}$$

$$A = 673 \text{ liters/mole second}$$

$$A' = 547 \text{ liters}^2/\text{mole second mmole catalyst}$$

$$H^+ = \text{catalyst concentration mmole/liter}$$

In terms of transition state theory, the rate constant can be represented as

$$k_f = \frac{K^{\circ} T}{h \nu_m} e^{+\frac{\Delta S_1^*}{R} - \frac{\Delta H_1^*}{RT}} + e^{+\frac{\Delta S_2^*}{R} - \frac{\Delta H_2^*}{RT}}$$

where the standard states are the pure reactants and complex at one atmosphere pressure at the indicated temperature.

where k_f = forward rate constant, liter/mole second
 K° = Boltzmann constant $(1.3805) \cdot 10^{-16}$ erg/ $^\circ$ K molecule
 h = Planck constant $(6.6240) \cdot 10^{-27}$ erg-sec/molecule
 γ = activity coefficient of activated complex, 1.0
 v_m = average molal volume of system, .0619 liter/mole
 ΔS_1^* = - 59.8 entropy units
 ΔH_1^* = 10,480 calories
 ΔS_2^* = - 60.6 entropy units
 ΔH_2^* = 10,590 calories

3. The equilibrium constant for the esterification reaction was 3.02 and was independent of the temperature and catalyst concentration.
4. The catalyzed and uncatalyzed reaction in all probability travel the same reaction path as evidenced by their similar activation energies.
5. Dimeric acid in the range of small concentrations did not appear to react during the course of the reaction.
6. The equilibrium constant for the dimer reaction was determined to be 0.363. The kinetic parameters for the dimerization reaction were not fully determined since the main concern of this investigation was the ester reaction but an approximate value for the activation energy was found to be in the range of 16,200 calories to 17,200 calories. An approximate value for the frequency factor was found to be $3.12 (10^5)$ liter/mole second.

CHAPTER VI

RECOMMENDATIONS

1. The kinetic parameters of the esterification reaction should be used as a basis for the design of the reaction vessels and equipment for the butanol-lactic acid esterification reaction.
2. As an academic aside, kinetic investigation into the reaction of dimeric acid and butyl alcohol should also be studied.
3. Investigation should be made into the ionization of lactic acid in a butanol-water-lactic acid system to determine the ionization constant as a function of the composition of the ionizing medium. This should be done so that equation (51) can be solved. Also this investigation would readily determine if there is a free proton, supplied by the lactic acid, available for protonation of the lactic acid.
4. Work should also be done on the hydrolysis of butyl lactate in an acid medium to check on the constants of hydrolysis which can only be inferred in this work.

APPENDIX A

Table 20

DIMER REACTION RUN NO. D654

Temperature	65.40°C	Initial Dimer Concentration	
HCl Catalyst Concentration	18.4 mmoles/liter		1.012 moles/liter
Initial Lactic Acid Concentration	9.522 moles/liter	Initial Water Concentration	7.1180 moles/liter
		Equilibrium Constant	0.362

<u>Time, seconds</u>	<u>Conversion of Lactic Acid moles/liter</u>	<u>Rate Constant, k_{forward} liter/moles, second 10^6</u>
180	0.1395	11.20
450	0.2614 0.2819	8.70 9.42
792	0.4651	9.24
1200	0.6966 0.7044	9.73 9.86
1800	0.8890 0.9164	8.76 9.11
2400	1.0843 1.1289	8.55 9.05
3009	1.3419 1.3453	9.32 9.36
3900	1.5962 1.4852	9.64 8.48
4800	1.7220 1.7396	9.07 9.26
6000	1.9673 1.9317	9.89 9.42

average $k = 9.34 \pm 0.62$

Table 21

DIMER REACTION RUN NO. D800

Temperature	80.40°C	Initial Dimer Concentration	
HCl Catalyst Concentration	0.0 mmoles/liter		0.513 moles/liter
Initial Lactic Acid Concentration	10.04 moles/liter	Initial Water Concentration	9.12 moles/liter
		Equilibrium Constant	0.362

<u>Time, seconds</u>	<u>Conversion of Lactic Acid moles/liter</u>	<u>Rate Constant, k_{forward} liter/moles, second 10^6</u>
300	0.0496	1.88
600	0.1416	2.74
	0.0736	1.40
1020	0.1220	1.38
3000	0.2823	1.12
4200	0.4060	1.18
	0.3919	1.13
5400	0.7202	1.75
	0.5954	1.41
7200	0.7119	1.29
	0.7894	1.46
9000	0.9454	1.46
	1.0198	1.60
12000	1.2719	1.62
34800	2.2325	1.51
	2.2083	1.47

average $k = 1.52 \pm 0.38$

Table 22

DIMER REACTION RUN NO. D801

Temperature 65.40°C	Initial Dimer Concentration
HCl Catalyst Concentration 4.6 mmoles/liter	0.444 moles/liter
Initial Lactic Acid Concentration 10.033 moles/liter	Initial Water Concentration 9.698 moles/liter
	Equilibrium Constant 0.362

Time, seconds	Conversion of Lactic Acid moles/liter	Rate Constant, k_{forward} liter/mole, second 10^6
180	0.0737	4.68
420	0.2470	6.96
	0.2075	5.80
786	0.5351	8.58
	0.4573	7.20
1200	0.6675	7.23
	0.6018	6.42
1692	0.8541	6.88
	0.8563	6.90
2280	1.0332	6.48
	0.9816	6.07
3000	1.3252	6.92
	1.2514	6.38
3600	1.4688	6.72
	1.4332	6.47
4500	1.6327	6.37
	1.6303	6.35
5400	1.8716	6.78
	2.0018	7.79
7200	2.0769	6.34
	2.0519	6.17
9360	2.3698	7.09
	2.2806	6.25

average $k = 6.73 \pm 0.64$

Table 23

DIMER REACTION RUN NO. D802

Temperature	80.40°C	Initial Dimer Concentration	
HCl Catalyst Concentration	9.4 mmoles/liter		0.5081 moles/liter
Initial Lactic Acid Concentration	9.9088 moles/liter	Initial Water Concentration	9.1415 moles/liter
		Equilibrium Constant	0.362

Time, seconds	Conversion of Lactic Acid moles/liter	Rate Constant, k_{forward} liter/mole, second 10^6
192	0.2582	16.92
	0.2664	17.49
366	0.5691	21.00
	0.4717	17.01
600	0.6317	14.44
	0.7262	17.00
900	0.9002	14.72
	0.8977	14.67
1320	1.1411	13.67
	1.1110	13.18
1800	1.3903	13.30
	1.4679	14.46
2400	1.7323	14.35
	1.7321	14.35
3045	1.9037	13.61
	1.9083	13.67
3900	2.1159	13.60
4800	2.2262	12.78
6000	2.3718	12.88
	2.4098	13.87

average $k = 14.85 \pm 0.20$

Table 24

DIMER REACTION RUN NO. D804

Temperature 80.40°C	Initial Dimer Concentration
HCl Catalyst Concentration 18.6 mmoles/liter	0.390 moles/liter
Initial Lactic Acid Concentration 10.14 moles/liter	Initial Water Concentration 9.52 moles/liter
	Equilibrium Constant 0.362

<u>Time, seconds</u>	<u>Conversion of Lactic Acid moles/liter</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
120	0.3854	37.40
	0.3669	35.53
240	0.6083	31.02
	0.6195	31.67
480	1.0796	30.90
	1.1950	35.35
780	1.2971	24.45
	1.3381	25.43
1200	1.7486	24.98
	1.7304	24.54
1800	2.0915	23.43
	2.1491	24.89
2400	2.3634	23.84
	2.3118	22.39
3600	2.7535	35.61
	2.7106	29.75

average $k = 29.23 \pm 5.15$

Table 25

DIMER REACTION RUN NO. 951

Temperature 95.40°C	Initial Dimer Concentration
HCl Catalyst Concentration 9.20 mmoles/liter	0.558 moles/liter
Initial Lactic Acid Concentration 9.979 moles/liter	Initial Water Concentration 8.925 moles/liter
	Equilibrium Constant 0.362

<u>Time, seconds</u>	<u>Conversion of Lactic Acid moles/liter</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
123	0.5394	57.19
	0.2187	21.62
240	0.9043	53.82
	0.9597	57.98
483	1.1582	36.83
	1.2884	42.70
780	1.5911	36.44
	1.5998	36.76
1209	2.0426	37.69
	2.1129	40.81
1800	2.2945	34.37
	2.2937	34.33
2445	2.3903	29.13
	2.4387	31.60
3000	2.5627	33.89
	2.5815	35.93
3900	2.5775	27.27
	2.6032	29.92
4926	2.6654	40.46
	2.7237	25.20
6150	2.6721	38.02
	2.6693	40.12

average $k = 38.19 \pm 2.90$

APPENDIX B

Table 26

ESTERIFICATION REACTION RUN NO. E650

Temperature 65.40°C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration	0.031 moles/kg
0.0 mmoles/liter	Initial Water Conc. 2.537 moles/kg
Initial Lactic Acid Monomer	Initial Dimer Conc. 0.196 moles/kg
Concentration 3.185 moles/kg	Equilibrium Constant 3.02
Initial Butyl Alcohol Concentration	
8.546 moles/kg	

<u>Time, seconds</u>	<u>Conversion of Lactic Acid moles/kg</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
900	0.379	1.79
3000	0.1870	2.74
	0.1653	2.41
4230	0.2168	2.27
	0.1969	2.05
5400	0.2515	2.08
	0.2671	2.22
7200	0.3232	2.04
	0.3372	2.14
9000	0.3856	1.98
	0.4042	2.09
11040	0.4491	1.91
13530	0.5226	1.85
16620	0.6250	1.86
	0.6118	1.81
20820	0.7338	1.80
	0.7450	1.83

average $k = 2.05 \pm 0.253$

Table 27

ESTERIFICATION REACTION RUN NO. E651

Temperature 65.40°C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration 13.42 mmoles/liter	0.103 moles/kg
Initial Lactic Acid Monomer Conc. 2.826 moles/kg	Initial Water Concentration
Initial Butyl Alcohol Concentration 8.584 moles/kg	4.100 moles/kg
	Initial Dimer Concentration
	0.175 moles/kg
	Equilibrium Constant 3.02

<u>Time, seconds</u>	<u>Conversion of Lactic Acid moles/kg</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
312	0.0704	10.98
	0.0812	12.71
648	0.1618	12.47
	0.1888	14.66
900	0.2635	15.05
	0.2457	13.97
1500	0.4338	15.26
	0.4005	14.31
2100	0.5387	14.38
	0.5708	15.40
3480	0.8017	14.19
	0.8291	14.83
4800	1.0062	14.05
	1.0329	14.59
7200	1.2580	13.24
	1.2893	13.80
18600	1.8273	11.67
	1.8386	11.90

average $k = 13.73 \pm 1.28$

Table 28

ESTERIFICATION REACTION RUN NO. E652

Temperature 65.40°C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration 12.90 mmoles/liter	0.120 moles/kg
Initial Lactic Acid Monomer Conc. 4.030 moles/kg	Initial Water Concentration
Initial Butyl Alcohol Concentration 6.954 moles/kg	3.909 moles/kg
	Initial Dimer Concentration
	0.228 moles/kg
	Equilibrium Constant 3.02

<u>Time, seconds</u>	<u>-Conversion of Lactic Acid moles/kg</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
300	0.0758	10.45
552	0.1626 0.1703	— 13.05
900	0.2855 0.2855	13.78 13.78
1500	0.4831 0.4832	14.70 14.71
2100	0.6480 0.6435	14.72 14.60
2712	0.7904 0.7802	14.48 14.25
3600	0.9832 0.9880	14.39 14.48
4800	1.1932 1.1967	14.05 14.11
6600	1.4453 1.4549	13.62 13.77
8520	1.6549	13.25
8478	1.6625	13.43
12018	1.9349 1.9426	12.77 12.89

average $k = 13.75 \pm 1.02$

Table 29

ESTERIFICATION REACTION RUN NO. E653

Temperature 65.40°C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration	0.083 moles/kg
15.60 mmoles/liter	Initial Water Concentration
Initial Lactic Acid Monomer Conc.	8.147 moles/kg
3.463 moles/kg	Initial Dimer Concentration
Initial Butyl Alcohol Concentration	0.172 moles/kg
6.762 moles/kg	Equilibrium Constant 3.02

<u>Time, seconds</u>	<u>Conversion of Lactic Acid moles/kg</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
126	0.0474	18.34
	0.0407	15.73
264	0.0895	16.72
	0.0998	18.69
486	0.1804	18.79
	0.1588	16.44
780	0.2716	18.13
	0.2712	18.10
1200	0.4028	18.24
	0.3999	18.09
1800	0.5612	17.90
	0.5576	17.76
2415	0.6911	17.25
	0.6968	17.43
3300	0.8662	17.01
	0.8611	16.88
4200	1.0103	16.67
	1.0087	16.63
5640	1.1918	16.11
	1.2008	16.32

average $k = 17.36 \pm 0.920$

Table 30

ESTERIFICATION REACTION RUN NO. E800

Temperature 80.40°C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration	0.073 moles/kg
0.0 mmoles/liter	Initial Water Concentration
Initial Lactic Acid Monomer Conc.	4.537 moles/kg
3.175 moles/kg	Initial Dimer Concentration
Initial Butyl Alcohol Concentration	0.226 moles/kg
7.990 moles/kg	Equilibrium Constant 3.02

<u>Time, seconds</u>	<u>Conversion of Lactic Acid moles/kg</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
1158	0.1008	3.96
	0.0936	3.67
1800	0.1639	4.21
	0.1618	4.15
2940	0.2487	4.17
	0.2572	4.15
3648	0.3388	4.51
	0.3342	4.42
4800	0.4217	4.36
	0.4282	4.44
6000	0.5136	4.37
	0.5073	4.31
7200	0.5691	4.11
	0.5860	4.25
8400	0.6268	3.95
	0.6654	4.25
11400	0.8208	4.07
	0.8208	4.07
15000	0.9835	3.94
15000	0.9549	3.78

average $k = 4.15 \pm 0.22$

Table 31

ESTERIFICATION REACTION RUN NO. E801

Temperature 80.40°C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration	0.120 moles/kg
3.53 mmoles/liter	Initial Water Concentration
Initial Lactic Acid Monomer Conc.	4.72 moles/kg
3.269 moles/kg	Initial Dimer Concentration
Initial Butyl Alcohol Concentration	0.205 moles/kg
7.702 moles/kg	Equilibrium Constant 3.02

Time, seconds	Conversion of Lactic Acid moles/kg	Rate Constant, k_{forward} liter/mole, second 10^6
420	0.0988	11.04
	0.1103	12.36
720	0.2044	13.70
	0.1989	13.31
1230	0.3302	13.41
	0.3385	13.78
1830	0.4643	13.18
	0.4770	13.18
2400	0.5926	13.35
	0.5898	13.28
3030	0.7164	13.32
	0.7163	13.31
3672	0.8344	13.34
	0.8422	13.50
4320	0.9153	12.81
	0.9339	13.17
5400	1.0639	12.64
	1.0694	12.73
7215	1.2604	12.23
	1.2570	12.18
12000	1.5944	11.20
	1.6062	11.37
21900	1.9436	10.11
	1.9412	10.07

average $k = 12.75 \pm 0.965$

Table 32

ESTERIFICATION REACTION RUN NO. E802

Temperature 80.40°C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration	0.173 moles/kg
10.23 mmoles/liter	Initial Water Concentration
Initial Lactic Acid Monomer Conc.	5.085 moles/kg
3.740 moles/kg	Initial Dimer Concentration
Initial Butyl Alcohol Concentration	0.200 moles/kg
6.958 moles/kg	Equilibrium Constant 3.02

<u>Time, seconds</u>	<u>Conversion of Lactic Acid moles/kg</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
120	0.0531	19.35
	— 0.0685	25.05
255	0.1425	24.97
	0.1560	27.44
480	0.2738	26.38
	0.2842	27.45
780	0.4576	28.54
	0.4583	28.59
1260	0.6830	28.22
	0.6717	27.65
1812	0.8905	27.41
	0.8627	26.30
2700	1.1866	27.43
	1.1745	27.02
3600	1.3666	25.67
	1.3844	26.22
5415	1.6786	24.85
	1.6847	25.03
7335	1.8910	24.12
	1.8977	24.34

average $k = 26.095 \pm 2.13$

Table 33

ESTERIFICATION REACTION RUN NO. E803

Temperature 80.40°C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration 2.0 mmoles/liter	0.180 moles/kg
Initial Lactic Acid Monomer Conc. 4.096 moles/kg	Initial Water Concentration
Initial Butyl Alcohol Concentration 7.893 moles/kg	4.206 moles/kg
	Initial Dimer Concentration
	0.204 moles/kg
	Equilibrium Constant 3.02

<u>Time, second</u>	<u>Conversion of Lactic Acid moles/kg</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
132	0.0876	25.07
	0.0849	24.28
249	0.1827	28.29
	0.1909	29.61
489	0.4055	33.64
	0.3938	32.57
786	0.6070	32.92
	0.6065	32.89
1215	0.8690	32.70
	0.8770	33.07
1800	1.1514	31.82
	1.1519	31.84
2400	1.3776	30.82
	1.3698	30.56
3315	1.6425	29.50
	1.6420	29.48
4200	1.8615	29.17
	1.8546	28.97
5700	2.0626	26.61
	2.0666	26.72

average $k = 30.03 \pm 2.74$

Table 34

ESTERIFICATION REACTION RUN NO. E804

Temperature 80.40°C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration	0.012 moles/kg
13.00 mmoles/liter	Initial Water Concentration
Initial Lactic Acid Monomer Conc.	10.681 moles/kg
4.331 moles/kg	Initial Dimer Concentration
Initial Butyl Alcohol Concentration	0.210 moles/kg
4.620 moles/kg	Equilibrium Constant 3.02

<u>Time, seconds</u>	<u>Conversion of Lactic Acid moles/kg</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
120	0.0667	30.25
285	0.1597	31.42
	0.1733	34.25
393	0.2308	33.73
	0.2221	32.36
600	0.3477	34.73
	0.3113	30.68
900	0.4242	29.08
	0.4378	30.17
1500	0.6491	29.33
	0.6510	29.44
2400	0.9042	29.00
3660	1.1491	28.20
	1.1494	28.21
5700	1.4346	29.31
	1.4063	27.81
9900	1.6951	33.64
	1.7010	34.62

average $k = 30.88 \pm 2.39$

Table 35

ESTERIFICATION REACTION RUN NO. E805

Temperature 80.40°C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration 17.17 mmoles/liter	0.160 moles/kg
Initial Lactic Acid Monomer Conc. 3.486 moles/kg	Initial Water Concentration
Initial Butyl Alcohol Concentration 7.191 moles/kg	5.084 moles/kg
	Initial Dimer Concentration
	0.153 moles/kg
	Equilibrium Constant 3.02

<u>Time, second</u>	<u>Conversion of Lactic Acid moles/kg</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
243	0.2064	40.43
	0.2003	39.16
480	0.4107	43.13
780	0.6157	42.36
1212	0.8835	42.89
	0.8844	42.95
1800	1.1610	42.41
	1.1617	42.45
2400	1.3701	41.45
	1.2253	34.55
3300	1.5967	40.02
	1.6004	40.21
4980	1.8588	37.81
	1.8577	37.74

average $k = 40.53 \pm 2.51$

Table 36

ESTERIFICATION REACTION RUN NO. E806

Temperature 80.40 °C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration	0.043 moles/kg
8.50 mmoles/liter	Initial Water Concentration
Initial Lactic Acid Monomer Conc.	4.868 moles/kg
2.109 moles/kg	Initial Dimer Concentration
Initial Butyl Alcohol Concentration	0.152 moles/kg
9.365 moles/kg	Equilibrium Constant 3.02

<u>Time, seconds</u>	<u>Conversion of Lactic Acid moles/kg</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
66	0.0329	30.60
	0.0329	30.67
144	0.0846	36.72
126	0.0846	41.97
	0.0573	28.16
243	0.1444	37.95
	0.1506	39.65
486	0.2996	41.70
	0.2996	41.70
780	0.4534	41.89
	0.4462	41.08
1200	0.6353	41.47
	0.6203	40.20
1806	0.8374	40.48
	0.8286	39.85
2400	0.9832	39.24
	0.9715	38.46
3600	1.1877	37.17
	1.1857	37.04
5400	1.3684	34.96
	1.3871	36.39
7470	1.4593	31.22
	1.4619	31.43

average $k = 37.38 \pm 4.26$

Table 37

ESTERIFICATION REACTION RUN NO. E950

Temperature 95.40°C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration 0.0 mmoles/liter	0.100 moles/kg
Initial Lactic Acid Monomer Conc. 3.187 moles/kg	Initial Water Concentration
Initial Butyl Alcohol Concentration 8.211 moles/kg	3.532 moles/kg
	Initial Dimer Concentration
	0.215 moles/kg
	Equilibrium Constant 3.02

<u>Time, seconds</u>	<u>Conversion of Lactic Acid moles/kg</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
600	0.1386	10.97
	0.1369	10.83
1200	0.2722	11.15
	0.2788	11.44
1800	0.3489	9.72
	0.3903	11.01
2700	0.5438	10.68
3600	0.6853	10.55
	0.6787	10.42
4800	0.8330	10.09
6300	0.9867	9.62
9600	1.1381	7.72
	1.1378	7.71

average $k = 10.24 \pm 1.33$

Table 38

ESTERIFICATION REACTION RUN NO. E951

Temperature 95.40°C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration	0.221 moles/kg
9.05 mmoles/liter	Initial Water Concentration
Initial Lactic Acid Monomer Conc.	3.994 moles/kg
3.762 moles/kg	Initial Dimer Concentration
Initial Butyl Alcohol Concentration	0.170 moles/kg
7.189 moles/kg	Equilibrium Constant 3.02

Time, seconds	Conversion of Lactic Acid moles/kg	Rate Constant, k_{forward} liter/mole, second 10^6
129	0.1479	50.21
	0.1261	42.59
246	0.3090	57.25
	0.3163	58.73
483	0.5989	61.13
	0.6177	63.39
780	0.9033	62.66
	0.8913	61.59
1200	1.1985	59.99
	1.2167	61.33
1800	1.5310	58.91
	1.5310	58.91
2400	1.7513	56.81
	1.7375	55.91
3300	1.9773	54.30
	1.9791	54.42
4200	2.1200	51.81
	2.1289	52.49
5400	2.2274	47.75
	2.2518	49.86
7200	2.3679	48.04
	2.3729	48.68

average $k = 54.85 \pm 2.34$

Table 39

ESTERIFICATION REACTION RUN NO. E952

Temperature 95.40°C	Initial Butyl Lactate Concentration
HCl Catalyst Concentration	0.283 moles/kg
4.50 mmoles/liter	Initial Water Concentration
Initial Lactic Acid Monomer Conc.	8.034 moles/kg
3.371 moles/kg	Initial Dimer Concentration
Initial Butyl Alcohol Concentration	0.134 moles/kg
6.658 moles/kg	Equilibrium Constant 3.02

<u>Time, seconds</u>	<u>Conversion of Lactic Acid moles/kg</u>	<u>Rate Constant, k_{forward} liter/mole, second 10^6</u>
480	0.2451	28.12
	0.2554	29.40
780	0.4455	33.71
	0.4294	32.31
1200	0.6618	35.41
	0.6471	34.42
1800	0.9026	35.91
	0.9018	35.87
2400	1.0868	35.80
	1.1047	36.78
3300	1.2535	33.41
	1.2963	35.63
4200	1.4162	33.71
	1.4372	34.87
6180	1.6275	33.32
	1.6266	33.26
11580	1.7802	26.44
	1.8544	39.73
18120	1.8700	31.99
	1.8642	28.64

average $k = 33.89 \pm 3.07$

APPENDIX C

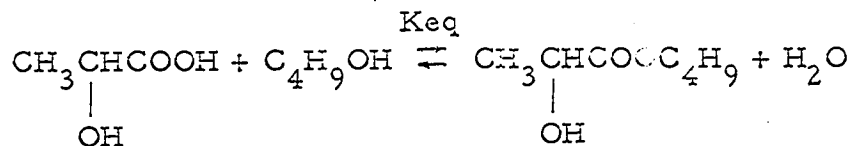
Solution for 2 1/2-Order Reversible Reaction

$$\frac{Vdx}{dt} = k_1(F_o - X)(A_o - X)(F_o - X)^{\frac{1}{2}} - k_2(E_o + X)(W_o + X)(F_o - X)^{\frac{1}{2}} \quad (1)$$

Divide through by k_1 ,

$$\frac{Vdx}{dt} = (F_o - X)^{\frac{1}{2}} \left[(F_o - X)(A_o - X) - \frac{1}{K_{eq}} (E_o + X)(W_o + X) \right] \quad (2)$$

where $K_{eq} = \frac{k_1}{k_2}$ and is the equilibrium constant of the reaction



separating variables

$$\int_0^X \frac{dX}{(F_o - X)^{\frac{1}{2}} \left[(F_o - X)(A_o - X) - \frac{1}{K_{eq}} (E_o + X)(W_o + X) \right]} = \int_0^t \frac{k_1 dt}{V} \quad (3)$$

From here on we shall concern ourselves with the integration of the left hand member of equation (3).

Multiplying parentheses and grouping

$$\int_0^X \frac{dX}{(F_o - X)^{\frac{1}{2}} \left[(F_o A_o - \frac{1}{K_{eq}} E_o W_o) + X(-A_o - F_o - \frac{E_o}{K_{eq}} - \frac{W_o}{K_{eq}}) + X^2(1 - \frac{1}{K_{eq}}) \right]} \quad (4)$$

let

$$(F_o A_o - \frac{1}{K_{eq}} E_o W_o) = C \quad (5)$$

$$\left(-A_o - F_o - \frac{E_o}{K_{eq}} - \frac{W_o}{K_{eq}}\right) = B \tag{6}$$

$$\left(1 - \frac{1}{K_{eq}}\right) = R \tag{7}$$

$$\int_0^X \frac{dX}{(F_o - X)^{\frac{1}{2}} [R X^2 + B X + C]} \tag{8}$$

Let $Z^2 = (F_o - X)$, $X = (F_o - Z^2)$, $2ZdZ = -dX$

Substituting in (8)

$$\int_0^X \frac{-2ZdZ}{Z[R(F_o - Z^2)^2 + B(F_o - Z^2) + C]} \tag{9}$$

Multiplying parentheses and grouping like terms,

$$-2 \int \frac{dZ}{R Z^4 + (-2R F_o - B)Z^2 + (C + R F_o^2 + B F_o)} \tag{10}$$

Let $(C + R F_o^2 + B F_o) = L$ (11)

$(-2R F_o - B) = J$ (12)

Then

$$-2 \int \frac{dZ}{R Z^4 + J Z^2 + L} \tag{13}$$

Dividing the numerator and denominator by R, and adding and subtracting $1/4 (J/R)^2$ in order to complete the square, equation (13)

becomes

$$-\frac{2}{A} \int \frac{dZ}{(-Z^4 + \frac{J}{R} Z^2 + \frac{1}{4}(\frac{J}{R})^2) + \frac{L}{R} - \frac{1}{4}(\frac{J}{R})^2} \quad (14)$$

$$-\frac{2}{A} \int \frac{dZ}{(Z^2 + \frac{J}{2R})^2 + (\frac{L}{R} - \frac{1}{4}(\frac{J}{R})^2)} \quad (15)$$

Let $-(\frac{L}{R} - \frac{1}{4}(\frac{J}{R})^2) = M^2$,

then $-\frac{2}{R} \int \frac{dZ}{[(Z^2 + \frac{J}{2R})^2 - M^2]} \quad (16)$

Factoring the denominator

$$-\frac{2}{R} \int \frac{dZ}{[(Z^2 + \frac{J}{2R}) + M][(Z^2 + \frac{J}{2R}) - M]} \quad (17)$$

let $N = (\frac{J}{2R}) + M$, and $P = (\frac{J}{2R}) - M$

$$-\frac{2}{R} \int \frac{dZ}{(Z^2 + N)(Z^2 + P)} \quad (18)$$

Equation (18) can now be integrated by the method of partial fractions where

$$\frac{1}{(Z^2 + N)(Z^2 + P)} \equiv \frac{S Z + G}{(Z^2 + N)} + \frac{Q Z + D}{(Z^2 + P)} \quad (19)$$

Solving equation (19) for the values of S, G, Q and D, it is found that

$$S = Q = 0, \text{ and } D = \frac{1}{N - P}, \text{ } G = -\frac{1}{N - P} .$$

□

Equation (18) can now be written as

$$-\frac{2}{R} \int \frac{dZ}{(N-P)(Z^2+N)} - \frac{2}{R} \int \frac{dZ}{(N-P)(Z^2+P)} \quad (20)$$

The integral of equation (20) is

$$\left(-\frac{2}{R}\right)\left(\frac{1}{N-P}\right) \frac{1}{2\sqrt{-N}} \log \frac{N+Z\sqrt{-N}}{N-Z\sqrt{-N}} - \frac{1}{2\sqrt{-P}} \log \frac{P+Z\sqrt{-P}}{P-Z\sqrt{-P}} \quad (21)$$

but $Z = \sqrt{F_o} - X$.

$$-\frac{2}{R} \left(\frac{1}{N-P}\right) \frac{1}{2\sqrt{-N}} \log \frac{N+\sqrt{F_o}-X\sqrt{-N}}{N-\sqrt{F_o}-X\sqrt{-N}} - \frac{1}{2\sqrt{-P}} \log \frac{P+\sqrt{F_o}-X\sqrt{-P}}{P-\sqrt{F_o}-X\sqrt{-P}} \Big|_0^X = \frac{k_1 t}{V} \quad (22)$$

The final form of equation (22) between the limits of zero and X is

$$k_1 t = -A \left(\frac{V}{N-P}\right) \frac{1}{\sqrt{-N}} \ln \frac{N+\sqrt{(F_o-X)}\sqrt{-N}}{N-\sqrt{(F_o-X)}\sqrt{-N}} - \frac{1}{\sqrt{-P}} \ln \frac{P+\sqrt{F_o-X}\sqrt{-P}}{P-\sqrt{F_o-X}\sqrt{-P}} \\ - A \left(\frac{V}{N-P}\right) \frac{1}{\sqrt{-N}} \ln \frac{N+\sqrt{F_o}\sqrt{-N}}{N-\sqrt{F_o}\sqrt{-N}} - \frac{1}{\sqrt{-P}} \ln \frac{P+\sqrt{F_o}\sqrt{-P}}{P-\sqrt{F_o}\sqrt{-P}} \quad (23)$$

where $P = \frac{J}{2R} - M$

$$N = \frac{J}{2R} + M$$

$$J = (-2R F_o - B)$$

$$R = \left(1 - \frac{1}{Keq}\right)$$

$$B = \left(-A_o - F_o - \frac{E_o}{Keq} - \frac{W_o}{Keq}\right)$$

--

$$M = \frac{L}{R} - \frac{1}{4} \left(\frac{J}{R}\right)^2$$

$$L = (C + R F_o^2 + B F_o)$$

$$C = [F_o A_o - \frac{1}{K_{eq}} (E_o W_o)]$$

V = volume per unit mass.

Table 40

EXPERIMENTAL DESIGN FOR DENSITY EXPERIMENTS

Run No.	Response Density gr/ml. Y	Mole Ratio Alcohol to Acid X ₁		Temperature °C X ₂		Conversion X ₃		Initial Ratio, Weight Lactic Acid/Water X ₄	
		coded	uncoded	coded	uncoded	coded	uncoded	coded	uncoded
1	0.9206	- 1	2.0	- 1	45.0	- 1	25	- 1	3.0
2	0.8696	+ 1	4.0	- 1	45.0	- 1	25	- 1	3.0
3	0.8864	- 1	2.0	+ 1	85.0	- 1	25	- 1	3.0
4	0.9173	- 1	2.0	- 1	45.0	+ 1	75	- 1	3.0
5	0.9174	- 1	2.0	- 1	45.0	- 1	25	+ 1	4.0
6	0.8655	+ 1	4.0	+ 1	85.0	+ 1	75	+ 1	4.0
7	0.9153	- 1	2.0	+ 1	85.0	+ 1	75	+ 1	4.0
8	0.8328	+ 1	4.0	- 1	45.0	+ 1	75	+ 1	4.0
9	0.8416	+ 1	4.0	+ 1	85.0	- 1	25	+ 1	4.0
10	0.8357	+ 1	4.0	+ 1	85.0	+ 1	75	- 1	3.0
11	0.8368	+ 1	4.0	+ 1	85.0	- 1	25	- 1	3.0
12	0.8685	+ 1	4.0	- 1	45.0	+ 1	75	- 1	3.0
13	0.8745	+ 1	4.0	- 1	45.0	- 1	25	+ 1	4.0
14	0.8841	- 1	2.0	+ 1	85.0	- 1	25	+ 1	4.0
15	0.8824	- 1	2.0	- 1	45.0	+ 1	75	+ 1	4.0
16	0.8834	- 1	2.0	+ 1	85.0	+ 1	75	- 1	3.0
17	0.9623	- 2	1.0	0	65.0	0	50	0	3.5
18	0.8377	+ 2	5.0	0	65.0	0	50	0	3.5
19	0.9040	0	3.0	- 2	105.0	0	50	0	3.5
20	0.8463	0	3.0	+ 2	25.0	0	50	0	3.5
21	0.8721	0	3.0	0	65.0	- 2	0	0	3.5
22	0.8686	0	3.0	0	65.0	+ 2	100	0	3.5
23	0.8774	0	3.0	0	65.0	0	50	- 2	2.5
24	0.8692	0	3.0	0	65.0	0	50	0	4.5
25	0.8712	0	3.0	0	65.0	0	50	0	3.5
26	0.8697	0	3.0	0	65.0	0	50	0	3.5
27	0.8685	0	3.0	0	65.0	0	50	0	3.5
28	0.8693	0	3.0	0	65.0	0	50	0	3.5
29	0.8682	0	3.0	0	65.0	0	50	0	3.5
30	0.8684	0	3.0	0	65.0	0	50	0	3.5

APPENDIX D

COMPUTER PROGRAM
ESTERIFICATION REACTION
USING SEVEN MECHANISMS

```

20  READ, X, Y, V, K, SP, N
    READ, DI, HI, EI, ALI, FI, CK
    DO 10 I=1, K
    READ, A, B, C, W, TR
    T=60.*TR
    F=((A-W*V)*X)/W-DI
    E=(B*X-C*Y)/W-DI
    XX=FI-F
    VL=1000./SP
    S=(CK*ALI*FI)-(EI*HI)
    Z=(-CK*ALI)-(CK*FI)-EI-HI
    CC=CK-1.0
    Q=(4.*S*CC)-(Z*Z)
    TT=((2.*CC*XX)+Z-SQRT(-Q))*(Z+SQRT(-Q))
    BB=((2.*CC*XX)+Z+SQRT(-Q))*(Z-SQRT(-Q))
    AA=TT/BB
    RK=((VL*CK)/(T*SQRT(-Q)))*LOG(AA)
    G=(FI*(ALI-XX))/(ALI*(FI-XX))
    RKK=(VL/(T*(ALI-FI)))*LOG(G)
    RKF=(1./T)*LOG(FI/(FI-XX))
    RKA=(1./T)*LOG(ALI/(ALI-XX))
    EE=(FI*(ALI-.5*XX))/(ALI*(FI-XX))
    CCC=XX/(FI*(FI-XX))
    DD=(1./(FI-2.*ALI))*LOG(EE)
    RKKK=(VL*VL/(T*(ALI-.5*FI)))*LOG(CCC+DD)
    SS=(VL*CK*FI)-(HI*EI)
    ZZ=-VL*CK-HI-EI
    WW=-1.
    QQ=(4.*SS*WW)-(ZZ*ZZ)
    TTT=((2.*WW*XX)+ZZ-SQRT(-QQ))*(ZZ+SQRT(-QQ))
    BBB=((2.*WW*XX)+ZZ+SQRT(-QQ))*(ZZ-SQRT(-QQ))
    AAA=TTT/BBB
    RKRK=((VL*CK)/(T*SQRT(-QQ)))*LOG(AAA)
    GG=(CK*FI*FI)-(HI*EI)
    HH=(-2.*CK*FI)-.5*(HI+EI)
    FF=CK-.25
    QQQ=(4.*GG*FF)-(HH*HH)
    GGG=((2.*FF*XX)+HH-SQRT(-QQQ))*(HH+SQRT(-QQQ))
    HHH=((2.*FF*XX)+HH+SQRT(-QQQ))*(HH-SQRT(-QQQ))
    FFF=LOG(GGG/HHH)
    RKKF=((VL*CK)/(T*SQRT(-QQQ)))*LOG(FFF)
    PUNCH 1, RKF, RKA, RKK, RKKK, RK, RKRK, RKKF, T
1  FORMAT(3F9.6, 1X, F9.2, 3F9.6, 1X, F7.0)
10  CONTINUE
    GO TO 20
    END

```

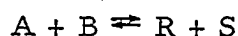
Table 41NOMENCLATURE FOR ESTERIFICATION REACTION,
SEVEN MECHANISMS, COMPUTER PROGRAMS

X	=	Molarity of sodium hydroxide
Y	=	Molarity of hydrochloric acid
V	=	Correction factor for catalyst concentration
K	=	Number of computation
SP	=	Density of reacting system
N	=	Record mark
DI	=	Initial dimer concentration
HI	=	Initial water concentration
EI	=	Initial ester concentration
ALI	=	Initial alcohol concentration
FI	=	Initial monomer concentration
CK	=	Equilibrium constant
A	=	Ml. NaOH first titrated
B	=	Ml. NaOH excess
C	=	Ml. HCl backtitrated
W	=	Weight of sample
T	=	Time, minutes
F	=	Monomer concentration at time T
E	=	Ester concentration at time T

Table 41 continued

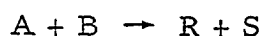
VL = Volume of reacting system

S, Z, CC, Q, TT, BB, AA = Dummy variables for solution of
second order reversible reaction

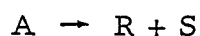


RK = Forward rate constant for second order reversible reaction

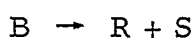
RKK = Forward rate constant for irreversible second order
reaction



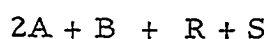
RKF = Rate constant for irreversible reaction, first order in
lactic acid



RKA = Rate constant for irreversible reaction, first order in butyl
alcohol

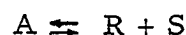


EE, CCC, DD = Dummy variables for solution of third order
irreversible reaction



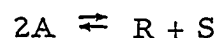
RKKK = Rate constant for third irreversible reaction

SS, ZZ, WW, QQ, TTT, BBB, AAA = Dummy variables for
reversible reaction first order
in lactic acid



RKRRK = Rate constant for first order reversible reaction

GG, HH, FF, QQQ, GGG, HHH, FFF = Dummy variables for solution
of reversible reaction second
order in lactic acid



RKKF = Forward rate constant for second order reversible reaction
in lactic acid.

COMPUTER PROGRAM
DIMERIZATION REACTION

```

READ, FI, DI, HI
20 READ, X, Y, P, V, K, N
   READ, AI, BI, CI, WI, TI
   DI = ((BI*X - CI*Y)*P)/WI
   FI = (((AI - BI)*X) + CI*Y)*P)/WI
   DXI = ((BI*X - CI*Y)*0.162)/WI
   FXI = (((AI - BI)*X) + CI*Y)*0.090)/WI
   HXI = (1.0 - FXI - DXI)
   HI = ((HXI/18.)*P)*1000.
   DO 10 I=1, K
   READ, A, B, C, W, T
   TT = T*60.
   D = ((B*X - C*Y)*P)/W
   F = (((A - B - W*V)*X) + C*Y)*P)/W
   DX = ((B*X - C*Y)*0.162)/W
   FX = (((A - B - W*V)*X) + C*Y)*0.090)/W
   HX = (1.0 - FX - DX)
   H = ((HX/18.)*P)*1000.
   CK = .365
   XX = FI - F
   AA = (CK*FI*FI) - (DI*HI)
   BB = -(2.*CK*FI) - (DI/2.) - (HI/2.)
   CC = CK - .25
   Q = (4.*AA*CC) - (BB*BB)
   S = ((2.*CC*XX) + BB - SQRT(-Q))*(BB + SQRT(-Q))
   Z = ((2.*CC*XX) + BB + SQRT(-Q))*(BB - SQRT(-Q))
   E = S/Z
   RK = (CK/(TT*SQRT(-Q)))*LOG(E)
   PUNCH 3, D, H, F, XX, RK, TT, N
3   FORMAT( 4X, 4F9.4, 2X F12.10, 3X F9.0, 3X 14)
10  CONTINUE
   GO TO 20
   END

```


Table 42

NOMENCLATURE FOR DIMERIZATION REACTION
COMPUTER PROGRAM

FI	=	Initial mono lactic acid, moles/kg
DI	=	Initial dimer, moles/kg
HI	=	Initial water, moles/kg
X	=	Molarity of sodium hydroxide, moles/liter
Y	=	Molarity of hydrochloric acid, moles/liter
P	=	Density of reaction system, liter/kg
V	=	Concentration of acid catalyst expressed as mls of sodium hydroxide per gram of sample
AI	=	Mls. of sodium hydroxide titrated
BI	=	Mls. of sodium hydroxide backtitrated
CI	=	Mls. of hydrochloric acid titrated
WI	=	Weight of sample, gms
TI	=	Reaction time, minutes
K	=	Number of calculations to be done
N	=	Record mark
DXI	=	Weight per cent of dimer
FXI	=	Weight per cent of monomer
HXI	=	Weight per cent of water
T	=	Time of reaction, minutes
D	=	Dimer concentration, moles/liter at time T

Table 42 continued

F	=	Monomer concentration, moles/liter at time T
H	=	Water concentration, moles/liter at time T
DX	=	Weight per cent dimer
FX	=	Weight per cent monomer
HX	=	Weight per cent water
CK	=	Equilibrium constant for dimer reaction
XX	=	Molar concersion of lactic acid
AA, BB, CC, Q, S, Z and E	=	dummy variables for the solution of the integrated equation for the reversible reaction
		$2A \rightleftharpoons R + S$
RK	=	Rate constant, liter/mole second.

COMPUTER PROGRAM
ESTERIFICATION REACTION
2 1/2 ORDER MODEL

```

READ,DI,HI,EI,ALI,FI,CK
PUNCH 2
20 READ,X,Y,V,K,SP,N
DO 10 I=1,K
READ,A,B,C,W,TR
T=60.*TR
F=((A-W*V)*X)/W-DI
E=(B*X-C*Y)/W-DI
XX=FI-F
VL=1000./SP
S=(CK*ALI*FI)-(EI*HI)
Z=(-CK*ALI)-(CK*FI)-EI-HI
CC=CK-1.0
Q=(4.*S*CC)-(Z*Z)
TT=((2.*CC*XX)+Z-SQRT(-Q))*(Z+SQRT(-Q))
BB=((2.*CC*XX)+Z+SQRT(-Q))*(Z-SQRT(-Q))
AA=TT/BB
PK=((VL*CK)/(T*SQRT(-Q)))*LOG(AA)
AAA=1.0-1.0/CK
BBB=-ALI-FI-(EI+HI)/CK
CJ=-2.0*AAA*FI-BBB
CCC=FI*ALI-EI*HI/CK
AK=CCC+(AAA*FI+BBB)*FI
CM=SQRT(AK/AAA-0.25*(CJ/AAA)**2)
CN=CJ/(2.0*AAA)+CM
P=CN-2.0*CM
PP=SQRT(-P)
CCN=SQRT(-CN)
FX=SQRT(FI-XX)
FFI=SQRT(FI)
G=-VL/(AAA*T*(CN-P))
GA=(CN+F*CCN)/(CN-FX*CCN)
GB=(P+FX*PP)/(P-FX*PP)
GC=(CN+FFI*CCN)/(CN-FFI*CCN)
GD=(P+FFI*PP)/(P-FFI*PP)
RKK=G*(LOG(GA)/CCN-LOG(GB)/PP-LOG(GC)/CCN-LOG(GD)/PP)
PUNCH 1,XX,E,F,RK,RKK,T,N
10 CONTINUE
GO TO 20
1 FORMAT(3F10.4,3X,2F12.10,2X,F6.0,2X,I4)
2 FORMAT(5X,2HXX,9X,1HE,9X,1HF,10X,2HRK,10X,3HRKK,10X,1HT,6X,1HN)
END

```

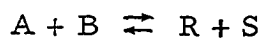
Table 43NOMENCLATURE FOR 2-1/2 ORDER REVERSIBLE
REACTION, COMPUTER PROGRAM

X	=	Molarity of NaOH
Y	=	Molarity of HCl
V	=	Correction factor for catalyst
K	=	Number of computations
SP	=	Density of reacting system
N	=	Record mark
DI	=	Dimer concentration
HI	=	Water concentration
EI	=	Ester concentration
ALI	=	Alcohol concentration
FI	=	Monomer concentration
CK	=	Equilibrium constant
A	=	Ml. NaOH first titrated
B	=	Ml. excess NaOH
C	=	Ml. of HCl backtitrated
W	=	Weight of sample
TR	=	Time of reaction
F	=	Monomer concentration at time TR
E	=	Ester concentration at time TR

Table 43 continued

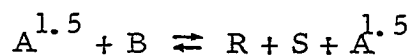
XX = Conversion of monomer

VL, S, Z, CC, Q, TT, BB, AA = Dummy variables for solution of second order reversible reaction



RK = Forward rate constant for second order reversible reaction

AAA through GD = Dummy variables for solution of 2-1/2 order reversible reaction



RKK = Forward reaction rate constant for 2-1/2 order reversible reaction.

REFERENCES

1. Needle, H. and Aries, R. Sugar p. 44, 32 (1949).
2. Inskip, G. IEC p. 1955, 44, No. 9, Sept. 1952.
3. Jenneman, J. U.S. Pat. 1, 906, 068 (1933).
4. Oil Paint and Drug Reporter, May 2, 1966.
5. Handbook of Physics and Chemistry p. 1008, vol. 38, 3rd edition.
6. Physics Handbook, p. 633, vol. 3.
7. Berman, Sedoff and Othmer IEC, 40, 2139-1948.
8. Filachione, E. and Fisher, C. U.S. Pat. 2, 420, 234, May 6, 1947.
9. Schulz, W. and Richardson, W. U.S. Pat. 2, 722, 541, Nov. 1, 1955.
10. Wenker, H. U.S. Pat. 2, 334, 524, Nov. 16, 1943.
11. Gabriel, C. and Bogen, C. U.S. Pat. 1, 668, 806, May 8, 1938.
12. Weisberg, S. and Stimpson, E. U.S. Pat. 2, 465, 772, May 29, 1949.
13. Schopmeyer, H. and Arnold, C. U.S. Pat. 2, 350, 370, June 6, 1944.
14. Filachione, E. and Fisher C. U.S. Pat. 2, 447, 693.
15. Jones, L. J., U.S. Pat. 2, 410, 740, Oct. 5, 1946.
16. Sly, G. Australian Pat. 129, 176, Sept. 30, 1948.
17. Weisberg, S and Othmer, P. U.S. Pat. 2, 406,648, August 27, 1946.
18. Gonzalez, R. Ciencia 8, 175 (1947).
19. Mishima, Y. Japanese Pat. 8061, Nov. 7, 1955.

20. Arnold, H. and Childs, C. , British Pat. 907, 322, Oct. 3, 1962.
21. Maatschappij, British Patent 839, 831, June 29, 1960.
22. Smith, L. and Claborn, IEC. 32, 692 (1940).
23. Filachione, E. and Castello, E. , IEC. 44, 2189 (1952).
24. Knapsack-Greesheim A. G. , Belgian Patent 630, 716, Aug. 1, 1963.
25. Troupe, R. and Kobe, K. , IEC. 42, 801 (May 1950).
26. Troupe, R. and Kobe, K. , IEC. 42, 1403 (July 1950).
27. Troupe, R. and Di Milla, E. , IEC 49, 847 (May 1957).
28. Watson, P. IEC. 32, (May 1944).
29. Eder, R. and Kutter, F. , Helv. Chem. Acta, 9, 557 (1926).
30. Montgomery, R. , J. ACS. 74, 466 (1952).
31. Monsanto's Technical Bulletin on Food Grade Lactic Acid, p. 5.
32. Troupe, R. , Aspy, W. and Schrodt, P. , IEC. 43, 1143 (1951).
33. Datta, Day and Ingold, J. Chem. Soc. , 839, 1939.
34. Lang and Friedman, J. Am. Chem. Soc. , 72, 3692 (1950).
35. Bender, W. , J. Am. Chem. Soc. , 75, 5986 (1953).
36. Roberts and Urey, J. Am. Chem. Soc. , 60, 2391 (1938).
37. Reed, Am. Chem. J. , 43, 489 (1910).
38. Gould, E. , Mechanism and Structure in Organic Chemistry, p. 321, Holt, Rinehart and Winston Inc. , 1959, New York.
39. Hougen and Watson, Chemical Process Principles, Vol. 3, p. 825, John Wiley and Sons, Inc. , 1961, New York.

40. Flory, P. , Am. J. Chem. Soc. 61, p. 3335, 1939.
41. Hinshelwood and Ralfe, Trans. Faraday Soc. 30, 935, 1934.
42. Mason, B. and Kilpatric , J. Am. Chem. Soc. 59, 572 (1937).
43. Davies, C. W. , "Progress in Reaction Kinetics", p. 161, 1961, Pergamon Press.
44. Bell, R. , Acid Base Catalyses, Clarendon Press, Oxford, 1941.
45. Glasstone, S. , Textbook of Physical Chemistry, p. 1127, Van Nostrand Co. , 1946.
46. Jones and Lapworth, J. Am. Chem. Soc. , 1911.
47. Kendall, J. , J. Am. Chem. Soc. , 1914.
48. Box, S. E. P. and Hunter, J. S. , Biometrika, p. 193, Sept. 1961.
49. Goldschmidt, Z. Physik. Chem. 60, 728, 1907.
50. Peng, J. Chem. Soc. London, p. 784, 1938.
51. Wezowicz, Purification of Lactic Acid, Newark College of Engineering, Thesis, June 1958.
52. Swier, Purification of Lactic Acid, Newark College of Engineering, Thesis, June 1958.
53. Eyring, Glasstone and Laidler, Theory of Rate Processes, Mc Graw Hill, 1940.