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CONTINUOUS ESTERIFICATION OF LACTIC ACID  
WITH n-BUTYL ALCOHOL

BY  
ROBERT DIX

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  
1970

APPROVAL OF DISSERTATION  
CONTINUOUS ESTERIFICATION OF LACTIC ACID  
WITH n-BUTYL ALCOHOL

BY

ROBERT DIX

FOR

DEPARTMENT OF CHEMICAL ENGINEERING  
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: \_\_\_\_\_ CHAIRMAN

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NEWARK, NEW JERSEY

JUNE, 1970

## ABSTRACT

A model is proposed for the reactions occurring when an aqueous 30% lactic acid solution is contacted with a primary alcohol, normal butanol. Kinetic and equilibrium data for the esterification reactions of monomeric lactic acid and dimeric lactic acid were determined in a series of experiments using an ideal overflow back-mix reactor. The variables studied were reaction temperature and catalyst concentration.

It was determined that the significant reactions occurring within this system are the esterification of monomeric lactic acid with n-butanol and the esterification of dimeric lactic acid with n-butanol. Other reactions that may be postulated to occur within the system are negligible.

The data is successfully correlated using this reaction model. Rate constants were evaluated at three temperature levels and catalyst levels ranging from zero to 44 mmoles/liter. The observed rate constants vary linearly with catalyst concentration. The Arrhenius parameters for the reactions were determined. The activation energy and frequency factor for the uncatalyzed formation of butyl lac-

tate were found to be  $21220 \pm 715$  cal and  $(6.258 \pm 0.97) \times 10^8$  liter/mole-second, respectively. The activation energy and frequency factor for the catalyzed formation of butyl lactate were found to be  $10870 \pm 650$  cal and  $8.91 \pm 1.10$  liter<sup>2</sup>/mole-second-mmole of cat, respectively. The activation energy and frequency factor for the uncatalyzed formation of butyllactyllactate were found to be  $17580 \pm 300$  cal and  $(1.303 \pm 0.080) \times 10^6$  liter/mole-sec, respectively. The activation energy and the frequency factor for the catalyzed formation of butyllactyllactate were found to be  $7980 \pm 645$  cal and  $(4.54 \pm 0.55) \times 10^{-2}$  liter<sup>2</sup>/mole-sec-mmole catalyst.

The equilibrium constant for the butyllactate formation reaction was determined to be  $3.13 \pm 0.16$ . The equilibrium constant for the butyllactyllactate formation reaction was determined to be  $2.75 \pm 0.15$ .

Equilibrium constants were evaluated at 25<sup>o</sup> C and were assumed to be constant with respect to temperature and catalyst concentration.

Kinetic and equilibrium data for the hydrolysis of dimeric lactic acid were determined in a series of experiments using an ideal overflow backmix reactor. The variables studied were reaction tem-

perature and catalyst concentration.

Rate constants were evaluated at three temperature levels and catalyst levels ranging from zero to 35 mmoles/liter. The observed rate constants vary linearly with catalyst concentration. The Arrhenius parameters for the reaction were determined. The activation energy and frequency factor for the uncatalyzed hydrolysis of lactyllactic acid were found to be  $22930 \pm 1617$  cal and  $(6.307 \pm 1.88) \times 10^8$  liter/mole-second, respectively. The activation energy and frequency factor for the catalyzed hydrolysis of lactyllactic acid were found to be  $12360 \pm 219$  cal and  $6.821 \pm 0.253$  liter<sup>2</sup>/mole-second-mmole of catalyst, respectively.

The equilibrium constant for the hydrolysis of lactyllactic acid was determined to be  $1.27 \pm 0.07$ .<sub>o</sub> The equilibrium constant was evaluated at 25 C and was assumed to be temperature and catalyst independent.



## ACKNOWLEDGMENTS

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To Dr. Saul I. Kreps, I wish to express my warmest thanks and sincerest appreciation for the guidance and advice that has made my graduate years at N.C.E. the most rewarding years of my academic life. Thank you.

I thank also my loving wife for her patience and understanding through the long days and late nights. My eternal debt to her would take more than a lifetime to repay.

Finally, I wish to dedicate this work to my father who would have liked so much to have seen this day.

Thank you,

R.D.

## VITA

Robert Dix was born in \_\_\_\_\_ on \_\_\_\_\_. He received his Bachelor of Science degree in Chemical Engineering from Newark College of Engineering in 1965. In 1966 he received his Master of Science degree from the same institution on a National Defense and Education Act Fellowship. He was granted a National Science Foundation Fellowship and an Esso Industrial Fellowship for one year each for doctoral study at Newark College of Engineering in 1967 and 1968, respectively.

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## CHAPTER I

### Introduction

#### A. SCOPE AND PURPOSE OF INVESTIGATION

The object of this work was to determine the rates of the various reactions occurring when a water solution of lactic acid is reacted with normal butyl alcohol. A kinetic determination was made of the rate constants and Arrhenius parameters for the system of esterification reactions.

The mechanistic results obtained from this study should not be restricted to the one alcohol selected for use in this system, but should be generally applicable to any primary alcohol.

The present investigation was initiated by the desire to develop an economical process for purification of technical grade lactic acid obtained by the fermentation route.

#### Lactic Acid Production

In recent years there has been a trend of industry away from the purification of fermentation lactic acid. At present, only one company, (Clinton

Corn Processing Company,) is still using the fermentation process.

A new synthetic process for the production of lactic acid has been developed (1,14,2) and will undoubtedly bring about the demise of the method of fermentative production in the near future. The motivating force behind this thesis is the final determination of the kinetics of the esterification of water solutions of lactic acid.

A conspicuous feature of the fermentation lactic acid industry is the sale of the acid in varying grades at prices somewhat higher than the cost of the sugars used as raw materials. Since the dilute fermentation liquors of lactic acid are relatively inexpensive, the high cost of the purified grades can only be attributed to difficulties encountered in its purification (22).

#### Purification of Fermentation Acid

The purification of fermentation lactic acid is made difficult by its low vapor pressure, its tendency to undergo self-esterification (23), its similarity in solubility characteristics to water, and the presence of several impurities such as dextrans, proteins, inorganic salts and unfermented



sugars (4,33,43,45,50).

Several methods of purification procedures have been reviewed by Smith and Claborn (50), who recommend conversion of calcium lactate to methyl lactate, purification of the methyl ester by distillation, and then the hydrolysis of the ester back to the acid (64,65).

Other proposed purification methods include crystallization of the calcium (13,40,42,64), aniline (8), or zinc salts (50,61); extraction with a solvent such as isopropyl ether (32,54,60,29); and, distillation (50) techniques, such as, vacuum distillation (34,52), steam distillation under reduced pressure (27,38,39,48,49), distillation in a gas stream (41), and passage of superheated steam through condensation polymers of lactic acid (43).

A more detailed review of purification methods used is given by Kaplan (30).

Backhaus (3) obtained the first of a series of patents in 1922 describing an esterification process whereby alcohol, acetic acid, and sulfuric acid were fed into a distilling column and the ester continuously removed. This process was improved upon by subsequent workers (31). Until 1945, almost all continuous esterification column design was

done on an empirical basis, with the factors determining the amount of esterification taking place on a given plate or the number of plates required to produce the desired completeness of reaction and separation not being considered. Leyes and Othmer (36) have shown that with both kinetic data and vapor-liquid equilibrium data, it was possible to calculate what was occurring in a continuous esterification column after steady state conditions had been attained. Berman (6) has also approached this problem from a similar point of view.

A preliminary empirical investigation by Dix (18) was performed on a method for the continuous esterification of technical grade (44%) lactic acid. This is one step in a proposed industrial process for the purification of lactic acid. Technical grade lactic acid was treated with n-butyl alcohol in the presence of hydrochloric acid catalyst, to yield the ester, butyl lactate, and water. The water formed and the water present in the initial feed was removed by continuous azeotropic distillation. This water removal served to drive the reaction toward completion and thereby increase the yield of the ester.

The reaction was performed in an overflow back-

mix reactor connected in series with a bubble cap plate distillation column of original design. The reactants were fed into the reactor, the product of which was in turn fed to the distillation column. The greatest amount of reaction occurred in the reactor, with the column serving to drive the reaction to near completion. The azeotrope, (composed of 79 mole per cent water) was cooled and condensed. Phase separation occurred upon condensation, allowing the condensate to be continuously decanted to recycle the alcohol. In this way, almost all of the unreacted butanol feed may be recovered for recycle.

The results showed that equilibrium was approached in the reactor, and that the equilibrium conversion based on the initial feed was exceeded in the column.

The feasibility of this approach to the continuous esterification of lactic acid has clearly been demonstrated. This key step in turn fits into an over-all industrial design for the purification process as outlined by Kaplan (30). In his process:

1. Crude fermentation lactic acid is continuously fed into an esterification column, such as described above, and is esterified by n-butyl alcohol.

2. Unreacted alcohol, water and ester are separated from the reaction mixture.

3. Purified butyl lactate is steam-hydrolyzed to yield lactic acid and n-butyl alcohol. The butyl alcohol is recovered and recycled to the esterification column. A column design similar to the esterification column would be required, with kinetic design considerations merely approaching equilibrium from the other direction.

#### Continuous Esterification Processes

The major factors involved in the design of columns for the process described are the law of mass action, the laws of kinetics, and the distillation laws, all operating simultaneously. Esterification can occur only when the concentrations of the components give calculated values of the equilibrium ratio which are less than the value of the true equilibrium constant; otherwise, hydrolysis must occur. The kinetics of a homogeneous liquid phase reaction such as the esterification of lactic acid with butyl alcohol, are modelled by the equations governing the rate of reaction and the variation of the rate constant (which varies as a function of the temperature and catalyst concentration). The usual distillation laws may have to be modified since moles of reactants disappear while moles of products appear on each plate. Since these kinetic

considerations are super-imposed on distillation operations, each plate must be treated separately by successive calculations after the number of moles converted has been determined (36).

Due consideration must also be given to the design of the distillation operations to drive the reaction toward completion by separation of one of the products of the reaction. In the present system, the water formed is distilled overhead to remove it from the reaction zone.

### Reaction Kinetics

In order to design a system such as that described above the kinetics of all possible reactions occurring in the system must be known and the effects of temperature, catalyst concentration, and the mole ratio of the reactants of these kinetics must be available.

Prior investigations (56,57,58,30) into the kinetics of the lactic acid system have yielded inconsistent results in terms of the effect of initial acid concentration.

In the present work the various possible reaction schemes occurring in the esterification of lactic acid

solution were investigated. Based on a preliminary analysis of experimental data, a preferred reaction scheme was selected. This scheme was fully analyzed with the various kinetic aspects of this system being determined.

## B. BACKGROUND

Lactic acid (Acidum Lacticum,  $\alpha$  -hydroxypropionic acid, 2-hydroxy propanoic acid, milk acid),  $\text{CH}_3\text{CHOHCOOH}$ , with a formula weight of 90.08, is the simplest hydroxy acid containing an asymmetric carbon atom. It exists in nature as the two optically active d- and l-forms and a dl-inactive mixture. Lactic acid derives its name from its presence in sour milk where it was first discovered in 1780 by Scheele.

"Scheele allowed milk to ferment for 3 weeks, separated the protein, and added calcium hydroxide to precipitate the phosphate. The calcium lactate remained dissolved and was decomposed with oxalic acid. The filtrate was concentrated and taken up in alcohol. After concentrating the alcohol, the acid lactate was obtained as a thick sirup which could not be distilled or crystallized. From this work, as well as subsequent work, Scheele concluded that the acid was free of acetate and that a new acid had been obtained. Pasteur, in 1867, discovered that the souring of milk was caused by an organized ferment and described the organism which was responsible for the fermentation of sterilized milk. Lister, in 1878, showed that the lactic fermentation is similar to the so-called alcoholic fermentation and is produced by microorganisms which he isolated from sour milk by dilution." (59)

Other early discoveries in the chemistry of lactic acid by such notable chemists as Liebig, Berzelius, Kekule and others, have contributed to the historical and classical development of our knowledge of this widely used acid. Commercial exploitation of this

readily prepared material soon followed. The manufacture and chief uses for lactic acid were developed by Americans; the industry was well established in the U.S. before the manufacture of lactic acid was undertaken in foreign countries. Commercial production of lactic acid was first initiated by Charles Avery, at Littleton, Massachusetts, in 1881 in an attempt to make calcium lactate which was to be used as a substitute for cream of tartar in baking powder.

Many of the recent studies reflect an increasing interest in the synthetic and industrial aspects of lactic acid chemistry and the transformation of abundant carbohydrates-via lactic acid as an intermediate-into various industrially valuable products, including chemical intermediates, solvents, plasticizers and resins (24,66).



### C. STRUCTURE AND PHYSICAL PROPERTIES

Lactic acid is a slightly hygroscopic syrup (the racemic mixture more hygroscopic than the optically active isomers), varying in color from colorless to pale yellow (62). The specific gravity of lactic acid is variable, depending on the extent of self esterification it has undergone. It is completely miscible with water, alcohol, and ether, but is insoluble in chloroform. The viscosity and density of aqueous solutions of lactic acid as a function of the concentration are given in Table I. The acid represented by this table is assumed to be the racemic mixture.

As mentioned previously, lactic acid contains an asymmetric carbon atom and exists in the d- and l-, active and dl-, inactive, forms. Both optical isomers of lactic acid occur naturally, but commercial fermentation acid is mostly the optically inactive form (44). Optically active acids may be prepared under controlled conditions with selected organisms and substrates, or by resolution of the racemic mixture via the zinc ammonium salt or the salt with alkaloids such as morphine (5,25). The two optical isomers have also been separated by fractional

(55)  
TABLE I

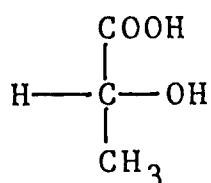
Viscosity and Density of Aqueous Lactic Acid at 25 °C

<u>Lactic Acid Conc., %</u>	<u>Viscosity Centipoises</u>	<u>Density g/ml</u>
0	0.89	-
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

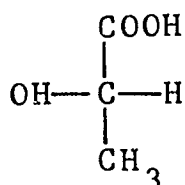
crystallization of pure lactic acid from mixed ethyl ether and ispropyl ether solution (9).

Schopmeyer (59) points out that much confusion exists regarding the nomenclature of the optical isomers, since d- and l- have been used to refer to either optical rotation or to configuration. That which shows dextro rotation (commonly known as sarcolactic acid, paralactic acid or d-lactic acid), but the L-configuration is correctly designated by modern nomenclature as L-(+)-lactic acid (II). This form of lactic acid is metabolized by the human body. Salts of the dextrorotatory acid are levorotatory.

The enantiomorph, levorotary lactic acid, is properly referred to as D-(-)-lactic acid (I). This isomer is not metabolized by the human body. Its salts are dextrorotatory. Heating of either of the optically active lactic acids converts them into the optically inactive racemic forms containing equal proportions of the dextro and levo modifications. The configurational relationships are shown in formulas (I) and (II).



(I) D-(-)-lactic acid



(II) L-(+)-lactic acid

Lactic acid, upon heating, self-esterifies, (see section on Chemistry of Lactic Acid), making the determination of its boiling point impossible at atmospheric pressure, and extremely difficult at lower pressure. The boiling point of lactic acid at reduced pressure has been reported as 119<sup>o</sup> C at 12mm and 82-85<sup>o</sup> C at approximately 1mm of mercury.

Since lactic acid is commonly encountered as an aqueous solution, the properties of the lactic acid-water system are extremely important. Dilute aqueous solutions, those with less than approximately 25% lactic acid, are composed essentially of monomeric lactic acid and water. However, more concentrated solutions show a complex composition due to self-esterification of the acid to longer chain length polylactic acids. The equilibrium composition of aqueous lactic acid then, depends on the concentration (7,25,62). Further discussion of the composition of aqueous lactic acid solutions is presented in the section entitled The Chemistry of Lactic Acid.

#### D. OCCURRENCE

Lactic acid occurs abundantly in nature in one or another of its three forms. It is a normal constituent in the blood and muscle tissue of animals and the principle acid constituent of sour milk. It has been observed that an abnormally high lactic acid value in human blood is present in some diseases, such as pneumonia, TB and heart failure. Biochemically speaking, lactic acid is also a very important compound; apparently, the energy necessary for muscular activity is normally supplied when glycogen is converted into lactic acid through a complicated series of reactions. Lactic acid has been identified in yeast fermentation and is a component of a by-product of the corn processing industry-corn steep liquor. Some food products containing lactic acid are sauerkraut, pickles, beer, buttermilk, and cheese (44,66).

#### Fermentation Production of Lactic Acid

Lactic acid is industrially produced by the fermentation of refined glucose, hydrolyzed starch, whey, and molasses. To reduce purification cost, the more refined substrates are used for the production of higher grades of lactic acid. Among the substances proposed as substrates are sulfite waste

liquor, juice of culled citrus fruits, enzymatically hydrolyzed potatoes, acid hydrolyzed wood, mill sawdust, straw, corncobs, extracted beet slices, and Jerusalem artichokes.

Bacteria isolated from souring foods, grains, malt sprouts, or soil may be suitable for commercial production of lactic acid. The nutritional requirements of these organisms are complex. Lactobacillus delbrueckii, for example, illustrates this complexity; it requires 14 amino acids, 4 vitamins, and stimulation by a number of other substances. Addition of small amounts of malt sprouts, corn steep liquor, distillers' grains or solubles, koji, rice bran, peanut oil cake, soybean cake, undenatured milk, or extracts of liver and yeast provide these growth factors. The culture may be maintained by frequent transfer in media of low sugar content such as 5% corn mash.

A more complete listing of the practices in industrial fermentative production of lactic acid is presented by Schopmeyer in Industrial Fermentations, volume I (59).

Lactobacillus delbrueckii, in one commercial process, is transferred consecutively from test tube to flasks, to seed tanks, and finally to the

wooden or stainless steel fermentor, at all times maintaining an inoculum level of 10%. Culture transfer is made after 16-20 hours of growth at 49<sup>o</sup> C. The medium, which consists of 15% glucose, 0.4% malt sprouts, 0.25% diammonium phosphate and 10% calcium carbonate, is not sterile. Cleanliness, high temperature and low pH are relied on heavily by the industry to restrict and retard contaminants. Butyric bacteria produce volatile acids in addition to a racemase and are therefore considered the most troublesome.

When the fermentation is complete, ( 4 to 6 days required), the concentration of sugar falls to 0.1% or less and the yield reaches 90-95%. Automatic control of pH is considered advantageous during fermentation since small changes in pH adversely affect the process. Sufficient addition of a calcium carbonate initially or intermittently, as required, helps maintain optimum pH of 5.6-5.8.

Recovery of lactic acid from fermented liquors is a rather difficult process for several reasons. Lactic acid has a low vapor pressure and tends to form anhydrides and undergo self-esterification

when heated and concentrated above 20%. Extraction techniques are difficult because lactic acid has a solubility similar to water. Proteins, unfermented sugars, inorganic salts, and colored materials are the important contaminants. The protein as a contaminant, is usually removed by coagulation during the complete neutralization of the lactic acid by heating to 90°C with excess lime. The insoluble matter is filtered from the system and colored materials and soluble proteins are adsorbed by treatment with charcoal. The purified lactate is then cooled and allowed to crystallize or is concentrated and spray dried. Treatment of a solution of calcium lactate with sulfuric acid followed by filtering off the insoluble calcium sulfate will result in the preparation of lactic acid. The acid may then be repeatedly bleached to attain the desired purity. By treatment with hypochlorites or nitric acid, strong oxidizing agents, some organic impurities in lactic acid can be destroyed.

Theoretically the yield of lactic acid is 100% of the weight of fermentable sugar; in practice, this yield is never obtained. Presumably a portion of the carbohydrate is metabolized by the organism. In commercial practice, yields of about 85% are considered normal since further losses occur during



subsequent processing.

The technology of the recovery of lactic acid from the fermentation liquor varies considerably, depending on the grade of acid desired (44).

Crude lactic acid. The crude acid (15%), can be made by directly acidifying the fermentation liquor obtained from a relatively impure carbohydrate substrate. The quantity and nature of the impurities in the final acid is dependent upon the initial substrate and also on the manufacturing method and the degree of refining (44).

Edible (or Food-Processing) lactic acid. There are two methods currently being used for the manufacture of edible lactic acid. One method refines the sugar, and the other refines the lactate or lactic acid. The components of the fermentation mash of the first method are a highly refined sugar, a minimum of nutrient material, and a relatively pure calcium carbonate. After the fermentation is completed the mash is acidified with sulfuric acid and the calcium sulfate is removed by filtration. Treatment with vegetable carbon refines and concentrates the light-colored lactic acid. Where applicable, removal of iron and copper is accomplished by precipitation as the ferrocyanides by adding the

stoichiometrical quantity of sodium or calcium ferrocyanide. The carbon and heavy-metal ferrocyanides are filtered out and finally the lactic acid is diluted to the proper strength (44).

An inexpensive carbohydrate substrate is fermented in the second type of process. The calcium lactate liquor produced by the neutralization may be filtered in order to clarify it, and it may be concentrated to approximately 25% at the elevated temperature of evaporation. The calcium lactate crystallizes when the solution is cooled. The crystals are filtered or centrifuged to separate them from the liquor, then they are redissolved in water and acidified with sulfuric acid. Filtration removes the calcium sulfate and the light colored lactic acid product is concentrated to the proper strength (44).

An alternative procedure is described by Jenemann (29). This procedure involves the use of isopropyl ether to extract the lactic acid from the crude solution. The lactic acid is then reextracted from the isopropyl ether with water. This process involves the continuous feeding of concentrated crude lactic acid solution into the top of an extraction tower, while isopropyl ether is introduced at the bottom. The isopropyl ether solution

of lactic acid is removed from the top of the first tower and pumped into a second extraction tower. Here it is passed upwards through a counter current stream of water, removing the lactic acid from the isopropyl ether. The withdrawal of the purified aqueous solution of lactic acid occurs at the bottom of the second tower. The isopropyl ether is pumped from the top of the second tower to the bottom of the first tower for recycling. The acid obtained by this process is of a somewhat higher purity than is required for edible grade. The lactic acid produced by this method has a low concentration of impurities, particularly ash, and frequently enters the market as plastic grade lactic acid (44,66).

U.S.P. XVI (formerly N.F.) Lactic Acid. Basically there are three procedures available for the production of U.S. P. lactic acid. U.S.P. grade acid may be a result of the solvent extraction process outlined above. One of the oldest procedures is distillation with steam under relatively high vacuum. The relatively high boiling point of lactic acid results in self-esterification to nonvolatile polyesters so this method is quite expensive. The steam in this distillation procedure is for the purpose of minimizing this self-esterification. The efficiency

in overcoming entrainment is important in this process. Usually the vapors are led to a particular condenser, where the bulk of distilled acid is stripped, resulting in a condensate of aqueous lactic acid which is 50% or higher in concentration. Acid remaining in the vapor stream beyond the dephlegmator is recovered by concentration of the final condensate (44).

Perhaps the most practical method for production of this grade of lactic acid involves the formation of the methyl ester as an intermediate (22,23,25). First a solution of high acid content is obtained by dehydration; this concentrated solution is subsequently esterified with methanol. The esterification may be accomplished by passing the vapors of methanol through the acidified lactic acid at approximately 100 °C, or by refluxing the solution in the presence of a sulfuric acid catalyst. The former method gives higher yields of methyl lactate, since by removal of volatile methyl lactate (in the vapor stream) from the reaction, the equilibrium is favorably shifted. If desired, the methyl lactate may be fractionated and then hydrolyzed completely by boiling in an excess of water and continuously removing the regenerated methanol. The residual

aqueous solution from this treatment is U.S.P.  
grade lactic acid, which requires some concentration  
to the final composition.

## E. SYNTHESIS OF LACTIC ACID

Mention should be made at this point of some of the other possible methods for the manufacture of lactic acid. Lactic acid can be synthesized by purely chemical methods such as the degradation of carbohydrates as described by Braun (10). In this method, a suitable carbohydrate, for example sucrose, is heated with a strong alkali, such as sodium hydroxide, at a high temperature and pressure to produce lactic acid.

Another method for synthesizing lactic acid is the heating of carbon monoxide and acetaldehyde in the presence of sulfuric acid at 130 °C to 200 °C under 900 atm. pressure (37).

In addition to the above methods, several other techniques are available for preparing lactic acid, including:

1. Hydrolysis of acetaldehyde cyanohydrin (prepared from acetaldehyde and hydrogen cyanide).
  2. Hydrolysis of  $\alpha$ -chloropropionic acid (prepared by chlorination of propionic acid).
  3. By action of nitrous acid on alanine.
  4. By oxidation of propylene glycol, and others.
- Synthetic methods, however, are generally more

expensive than fermentation.

One notable exception to the above statement is the process of the Monsanto Company, a relative newcomer in the production of lactic acid. Monsanto, utilizing a proprietary process, produces lactic acid synthetically without the use of an agricultural substrate. Kaplan (30) has speculated that this process proceeds from acetaldehyde to lactonitrile to lactic acid, probably by technique (1) given above.

## F. USES OF LACTIC ACID

Lactic acid is a weak acid with a pleasant sour taste and very little odor. It has good solvent properties, polymerizes readily, and most of its salts are highly soluble. Because of these properties, lactic acid has many uses both in food products and industrially. The uses of lactic acid can therefore be divided into two categories: Food and Non-food.

Food uses. About half of the total annual lactic acid production is of the edible grade. In general, lactic acid can be used as an acidulant in any kind of food or beverage. The properties of lactic acid which make it ideal in a variety of food products are:

1. Its taste is mildly acid as opposed to the sharp biting taste of other food acids.
2. Flavors are not masked or overpowered by it.
3. It prevents deterioration in some foods.
4. Its liquid form makes it ready to use.

Because of one or more of the above properties, edible grade lactic acid has found increasing use in animal foods and remedies, bakery products, beer, butter, candy, cheese, dried egg whites, flavoring extracts, jelly, liquid pectin, mincemeat, olives, pickles, sauerkraut, soft drinks, soups and sherberts.



It is also used to adjust the pH of brewery worts to yield proper saccharification and reduce undesirable bacterial fermentations. It is also added to cows milk for baby feeding as an aid in digestion.

As mentioned previously, the first lactic acid process in America was developed for the production of calcium lactate for use in baking powder. It is interesting to note that this is still an important outlet for this acid and considerable quantities of calcium lactate are used in certain baking powders to stabilize them and control the rate of gas evolution. Calcium lactate is also used in certain pharmaceuticals as a source of calcium, a hemostatic and an anti-spasmodic.

Non-food uses. Crude lactic acid has long been used in the leather industry for deliming hides, in vegetable tanning, and for bating and plumping sole leather. It is also the raw material for preparing the esters such as methyl, ethyl, and n-butyl lactates, which are used as solvents. Lactic acid is also used in the acid dyeing of wool and other textile fibers. Other non-food uses include applications such as adhesives, electroplating and electropolishing, cleaning and polishing formulation, insecticides and fungicides, oil and water well treating, lithographic

developers, plastics and resins, and special inks and textiles. Lactic acid is useful in neutralizing the alkali catalyst in the manufacture of phenol formaldehyde resins, since a noncrystallizable salt is formed, which does not impair the clarity and strength of the resin. In this application a high purity lactic acid, essentially free of iron is desired.

In recent years several publications have appeared indicating new potential applications of lactic acid and its derivatives. The use of lactic acid as an extender for glycerol in alkyd resins (53) has been described. The preparation of coatings by reaction of polylactic acid with drying oils or with small amounts (1-6%) of salts of polyvalent metals has been reported (63). The addition of dicyclopentadiene to lactic acid (11) results in a dihydrodicyclopentadienyl ether-ester of lactic acid, which in the presence of driers rapidly absorbs oxygen from the air, to give an insoluble varnish-like film, behaving like a drying oil in this way. By heating to a viscous autoxidizable oil with peroxides this ether-ester can be polymerized. Many high-boiling lactic esters have been evaluated in a preliminary manner as plasticizers for resins (20,24,46,47). Lactic and adipic acid mixed

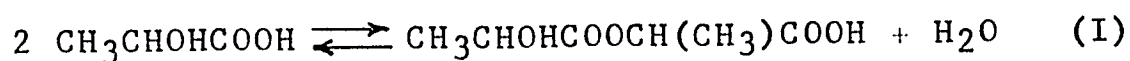
esters of the types  $\text{ROOC}(\text{CH}_2)_4\text{COOCH}(\text{CH}_3)\text{COOR}$  and  $(\text{CH}_2\text{CH}_2\text{COOCH}(\text{CH}_3)\text{COOR})_2$  have been shown to be efficient plasticizers for vinyl chloride copolymers (46). A smooth conversion of lactic acid into methyl acrylate can be accomplished by the following reaction scheme: conversion to methyl lactate, acetylation, and pyrolysis at  $550^\circ\text{C}$  (12,51).

## G. CHEMISTRY OF LACTIC ACID

### Composition of Lactic Acid

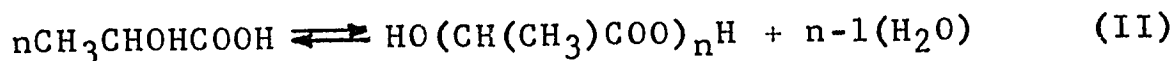
Watson (62) points out that there are many conflicting statements concerning the composition of lactic acid to be found in the literature. This results because lactic acid solutions, except those of less than approximately 25% concentration, contain two or more compounds besides water.

Because it contains both hydroxyl and carboxyl functional groups, difunctional lactic acid undergoes self-esterification when heated to form linear polyesters as well as lactide. As dilute aqueous lactic acid is concentrated by distillation, the removal of water results in a shift in the concentration in favor of self-esterification. The first esterification product is lactyllactic acid. The reaction may be represented as:

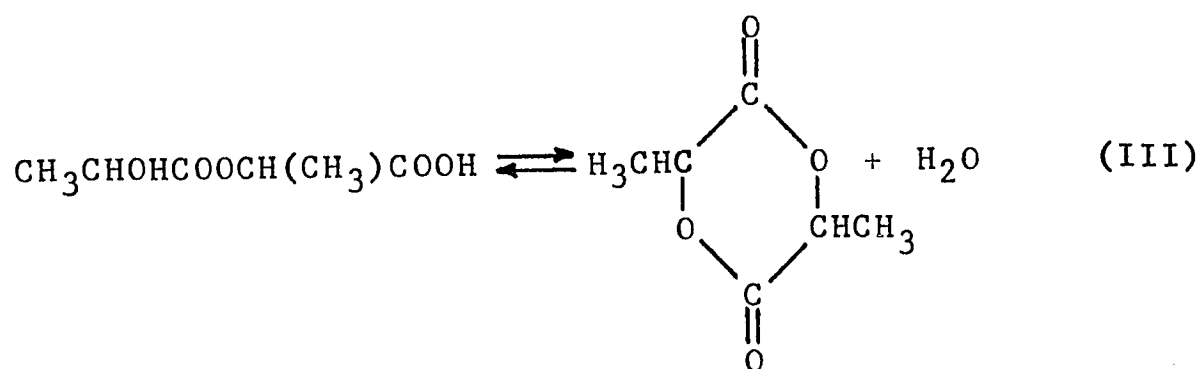


As the concentration proceeds, lactide and higher linear esters, that is, the so-called polylactic acids (referred to in earlier literature as "anhydrides") or trimeric, tetrameric, and polymeric lactic acids, are formed (7,21,25,62). The formation of polylactic

acid may be represented as:



The formation of the lactide may be represented as:



Equilibrium between the several components is attained slowly (several weeks) at room temperature, but may be accelerated by the addition of a strong acid catalyst.

All of the self-esterification reactions presented above are readily reversible. Therefore, the equilibrium composition of a particular aqueous solution of lactic acid is a function only of the concentration of acid in the solution.

Eder and Kutter (19) studied the composition of aqueous lactic acid solutions as a function of acid concentration and found that solutions below 90% lactic acid consist of monomeric acid, dimeric acid and water. These results were subsequently

confirmed by Watson (62) and more recently reconfirmed by Kaplan (30). Figure 1 represents the results obtained by Watson in a study of the equilibrium compositions of aqueous solutions of lactic acid.

#### Other Reactions of Lactic Acid

Lactic acid undergoes reactions typical of organic acids, and many salts of this acid have been reported. Since lactic acid undergoes esterification readily with many alcohols, numerous lactic esters have been prepared by acid-catalyzed esterification. The esterification is complicated because the esters of polylactic acid are simultaneously produced (25). By using an excess of alcohol in the esterification the formation of ester of polylactic acid can be minimized. The conversion of lactic acid to ester usually occurs in high yields. Esters of polylactic acid, the by-products, are actually a source of lactic acid, so they may be recycled and the ultimate yield of lactic ester is usually high.

Polylactic acid is formed when lactic acid is heated in the presence of catalytic amounts of mineral acid; however, decomposition into acetaldehyde, carbon monoxide, formic acid, and water occurs with larger amounts of mineral acid (25).

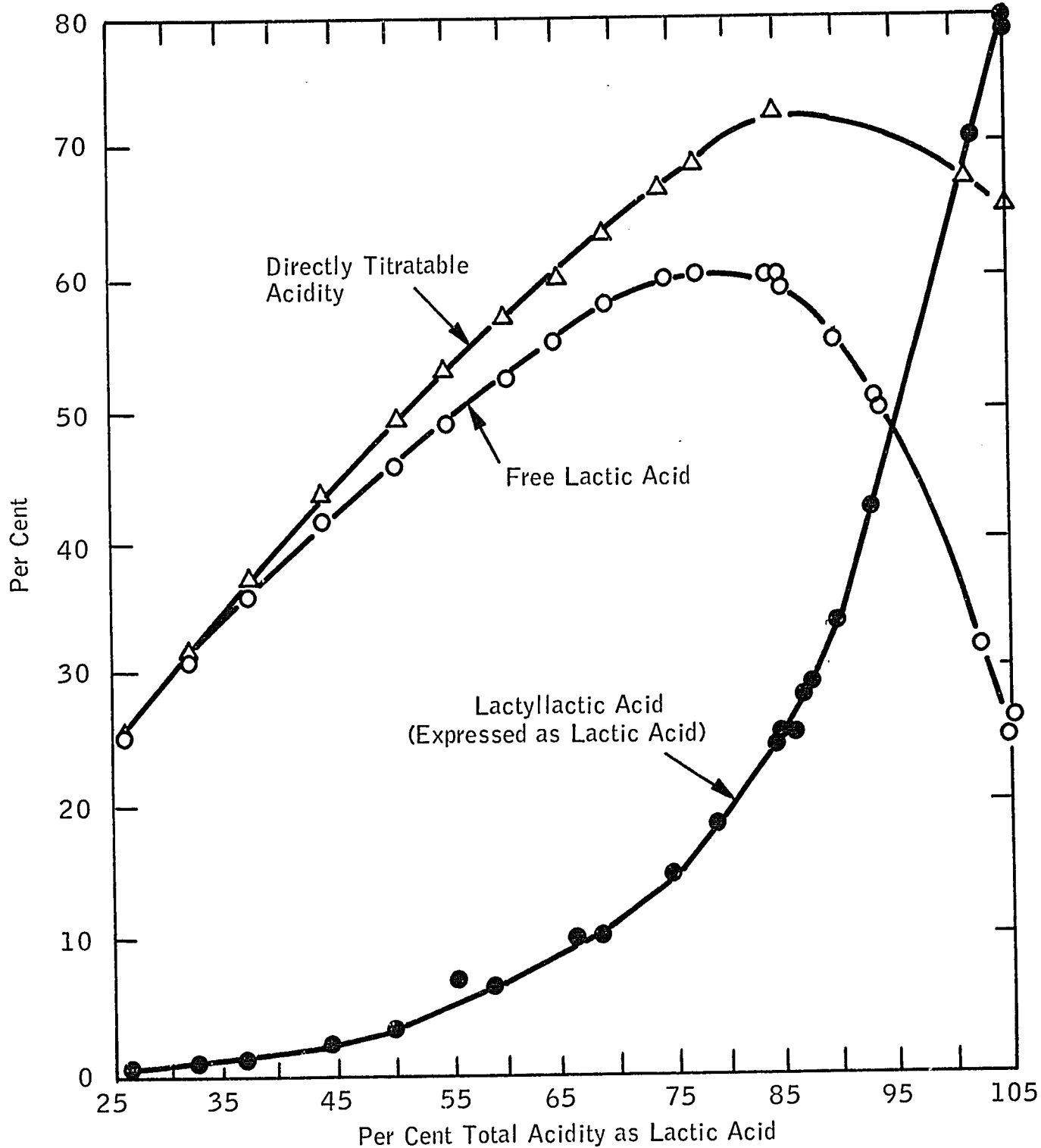
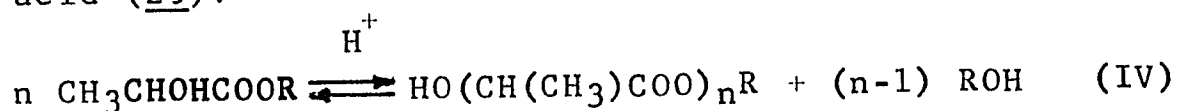


Figure 1  
RELATION OF TOTAL ACIDITY TO COMPOSITION IN  
EQUILIBRATED LACTIC ACID SOLUTIONS

When concentrated solutions of the monoesters of lactic acid are heated, particularly in the presence of a mineral acid catalyst, they undergo self-alcoholysis to produce esters of polylactic acid (25):



In these reactions, the lactic esters exhibit behavior similar to lactic acid. Then, similar to the behavior of aqueous lactic acid systems, (where chain lengths greater than the dimer occur only in highly concentrated solutions), it is surmised by this investigator that chain lengths greater than the ester of the dimer, that is, butyllactyllactate may also not be expected to occur, except in extremely concentrated systems.

Lactic esters hydrolize less readily than esters of glycolic acid, but more readily than esters of the fatty acids, such as acetic acid. In general, the lactic esters of secondary alcohols are considerably more resistant to hydrolysis than the esters of corresponding primary alcohols (25). Lactic esters and lactide undergo alcoholysis readily with various alcohols. In the presence of a trace of catalyst, alcoholysis of lactide produces esters

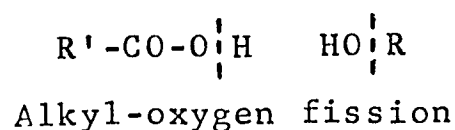
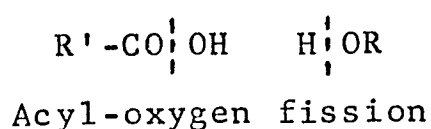


of lactyllactic acid (15), but larger amounts of catalyst yield the monomeric lactic ester. Alcoholysis of methyl lactate with a higher alcohol is an excellent method for preparing lactic esters.

## H. ESTERIFICATION MECHANISMS

### Classification of Mechanisms

Since esterification and hydrolysis can be part of the same equilibrium, information about the mechanism of both may be obtained by a study of one. In the reactions of carboxyl esterification and hydrolysis, a number of distinct mechanisms may be recognized. In general, the bulk of all the suggested mechanisms may be classified (16,17) on three different bases depending upon (1) whether or not the reaction is acid- or base-catalyzed, (2) the position of rupture of the carboxyl compound; i.e., whether acyl-oxygen fission or alkyl-oxygen fission occurs. These types of fission are represented below:



and (3) the reaction kinetics of the steps occurring in the mechanism, i.e., whether the reaction scheme is unimolecular or bimolecular.

The classification described is summarized in Table II. For convenience, basic mechanisms are represented by B and acidic mechanisms by A; acyl-

TABLE IIMechanism of Carboxyl Hydrolysis and Esterifications

Type of Mechanism	Form Attacked	Known Reactions	Fission	
			Acyl-	Alkyl
Basic	$R'-CO_2R$	Hydrolysis	-	$B_{AL}^1$
			$B_{AC}^2$	$B_{AL}^2$
Acidic	$R'-CO_2HR^+$	Hydrolysis and Esterification	$A_{AC}^1$	$A_{AL}^1$
	or $R'-CO_2H_2^+$		$A_{AC}^2$	-

oxygen and alkyl-oxygen fission are represented by the subscripts AC and AL, respectively; and molecularity is indicated by 2 or 1, depending on whether the reaction is bimolecular or unimolecular. Based on the classifications, eight mechanisms are possible, but only the six that have been observed are entered in the Table (28).

The applicability of these mechanisms may now be examined in light of the subject system; the esterification of lactic acid with a primary alcohol.

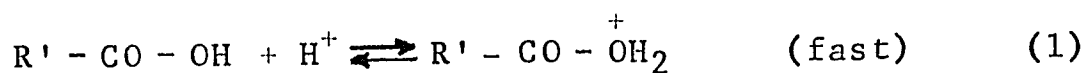
Alkaline esterification may be immediately discounted because of the stability of the carboxylate ion. Acid-catalyzed esterification is well known, with the reacting entity being  $R' - CO_2H_2^+$ .

Ingold (28) has examined in depth the relative merits of the remaining three possible esterification mechanisms, and has concluded that in aqueous or alcoholic solvents, such as would be encountered in the system studied here, the  $A_{AC}^2$ , or acid-catalyzed, acyl-oxygen fission, bimolecular mechanism is favored. The reader is referred to Ingold's (28) work for a detailed explanation of the reasoning behind this selection.

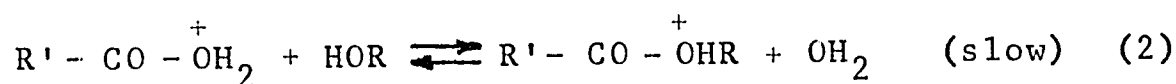
### The A<sub>AC</sub>2 Mechanism

The mechanistic model consistent with acid catalyzed esterification, the A<sub>AC</sub>2 mechanism, is envisioned as occurring in the following manner:

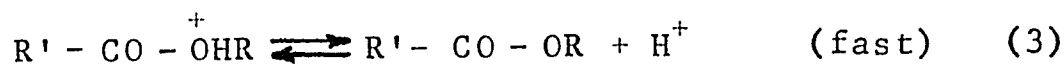
1. A preliminary addition of a proton forming a conjugate acidic ion (or oxonium ion).



2. This then undergoes an exchange reaction with an alcohol molecule which approaches along the line of the C-O dipole.



3. Loss of a proton to yield the ester.



Certain kinetic characteristics may be predicted from the A<sub>AC</sub>2 mechanism (28). These are:

1. The rate of esterification should be a function of the concentration of the alcohol.
2. The rate of esterification is a function of the acidity of the system.
3. The rate of esterification is not greatly affected by electropositive substituents in the acyl group.

4. Rates by mechanism  $A_{AC}^2$  are sensitive to steric hindrance. That is, if either R or R' has a branched chain structure and is therefore bulky, it will exert a hindering influence in the formation of the bimolecular complex in (2) and esterification will be accordingly more difficult.

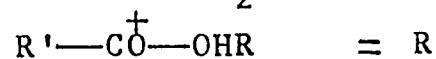
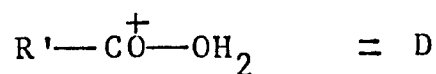
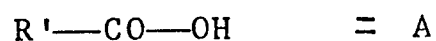
5. The rate should be relatively insensitive to the solvent.

The  $A_{AC}^2$  reaction mechanism is assumed to be consistent with all of the reactions encountered in this work and will be taken as an accurate depiction of the system. Alcoholysis reactions, being a modification of the hydrolysis reaction, are also described by this mechanism.

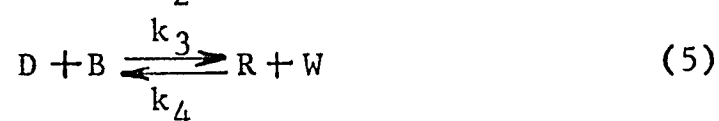
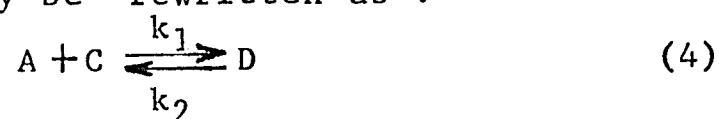
# I. DERIVATION OF RATE EXPRESSIONS

Based on the esterification mechanism presented in the previous section, and with the aid of the steady-state approximation, the kinetic rate expression for the reactions actually occurring in this system can be derived.

To simplify the presentation of this derivation, the components and intermediates of the reaction system are redefined as follows:



Using this key to the identification of components and introducing rate constants, the reaction mechanism may be rewritten as :



Consistent with the relative rates given by the mechanism,  $k_1$ ,  $k_2$ ,  $k_5$ , and  $k_6$  are very large, and  $k_3$  and  $k_4$  are very small in magnitude.

The intermediate compounds D and R are not detectable in the reaction mixture, but product P is formed as rapidly as product W. It may be said then that intermediate R rapidly decomposes to form product P.

The rate of formation of products P and W may be written directly from equations (5) and (6) above as the algebraic sum of the rates of formation by all pertinent reactions in terms of the concentration of the individual components, or,

$$r_P = k_5 C_R - k_6 C_P C_C \quad (7)$$

$$r_W = k_3 C_D C_B - k_4 C_R C_W \quad (8)$$

The evaluation of  $r_P$  and  $r_W$  requires the evaluation of  $C_R$  and  $C_D$ ; quantities which are not experimentally available.

It may be postulated at this point that although  $C_R$  and  $C_D$  are never detectable, they can never be zero, or the reaction could not proceed. Since  $C_R$  and  $C_D$  are so low, the finite rates of formation and disappearance of R and D respectively, must



be approximately identical and the net rate of formation of the intermediate compounds must tend toward zero, and thus may be taken as zero. This is a statement of the steady state hypothesis, i.e., the net rate of change in the concentration of an intermediate compound may be taken as zero.

The steady state approximation is applied as follows. The total rate of formation of components R and D is zero, but is also equal to:

$$0 = r_R = k_3 C_D C_B - k_4 C_R C_W - k_5 C_R + k_6 C_P C_C \quad (9)$$

$$0 = r_D = k_1 C_A C_C - k_2 C_D - k_3 C_D C_B + k_4 C_R C_W \quad (10)$$

Solving these expressions simultaneously for  $C_R$  yields:

$$C_R = \frac{k_1 k_3 C_A C_B C_C + k_2 k_6 C_P C_C + k_3 k_6 C_B C_P C_C}{k_2 k_4 C_W + k_2 k_5 + k_5 k_3 C_B} \quad (11)$$

Substituting Eq. (11) into Eq. (7) and simplifying yields:

$$r_P = \frac{k_1 k_3 k_5 C_A C_B C_C - k_2 k_4 k_6 C_P C_W C_C}{k_2 k_4 C_W + k_2 k_5 + k_3 k_5 C_B} \quad (12)$$

Realizing that by initial conditions  $k_3$  and  $k_4$  are very small as compared to  $k_1$ ,  $k_2$ ,  $k_5$ , or  $k_6$ , it may be said that the products of  $k_2$ ,  $k_4$ , and

$C_W$ , and  $k_3$ ,  $k_5$ , and  $C_B$  are negligible compared to the product of  $k_2$  and  $k_5$ . The expression then reduces to:

$$r_P = \frac{k_1 k_3 k_5 C_A C_B C_C - k_2 k_4 k_6 C_P C_W C_C}{k_2 k_5} \quad (13)$$

By allowing:

$$k_{\text{forward}} = k_f = \frac{k_1 k_3}{k_2}$$

$$k_{\text{backward}} = k_b = \frac{k_4 k_6}{k_5}$$

the kinetic rate expression for any esterification or hydrolysis reaction satisfying the  $A_{AC}^2$  mechanism may be written as:

$$r_P = k_f C_A C_B C_C - k_b C_P C_W C_C \quad (14)$$

Finally, converting back to the original nomenclature:

$$r_P = k_f (R' - \text{CO} - \text{OH}) (\text{ROH}) (\text{H}^+) - k_b (R' - \text{CO} - \text{OR}) (\text{H}_2\text{O}) (\text{H}^+) \quad (15)$$

This rate expression may be made specific for any acid catalyzed esterification by substituting in the radicals used for R and R'.

## J. RATE OF CHEMICAL REACTION

The rate at which a chemical reaction proceeds,  $-r_A$ , expressed in terms of the number of molecules converted per unit time per unit volume depends on the frequency of collisions between the reacting molecules, and the fraction of these collisions occurring with sufficient energy to overcome the activation energy barrier. The fraction of collisions meeting this energy criterion can be expressed by the Maxwell Distribution Law as a function of the absolute temperature, and is equal to  $\exp(-E/RT)$ .

Several other factors influence the effectiveness of these collisions. Among these are structural effects such as steric hindrance, which has been mentioned earlier, and energy-dissipation considerations. Factors such as these are essentially temperature independent, and may be combined in a temperature-independent probability constant  $P$ . In addition, a frequency factor,  $A$ , may be defined as a measure of the frequency of the collisions of the reacting species. The frequency of collisions (which is inversely proportional to the mean free path of the molecules) increases as a function of temperature.

Therefore, it may be said that the rate of reaction is equal to the product of:

1. The frequency of the collisions between reacting species, which is a function of the concentration of the reacting species in the reaction mass.

2. The fraction of molecules colliding with sufficient energy to react.

3. The probability that these collisions will be fruitful in terms of orientation, quantum and energy-dissipation considerations.

The equation governing the reaction rate may be expressed as:

$$-r_A = P_A \exp(-E/RT) \prod_{i=1}^n (C_i)^{\beta_i} \quad (16)$$

The constant product,  $P_A$ , is seen to be dependent upon temperature, but is generally treated as a temperature-independent constant  $k_0$ . This may be justified by the fact that the effect of temperature in the exponential term greatly outweighs its effect in the pre-exponential constant.

The rate expression may then be divided into three characteristic portions:

1.  $k_0$ , a constant with dimensions of  $(\text{time})^{-1} \times (\text{concentration})^{1-n}$ , where  $n$  is order of reaction.

2.  $\exp(-E/RT)$  an exponential temperature function which is dimensionless, and

3.  $\prod_{i=1}^n (C_i)^{\beta_i}$ , a concentration function explicit

in the concentration of each species present.

$\alpha_i$  is the order of reaction with respect to the particular species.

### The Arrhenius Equation

The non-concentration dependent functions in the rate expression described above can be stated by the Arrhenius equation.

$$k = k_0 \exp(-E/RT) \quad (17)$$

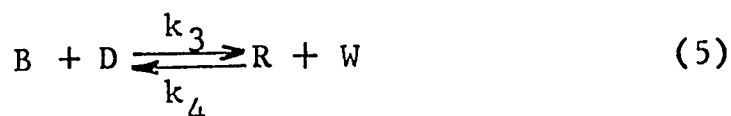
This equation describes the exponential increase in reaction rate constant with temperature, resulting from an increasing proportion of molecules possessing sufficient energy to overcome the activation energy barrier. Once the rate constants at two temperatures are known, the Arrhenius parameters may be calculated, enabling the calculation of the rate constant at any other temperature.

Other expressions have been developed to predict the temperature dependence of the reaction rate constant. The increased accuracy if any, obtained in using these relationships is far outweighed by the cumbersome calculational techniques and additional information required in their usage. The Arrhenius equation in general fits experimental data well over a wide range of temperatures, and

for most engineering applications is preferred because of its simplicity. For this reason, the Arrhenius equation was used throughout this work.

# K. EQUILIBRIUM CONSTANT

The equilibrium constant for a reversible reaction system may be mathematically derived in terms of the  $A_{AC}^2$  mechanism discussed earlier. The reactions occurring within the system may be written as:



It is assumed that each reversible reaction given is elementary in either direction.

Consider reaction (4). The rate equation for the forward reaction is:

$$-r_A = k_1 C_A C_C \quad (18)$$

and that for the reverse reaction is:

$$-r_A = -k_2 C_D \quad (19)$$

The net rate of disappearance of reactant A is the algebraic sum of the two reactions.

$$-r_A = k_1 C_A C_C - k_2 C_D \quad (20)$$

When equilibrium is established, the net rate of disappearance of A is zero,

$$-r_A = k C_{Ae} C_{Ce} - k_2 C_{De} = 0 \quad (21)$$

This equation describes the concept of dynamic equilibrium as the condition at which the rate of the forward reaction is identical to the rate of the reverse reaction, or

$$k_1 C_{Ae} C_{Ce} = k_2 C_{De} \quad (22)$$

This equation may be rearranged to

$$\frac{k_1}{k_2} = \frac{(C_{De})}{(C_{Ae} C_{Ce})} = K_1 \quad (23)$$

where  $K_1$  is the equilibrium constant for this reaction.

The equilibrium expressions for Eq(5) and Eq(6) may be derived in a similar manner.

$$\frac{k_3}{k_4} = \frac{C_{Re} C_{We}}{C_{Be} C_{De}} = K_2 \quad (24)$$

$$\frac{k_5}{k_6} = \frac{C_{Pe} C_{Ce}}{C_{Re}} = K_3 \quad (25)$$

Solving Eq(23) for  $C_{De}$  and Eq(25) for  $C_{Re}$  and substituting the result in Eq(24) yields, with rearrangement

$$K_1 K_2 K_3 = \frac{(C_{Pe}) (C_{We})}{(C_{Ae}) (C_{Be})} = \frac{k_1 k_3 k_5}{k_2 k_4 k_6} \quad (26)$$

Realizing that

$$k_i = k_{0i} \exp(-E_i/RT) \quad (27)$$



it may be written

$$\frac{k_1 k_3 k_5}{k_2 k_4 k_6} = \frac{k_{01} k_{03} k_{05} \exp (-E_1 - E_3 - E_5) / RT}{k_{02} k_{04} k_{06} \exp (-E_2 - E_4 - E_6) / RT} \quad (28)$$

Defining the following quantities,

$$k_{0f} = k_{01} k_{03} k_{05} \quad (29)$$

$$k_{0b} = k_{02} k_{04} k_{06} \quad (30)$$

$$E_f = E_1 + E_3 + E_5 \quad (31)$$

$$E_b = E_2 + E_4 + E_6 \quad (32)$$

the final form of the equilibrium expression may be stated

$$K_{eq} = \frac{(C_{Pe})(C_{We})}{(C_{Ae})(C_{Be})} = \frac{k_{0f} \exp (-E_f / RT)}{k_{0b} \exp (-E_b / RT)} = \frac{k_f}{k_b} \quad (33)$$

The overall equilibrium constant for the reaction,  $K_{eq}$ , is therefore defined.

The temperature dependency of the equilibrium constant is given by the van't Hoff equation,

$$\frac{d(\ln K_{eq})}{dT} = \frac{\Delta H_r}{RT^2} \quad (34)$$

where

$T$	$\equiv$ absolute temperature
$R$	$\equiv$ universal gas constant
$\Delta H_r$	$\equiv$ heat of reaction

and

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

As Kaplan (30) points out, most esterification reactions have negligibly small heats of reaction. In terms of the van't Hoff equation it may be said that the equilibrium constants for esterification reactions are functionally independent of temperature.

Glasstone (26) has indicated that the effect of catalyst on the equilibrium constant is negligible in all cases except those in which the catalyst affects the activities of the reactants. The effect of added hydrogen ions (in the form of mineral acid catalyst) on the equilibrium position of the reaction system in this study, may be examined in light of the derivation of the equilibrium constant consistent with the  $A_{AC}^2$  mechanism. It can be seen by Eq (33), the final equilibrium expression in terms of the concentrations of the reacting compounds, that the equilibrium constant is independent of hydrogen ion concentration. In addition, lactic acid may be classified as a weak electrolyte and as such, the activity of this species may be satisfactorily expressed in terms of its concentration. On this basis,

the effect of catalyst on the equilibrium constant is assumed to be negligible in the present system.

## L. HOMOGENEOUS CATALYSIS

A homogeneous catalyst is defined as a non-stoichiometric quantity of an acid, base or specific ion that is miscible with the reactants and products, which has no effect on the stoichiometry of the reacting system, but results in an increase in the reaction rate. The phenomenon of homogeneous catalysis may be modelled as two reactions occurring in parallel, the catalyzed and uncatalyzed reactions.

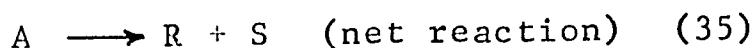
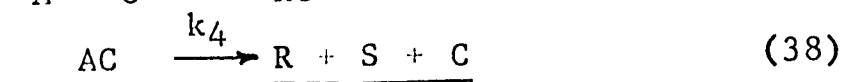
Consider the following reaction scheme



whose rate of reaction may be expressed as

$$-r_A = k_1 C_A \quad (36)$$

The catalytic reaction may be postulated as occurring by the following mechanism



Assuming that the first step of the above reaction is rate controlling, the rate of disappearance of reactant A may be expressed as

$$-r_A = k_2 C_A C_C \quad (39)$$

The total rate of disappearance of A is then

$$-r_A = k_1 C_A + k_2 C_A C_C \quad (40)$$

or,

$$-r_A = (k_1 + k_2 C_C) C_A \quad (41)$$

Since the catalyst is regenerated in the catalyzed reaction, its concentration remains essentially constant in the system, and the term  $k_2 C_C$  is therefore also constant. The observed overall rate constant for a homogeneously catalyzed reaction may then be given by

$$k_{\text{obs}} = k_1 + k_2 C_C \quad (42)$$

The observed constant,  $k_{\text{obs}}$ , will be constant for a given temperature and catalyst concentration, but it will vary linearly as a function of catalyst concentration.

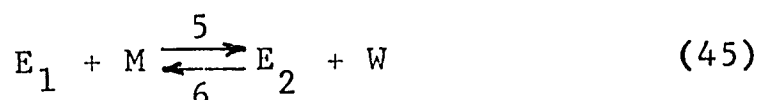
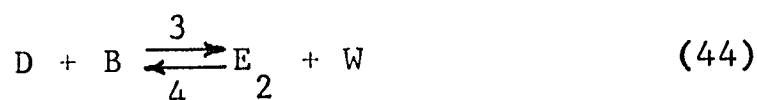
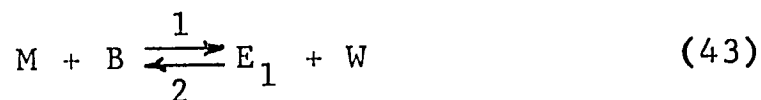
It should be pointed out at this juncture that the foregoing technique does not rigorously apply to the lactic acid-butanol system. According to the  $A_{AC}^2$  mechanism for esterification, the "uncatalyzed" reaction cannot proceed without the initial presence of some hydrogen ions. In the "uncatalyzed" system these ions would normally be supplied via dissociation of some carboxylic acid groups of the lactic acid. It is speculated that the addition of hydrogen ions by the catalyst would suppress the dissociation of the lactic acid yielding, at

extremely low catalyst concentrations, no net increase in hydrogen ion concentration. The effect would be offset as the catalyst concentration increases.

It is assumed for the purposes of this study that because lactic acid is a mild acid, with a dissociation constant of  $1.374 \times 10^{-4}$  @25°C, the approach presented above for correlation of the effect of catalyst concentration may be used with introduction of negligible error in the lower catalyst concentration ranges.

M. REACTION SCHEME

Consistent with the reaction scheme proposed by Filachione and Fisher (25) for the reactions occurring in the esterification of lactic acid, the following expressions may be written:



where,

M = monomeric lactic acid  
 $\text{CH}_3\text{CHOHCOOH}$

D = dimeric lactic acid  
 $\text{CH}_3\text{CHOHCOOCH}(\text{CH}_3)\text{COOH}$

B = n-butyl alcohol  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

W = water  
 $\text{H}_2\text{O}$

$E_1$  = butyllactate  
 $\text{CH}_3\text{CHOHCOOC}_4\text{H}_9$

$E_2$  = butyllactyllactate  
 $\text{CH}_3\text{CHOHCOOCH}(\text{CH}_3)\text{COOC}_4\text{H}_9$

In water solutions of lactic acid ranging up to 85%, an equilibrium exists between monomeric (M) and dimeric (D) acid. It has been shown by Watson (62) that the higher weight polylactic acids are not present.

Assuming the added inhibition of steric hindrance in the esterification of butyllactylactate, the probability of higher chain length esters is very small. It is therefore assumed that no further reactions are occurring in this system.

In the case of the self-esterification of monomeric lactic acid, it has been shown by Kaplan (30), and confirmed in this investigation that the reaction is extremely slow, even in the presence of a catalyst at elevated temperatures, (Appendix A). It is therefore assumed that the effects of this reaction are unimportant and it therefore need not be considered.



## N. REACTOR DESIGN EQUATIONS

The major equipment used throughout this kinetic study was a constant flow stirred tank reactor, commonly called a backmix or total backmix reactor. This reactor system offers the advantage of simplicity in operation combined with relatively easy interpretation of results. In the ideal steady-state backmix reactor the contents are well stirred and the composition of the reaction mass is homogeneous throughout the system. The effluent stream from this reactor has the same composition as the fluid within the reactor. The reactor design equation for a constant flow stirred tank reactor may be derived using the techniques presented in Levenspiel (28).

The starting point for all design is the general material balance expressed for any reaction component. Such a material balance for any reactant may be expressed for any bound system in the following form:

$$\begin{aligned} & \left( \begin{array}{l} \text{rate of reactant} \\ \text{flow into system} \end{array} \right) = \left( \begin{array}{l} \text{rate of reactant flow} \\ \text{out of system} \end{array} \right) + \dots \\ \dots & \left( \begin{array}{l} \text{rate of reactant} \\ \text{loss due to chemical} \\ \text{reaction within system} \end{array} \right) + \left( \begin{array}{l} \text{rate of accumulation} \\ \text{of reactant within} \\ \text{system} \end{array} \right) \quad (46) \end{aligned}$$

In the present case, the system is the reaction

mass and the boundary is the wall of the reactor.

Assuming only the steady-state case, the rate of accumulation of reactant within the system is zero, and the material balance reduces to:

$$\begin{aligned} \left( \begin{array}{l} \text{rate of reactant} \\ \text{flow into system} \end{array} \right) &= \left( \begin{array}{l} \text{rate of reactant} \\ \text{flow out of system} \end{array} \right) + \dots \quad (47) \\ &\dots \left( \begin{array}{l} \text{rate of reactant} \\ \text{loss due to chemical} \\ \text{reaction within system} \end{array} \right) \end{aligned}$$

Since the composition is uniform throughout, the balance may be applied about the reactor as a whole. Expressing the molar feed rate of component A into the reactor in terms of the volumetric feed rate, and the concentration of component A in the feed,

$$F_{Ai} = v_i C_{Ai} \quad (48)$$

where

$F_{Ai}$  = molar feed rate, moles/time

$v_i$  = volumetric feed rate, volume/time

$C_{Ai}$  = concentration of A in feed, moles A/unit volume

The following rates can be written

$$\text{Input of A, moles/time} = F_{Ai} = F_{Ai}(1-X_{Ai}) \quad (49)$$

$$\text{Output of A, moles/time} = F_{Af} = F_{Ai}(1-X_{Af}) \quad (50)$$

Disappearance of A by reaction, moles/time =

$$(-r_A)_f V = \left( \frac{\text{moles of A reacting}}{(\text{time})(\text{volume of reacting fluid})} \right) \times \left( \frac{\text{volume of reactor occupied by reacting fluid}}{\text{fluid}} \right) \quad (51)$$

where

$X_{Ai}$  = initial conversion of reactant A

$X_{Af}$  = final conversion of reactant A

$(-r_A)_f$  = rate of disappearance of component A at existing reactor conditions, (moles)/(unit volume)(time)

$V$  = volume of reacting fluid.

Substituting equations (49), (50) and (51) into equation (47) yields

$$F_{Ai}(1-X_{Ai}) = F_{Ai}(1-X_{Af}) + (-r_A)_f V \quad (52)$$

or, with simplification,

$$F_{Ai}(X_{Af}-X_{Ai}) = (-r_A)_f V \quad (53)$$

Rearrangement gives

$$\frac{V}{F_{Ai}} = \frac{V}{v_i C_{Ai}} = \frac{X_{Af}-X_{Ai}}{(-r_A)_f} \quad (54)$$

In the subject system, the reactants are not contacted until they enter the reactor. Therefore, the initial conversion,  $X_{Ai} = 0$ . Then,

$$\frac{V}{v_i} = \frac{C_{Ai} X_{Af}}{(-r_A)_f} \quad (55)$$

Finally, the quantity space time,  $\tau$ , having units of time, may be defined as the time required to process one reactor volume of feed measured at specified conditions. The space time may be expressed as:

$$\tau = \frac{V}{v_i}$$

(reactor volume)/(volumetric feed rate) (56)

Combining equation (55) and (56) yields the final working form of the design equation for the backmix reactor.

$$\tau = \frac{V}{v_i} = \frac{VC_{Ai}}{F_{Ai}} = \frac{C_{Ai} X_{Af}}{(-r_A)_f} \quad (57)$$

Knowing the reactor volume, volumetric feed rates, and reactor effluent concentrations, permits the calculation of the observed rate constants of the reactions occurring within the system.

## O. PRIOR LACTIC ACID KINETIC INVESTIGATIONS

In previous sections of this report, the long and varied history of lactic acid has been discussed. In spite of lactic acid's early discovery and the extensive commercial exploitation of this versatile acid, basic studies into the kinetics of this system have been few. To date only four investigations have appeared dealing with the kinetics of esterification of lactic acid.

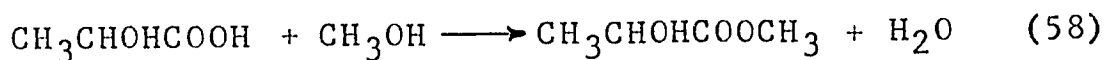
Three of the investigations appearing in the literature, those of Troupe and Kobe (56), Troupe and Kobe (57), and Troupe and Dimilla (55), are similar in their approach to the determination of the rate constant and will therefore be discussed together. Troupe and Kobe studied the esterification of lactic acid with methanol in the presence of sulfuric acid catalyst. Troupe and Dimilla investigated the kinetics of the ethanol-lactic acid reaction catalyzed by sulfuric acid.

Two grades of lactic acid were used in these studies; reagent grade, 85% lactic acid, and 44% technical grade lactic acid. In total, four systems were studied; each alcohol with each of the acid concentrations given above.

Before presenting the results of these investigations it is pertinent to discuss the assumptions made by the investigators in the analysis of their findings.

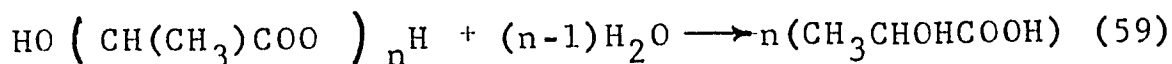
The only reactions assumed to be occurring within the system were:

1. The Esterification of Monomeric Acid



and,

2. The Hydrolysis of Lactic Acid Condensation Polymers



The investigators were aware of the presence of lactyllactic acid in their reaction system but chose to neglect any reaction of alcohol with this component. Further esterification of the esters was not considered.

In addition, the correlation of the kinetic rate data was done entirely on an empirical basis. No reaction mechanisms were postulated nor were any rate expressions derived. The general kinetic relationship arrived at in all three investigations was of the form:

$$kt = \frac{X}{(A-b)(A-b-x)} \quad (60)$$

where:

A = total lactic acid originally present, moles

b = a function of the reactant ratio, moles

x = the amount of lactic acid converted in time

= t, moles

t = reaction time, minutes

k = specific reaction rate constant, liter/mole-minute

The functional relationships between the rate constant and the reaction temperature, catalyst concentration and mole ratio of reactants were also determined.

The final forms of the four correlations are given below. In all the forms presented, the following consistent nomenclature is used.

(A/L) = mole ratio of alcohol to acid

C = weight percent sulfuric acid catalyst

T = temperature, °K

Methanol-85% Lactic Acid (Reagent Grade)

$$k = \left( 0.08750 (A/L)C - 0.08955C + 0.00435 \right) \times \left( \frac{10(10.91369 - 3139.3/T)}{314.3} \right) \quad (61)$$

Methanol - 44% Lactic Acid (Technical Grade)

For catalyst concentrations up to 0.417% sulfuric acid,

$$k = (0.0001755(A/L) + 0.0005807) \left( \frac{10^{(10.36400-3069.3/T)}}{136.5} \right) \quad (62)$$

For catalyst concentrations above 0.417% sulfuric acid,

$$k = (0.000422(A/L)(C) + 0.014175C - 0.005334) \times \left( \frac{10^{(10.36400-3069.3/T)}}{136.5} \right) \quad (63)$$

Ethanol - 35% Lactic Acid (Reagent Grade)

$$k = (0.03120(A/L)C - 0.0150C + 0.001895) \times \left( \frac{10^{(11.086-3265/T)}}{215.1} \right) \quad (64)$$

Ethanol - 44% Lactic Acid (Technical Grade)

For catalyst concentrations up to 0.263% sulfuric acid,

$$k = (0.0001031(A/L) + 0.00024) \left( \frac{10^{(8.721-2579/T)}}{64.1} \right) \quad (65)$$

For catalyst concentrations above 0.263% sulfuric acid,



$$k = (0.000342(A/L)C + 0.00177C - 0.000218) \times \left( \frac{10^{(8.721-2579/T)}}{64.1} \right) \quad (66)$$

The level response of rate constant to catalyst concentration for technical grade lactic acid in the low catalyst ranges is explained by the authors as the result of reaction of the catalyst with impurities in the acid.

An interesting effect is noted when the predicted rate constants at the two acid concentrations with either alcohol are compared. (Table III). The predicted constants for 88% lactic acid are 20 to 30 times those for 44% acid. Theory predicts that the rate constant for a reaction should be independent of the reactant concentration. It is felt by this author that the deviation of these results from theory is a result of the neglect of certain reactions occurring in the system. These are namely, the esterification of lactylactic acid and the esterification of the alcoholic esters of lactate with lactic acid.

Kaplan (30) investigated the kinetic data of the somewhat "synthetic" system of monomeric lactic acid and normal butyl alcohol. The variables

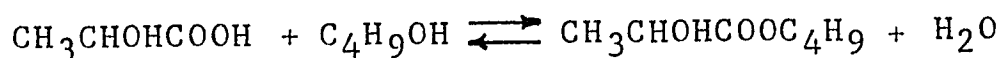
TABLE III

Predicted Rate Constants For Different Lactic  
Acid Solutions (55,56,57)

Temperature	350°K
Catalyst Concentration, Weight Per Cent	0.10
Mole Ratio of Alcohol To Acid	5.00

<u>Alcohol</u>	<u>Predicted Rate Constant</u> <u>liter/mole-min</u>	
<u>Lactic Acid</u> <u>Concentration</u>	<u>85%</u>	<u>44%</u>
Methanol	0.01093	0.000365
Ethanol	0.00424	0.000264

studied were reaction temperature and catalyst concentration. Only one reaction was assumed to occur within the system, the reaction between monomer and alcohol:



The data were correlated as a second order reversible reaction, and the Arrhenius parameters were determined for the system. For the uncatalyzed system the activation energy was found to be 13,190 calories and the pre-exponential constant was 673 liter/mole-second. The activation energy for the catalyzed reaction was found to be 13,580 calories with a frequency factor of 547 liters<sup>2</sup>/mole-second-mmole catalyst. The equilibrium constant for the esterification reaction found was 3.02.

A further discussion of Kaplan's work is warranted at this point. As mentioned, the system studied by Kaplan was "synthetic". That is, concentrated solutions of lactic acid with dimer concentrations of approximately 4.5-9% do not occur naturally. The utility of kinetic data derived from this is therefore quite limited in an application such as the industrial design suggested.

In addition, Kaplan, as did the investigations of Troupe, neglected the possibility of reaction between dimer and alcohol. The experimental design used by Kaplan was intended to reduce the importance of the dimer esterification by reducing the concentration of dimer in the reaction mass. However, the dimer concentration in his initial lactic acid mixture was as high as 9% by weight, with a corresponding monomer concentration of 71%. In terms of reacting species, the percentage of total carboxylic acid groups in the reaction mass attributable to dimer ranged from 3.5 to 6.5%. At equilibrium, the dimer carboxylic acid groups represent 24.2% of the total. On this basis, it is felt that the assumption of negligible dimer esterification is invalid.

The experimental results presented in this work differ from prior investigations in one major respect. All possible reactions occurring in the system have been included. As mentioned previously, the works of Troupe (56,57,58) approached the study of the kinetics of lactic acid-alcohol reactions from a completely empirical viewpoint. No mechanistic assumptions were made. In addition, Troupe chose to neglect the possible reactions of other acid and

alcoholic constituents within the reaction system.

Kaplan attempted to reduce the importance of the dimer-alcohol reaction by reducing the concentration of dimer to negligible proportions. As explained above, he was not successful, and his correlations were in error in this respect.

The current work has approached the lactic acid-alcohol kinetic study from a theoretical direction and has made only justifiable assumptions regarding the mechanisms of the reaction scheme.

## CHAPTER II

### Experimental Procedures

#### A. RAW MATERIALS

##### Lactic Acid

The lactic acid used in this experiment was purchased from the Clinton Corn Processing Company. Clinton lactic acids are made with the use of special strains of the lactic acid-producing bacteria, (lactobacillus), which produce the acid by their action on various grades of dextrose. The resulting dilute acid solutions are refined to meet the specifications of the different grades of lactic acid and concentrated (by the evaporation of water), to the percent acid required.

Two Clinton lactic acid products are available for industrial use: Light Technical Grade Lactic Acid and Dark Technical Grade Lactic Acid. The differences between them are primarily attributed to the refining each receives. The light Technical may be considered to be intermediate between the Food Processing and Dark Technical Grades. The Light is of higher purity than the Dark, having a lighter color and containing smaller percentages

of protein, carbohydrates and metal salts.

The grade of lactic acid used throughout this work was the Light Technical Grade, 80 percent acid. The acid was used as it came from the drum, with no further purification or modification of composition. Acid analyses were performed periodically throughout the course of this investigation and the composition was found to be essentially constant.

Acid composition was analyzed by the method of Eder and Kutter (19), which was modified (see page 76) to fit the equipment of this investigator. The analysis of the lactic acid solution, based on several sets of replicate samples is presented in Table IV. The Table also gives the 95 percent confidence range of the component concentrations.

#### n-Butyl Alcohol

Technical grade n-butyl alcohol purchased from Commercial Solvents Corporation was used as the alcoholic component of the esterification reaction. Commercial Solvents butanol is sold as 99% pure. (Chromatographic analysis of the butanol showed only one peak, indicating no detectable impurities). The alcohol was used straight from the drum with no further purification.

TABLE IVAnalysis of 80% Light Technical Grade Lactic Acid

<u>Component</u>	<u>Weight Percent Average</u>	<u>95% Confidence Range</u>
Monomeric Acid $\text{CH}_3\text{CHOHCOOH}$	46.278	$\pm 0.407$
Dimeric Acid $\text{CH}_3\text{CHOHCOOCH}(\text{CH}_3)\text{COOH}$	35.155	$\pm 0.916$
Water, $\text{H}_2\text{O}$	<u>18.567</u>	$\pm$ <u>0.509</u>
Total	100.000	$\pm 1.832$



### Butyl Lactate

Reagent grade butyl lactate from the Baker Chemical Company was used as a chromatographic standard. Water content of the butyl lactate by Fisher water assay was less than 0.20 per cent. Chromatographic analysis of the butyl lactate showed the presence of no major impurities.

### Hydrochloric Acid

Reagent grade hydrochloric acid, obtained from the Baker Chemical Company, was used as the acid catalyst in this investigation. The hydrochloric acid is sold as a 37 per cent aqueous solution.

## B. ANALYTICAL TECHNIQUES

### Titration Techniques

The technique used to determine the total acid and total ester content of a sample was a modification of the method of Eder and Kutter (19). Simply stated, the method involved the titration of total acid groups present using a standard base, addition of excess base with subsequent saponification of the ester groups, and back titration of the remaining base with standard acid to determine the amount of base consumed in saponification. The method routinely followed in all total acid and total ester analyses is as follows:

1. An aliquot sample, P grams, (approximately 0.8cc) was weighed by difference, via a 1.0cc syringe, into a 250 ml beaker.
2. The sample was diluted to approximately 100 cc with distilled water.
3. This solution was titrated to pH 7.0 with 0.1 N NaOH, (A mls), using a Beckman automatic titrator.
4. Sufficient excess of 0.1 N NaOH was added to saponify all ester groups present. (B mls) generally, 20 cc of excess base was enough.
5. Saponification was speeded by heating

the sample in a hot water bath for 3 hours at 90°C.

6. The solution was cooled to room temperature and backtitrated to pH 7.0 with a standard 0.05 N HCl solution, (C mls).

At this point, the modification of the technique of Eder and Kutter (19), made by this author should be explained. The suggested technique involved the saponification of the ester in a steam bath at 100°C for 15 minutes. Since a hot water bath at 90°C was used in this work, it was found that 15 minutes was not sufficient to saponify all ester present. A minimum of 2 hours in the bath was required to obtain reproducible results. To be certain all ester reacted, a time of 3 hours at 90°C was taken as standard.

The analysis of the experimental data taken by the above technique varied slightly depending on whether the sample was feed lactic acid or reactor product. The calculational approach used in each case is outlined below.

Calculation of lactic acid composition was performed as follows. By knowledge of the components present, it is realized that each monomer molecule

contains one acid group. It is also known that each dimer molecule contains one acid group and one ester group. Therefore, the total ester present in the feed sample is equal to the total amount of dimer. The difference between the amount of dimer and the total acid present is the amount of monomer. In equation form this is written as:

$$\begin{aligned}\text{Total acid} &= (A, \text{ ml NaOH}) \times (X, \text{ mmoles/ml NaOH}) \\ &= \text{mmoles acid} \quad (67)\end{aligned}$$

$$\begin{aligned}\text{Total ester} &= (B, \text{ ml NaOH}) \times (X, \text{ mmoles/ml NaOH}) - \\ &\quad (C, \text{ ml HCl}) \times (Y, \text{ mmoles/ml HCl}) \\ &= \text{mmoles base reacting with ester} \\ &= \text{mmoles ester} \quad (68)\end{aligned}$$

Where X and Y are the molarities of the standard base and acid respectively. Then,

$$\text{mmoles ester} = \text{mmoles dimer} \quad (69)$$

$$\begin{aligned}\text{mmoles acid} - \text{mmoles ester} &= \text{mmoles} \\ &\quad \text{monomer} \quad (70)\end{aligned}$$

The mmoles of acid and ester per gram are obtained by dividing through by the sample weight. Thus,

$$\text{mmoles dimer/gram} = \frac{BX - CY}{P} \quad (71)$$

$$\text{mmoles monomer/gram} = \frac{AX - BX + CY}{P} \quad (72)$$

Weights may be obtained by multiplying through by the proper molecular weight. Water content is obtained by difference.

Calculation of reaction products was basically the same as the approach given above, except that since the relative amounts of ester groups attributable to dimer, butyl lactate or butyllactyllactate are unknown, the calculation can not proceed past equation (68). That is,

$$\text{Total Acid} = AX/P, \quad \text{mmoles/gram} \quad (73)$$

$$\text{Total Ester} = BX-CY/P, \quad \text{mmoles/gram} \quad (74)$$

#### Catalyst Determination

Catalyst was added to the reaction mass via the n-butanol feed stream. Varying amounts of HCl catalyst were injected into the butanol feed flask immediately prior to the start of a run. Catalyst was analyzed for by titration of the feed butanol-catalyst mixture to pH 7.0 immediately after the termination of the run. Since the moles of catalyst per gram of butanol were known, and the grams of butanol per gram of reaction mass were

known from the feed rates, the moles of catalyst per gram of reaction mixture could be calculated.

#### Automatic Titrator

All acid-base titrations were performed using a Beckman Model K Automatic Titrator. The Model K Titrator, consisting of one control unit and two delivery units (one each for acid and base), provided a convenient, rapid means of conducting the titrations. Titrating accuracy of up to 0.1 per cent can be expected from this unit. The end point of the titrations was established by standardization with buffer solution of pH 7.0. The unit was standardized prior to the analysis of a particular run. Standard glass and calomel electrodes were used as the electrode pairs on the titrator.

#### Chromatographic Techniques

The determinations of the butanol and butyl lactate components of the reaction mass were performed by chromatographic techniques. The chromatograph used in this study was a dual column, F and M model 810 flame ionization gas chromatograph. The column was 8 feet long by 1/8 inch diameter, packed with 10 per cent phosphoric acid on Diatoport S 80-100 substrate. The standard operating conditions on

the chromatographic unit were:

gas flow rate	2.5 scale reading
helium pressure	56.0 psi
hydrogen pressure	26.0 psi
oxygen pressure	40.0 psi
detector temperature	210°C
injection block temperature	140°C
oven temperature (isothermal)	140°C
attenuation	32

These conditions gave excellent separation of the butanol and butyl lactate peaks.

Calibration of the unit was done via an internal standard incorporated with the sample of the reaction product. The technique used is as follows. Prior to each day's run, a chromatographic standard was carefully weighed; it consisted of drum butanol, butyl lactate, and diphenyl ether. Diphenyl ether was selected as the standard material on the basis of its miscibility with the reaction mixture, its inertness with respect to the components of the reaction mixture, and its relatively high boiling point. The diphenyl ether peak came out of the chromatograph several minutes after the butanol and butyl lactate peaks.

Several injections of the standard were made to determine the calibration in terms of the butyl lactate to diphenyl ether and the butanol to diphenyl ether area ratios. The premise in this calibration technique was that the butanol, butyl lactate, and diphenyl ether peak areas are related to the relative quantity of that material present. In addition, the response of the area-to-weight ratio of one component relative to another are proportional. The technique is commonly used in quantitative chromatographic analysis. The relationship may be summed up as

$$\frac{(\text{Area A/wt. A})_1}{(\text{Area B/wt. B})_1} = \frac{(\text{Area A/wt. A})_2}{(\text{Area B/wt. B})_2} = \text{constant} \quad (75)$$

From this standard, the constant may be evaluated.

The sample analysis proceeded as follows. A sample of reaction product was weighed by difference into a known weight of diphenyl ether. Generally 4.0 to 4.5 grams of sample to 0.5 grams of ether was used. This mixture was then immediately injected into the chromatograph and the response peaks obtained. The samples were cooled prior to mixing but not cooled after mixing. For this reason, the samples were never allowed to age more than 20 minutes to decrease the chance of additional reaction. Three injections were made of each sample.



Data for a typical analysis is given in Table V.

All chromatographic peak areas were determined by means of a Gelman Model 39231 Compensating Polar Planimeter. Each peak was transversed four times to determine an average value of the area.

It should be mentioned at this point that the constants evaluated from the standard were reproducible within the day but varied from day to day. The butanol constant varied from 0.929 to 1.075. The butyl lactate constant varied from 0.503 to 0.620. This is most probably due to the result of the slight uncertainty in resetting the conditions of the chromatograph. Resetting was necessitated by the fact that the same chromatograph was being used simultaneously by other investigators.

TABLE V

Calculation of Butanol and Butyl Lactate  
Concentration by Chromatographic Standards

Run #107

Temperature - 60°C

Catalyst Concentration - 0.04929 mmoles/gram

Initial Lactic Acid - 2.9057 mmoles/gram

Initial Dimer - 1.2262 mmoles/gram

Initial Butanol - 5.861 mmoles/gram

Initial Water - 5.8277 mmoles/gram

Feed Rate - 29.781 ml/min

Residence Time - 1315 sec

Standard

<u>Area BuOH</u>	<u>Area Bulac</u>	<u>Wt DPE</u>	<u>Wt DPE</u>	<u>C<sub>BuOH</sub></u>	<u>C<sub>Bulac</sub></u>
<u>Area DPE</u>	<u>Area DPE</u>	<u>Wt BuOH</u>	<u>Wt Bulac</u>		
2.376	0.858	0.4223	0.6951	1.0034	0.596
2.405	0.866	0.4223	0.6951	1.0156	0.602
2.415	0.854	0.4223	0.6951	1.0199	0.594
Ave.				1.0130	0.597

Sample

<u>Area BuOH</u>	<u>Area Bulac</u>	<u>Wt DPE</u>	<u>Wt BuOH</u>	<u>Wt Bulac</u>
<u>Area DPE</u>	<u>Area DPE</u>	<u>g-sam</u>	<u>g-sam</u>	<u>g-sam</u>
2.767	0.372	0.1398	0.382	.0870
2.765	0.359	0.1398	0.382	.0841
2.804	0.356	0.1398	0.387	.0832
Ave.			0.384	.0847

### C. DESCRIPTION OF ESTERIFICATION EQUIPMENT

Figure 2 is a schematic drawing of the continuous esterification apparatus used throughout this investigation. Feed reservoirs consisted of two 4-l Erlenmeyer flasks; one each for the butanol-catalyst mixture and the 80 per cent lactic acid solution. The reactants were pumped from their respective feed flasks to the reaction vessel by means of a DCL Series II Micropump. The pump heads (both #3 DCL) were driven from the same shaft, with the volumetric flow rates delivered being controlled by a micrometer dial adjustment of piston stroke. Throughout the series of runs performed, micrometer settings of 5.0 were maintained on both pump heads. All lines connecting equipment pieces were either glass or tygon. The lines between the pump heads and the reactor were tygon, and these lines were elevated above the level of the liquid in the reactor to trap any air bubbles entering the system and to reduce any possible back flow of reaction mass from the vessel into the pumping lines. Periodic checking of pumping rates showed them to be reproducible with approximately one per cent error.

The 670 ml overflow backmix reactor was equipped with an outer jacket to permit the circulation of a

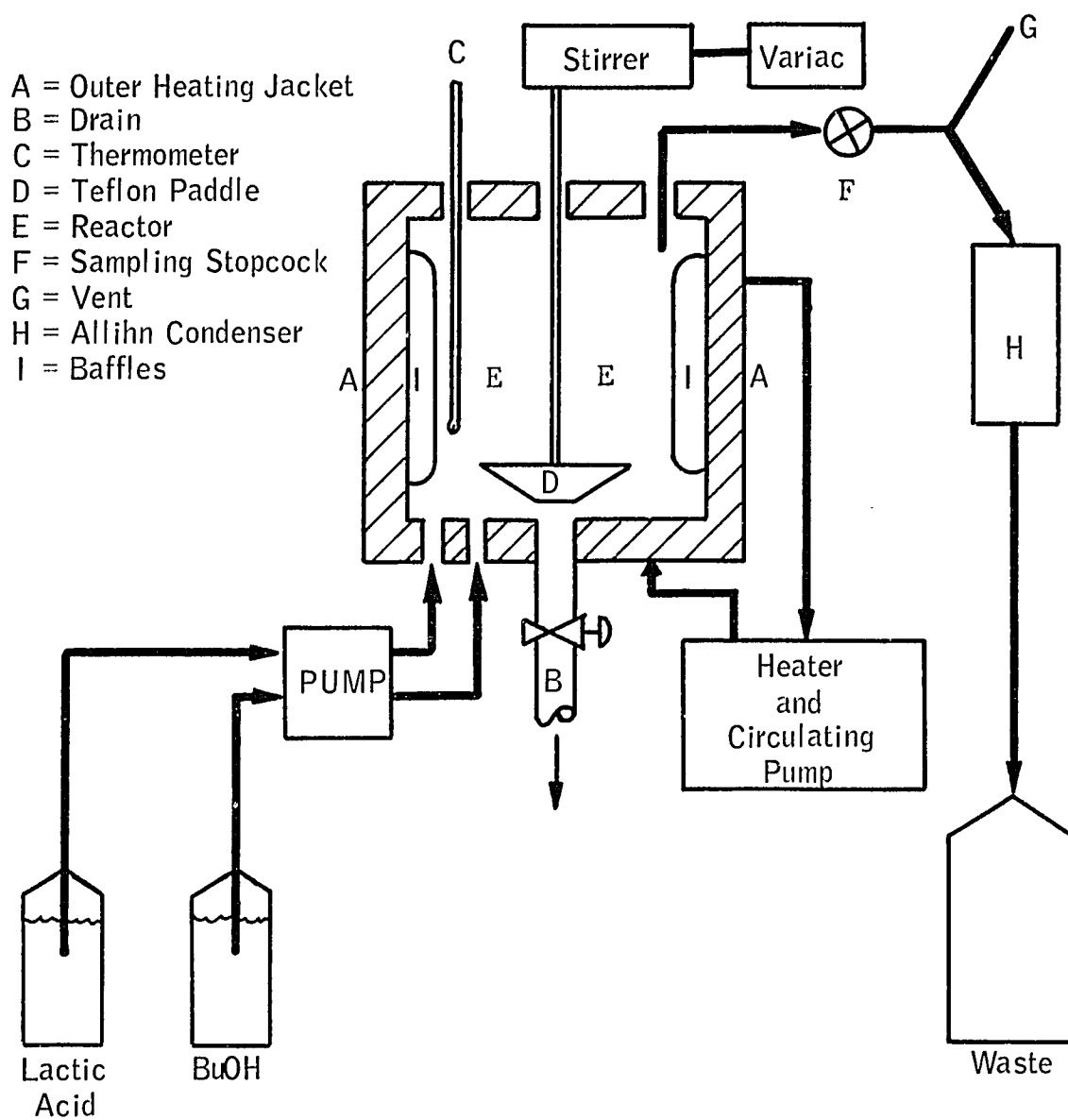


Figure 2

SCHMATIC OF EXPERIMENTAL EQUIPMENT CONFIGURATION

heating medium which consisted of 80% glycerin and 20% water. The reaction volume was completely surrounded by the heating medium. The reactor also contained four baffles to retard any vortex formation and thereby produce better mixing. The reactor contained the following openings: 1. Two connections at the base of the reactor for feed entrance. 2. One overflow connection at the top of the reactor for product exit. 3. Two jacket connections for heating medium circulation. 4. One jointed opening at the top for entrance of agitator shaft. 5. One jointed thermometer opening. 6. One stopcock at the base of the reactor for draining and/or sampling.

Mixing was accomplished using a Bodine Electric Company 36:1 Speed Reducer Motor Type NSE-11R whose speed of rotation was controlled by means of a Variac. The speed was kept constant throughout the series of experiments at 2050 rpm. This motor drove a teflon paddle at the end of a glass stirring rod. The paddle height was adjusted below the center of the reactor, near the entrance reactant streams, to insure rapid and complete mixing.

Verification of thorough mixing in the reactor

was made by variation of stirrer speed and product sampling point. Samples were taken at 80 to 100 per cent of maximum speed. These samples were taken from the bottom drain stopcock and immediately after the overflow connection. Titration of these samples indicated only statistical variation in the total acid obtained. To insure maximum effectiveness, the stirrer was run at maximum speed throughout all runs. Sampling was done after the overflow connection to eliminate the possibility of reactant "short circuiting" the reactor.

A thermometer entering through the other jointed neck of the reactor provided the temperature readout. The accuracy of the thermometer was  $\pm 0.2^{\circ}\text{C}$ . It was determined in the course of running that the temperature of the reactor varied  $\pm 0.3^{\circ}\text{C}$ , varying with the temperature of the heating medium reserve tank.

The product exited through the overflow connection. The exit line was vented by means of a "Y" tubing connection. This vent served to prevent vacuum locking and thus eliminated siphoning of product from the reactor. The overflow led to a water-cooled Allihn condenser to cool the product stream and thereby decrease the amount

of butanol vapors in the room. The product finally dripped into a five gallon waste bottle.

Sampling was done via a three way stopcock in the exit line, located immediately after the overflow port of the reactor. The samples were cooled during the sampling by passage through a condenser. This served to prevent the escape of butanol and water vapors, thereby giving a true sample of the reactor product.

#### D. RUN PROCEDURE

Immediately prior to the start of a run, the lactic acid feed supply flask was flushed with fresh lactic acid and filled; the butanol feed flask was flushed with butanol to remove residual butanol-catalyst mixture and filled with butanol. An approximate volume of HCl catalyst was added to the butanol by means of a 20cc syringe. The hydrochloric acid volume was not carefully measured because exact catalyst determination was subsequently performed on the mixture. The butanol-catalyst mixture was thoroughly stirred to insure complete mixing.

The pumps were turned on and the reactor began to fill. The heater was turned on, set approximately ten degrees above the reactor temperature. This setting was later adjusted to yield the desired temperature. When the reactor was about one third full, the stirrer was begun at a low speed so as to avoid the mixing of air with the reactants. As the reactor filled, the rate of stirring was increased. When the reactor began to overflow, the stirrer was set at the proper speed, and the water flow through the condenser was begun. After running for three hours, (approximately six reactor volumes), the sampling stopcock was flushed and several samples



were taken at once in 5 ml test tubes. To verify the attainment of steady-state, earlier runs were sampled at two and one-half hours and three hours after the reactor began to overflow (sample separation about one reactor volume). No detectable difference was noted between total acid and total ester results at the two times. The system was therefore considered to be at steady state after three hours on all subsequent runs. Product samples were sealed and immediately immersed in a dry-ice-acetone bath; remaining there until immediately prior to analysis.

### E. SAMPLE EXPERIMENTAL RUN

All runs were performed using the previously outlined experimental procedures. The outline of a typical experimental run and the presentation of the raw data taken from this run will be presented in this section. The presentation of this sample experimental run will be helpful in visualizing how all the experimental data in this investigation was obtained.

Run No. 107 was performed within a series of runs at a reactor temperature of 60.0°C. Circulation bath temperature was therefore initially set. Pumping rates were held constant at a vernier setting of 5.0 on both heads. These settings were not changed throughout all experimental runs. Subsequent to the experimental runs, two verification runs were made at varying alcohol/acid feed ratios. These runs are discussed in Chapter III.

Immediately prior to the initiation of the run, 37 cc of HCl catalyst were injected into approximately 2.5 l of butanol contained in the butanol feed flask. After the mixture was thoroughly stirred, pumping was started. Three hours after the reactor had begun to overflow, four 5 ml samples were

taken by the afore-mentioned procedure. Customarily, two of these four samples were analyzed. The remaining two were taken as back-up samples in the event of a mishap. The samples were removed from the ice bath just before analysis and allowed to thaw to the point where the sample would flow.

Prior to the start of product analysis, samples of the butanol-catalyst mixture were taken. These samples were weighed by difference into 250 ml beakers and titrated to pH 7.0. The results of these titrations are given in Table VI. The acid concentration in the feed butanol mixture, in units of mmoles per gram of mix, are known directly by this titration. The final catalyst concentration in the product mixture may be calculated from the mmoles per gram of mixture and the weight ratio of grams of butanol per gram of total feed.

Product titration samples were weighed by difference, via a syringe, into 250 ml beakers. Initially, four titration samples were prepared. This number was later cut to three when it was found that titration analysis was very reproducible. The samples were diluted one at a time with approximately 100 cc of distilled water and titrated to pH 7.0. The results of these titrations are given

in Table VI. Elapsed time from the initiation of weighing to the final acid titration was approximately 10 minutes.

When initial acid titrations were completed, excess base was added to each sample, the samples were saponified for 3 hours at 90°C, cooled to room temperature and back-titrated with standard acid. These results are also presented in Table VI.

Chromatographic samples were prepared by first difference weighing the diphenyl ether into 20 ml jointed erlenmeyer flasks. The product sample was removed from the ice bath, thawed, and weighed by difference into the diphenyl ether. The sample was thoroughly mixed, and chromatographic injections begun. Elapsed time from the initiation of weighing until the completion of chromatographic injection was approximately 20 minutes. The results of these analyses are given in Table VI.

Total acid (corrected for catalyst), total ester, weight fraction butanol and weight fraction butyl lactate may be obtained directly from this data.

TABLE VI  
Sample Experimental Run  
Run No. 107

Temperature - 60°C	Initial Lactic Acid- 2.9057 mmoles/gram
Feed Rate - 29.781 ml/min	Initial Dimer- 1.2262 mmoles/gram
Residence Time - 1315 sec	Initial Butanol- 5.861 mmoles/gram
Feed Ratio - 0.434g BuOH/g-feed	Initial Water- 5.8277 mmoles/gram
N, NaOH - 0.09705N	
N, HCl - 0.04554N	

Catalyst Determination

	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>
Weight, g	84.2447	91.8263	88.2041
ml NaOH	42.73	46.68	44.82
mmole cat/g	0.04922	0.04933	0.04932

Sample Titration

	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>	<u>Sample 4</u>
Weight, g	0.7142	0.6453	0.7863	0.7699
ml NaOH	25.56	23.06	28.12	27.52
ml excess	20.00	20.00	20.00	20.00
ml HCl	12.28	19.07	9.14	9.86
mmoles acid/g (uncorr)	3.4732	3.4679	3.4703	3.4691
mmoles ester/g	1.9344	1.9411	1.9389	1.9378

TABLE VI, Cont'd.

<u>Chromatographic Samples</u>			
wt. DPE/gram-sample - 0.1398			
$C_{\text{BuOH}}$ - 1.0130			
$C_{\text{Bulac}}$ - 0.597			
	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>
Area BuOH	670	857	729
Area Bulac	90	111	87
Area DPE	242	310	260
wt. BuOH, g/g-sam	0.382	0.382	0.387
wt. Bulac, g/g-sam	0.0870	0.0841	0.0832

### CHAPTER III

#### EXPERIMENTAL RESULTS

The esterification of an aqueous 80 percent lactic acid solution with n-butanol was studied at three temperature levels and varying catalyst levels. The catalyst levels determined ranged from zero to 45 mmoles/liter. Reaction was performed in an overflow backmix reactor with volumetric input rate maintained constant. Reactor residence time varied slightly with the reaction temperature and the composition of the product stream. Experimental residence times varied from 1315 sec at 60 °C to 1244 sec at 80 °C.

The data taken for a typical run are presented in Table VI. A tabulation of total acid, (corrected for catalyst), total ester, butanol, butyl lactate and catalyst data are presented in Appendix B. Mean values of total acid, total ester, butanol, and butyl lactate are plotted versus catalyst concentration in Figures 3, 4, 5, and 6.

To smooth the raw experimental data and to simplify further calculations, all experimental data at the three temperature levels were correlated by curvilinear regression using least squares poly-

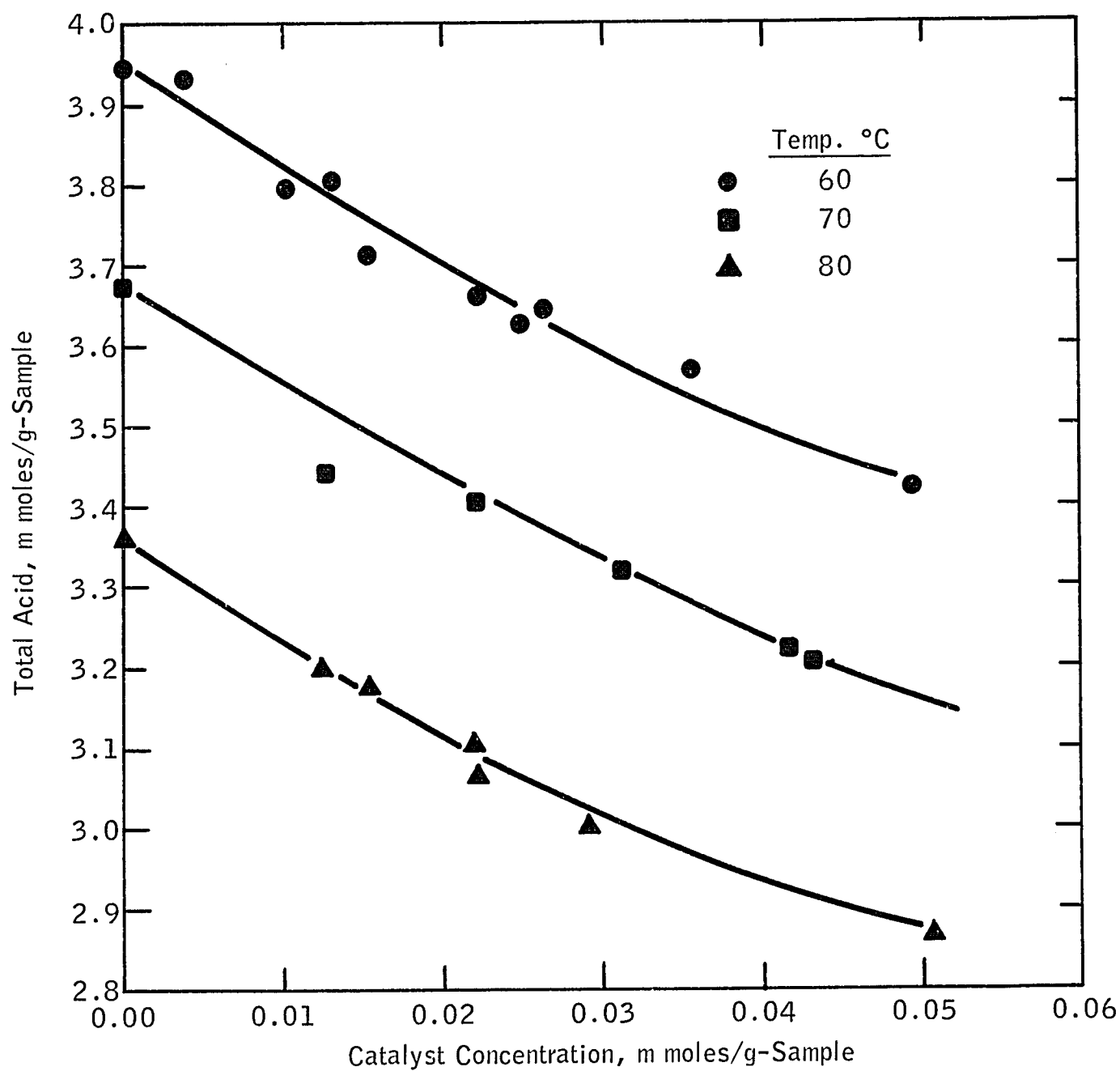


Figure 3  
MEAN TOTAL ACID DATA VS.  
CATALYST CONCENTRATION  
(m moles/g-Sample)



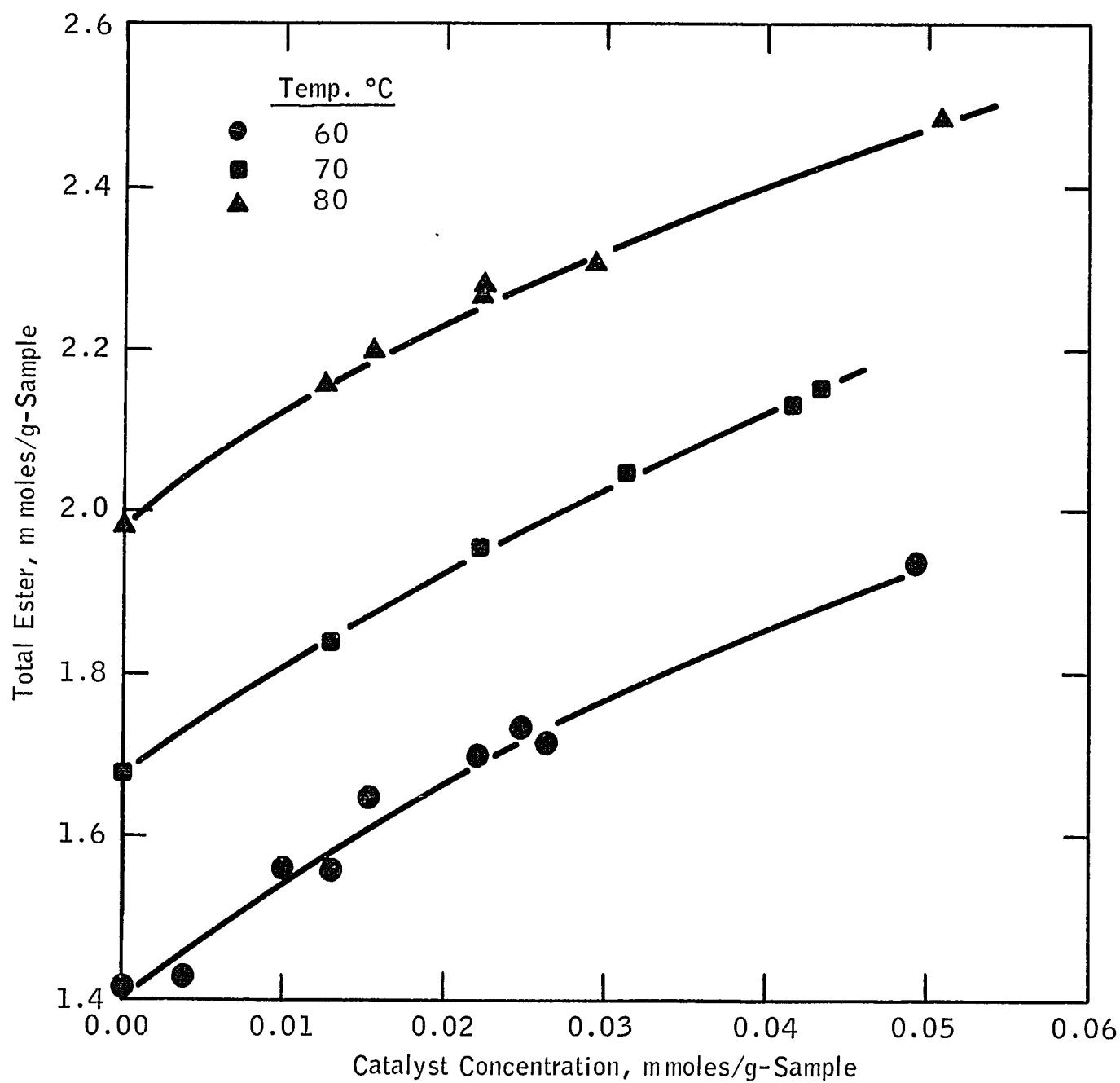


Figure 4

TOTAL ESTER VS. CATALYST CONCENTRATION  
(m moles/g-Sample)

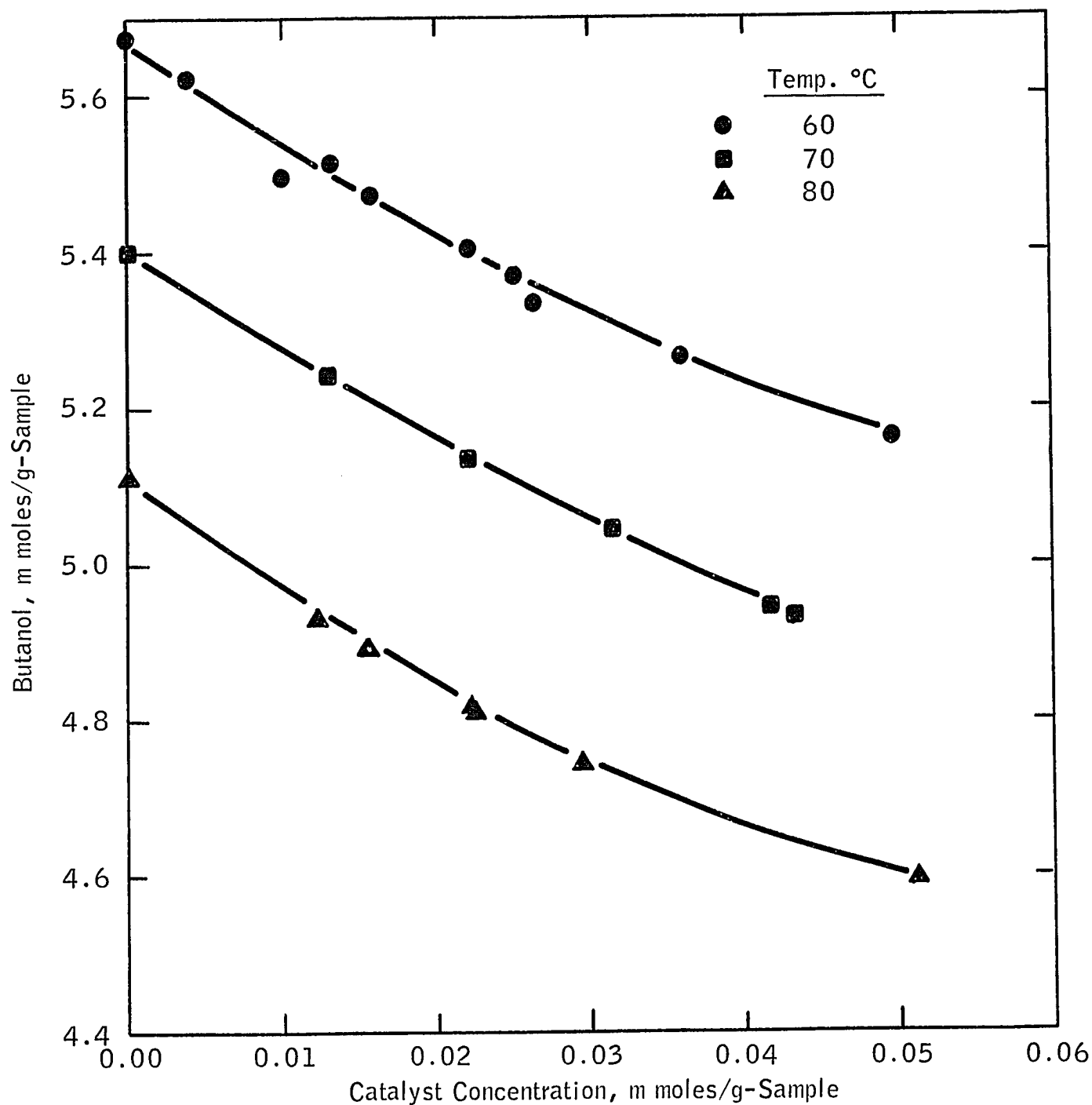


Figure 5  
BUTANOL VS. CATALYST CONCENTRATION  
(m moles/g-Sample)

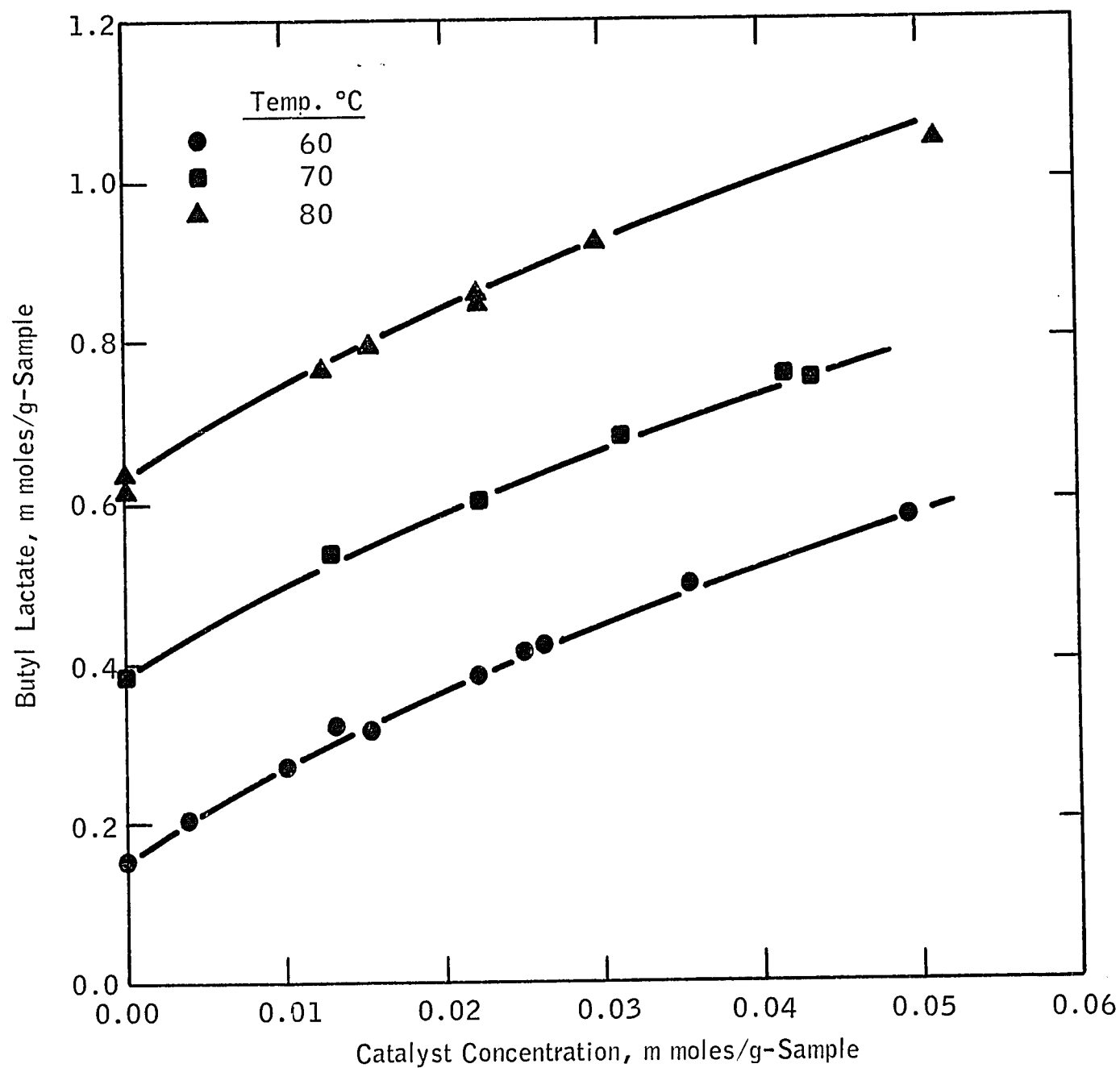


Figure 6

BUTYL LACTATE VS. CATALYST CONCENTRATION  
(m moles/g-Sample)

nomials. Excellent fit to all data was obtained with second order polynomial equations in terms of catalyst concentration. The resultant polynomials are presented in Table VII, and shown in Figures 3, 4, 5, and 6. Table VII also presents the index of determination of the correlation, (a measure of the probability that this data can be represented as a second degree polynomial), and the standard error of the estimate for the dependent variable. As can be seen from this table, correlation was quite good.

Summary computer printouts for all experiments, showing the actual data, predicted data and the percent difference between the two are given in Appendix C.

### Material Balances

Consistent with the possible reaction models proposed earlier and with the knowledge of initial feed compositions, material balances may be written to determine the amounts of the various components within the reaction mass.

It is known from the reaction stoichiometry that the total acid (corrected for catalyst content), must be equal to the acid groups attributable to the

TABLE VII  
Smoothing Polynomials for Raw Data

<u>Temp C</u>	<u>Least Squares Equation*</u>	<u>Total Acid Data</u>	<u>Index of Determ</u>	<u>Std Error of Est for Y</u>
60	$Y_1 = 3.95445 - 14.618C + 81.8023C^2$		0.9770	0.024332
70	$Y_1 = 3.67204 - 13.3045C + 59.8682C^2$		0.9829	0.023690
80	$Y_1 = 3.36121 - 14.1355C + 86.7209C^2$		0.9849	0.0206556
<u>Total Ester Data</u>				
60	$Y_2 = 1.40342 + 14.6646C - 82.3866C^2$		0.9769	0.024427
70	$Y_2 = 1.67714 + 14.0901C - 72.1122C^2$		0.9879	0.020353
80	$Y_2 = 1.9754 + 15.3621C - 105.964C^2$		0.9741	0.028211
<u>Butanol</u>				
60	$Y_3 = 5.66912 - 14.151C + 78.719C^2$		0.9658	0.029295
70	$Y_3 = 5.39968 - 13.0834C + 53.2539C^2$		0.9900	0.018151
80	$Y_3 = 5.1124 - 15.7324C + 109.631C^2$		0.9890	0.018579

Cont'd.

Table VII, Cont'd.

<u>Temp C</u>	<u>Least Squares Equation*</u>	<u>Index of Determ</u>	<u>Std Error of Est for Y</u>
	<u>Butyl Lactate</u>		
60	$Y_4 = 0.157258 + 11.9354C - 68.5898C^2$	0.9869	0.014991
70	$Y_4 = 0.382067 + 11.3141C - 58.2879C^2$	0.9861	0.017494
80	$Y_4 = 0.528209 + 12.5541C - 84.8627C^2$	0.9853	0.017404

- \*  $Y_1$  = Total Acid, m.e./g-sample  
 $Y_2$  = Total Ester, m.e./g-sample  
 $Y_3$  = Butanol, mmoles/g-sample  
 $Y_4$  = Butyl Lactate, mmoles/g-sample  
C = Catalyst concentration, m.e./g-sample

monomer (M), plus the acid groups attributable to the dimer (D). This may be written in equation form as

$$\text{Total Acid} = M + D \quad (76)$$

It is also known from the reaction stoichiometry, that the total ester groups must be equal to the sum of the dimer ester groups plus the butyl lactate ( $E_1$ ) ester groups, plus twice the butyllactyllactate ester groups, ( $E_2$ ), or

$$\text{Total Ester} = D + E_1 + 2E_2 \quad (77)$$

Following the assumed model any reaction of butanol is to form butyl ester. By the model, the only butyl esters formed are butyllactate and butyllactyllactate. Therefore, the decrease in butanol is equal to the sum of the two butyl esters. This may be written as

$$B_i - B = E_1 + E_2 \quad (78)$$

where  $B_i$  is the initial butanol content and  $B$  is the final butanol content.

Finally, the butyl lactate content is known by analysis. Change in water content is found by difference, realizing that for every acid group that disappears, one water unit is formed. These balances may be written as

$$\text{Butyl lactate} = E_1 \quad (79)$$

$$W = W_i + \text{initial total acid} - P \quad (80)$$

where  $W_i$  is initial water content,  $W$  is final water content, and  $P$  is total acid.

It should be noted that these balances are independent of reaction path and are only based on the formation of the specified reaction products.

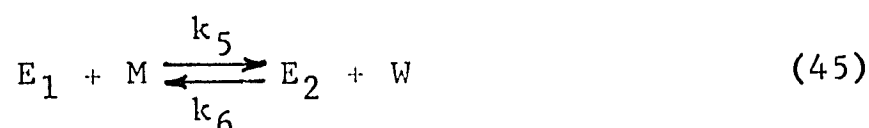
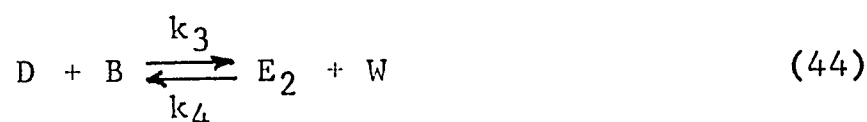
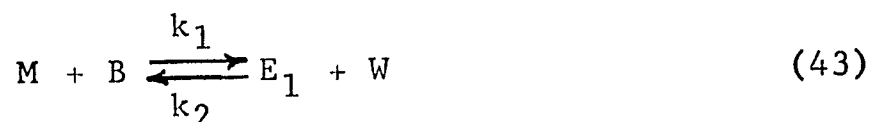
These material balances (Eqs. (76), (77), (78), (79), and (80)) were combined and solved for individual component concentrations using the smoothed data equations. These results are presented in Appendix D.

The component concentrations as a function of catalyst concentration were fit by regression to a least squares polynomial of second order. Since the solution of the material balance equations involves the addition and subtraction of the smoothed second order polynomials for the raw data and constants, the resultant component equations should be second order polynomials. That is, since the raw data were expressed as second order polynomials the resultant component concentration must also be perfectly expressed as second order polynomials. The equations for component concentration in mmoles



per gram versus catalyst concentration are given in Table VIII.

At this point, simplifying assumptions were made about the nature of the reaction scheme. Two possible paths may be followed to determine the reaction kinetics. First, all three suggested reactions may be assumed as occurring to an appreciable extent. That is,



If the reaction given by equation 45 is significant, the decrease in monomer content should be significantly larger than the increase in butyllactate content. Examination of the component equations in Table VIII reveals that the differences between these relative rates are small and may be assumed statistically insignificant. The assumption that this reaction is negligible is given further merit in light of the kinetics of the reaction of between two monomer groups to yield the dimer. This reaction is extremely slow in the present system

TABLE VIII  
Smoothed Component Concentration Equations

<u>Monomer</u>	
<u>Temp., °C</u>	<u>Least Squares Equation *</u>
60	$Y_5 = 2.77753 - 12.9153C + 75.3406C^2$
70	$Y_5 = 2.53547 - 12.5419C + 83.7611C^2$
80	$Y_5 = 2.2548 - 10.587C + 58.2873C^2$
<u>Dimer</u>	
60	$Y_6 = 1.17692 - 1.70256C + 6.45911C^2$
70	$Y_6 = 1.13657 - 0.762699C - 23.8908C^2$
80	$Y_6 = 1.10641 - 3.54878C + 28.438C^2$
<u>Butyllactate</u>	
60	$Y_7 = 0.157258 + 11.9354C - 68.5895C^2$
70	$Y_7 = 0.382067 + 11.3141C - 58.2878C^2$
80	$Y_7 = 0.628209 + 12.5541C - 84.863C^2$
<u>Butyllactyllactate</u>	
60	$Y_8 = 0.034623 + 2.21558C - 10.129C^2$
70	$Y_8 = 0.079253 + 1.76933C + 5.03357C^2$
80	$Y_8 = 0.120391 + 3.17828C - 24.768C^2$
<u>Butanol</u>	
60	$Y_9 = 5.66912 - 14.1509 + 78.7167C^2$
70	$Y_9 = 5.39968 - 13.0833C + 53.2522C^2$
80	$Y_9 = 5.1124 - 15.7323C + 109.628C^2$

Cont'd.

Table VIII, Cont'd.

<u>Temp., °C</u>	<u>Least Squares Equation*</u>	
	<u>Water</u>	
60	$Y_{10}$	$= 6.00515 + 14.6182C - 81.8072C^2$
70	$Y_{10}$	$= 6.28756 + 13.3042C - 59.8641C^2$
80	$Y_{10}$	$= 6.59839 + 14.1357C - 86.7227C^2$

- 
- \*  $Y_5$  = lactic acid, mmoles/g-sample  
 $Y_6$  = dimeric acid, mmoles/g-sample  
 $Y_7$  = butyl lactate, mmoles/g-sample  
 $Y_8$  = butyllactyllactate, mmoles/g-sample  
 $Y_9$  = butanol, mmoles/g-sample  
 $Y_{10}$  = water, mmoles/g-sample  
 $C$  = catalyst concentration, mmoles/g-sample

(Appendix A). The reaction between butyl lactate and monomer is characteristically the same as the dimerization, with the carboxylic acid group of the monomer reacting with the alcoholic group of the ester. If anything, considering the added steric hindrance of the butyl group, this reaction might be expected to be slower than the dimerization. On this basis, as an initial attempt, only the reactions given in equations 43 and 44 were assumed to be important. This assumption was later found to be sound by the excellent correlation of the results obtained, taking only the reactions given by equations 43 and 44 as significant.

The equilibrium constants for the reactions occurring were evaluated at 25 °C from five specially prepared samples covering an initial range of alcohol to lactic acid mole-ratio varying from 1.16:1 to 7.25:1; and alcohol to dimer mole-ratio varying from 3.69: 1 to 25.9:1. Uncatalyzed mixtures were used in these evaluations. The equilibrium constant for the esterification of lactic acid was found to be  $3.13 \pm 0.16$ . The equilibrium constant for the esterification of lactyllactic acid was found to be  $2.75 \pm 0.15$ . The equilibrium constants were assumed to be independent of temperature and catalyst concen-

tration, (see page 51-52).

Density correction for conversion of data from unit weight to unit volume was performed using an empirical expression derived by Kaplan (30). The density may be expressed as

$$y = 0.869 - 0.026x_1 - 0.010x_2 + 0.0073x_1^2 \quad (81)$$

where

$y$  = density, grams/ml

$x_1$  = coded mole ratio of alcohol to lactic acid

$x_2$  = coded temperature, °C

The coding relationship for  $x_1$  and  $x_2$  may be expressed as

$$x_1 = -1 + (B/M - 2.0) \quad (82)$$

$$x_2 = 0.05T - 3.25 \quad (83)$$

The component balance equations, equilibrium constants, residence times, density conversion, and reactor design equation were solved to yield the forward observed rate constant as a function of catalyst concentration. These results are presented in Tables IX and X, and plotted in Figures 7 and 8. The computer printouts of these results are given in Appendix E.

TABLE IX  
Observed Forward Rate Constant For  
Butyllactate Formation

<u>T = 60°C</u>	
<u>Catalyst</u> <u>mmoles/l</u>	<u>Observed Rate Constant</u> <u>l/mole-sec x 10<sup>6</sup></u>
0.0	6.99
9.01	13.05
18.00	19.29
26.95	25.53
35.89	31.50
44.80	36.93
<u>T = 70°C</u>	
0.0	20.67
8.93	29.05
17.82	37.93
26.90	47.08
35.55	56.19
44.41	64.82
<u>T = 80°C</u>	
0.0	43.79
8.83	58.17
17.64	73.50
26.41	89.20
35.16	104.43
43.89	118.03

TABLE X  
Observed Forward Rate Constant For  
Butyllactyllactate Formation

<u>Catalyst</u> <u>mmoles/l</u>	<u>Observed Rate Constant</u> <u>1/mole-sec x 10<sup>6</sup></u>
<u>T = 60°C</u>	
0.0	3.60
9.01	6.07
18.00	8.49
26.95	10.83
35.89	13.03
44.80	15.06
<u>T = 70°C</u>	
0.0	9.30
8.93	11.89
17.82	14.87
26.69	18.31
35.57	22.33
44.41	27.05
<u>T = 80°C</u>	
0.0	15.94
8.83	21.38
17.64	26.59
26.41	31.28
35.16	35.15
43.89	37.91

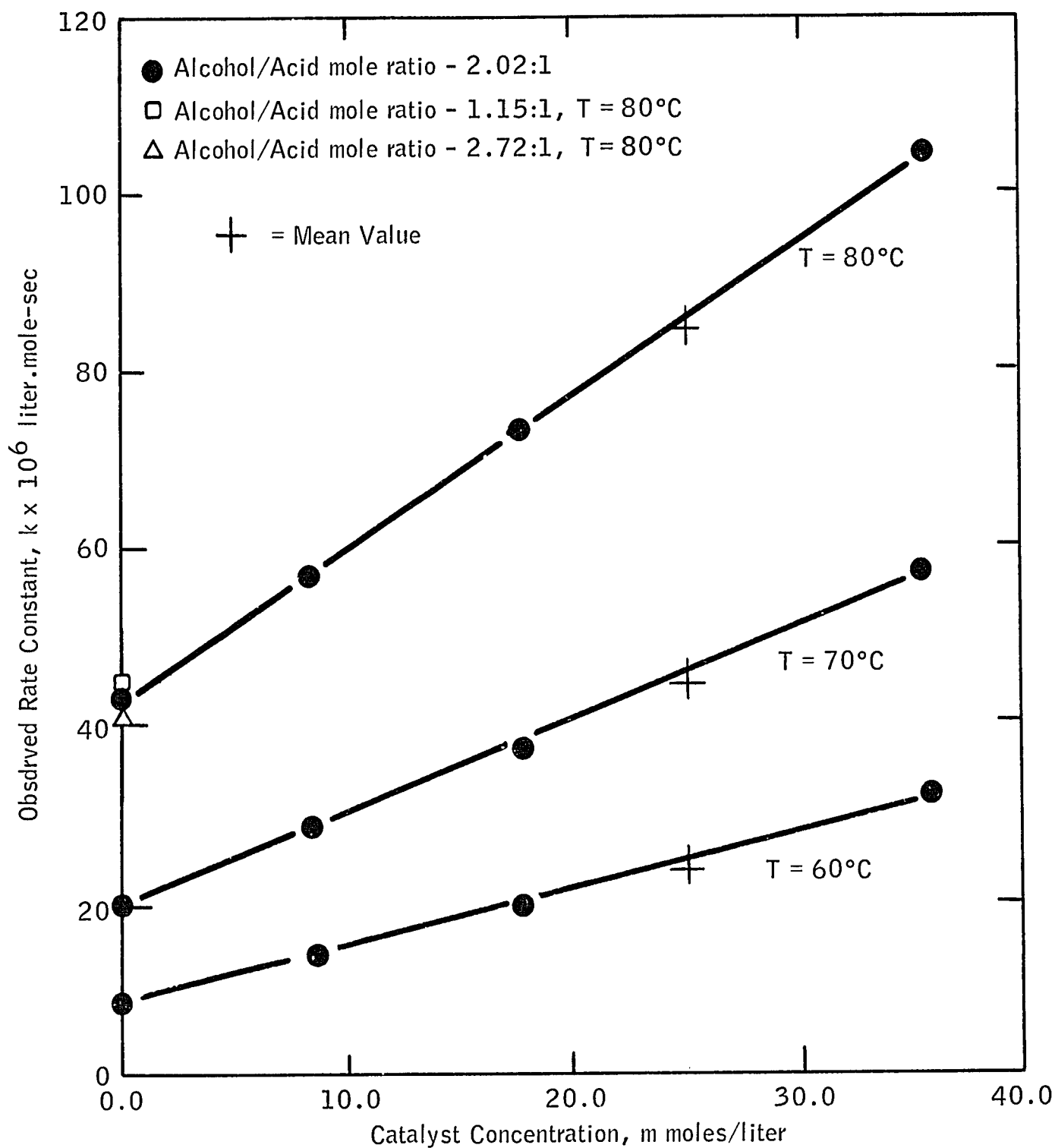


Figure 7

OBSERVED RATE CONSTANT FOR BUTYLLACTATE FORMATION, liter/mole-sec  
VS. CATALYST CONCENTRATION! m moles/liter



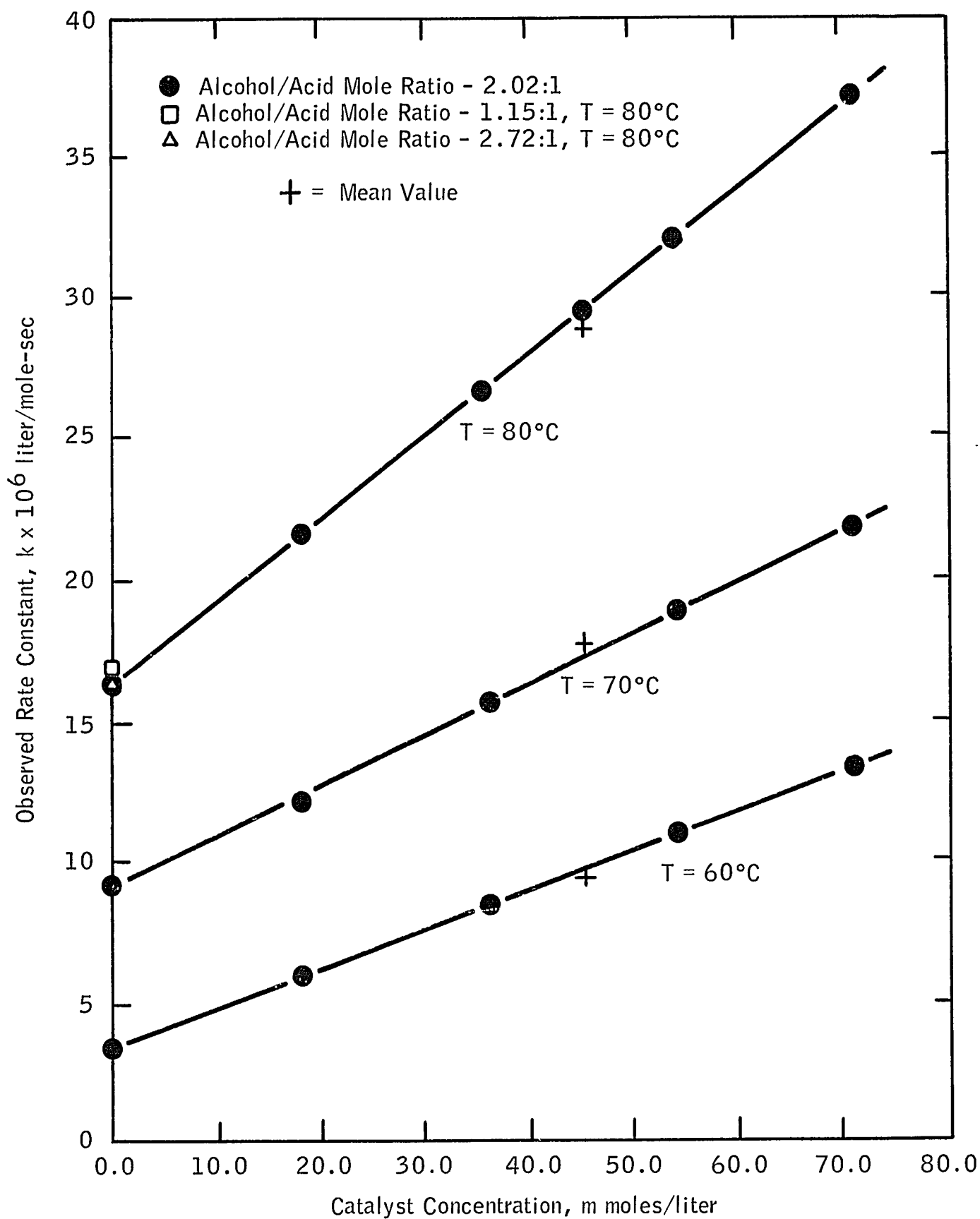


Figure 8

OBSERVED RATE CONSTANT FOR  
BUTYLLACTYLACTATE FORMATION, liter/mole-sec

First order Least Squares polynomials were then fit to these observed rate constants. The intercept of these linear relationships represents the uncatalyzed rate constants, while the slopes of these lines represent the catalyzed rate constants. The catalyzed and uncatalyzed rate constants are presented in Table XI. The computer printouts of the least squares fits are given in Appendix F.

Finally, first order least squares polynomials were fit to the catalyzed and uncatalyzed rate constants, using the natural log of the constant versus the reciprocal of the absolute temperature. The slope of this line represents  $-(E/R)$ , where  $E$  is the Arrhenius activation energy. The intercept represents the natural log of the pre-exponential constant,  $k_0$ . The Arrhenius parameters are presented in Table XII. Figure 9 shows the plot of the natural log of the rate constant,  $k$  versus the reciprocal of the absolute temperature for the butyl-lactate and the butyllactyllactate reactions, both catalyzed and uncatalyzed. Computer printouts for the least squares fit of  $\ln k$  versus  $1/T$  are given in Appendix G. It should be noted in Appendix G that the intercepts,  $\ln k_0$ , should be corrected by adding  $\ln(10^{-6})$ . This factor was not carried

TABLE XISummary of Catalyzed and Uncatalyzed Rate Constants

<u>Temp., °C</u>	<u>k, Catalyzed</u> <u>l<sup>2</sup>/mole-sec-mmole cat</u>	<u>k, uncatalyzed</u> <u>l/mole-sec x 10<sup>6</sup></u>
<u>Butyllactate Reaction</u>		
60	0.6737	7.095
70	1.0018	20.349
80	1.7113	43.557
<u>Butyllactyllactate Reaction</u>		
60	0.2568	3.750
70	0.3973	8.456
80	0.5075	16.884

TABLE XII  
Arrhenius Parameters

Butyllactate Reaction

<u>Reaction</u>	<u><math>k_o</math></u>	<u>E, cal</u>
Catalyzed	$8.91 \pm 1.10$ $l^2/\text{mole-sec-mmole cat}$	$10,870 \pm 650$
Uncatalyzed	$(6.258 \pm 0.97) \times 10^8$ $l/\text{mole-sec}$	$21,220 \pm 715$

Butyllactylactate Reaction

<u>Reaction</u>	<u><math>k_o</math></u>	<u>E, cal</u>
Catalyzed	$(4.54 \pm 0.55) \times 10^{-2}$ $l^2/\text{mole-sec-mmole cat}$	$7,980 \pm 645$
Uncatalyzed	$(1.303 \pm 0.08) \times 10^6$ $l/\text{mole-sec}$	$17,580 \pm 300$

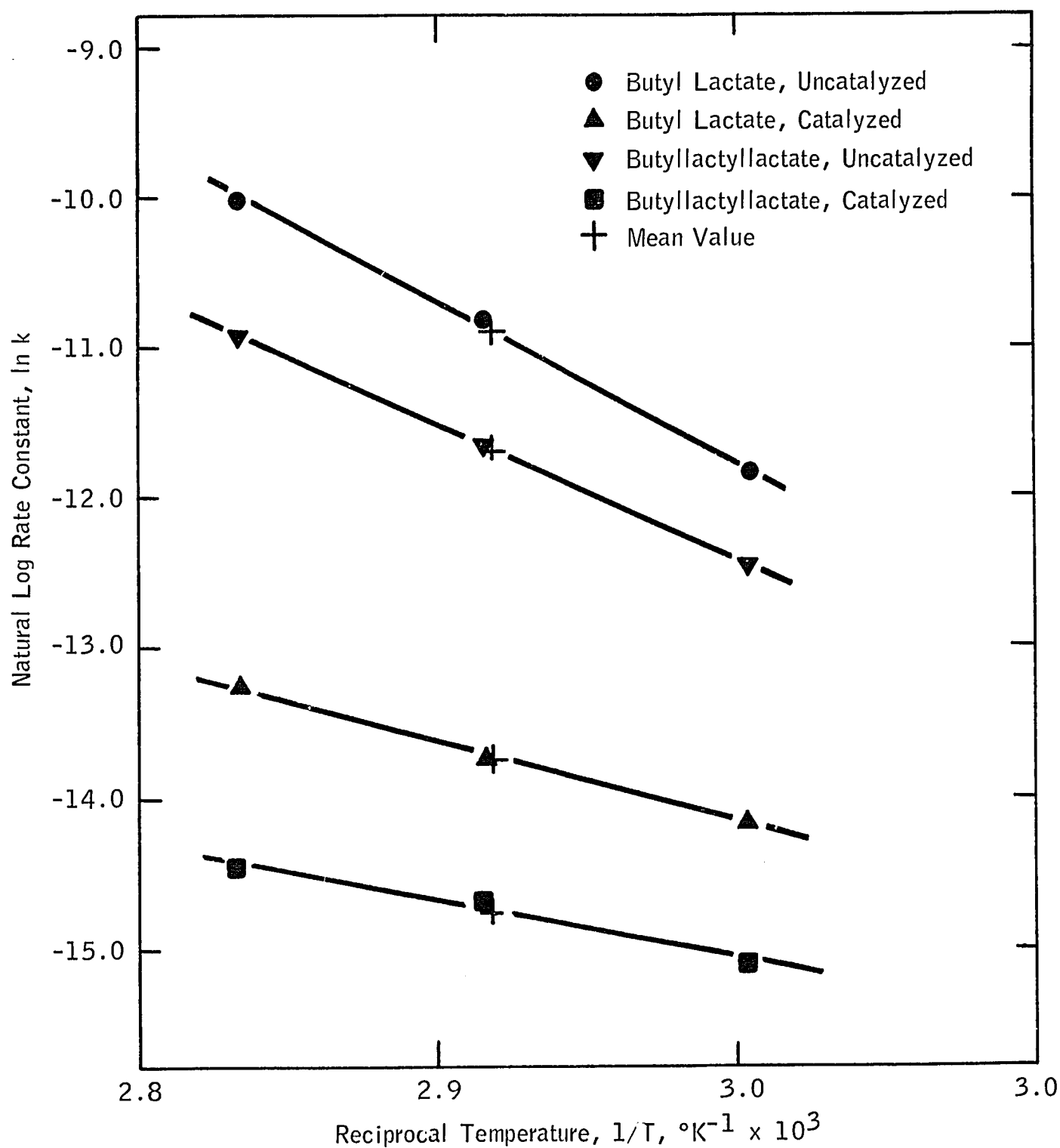


Figure 9

NATURAL LOG RATE CONSTANT,  $\ln k$  VS.  
 RECIPROCAL ABSOLUTE TEMPERATURE,  $1/T, ^{\circ}\text{K}^{-1}$

through in the calculation. The pre-exponential constants in Table XII are corrected.

### Verification Runs

To verify the independence of the observed rate constant from the effects of varying alcohol to acid ratio, two additional experimental runs were made subsequent to the experimental series previously discussed. Throughout that series of runs, lactic acid and butanol feed rates to the reactor were maintained constant. Pump head settings were kept at a micrometer reading of 5.0 for both reactant streams. In the two later runs, alcohol to acid feed ratios were varied by maintaining a lactic acid pump setting of 5.0 and varying the butanol setting to 3.0 and 7.0. Except as noted above, the run procedures and analytical techniques discussed in Chapter III were followed.

Both verification runs were made at 80°C with no added catalyst. Reactor residence times, reactant feed rates and initial reactant concentrations are given in Table XIII. Also given in Table XIII are the mean values of total acid, total ester, butanol and butyl lactate determined for the reaction products.

TABLE XIII

Variable Alcohol/Acid Ratio Runs Data

Temp. - 80.0°C

Catalyst concentration - 0.0 mmoles/liter

Lactic acid feed rate - 17.078 g/min

Reactor volume - 660 ml

	<u>Variable <math>\tau_1</math></u>	<u>Variable <math>\tau_2</math></u>
Weight rate butanol g/min	7.484	17.078
Residence time sec	1637	1063
Initial monomer conc., mmoles/g	3.575	2.528
Initial dimer conc., mmoles/g	1.506	1.064
Initial water conc., mmoles/g	7.160	5.050
Initial butanol conc., mmoles/g	4.115	6.875
Mean final total acid, mmoles/g	4.300	2.928
Mean final total ester, mmoles/g	2.284	1.728
Mean final butanol, mmoles/g	3.334	6.211
Mean final butyllactate mmoles/g	0.6575	.553

The reaction product analyses and initial feed compositions may be combined with the material balances presented previously to yield the individual component concentrations. This was done, and the results are presented in Table XIV.

Finally, the component concentrations, reactor residence time and reaction mass density, (calculated from empirical relationship of Kaplan (30)) may be combined in the reactor design equation to yield the rate constants for the butyl lactate and butyllactyl-lactate formation. The results of these calculations are given in Table XIV.

Also given in Table XIV are the percentage differences between these values and the values predicted by the Arrhenius parameters previously determined. Agreement between these values is good, thus indicating no relationship between observed rate constant and alcohol to acid mole ratio. For comparison purposes, these values are plotted in Figures 7 and 8.



TABLE XIV  
Variable Alcohol/Acid Ratio Run Results

<u>Product Conc., mmoles/g</u>	<u>Variable <math>\tau_1</math></u>	<u>Variable <math>\tau_2</math></u>
Monomer	2.917	1.975
Dimer	1.383	0.953
Butyllactate	0.658	0.553
Butyllactyllactate	0.123	0.111
Butanol	3.334	6.211
Water	7.941	5.714
Predicted butyllactate rate constant, 1/mole-sec x $10^6$	45.3	45.3
Observed butyllactate rate constant, 1/mole-sec x $10^6$	47.5	40.4
Percent difference	4.9%	-10.8%
Predicted butyllactyllactate rate constant, 1/mole-sec x $10^6$	17.0	17.0
Observed butyllactyllactate rate constant, 1/mole-sec x $10^6$	16.8	16.0
Percent difference	-1.1%	-5.9%

## CHAPTER IV

### DISCUSSION OF RESULTS

#### SUMMARY OF INVESTIGATION

The objective of this investigation was to determine the model for the system of reactions occurring when aqueous solutions of lactic acid are contacted with a primary alcohol. The alcohol selected for use in this study was n-butanol. The choice of butanol was not arbitrary, but was made on the basis of an industrial design proposed by Kaplan (30), for the purification of lactic acid. However, the mechanistic results obtained in this study need not be restricted to butanol alone. The final reaction model should be applicable to any primary alcohol.

Several possible reactions may be postulated as occurring within this system. These include the dimerization of monomeric lactic acid, the reaction of monomeric lactic acid with butanol to form butyllactate, the reaction of dimeric lactic acid with butanol to form butyllactyllactate, and the reaction of monomeric lactic acid with butyllactate to form butyllactyllactate. The system considered as a whole is quite complicated, with parallel and

series reactions occurring simultaneously. The reaction scheme, however, may be simplified considerably on the basis of previous investigations and logical conclusions drawn from an examination of the esterification mechanisms.

The dimerization reaction may be isolated and studied independently. The results of a preliminary investigation performed by Kaplan (30), showed that this reaction proceeds at an extremely slow rate. A thorough investigation of this reaction was performed by this investigator. The experimental data, calculations and results are presented in detail in Appendix A.

Kinetic data for the hydrolysis of the dimer were obtained through the use of an overflow back-mix reactor. The raw materials, analytical techniques, experimental equipment configurations and run procedures used were those previously discussed in Chapter II. Experimental data were analyzed in the manner presented in Chapter III.

The resultant functional relationships between the observed rate constants and catalyst concentration within the reaction system were found to be linear. Evaluation of the Arrhenius parameters

indicated that the reaction rate constant could be successfully characterized by the following relationship,

$$k_f = k_o e^{-E/RT} + (C)k_o' e^{-E'/RT}$$

where,

$k_f$  = the forward reaction rate constant, 1/mole-sec

$E$  =  $22930 \pm 1617$  cal

$E'$  =  $12360 \pm 219$  cal

$k_o$  =  $(6.307 \pm 1.88) \times 10^8$  1/mole-sec

$k_o'$  =  $6.821 \pm 0.253$  1<sup>2</sup>/mole-sec-mmole catalyst

$C$  = catalyst concentration, mmoles/l

The equilibrium constant for the monomer-dimer-water system was found to be  $1.27 \pm 0.07$  at 25°C, and was assumed to be temperature and catalyst independent. Estimation of the conversion of dimer to monomer in the butanol-lactic acid system showed this reaction to be negligible even in the most severe cases of temperature and catalyst concentration.

The other possible reactions occurring within the system may not be isolated in the manner that the dimerization reaction can. However, conclusions may be drawn about the importance of the reaction between monomeric lactic acid and butyl lactate. It is postulated by the  $A_{AC}2$  mechanism

that this reaction is mechanistically similar to the dimerization reaction. The carboxylic acid group of the monomer is reacting with the hydroxyl group of the butyl lactate. The structure of the butyl lactate molecule is similar to the structure of the monomer molecule, but is bulkier due to the added butyl group. This bulkier structure, resulting in increased steric hindrance, might be expected to reduce the rate of this reaction to a rate slower than the dimerization. This analysis allows the conclusion that the monomer-butyl lactate reaction may be neglected within this reaction system. The validity of this conclusion is illustrated by the excellent correlation of data obtained while neglecting this reaction.

Eliminating the above two reaction results in a simplified system. The only reactions occurring are the parallel reactions yielding butyl lactate ( $E_1$ ) and butyllactyllactate ( $E_2$ ) from monomer (M) and dimer (D), respectively. That is,



Where B is butanol and W is water.

These reactions are simple acid catalyzed esterifications which may be postulated as occurring

by the standard  $A_{AC}^2$  mechanism. Once a logical reaction model is available, a methodical approach to the evaluation of the rate constants may begin.

Kinetic data for this system were obtained through the use of an overflow back-mix reactor. The back-mix reactor system allowed the evaluation of a dynamic steady-state sample of reaction product. In total, twenty-four experimental runs were performed, using the butanol-lactic acid system. The resultant data were smoothed using least squares polynomials and correlated by the proposed reaction model.

The resultant functional relationships between the observed rate constants and the concentration of catalyst within the reaction system were found to be linear. Evaluation of the Arrhenius parameters indicated that the reactions could be successfully characterized by the following relationship

$$k_f = k_o e^{-E/RT} + (C)k_o' e^{-E'/RT}$$

where, for the reaction of butanol with lactic acid to form butyl lactate,

$k_f$  = the forward reaction rate constant, 1/mole-sec

$E = 21,220 \text{ cal} \pm 715 \text{ cal}$

$E' = 10,870 \text{ cal} \pm 650 \text{ cal}$

$$k_o = (6.25 \pm 0.97) \times 10^8 \text{ l/mole-sec}$$

$$k_o' = (8.91 \pm 1.10) \text{ l}^2/\text{mole-sec-mmole catalyst}$$

$$C = \text{catalyst concentration, mmole/l}$$

and for the reaction of butanol with lactyllactic acid to form butyllactyllactate,

$$k_f = \text{the forward reaction rate constant, l/mole-sec}$$

$$E = 17,580 \text{ cal} \pm 300 \text{ cal}$$

$$E' = 7,980 \text{ cal} \pm 645 \text{ cal}$$

$$k_o = (1.303 \pm .08) \times 10^6 \text{ l/mole-sec}$$

$$k_o' = (4.54 \pm 0.55) \times 10^{-2} \text{ l}^2/\text{mole-sec-mmole catalyst}$$

The above results were obtained from a series of runs performed at a constant feed molar ratio of alcohol to acid of 2.02:1. To verify these results and to check the independence of observed rate constant with respect to alcohol to acid ratio, two subsequent runs were performed. These runs were made with alcohol to acid molar feed ratios of 1.15:1 and 2.72:1, at a temperature of 80°C with no added catalyst. The results of these runs are presented in Table XIV. From the Arrhenius parameters presented above, predicted observed rate constants are  $45.3 \times 10^{-6} \text{ l/mole-sec}$  for the formation of butyllactate, and  $17.0 \times 10^{-6} \text{ l/mole-sec}$  for the formation of butyllactyllactate. Experimental values from the variable alcohol to acid ratio runs were

found to have a maximum error of approximately 11 percent based on the predicted value. The check was quite good. On the basis of these results it may be said that the observed rate constants are functionally independent of the molar feed ratio of butanol to lactic acid.



## DISCUSSION

The reliability of the Arrhenius parameters obtained in this study is a direct function of the accuracy of fit of the least squares polynomials to the raw data. Examination of the standard error of estimate for the least squares polynomials given in Table VII reveals an excellent fit to the data. The maximum error of estimate is of course, most significant in the determination of the butanol and butyl lactate contents of the reactor products. These two quantities control the amounts of butyl lactate and butyllactyllactate obtained by material balance. An analysis of the variability of the Arrhenius parameters with the component material balances may be obtained by examination of the standard error of estimate for these quantities. The deviation of the intercept value of  $\ln k_0$  for the catalyzed and uncatalyzed reactions in both the butyl lactate and butyllactyllactate formation reactions is equal to plus or minus the 95 percent confidence limit based on the standard error of estimate of  $\ln k$ .

The range of activation energy,  $E$ , may be evaluated about the mean value of the experimental data; that is, at the mean values of the natural log

of the rate constant and the reciprocal temperature. The maximum and minimum values of the slope,  $-E/R$ , are the lines passing through the mean value and encompassing 95 percent of all experimental data. In the current system, where only three points are available, the lines are drawn passing through the mean value and encompassing the extreme data points. The mean range of the activation energy for all correlations is 6.0 percent.

The confidence area of the correlation can be closely approximated by drawing smooth curves asymptotic to the lines of maximum and minimum slope and through the extremities of the confidence range of the mean value.

An explanation is needed as to the marked difference in Arrhenius parameters for the catalyzed and uncatalyzed mechanisms for both the butyllactate and butyllactyllactate reactions. The  $A_{AC}^2$  mechanism predicts that both catalyzed and uncatalyzed reactions proceed by the same path. This being the case, one would expect that the Arrhenius parameters for catalyzed and uncatalyzed reactions should be approximately the same. The difference most probably arises as a result of the correlation of data in terms of an "uncatalyzed" reaction. As

discussed previously, the application of the analytical expression

$$k_{\text{obs}} = k_{\text{uncat}} + Ck_{\text{cat}} \quad (42)$$

does not rigorously apply to a system of this type. The "uncatalyzed" reaction, per se, cannot occur. The results obtained in this work are reasonable in light of the fact that at a catalyst concentration of zero added catalyst, some hydrogen ions are present in the reaction system due to dissociation of carboxylic acid groups of the lactic acid and dimer lactic acid.

## COMPARISON OF RESULTS WITH OTHER INVESTIGATIONS

Prior investigations into the kinetics of the esterification of lactic acid with a primary alcohol have been discussed in an earlier section of this report. The empirical correlations of Troupe (56,57,58), for the esterifications of lactic acid with methanol and ethanol may not realistically be compared to the investigation performed in this work. The results of Troupe's work were derived without theoretical considerations, using alcohols different from the one used here. One result of Troupe's investigation should be mentioned. That is, that the rate constants arrived at by that investigator were different for 44% (with low dimer content) and 88% (with high dimer content) lactic acid. These results were obtained assuming no dimer esterification with the alcohol.

The investigation by Kaplan (30) into the kinetics of the esterification of lactic acid with n-butanol was subject to limitations. Initially, that work involved the study of a "synthetic" lactic acid solution. Dimer concentrations were reduced to 4.5-9%, where 35-40% dimer would be expected at equilibrium. In addition, Kaplan, as did the investigations of Troupe, neglected the dimer

alcohol reaction. The experimental design used by Kaplan was intended to reduce the importance of the dimer-butanol reaction by operating at low dimer contents. However, it is felt by this investigator that in light of the results of this investigation, that a dimer concentration of up to 9% was not low enough to be negligible. The analysis of the kinetic data taken by Kaplan was therefore confounded by the significant occurrence of both the monomer and dimer esterification reactions. The kinetic parameters resulting from this data are therefore incorrect.

It would be of interest at this point to apply the reaction scheme and kinetic parameters determined by this investigator to the kinetic data found by Kaplan. In his dissertation, Kaplan presents a typical set of experimental data for a sample batch esterification run. The data presented includes initial batch composition data (in terms of weights of reactants added and reactant concentrations) and titration data equivalent to the total acid and total ester per unit mass of sample. Calculated values of lactic acid and butyl lactate concentration are also given. Initial reactor conditions and the various experimental values as a

function of time are presented in Table XV.

The reactor design equation used by Kaplan for correlation of his data is the batch reactor equation solved for a second order reversible reaction. The design equation may be expressed as,

$$t = \frac{VK_{eq}}{k_f} \frac{1}{\sqrt{-q}} \ln \frac{(2cX_a + b - \sqrt{-q})(b + \sqrt{-q})}{(2cX_a + b + \sqrt{-q})(b - \sqrt{-q})}$$

where,

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

$$a = K_{eq}N_{Ao}N_{Bo} - N_{Ro}N_{So}$$

$$b = -K_{eq}N_{Bo} - K_{eq}N_{Ao} - N_{Ro} - N_{So}$$

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

where the terms are defined as

$t$  = time elapsed

$k_f$  = forward reaction rate constant

$K_{eq}$  = equilibrium constant

$N_{Ao}$ ,  $N_{Bo}$ ,  $N_{Ro}$ ,  $N_{So}$  = moles of reactants A and B,  
and products 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

TABLE XVCOMPARISON OF PREDICTED DATA TO EXPERIMENTAL DATA OF KAPLAN

<u>Initial Concentration*, moles/kg</u>	
Monomer - 4.112	Butyllactate - 0.173
Dimer - 0.124	Butanol - 7.070
Water - 4.321	Butyllactyllactate - assumed 0
Temperature - 80 °C	
Cat. conc. - 10.23 mmol/l	
Density - 0.8939 kg/l	
Butyllactate $k_f$ - $61.5 \times 10^{-6}$ l/mole-sec	
Butyllactyllactate $k_f$ - $22.1 \times 10^{-6}$ l/mole-sec	
Butyllactate $K_{eq}$ - 3.03	
Butyllactyllactate $K_{eq}$ - 2.75	

EXPERIMENTAL RESULTS OF KAPLAN

Time, min	Total Acid	Total Ester	Monomeric Acid	Bulac
	<u>moles/kg</u>	<u>moles/kg</u>	<u>moles/kg</u>	<u>moles/kg</u>
2	3.878	0.421	3.680	0.220
4.25	3.790	0.515	3.591	0.309
8.00	3.661	0.655	3.461	0.455
13.0	3.482	0.835	3.282	0.634
21.0	3.262	1.041	3.0632	0.839
30.0	3.053	1.259	2.863	1.058
45.0	2.759	1.539	2.559	1.329
60.0	2.564	1.720	2.365	1.521

TABLE XV, Cont'd.

PREDICTED EXPERIMENTAL RESULTS

Time, min	Total Acid	Total Ester	Monomeric Acid	Bulac
	<u>moles/kg</u>	<u>moles/kg</u>	<u>moles/kg</u>	<u>moles/kg</u>
2	4.057	0.476	3.955	0.350
4.25	3.872	0.661	3.751	0.534
8.0	3.594	0.939	3.478	0.807
13.0	3.282	1.251	3.170	1.115
21.0	2.885	1.648	2.780	1.505
30.0	2.552	1.981	2.454	1.831
45.0	2.174	2.359	2.089	2.196
60.0	1.969	2.592	1.863	2.422

Butyllactyl-  
lactate, moles/kg

0.002

0.003

0.008

0.012

0.019

0.026

0.037

0.046

---

\* Based on initial charge



Equation (84) may be rearranged to the more easily workable form,

$$X_A = \frac{(b^2 + q)(1 - e^k)}{2c(be^k - \sqrt{-q} e^k - b - \sqrt{-q})} \quad (85)$$

where

$$K = \frac{t k_f \sqrt{-q}}{V K_{eq}} \quad (86)$$

Equations (85) and (86) may be combined with the initial component concentrations as given by Kaplan and the rate constants and equilibrium constants determined by this investigator, to determine the conversion as a function of time of the initial monomeric and dimeric lactic acids. The computer program for the solution of equation (85) and (86) as well as the predicted butyl lactate and butyl-lactyllactate values obtained are given in Appendix H. Material balances may then be applied to calculate the monomer content and total acid and ester values as a function of time. A tabulation of these results for comparison to Kaplan's are presented in Table XV.

Initially it must be pointed out that certain assumptions have been made in the calculation of the predicted values. This calculation is based on the weights of reactants charged to the reactor and the

component concentrations given for these reactants. The individual component concentrations given in Table XV are those based on the initial charge. However, there is a discrepancy between these values and the values presented by Kaplan as data. For example, based on the initial charge, the total acid plus ester groups in the batch is 4.533 moles/kg. The only reactions occurring in the system are esterifications, such that each acid group reacting results in the formation of one ester group. The total acid plus ester content should be constant. From Kaplan's data, the acid plus ester total is equal to 4.308 moles/kg. In addition, based on initial charge, monomer content is 4.285 moles/kg. Since the reaction of monomer results only in the formation of butyl lactate, the total of monomer plus butyl lactate should equal a constant. It is a constant for Kaplan's data, but the constant is equal to 3.904 moles/kg.

Two possible conclusions may be drawn from the above discrepancies. Either the weights of the initial charge are in error or the analysis of the product samples are in error. These possibilities shall be discussed qualitatively as to their effects on the comparative predicted and experimental

values.

For the first case, an error in initial charge weights, the indication from the data is that the initial charge would have contained less lactic acid. If this were the case, the conversion to butyl lactate would be lower due to the lower initial concentration of the monomer. This would tend to bring the predicted values more in line with the experimental values of Kaplan.

The second possibility is that the experimental data is in error, resulting from an error in analytical technique. It was found by this investigator that a truly reproducible determination of ester content by saponification, required the samples to be heated for a minimum of two hours in a hot water bath at 90 °C. Three hours of heating were taken as standard in this investigation. The technique used by Kaplan involved heating at 90 °C for only 15 minutes. That procedure was initially tried by this investigator and it was found that fairly reproducible results could be obtained so long as the saponification time was maintained constant. However, the results were not reproducible as a function of time until at least two hours of saponification time were allowed. On this basis, it may be

surmised that the saponification results reported by Kaplan may not be a true measure of the total ester content of the sample.

The effect of this error would be two-fold. First the analysis of the feed lactic acid used by Kaplan should be higher in dimer content and lower in monomer content. This would tend to give lower butyl lactate concentrations than would be predicted. This is consistent with the observations in Table XV.

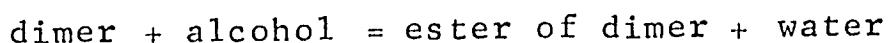
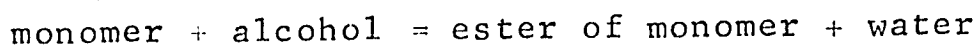
Secondly, the experimental total ester determination should be higher. This would again tend to bring the predicted values closer in line with what might be expected experimentally.

In summary, it may be said that discrepancies were found in the experimental data reported by Kaplan. Any explanation of these discrepancies that may be offered serves to indicate, at least qualitatively, an agreement between the data of Kaplan and the results of the correlations of the current investigation. In light of this, it may be said that the experimental data found by Kaplan are consistent with the results found by this investigator.

## CHAPTER V

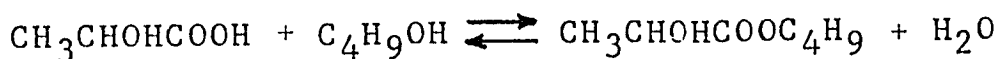
### CONCLUSIONS

1. The significant reactions occurring when an aqueous lactic acid solution and a primary alcohol are contacted are the esterification of monomeric lactic acid and the esterification of the dimeric lactic acid with the alcohol. The reactions may be represented as



In the system investigated, the alcohol was n-butanol with the esters formed being butyl esters.

2. The kinetic parameters for the butyl lactate formation reaction



can be represented as

$$k_f = k_o e^{-E/RT} + C k_o' e^{-E'/RT}$$

where

$k_f$  = the forward rate constant, 1/mole-sec

$E$  = 21,220 cal  $\pm$  715 cal

$E'$  = 10,870 cal  $\pm$  650 cal

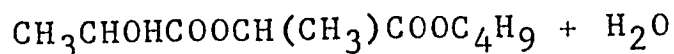
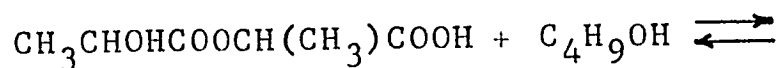
$k_o$  = (6.258  $\pm$  0.97)  $\times 10^8$  1/mole-sec

$$k_o' = (8.91 \pm 1.10) \text{ l}^2/\text{mole-sec-mmole cat}$$

C = catalyst concentration, mmoles/l

3. The equilibrium constant for the reaction resulting in the formation of butyllactate was  $3.13 \pm 0.16$ , evaluated at 25 °C.

4. The kinetic parameters for the butyllactyl-lactate formation reaction



can be represented by the above relationship, where

$k_f$  = the forward rate constant, l/mole-sec

$E = 17,580 \text{ cal} \pm 300 \text{ cal}$

$E' = 7,980 \text{ cal} \pm 645 \text{ cal}$

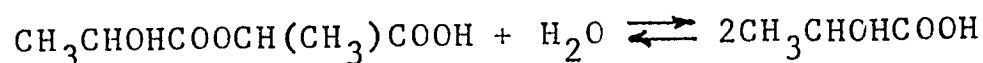
$k_o = (1.303 \pm .08) \times 10^6 \text{ l/mole-sec}$

$k_o' = (4.54 \pm 0.55) \times 10^{-2} \text{ l}^2/\text{mole-sec-mmole cat}$

C = catalyst concentration, mmoles/l

5. The equilibrium constant for the esterification of lactyllactic acid was  $2.75 \pm 0.15$ , evaluated at 25 °C.

6. The kinetic parameters for the hydrolysis of dimeric lactic acid,



may be represented as

$$k_f = k_o e^{-E/RT} + C k_o' e^{-E'/RT}$$

where

$k_f$  = the forward rate constant, 1/mole-sec

$E = 22,930 \pm 1617$  cal

$E' = 12,360 \pm 219$  cal

$k_o = (6.307 \pm 1.88) \times 10^8$  1/mole-sec

$k_o' = 6.821 \pm 0.253$  1<sup>2</sup>/mole-sec-mmole cat

$C$  = catalyst concentration, mmoles/l

7. The equilibrium constant for the hydrolysis of lactyllactic acid was  $1.27 \pm 0.07$  evaluated at 25 °C with no added catalyst.

## CHAPTER VI

### RECOMMENDATIONS

1. The kinetic parameters of the esterification reactions may be used to design a pilot scale system, for the continuous production of lactic acid.

2. The kinetic parameters of the esterification reactions may be used in an economic balance of an industrial design for the purification of lactic acid.

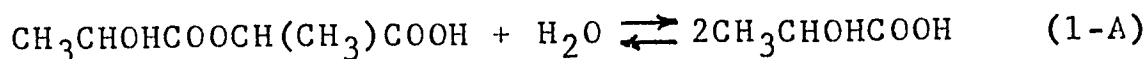
3. An investigation should be performed into the ionization of lactic acid in butanol-water-lactic acid systems to determine the ionization constant as a function of composition and temperature. Once this is done, the hydrogen ion concentration in an "uncatalyzed" reaction system may be calculated and the true single value of the "catalyzed" rate constant may be determined.



APPENDIX A

### MONOMER-DIMER REACTION

The hydrolysis of an aqueous 80 percent lactic acid solution with water was studied at three temperature levels and varying catalyst levels to evaluate the kinetic parameters of the reaction:



A preliminary investigation by Kaplan (30) had indicated that the self esterification of lactic acid was extremely slow and the effects of this reaction, relative to the esterification of lactic acid with n-butanol, were negligible. The scope of current investigation was to verify Kaplan's observations and to fully determine the kinetic parameters of the monomer-dimer reaction.

The raw materials, analytical techniques, experimental equipment configurations, and run procedures discussed in Chapter II were used throughout this series of runs. Experimental data were analyzed in the manner presented in Chapter III. A step by step procedure for data analysis is presented below.

### Experimental Results

The hydrolysis of lactyllactic acid was in-

vestigated at temperature levels of 59°C, 67°C, and 77°C and at catalyst concentrations ranging from zero to approximately 35 mmoles/liter. Reaction was performed in an overflow backmix reactor with volumetric input rates maintained constant. Reactor residence times varied slightly with the reaction temperature and the composition of the product stream. Experimental residence times were 1454 sec at 59°C, 1396 sec at 67°C, and 1340 sec at 77°C.

The mean total acid data for the run series are tabulated in Table A-1. This raw experimental data were fit with least squares polynomials to smooth experimental fluctuations. Summary computer printouts for all experiments, showing the actual data, predicted data and the percent difference between the two are given in Tables A-2, A-3 and A-4. The resultant polynomials are presented in Table A-5.

#### Material Balances

Consistent with the reaction model given above, and with the knowledge of initial feed compositions, material balances may be written to determine the amounts of the various components within the reaction mass.

It is known from the reaction stoichiometry that the total acid (corrected for catalyst content), must be equal to the acid groups attributable to the monomer (M), plus the acid groups attributable to the dimer (D). It is also known from the reaction stoichiometry that each dimer molecule reacting results in two monomer molecules with a net increase of one acid group. Therefore, it may be said that

$$\text{increase in monomer/gram} = (2)(\text{increase in acid/gram})$$

$$\text{decrease in dimer/gram} = \text{increase in acid/gram}$$

$$\text{decrease in water/gram} = \text{increase in acid/gram}$$

thus, the following material balances may be written:

$$\text{final monomer} = \text{initial monomer} + (2)(\Delta\text{acid/gram})$$

$$\text{final dimer} = \text{initial dimer} - \Delta\text{acid/gram}$$

$$\text{final water} = \text{initial water} - \Delta\text{acid/gram}$$

where

$$\Delta\text{acid} = (\text{final total acid/gram}) - (\text{initial total acid/gram})$$

The equilibrium constant for the monomer-dimer-water system was found to be  $1.27 \pm .07$  at  $25^{\circ}\text{C}$ . This constant was evaluated from multiple analyses of the feed lactic acid. The equilibrium constant was assumed to be independent of temperature and catalyst concentration.

-

Initial flow conditions and feed concentrations, which were maintained constant throughout the series of runs, are tabulated in Table A-6. This information, combined with the material balances given above and the smoothed raw data, yields the component concentrations as a function of catalyst concentration. The component concentrations may be combined with the reactor design equation to calculate the forward reaction rate constant as a function of catalyst concentration. These results were calculated at one time with the aid of the computer. A typical computer program for this calculation is given in Table A-7. The computer printouts of the results are given in Tables A-8 and A-9 and A-10. A plot of calculated observed rate constant versus catalyst concentration is shown in Figure 10.

The observed rate constants versus catalyst concentration data were fit with a first order least squares polynomials. These results are tabulated in Table A-11, where the intercepts are equal to the uncatalyzed rate constants and the slopes are equal to the catalyzed rate constants.

Finally, first order least squares polynomials were fit to the uncatalyzed and catalyzed rate con-

--

stants, using the natural log of the constant versus the reciprocal of the absolute temperature. The slope of this line represents  $-(E/R)$ , where  $E$  is the Arrhenius activation energy. The intercept represents the natural log of the pre-exponential constant,  $k_0$ . The Arrhenius parameters are presented in Table A-12. Figure 11 is a plot of the natural log of the rate constant,  $k$  versus the reciprocal of the absolute temperature. Computer printouts for the least squares fit of  $\ln k$  versus  $1/T$  are given in Tables A-13 and A-14.

## Discussion

Kinetic data for this system were obtained through the use of an overflow back-mix reactor. In total, seventeen experimental runs were performed, using the lactic acid-water system. The resultant data were smoothed using least squares polynomials and correlated by the proposed reaction model.

The resultant functional relationships between the observed rate constants and the catalyst concentration within the reaction system were found to be linear. Evaluation of the Arrhenius parameters indicated that the reaction rate constant could be successfully characterized by the following relationship

$$k_f = k_o e^{-E/RT} + (C)k_o' e^{-E'/RT}$$

where,

$k_f$  = the forward reaction rate constant, l/mole-sec

$E = 22,930 \pm 1617$  cal

$E' = 12,360 \pm 219$  cal

$k_o = (6.307 \pm 1.88) \times 10^8$  l/mole-sec

$k_o' = 6.821 \pm 0.253$  l<sup>2</sup>/mole-sec-mmole cat.

$C$  = catalyst concentration, mmole/l

The equilibrium constant for the monomer-dimer-water system was found to be  $1.27 \pm 0.07$  at  $25^{\circ}\text{C}$ , and was assumed to be temperature and catalyst independent.

No complete comparison may be drawn between this work and the previous preliminary investigation of Kaplan (30). Kaplan performed runs at varying catalyst concentrations at one temperature only and was therefore unable to evaluate the Arrhenius parameters of the system. A cursory comparison may be drawn from the observed rate constants evaluated by Kaplan. The functional relationship between observed rate constant and catalyst concentration found by Kaplan at  $80.4^{\circ}\text{C}$  may be expressed as,

$$k_o = 1.93 \times 10^{-6} + (1.82 \times 10^{-6})C$$

The like expression, evaluated by this investigator at  $77^{\circ}\text{C}$ , was found to be,

$$k_o = 2.85 \times 10^{-6} + 0.129 \times 10^{-6}C$$

The agreement, in terms of uncatalyzed rate constant is fairly good. Agreement in terms of catalyzed rate constant is poor, being different by an order of magnitude. The effect of catalyst found by this investigator is much less pronounced than the effect found by Kaplan. No explanation is



offered for this discrepancy.

The importance of the monomer-dimer reaction during the butanol-lactic acid esterification may be measured by calculating the amount of dimer that would react in the alcohol acid system. The dimer hydrolysis would be most rapid at the highest temperature and higher catalyst concentrations used during the alcohol-acid runs. This occurred during the alcohol run series at 80 C with a catalyst concentration of approximately 50 mmoles/l. Reactor residence time was 1244 sec. Based on the Arrhenius parameters given in Table A-12 and a catalyst concentration of 50 mmoles/l, the observed rate constant is approximately  $9.3 \times 10^{-6}$  1/mole-sec.

The initial component concentrations in the alcohol system based on feed rates are,

Initial Dimer	1.226 mmoles/g
Initial Monomer	2.91 mmoles/g
Initial Water	5.83 mmoles/g

Density of the reaction mass is 0.893 g/ml. Using this data and the reactor design equation, the concentration of dimer (assuming the case of no other competing reactions) may be calculated. This has been done and the exit dimer concentration was found

to be 1.219 mmoles/g. Dimer disappearance by the monomer-dimer reaction was 0.007 mmoles/g, or 0.57 percent of the feed dimer. On the basis of these calculations it is assumed that the monomer-dimer reaction is negligible in the lactic acid-butanol reaction system.

TABLE A-1  
Mean Total Acid Data For  
Monomer-Dimer Reaction

<u>T, °C</u>	<u>Catalyst m.e./g</u>	<u>Total Acid m.e./g</u>
59	0.0146	3.913
59	0.0000	3.884
59	0.00625	3.890
59	0.01225	3.916
67	0.01295	3.944
67	0.01228	3.959
67	0.0064	3.931
67	0.0098	3.948
67	0.0138	3.959
67	0.0259	3.986
67	0.0362	4.012
67	0.0184	3.974
77	0.0128	4.010
77	0.0065	3.987
77	0.0204	4.038
77	0.0244	4.053
77	0.0120	4.000

TABLE A-2

Least Square Polynomial Fit of  
Total Acid At 59 C versus Catalyst

## L E A S T - S Q U A R E S   P O L Y N O M I A L S

NUMBER OF POINTS = 4  
 MEAN VALUE OF X = .008275  
 MEAN VALUE OF Y = 3.90075  
 STD ERROR OF Y = 1.60267E-02

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .889918      WHAT NEXT?2

TERM	COEFFICIENT			
0	3.88151			
1	2.32487			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
.0146	3.913	3.91545	-2.45476E-03	-6.26941E-02
0	3.884	3.88151	2.48814E-03	6.41022E-02
.00625	3.89	3.89604	-.006042	-.155081
.01225	3.916	3.90999	6.00863E-03	.153674

STD ERROR OF ESTIMATE FOR Y = 6.51253E-03

WHAT NEXT?3

Table A-2, Cont'd.

POLYFIT OF DEGREE 2      INDEX OF DETERM = .903668      WHAT NEXT?2

TERM	COEFFICIENT
0	3.88298
1	1.24328
2	74.429

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
.0146	3.913	3.91699	-3.99351E-03	-.101953
0	3.884	3.88298	1.02329E-03	2.63533E-02
.00625	3.89	3.89365	-3.65448E-03	-9.38573E-02
.01225	3.916	3.90938	6.62422E-03	.169445

STD ERROR OF ESTIMATE FOR Y = 8.61573E-03

TABLE A-3

Least Square Polynomial Fit of  
Total Acid at 67 C Versus Catalyst

## L E A S T - S Q U A R E S   P O L Y N O M I A L S

NUMBER OF POINTS = 8  
 MEAN VALUE OF X = 1.69663E-02  
 MEAN VALUE OF Y = 3.96413  
 STD ERROR OF Y = .025869

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .949707      WHAT NEXT?2

TERM                      COEFFICIENT

0                      3.92018  
 1                      2.5899

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
.01295	3.944	3.95372	-9.72366E-03	-.245937
.01228	3.959	3.95199	7.01189E-03	.177427
.0064	3.931	3.93676	-5.75972E-03	-.146306
.0098	3.948	3.94557	2.43473E-03	.061708
.0138	3.959	3.95592	3.07512E-03	7.77346E-02
.0259	3.986	3.98726	-1.26266E-03	-3.16675E-02
.0362	4.012	4.01394	-1.93882E-03	-4.83022E-02
.0184	3.974	3.96784	6.16169E-03	.155291

Z                      STD ERROR OF ESTIMATE FOR Y = 6.26624E-03

WHAT NEXT?FN

3

Table A-3, Cont'd.

POLYFIT OF DEGREE 2

INDEX OF DETERM = .957119

WHAT NEXT?2

TERM	COEFFICIENT
------	-------------

0	3.91053
1	3.74T12
2	-26.7736

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
.01295	3.944	3.95452	-1.05233E-02	-.266108
.01228	3.959	3.95247	6.53315E-03	.165293
.0064	3.931	3.93339	-2.39277E-03	-6.08322E-02
.0098	3.948	3.94465	3.35217E-03	8.49801E-02
.0138	3.959	3.9571	1.90353E-03	4.81043E-02
.0259	3.986	3.98954	-3.53956E-03	-8.87211E-02
.0362	4.012	4.01098	1.02139E-03	2.54647E-02
.0184	3.974	3.97035	3.64590E-03	.091828

STD ERROR OF ESTIMATE FOR Y = 6.33833E-03

## TABLE A-4

Least Square Polynomial Fit of  
Total Acid at 77<sup>o</sup> C Versus Catalyst.

## L E A S T - S Q U A R E S   P O L Y N O M I A L S

NUMBER OF POINTS = 5  
 MEAN VALUE OF X = .01522  
 MEAN VALUE OF Y = 4.0176  
 STD ERROR OF Y = 2.73437E-02

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .987118      WHAT NEXT?2

TERM	COEFFICIENT			
0	3.95978			
1	3.79898			

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
.0128	4.01	4.00841	1.59359E-03	3.97562E-02
.0065	3.987	3.98447	2.52676E-03	6.34152E-02
.0204	4.038	4.03728	7.20978E-04	.017858
.0244	4.053	4.05247	5.25475E-04	1.29668E-02
.012	4	4.00537	-5.36728E-03	-.134002

STD ERROR OF ESTIMATE FOR Y = 3.58365E-03

WHAT NEXT?3



Table A-4, Cont'd.

POLYFIT OF DEGREE 2      INDEX OF DETERM = .9899      WHAT NEXT?2

TERM	COEFFICIENT			
0	3.96796			
1	2.55081			
2	39.7086			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
.0128	4.01	4.00712	2.88105E-03	7.18983E-02
.0065	3.987	3.98622	7.78675E-04	1.95342E-02
.0204	4.038	4.03652	1.47533E-03	3.65496E-02
.0244	4.053	4.05384	-8.44002E-04	-2.08198E-02
.012	4	4.00429	-4.29058E-03	-.10715

STD ERROR OF ESTIMATE FOR Y = 3.88618E-03

TABLE A-5  
Smoothing Polynomials for Raw Data

<u>Temp C</u>	<u>Total Acid Data</u>		<u>Index of Determ</u>	<u>Std Error of Est for Y</u>
	<u>Least Squares Equation*</u>			
59	$Y = 3.88298 + 1.24328C + 74.429C^2$		.9037	.008616
67	$Y = 3.91053 + 3.74712C - 26.7736C^2$		.9571	.006338
77	$Y = 3.96796 + 2.55081C + 39.7086C^2$		.9899	.003886

\* Y = Total acid, m.e./gram

C = Catalyst concentration, m.e./gram

TABLE A-6Initial Flow ConditionsMonomer-Dimer Reaction

Total weight rate lactic acid - 17.207 g/min

Total weight rate water - 15.371 g/min

Initial lactic acid solution - 0.5282 g/g-mix

Initial m.e. acid/g-mix - 3.8585 m.e./g

Initial Component Balance

<u>Component</u>	<u>Initial wt/g-mix</u>	<u>Initial mmoles/g-mix</u>
lactic acid	0.2444	2.7135
dimer	0.1857	1.1450
water	0.5699	31.6260

TABLE A-7

Typical Computer Program for Calculation  
of Component Concentrations and Observed  
Rate Constant

```

5 PRINT
10 LET X = 0.0
20 LET B = 3.88298 + 1.24328*X + 74.429*X*X
30 LET M = 2.7135 + 2*(B - 3.8585)
40 LET D = 1.1450 - (B - 3.8585)
50 LET W = 31.6260 - (B - 3.8585)
60 LET T = 1454
65 LET R = 1.105
70 LET K = -(1.1450-D)/((T)*((D*W) - (.787673*M*M)))
80 PRINT X*R*1000,M,D,W,K/R
90 LET X = X + 0.005
100 IF X > 0.055 THEN 9999
110 GO TO 20
9999 END

```

TABLE A-8  
Computer Results for Calculation of

Observed Rate Constants

T 59 C

<u>Catalyst</u> <u>Conc.,</u> <u>mole/l</u>	<u>Monomer</u> <u>m.e./g</u>	<u>Dimer</u> <u>m.e./g</u>	<u>Water</u> <u>m.e./g</u>	<u>Observed Rate</u> <u>Constant,</u> <u>l/mole-sec</u>
0	2.76246	1.12052	31.6015	5.18258E-07
5.525	2.77861	1.11244	31.5934	6.97196E-07
11.05	2.80221	1.10064	31.5816	9.66123E-07
16.575	2.83325	1.08512	31.5661	1.33428E-06
22.1	2.87173	1.06588	31.5469	1.81511E-06
27.625	2.91766	1.04292	31.5239	2.42764E-06
33.15	2.97103	1.01624	31.4972	3.19860E-06
38.675	3.03184	.98583	31.4668	4.16591E-06
44.2	3.1001	.951702	31.4327	5.38429E-06
49.725	3.17579	.913854	31.3949	6.93464E-06
55.25	3.25893	.872284	31.3533	8.94150E-06

TABLE A-9  
Computer Results for Calculation of

Catalyst Conc., mmole/l	Observed Rate Constants				Observed Rate Constant, 1/mole-sec
	Monomer m.e./g	Dimer m.e./g	Water m.e./g		
0	2.81756	1.09297	31.574		1.22929E-06
5.365	2.85369	1.0749	31.5559		1.70135E-06
10.73	2.88715	1.05818	31.5392		2.16215E-06
16.095	2.91793	1.04279	31.5238		2.60784E-06
21.46	2.94603	1.02874	31.5097		3.03442E-06
26.825	2.97145	1.01603	31.497		3.43767E-06
32.19	2.99419	1.00465	31.4857		3.81334E-06
37.555	3.01426	.994618	31.4756		4.15718E-06
42.92	3.03165	.985923	31.4669		4.46507E-06
48.285	3.04637	.978566	31.4596		4.73308E-06
53.65	3.0584	.972548	31.4535		4.95768E-06

TABLE A-10  
Computer Results for Calculation of

Catalyst Conc., mmole/l	<u>Observed Rate Constants</u> ° <u>T 77 C</u>				Observed Rate Constant, 1/mole-sec
	Monomer	Dimer	Water		
	<u>m.e./g</u>	<u>m.e./g</u>	<u>m.e./g</u>		
0	2.93242	1.03554	31.5165	3.03399E-06	
5.205	2.95991	1.02179	31.5028	3.49266E-06	
10.41	2.99138	1.00606	31.4871	4.04399E-06	
15.615	3.02681	.988344	31.4693	4.70158E-06	
20.82	3.06622	.96864	31.4496	5.48307E-06	
26.025	3.10959	.946953	31.428	6.41137E-06	
31.23	3.15694	.923278	31.4043	7.51713E-06	
36.435	3.20826	.897618	31.3786	8.84123E-06	
41.64	3.26355	.869974	31.351	1.04399E-05	
46.845	3.32281	.840343	31.3213	1.23923E-05	
52.05	3.38604	.808728	31.2897	1.48129E-05	

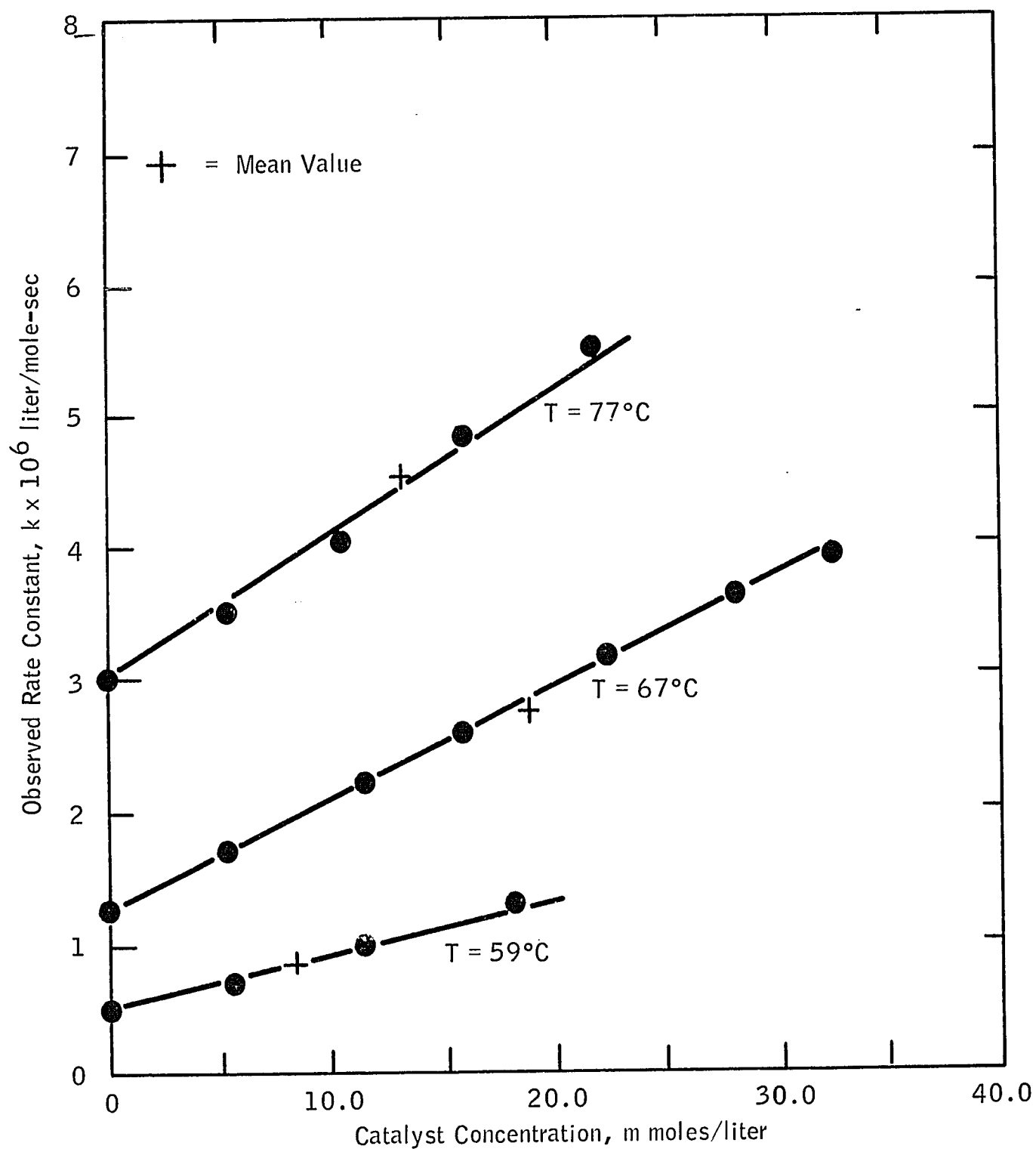


Figure 10

OBSERVED RATE CONSTANT FOR MONOMER-DIMER REACTION, liter/mole-sec  
VS. CATALYST CONCENTRATION, m moles/liter



TABLE A-11  
Least Square Polynomials for Observed

<u>Temp C</u>	<u>Rate Constants</u> <u><math>k_{obs}^*</math>, 1/mole-sec x <math>10^6</math></u>	<u>Index of</u> <u>Determ</u>	<u>Std Error of</u> <u>Est for Y</u>
59	$Y_D = 0.471415 + .0491763C$	0.9763	.066915
67	$Y_D = 1.29673 + .078348C$	0.9974	.056820
77	$Y_D = 2.84808 + .129083C$	0.9841	.178737

\*  $Y_D$  = observed rate constant, 1/mole-sec

C = catalyst concentration, mmoles/l

TABLE A-12  
Arrhenius Parameters

<u>Reaction</u>	<u>k<sub>o</sub></u>	<u>E, cal</u>
Catalyzed	$6.821 \pm .253$ l <sup>2</sup> /mole-sec-mmole cat.	12,360 $\pm$ 219
Uncatalyzed	$(6.307 \pm 1.88) \times 10^8$ l/mole-sec	22,930 $\pm$ 1617

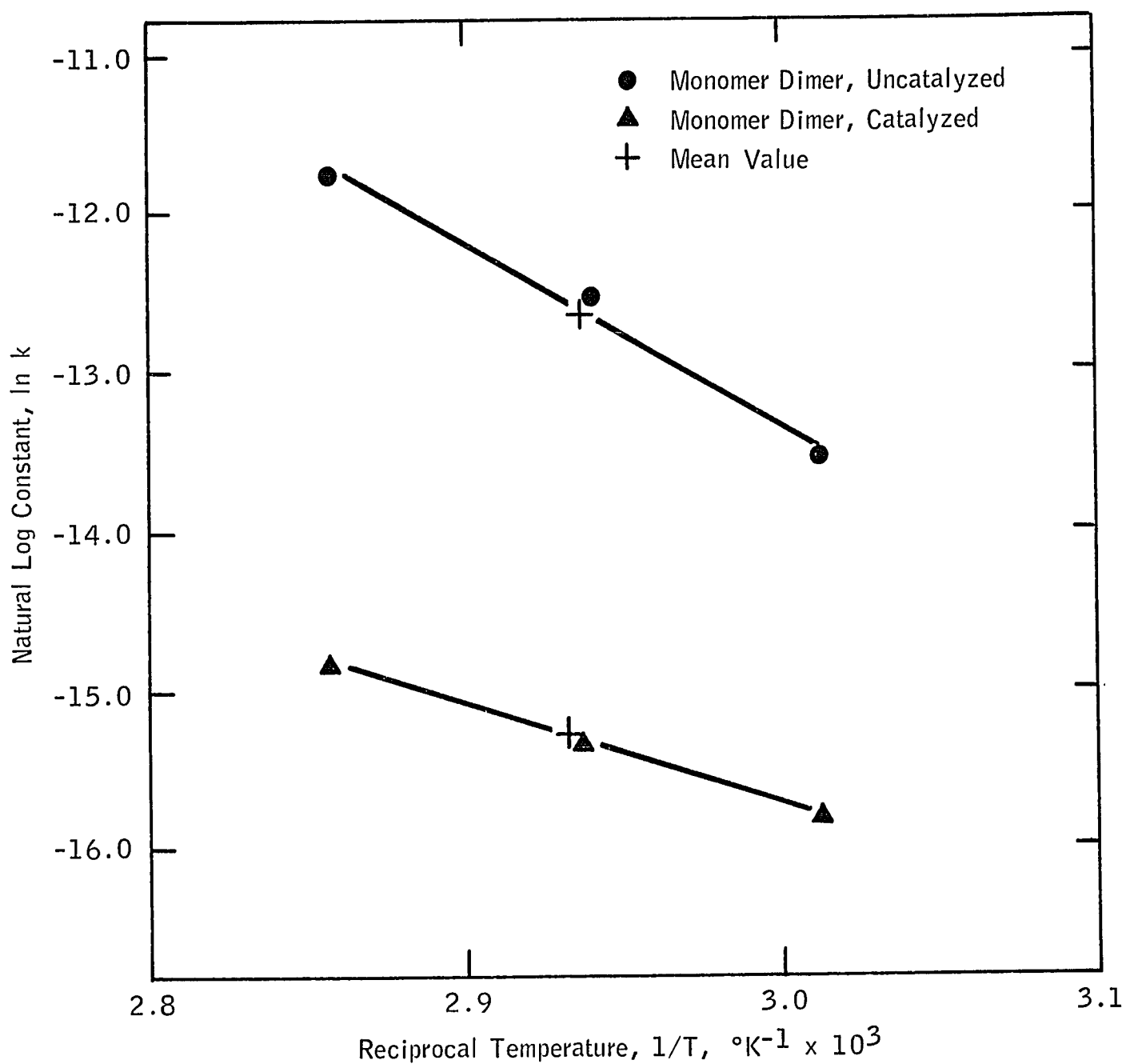


Figure 11

NATURAL LOG RATE CONSTANT,  $\ln k$  VS.  
RECIPROCAL ABSOLUTE TEMPERATURE,  $1/T, ^\circ K^{-1}$

TABLE A-13Least Square Fit for Arrhenius Parametersk Uncatalyzed

## L E A S T - S Q U A R E S   P O L Y N O M I A L S

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 2.93679E-03  
 MEAN VALUE OF Y = .184826  
 STD ERROR OF Y = .901677

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .985391      WHAT NEXT?2

TERM	COEFFICIENT			
0	34.0814			
1	-11542.			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
3.01205E-03	-.752017	-.683823	-6.81944E-02	9.97253
2.94118E-03	.259846	.134155	.125691	93.6905
2.85714E-03	1.04665	1.10416	-5.75066E-02	-5.20819

STD ERROR OF ESTIMATE FOR Y = .154129

TABLE A-14  
Least Square Fit for Arrhenius Parameters  
k Catalyzed

L E A S T - S Q U A R E S   P O L Y N O M I A L S

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 2.93679E-03  
 MEAN VALUE OF Y = -2.53541  
 STD ERROR OF Y = .482617

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .999161      WHAT NEXT?2

TERM	COEFFICIENT			
0	15.7341			
1	-6220.93			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
3.01205E-03	-3.01234	-3.0036	-8.73709E-03	.290887
2.94118E-03	-2.5466	-2.56273	1.61271E-02	-.629295
2.85714E-03	-2.0473	-2.03992	-7.38096E-03	.361826

STD ERROR OF ESTIMATE FOR Y = 1.97712E-02

APPENDIX B

### EXPERIMENTAL DATA

Throughout the course of this investigation, except where noted to the contrary, component feed rates to the reactor were maintained constant. Variation in pumping rates was found to be less than 1.0 percent as determined by periodic checks of component pumping rates. The volumetric feed rates and initial component concentrations, based on these feed rates are given below:

volumetric feed rate of lactic acid - 14.188 ml/min  
volumetric feed rate of butanol - 15.606 ml/min  
initial lactic acid - 0.2617 g/g-feed  
initial dimer - 0.1988 g/g-feed  
initial butanol - 0.4344 g/g-feed  
initial water - 0.1050 g/g-feed

The initial component concentrations in terms of moles may be obtained by multiplication by the proper molecular weights.

The remainder of this Appendix lists the experimental data obtained in this investigation given in terms of total acid, corrected for catalyst, total ester, butanol and butyllactate, all in mmoles/gram as a function of catalyst concentration.

°  
EXPERIMENTAL DATA AT 60 C

Cat. mmoles/g	Total Acid mmoles/g	Total Ester mmoles/g	Butyl Lactate mmoles/g	Butanol mmoles/g
0.00379	3.919	1.438	.215	5.644
"	3.938	1.422	.210	5.602
"	3.935	1.424	.190	5.622
"	3.940	1.416	--	--
0.01305	3.797	1.559	.315	5.520
"	3.801	1.556	.309	5.541
"	3.809	1.550	.329	5.477
"	3.798	1.562	--	--
0.0221	3.648	1.711	.352	5.399
"	3.660	1.697	.405	5.406
"	3.673	1.687	.394	5.392
"	3.664	1.692	--	--
0.01523	3.709	1.647	.328	5.485
"	3.721	1.639	.309	5.475
"	3.698	1.659	.315	5.464
"	3.718	1.641	--	--
0.01007	3.800	1.559	.284	5.554
"	3.793	1.563	.268	5.410
"	3.798	1.562	.256	5.526
"	3.802	1.555	--	--
0.0	3.946	1.413	.164	5.657
"	3.943	1.417	.149	5.684
"	3.945	1.410	.140	5.688
"	3.941	1.417	--	--
0.04929	3.424	1.934	.595	5.176
"	3.419	1.941	.575	5.156
"	3.421	1.939	.569	5.150
"	3.420	1.938	--	--
0.03549	3.562	1.798	.509	5.277
"	3.565	1.790	.496	5.268
"	3.563	1.794	.485	5.256
"	3.578	1.782	--	--
0.0263	3.641	1.721	.444	5.370
"	3.650	1.704	.413	5.332
"	3.644	1.719	.400	5.357
"	3.644	1.712	--	--
0.02491	3.625	1.730	.420	5.392
"	3.627	1.735	.410	5.361
"	3.630	1.726	.402	5.351
"	3.627	1.732	--	--



°  
EXPERIMENTAL DATA AT 70 C

Cat. mmoles/g	Total Acid mmoles/g	Total Ester mmoles/g	Butyl Lactate mmoles/g	Butanol mmoles/g
0	3.658	1.685	.399	5.425
0	3.683	1.672	.371	5.386
0	3.678	1.678	.378	5.391
.01258	3.560	1.849	.502	5.250
"	3.524	1.832	.516	5.231
"	3.454	1.838	.526	5.241
.02218	3.420	1.998	.625	5.160
"	3.383	1.936	.594	5.125
"	3.409	1.933	.588	5.126
.04151	3.228	2.172	.773	4.975
"	3.213	2.109	.769	4.925
"	3.226	2.132	.736	4.936
.04319	3.222	2.137	.780	4.954
"	3.193	2.152	.761	4.916
"	3.209	2.162	.722	4.937
.03122	3.340	2.028	.689	5.060
"	3.321	2.047	.675	5.054
"	3.298	2.070	.676	5.021

EXPERIMENTAL DATA AT 80<sup>o</sup> C

Cat. mmoles/g	Total Acid mmoles/g	Total Ester mmoles/g	Butyl Lactate mmoles/g	Butanol mmoles/g
0.0	3.350	1.983	.610	5.130
"	3.360	1.989	.621	5.124
"	3.361	1.975	.625	5.100
.01234	3.210	2.158	.789	4.961
"	3.156	2.163	.760	4.926
"	3.227	2.155	.761	4.909
.02214	3.124	2.234	.875	4.830
"	3.075	2.267	.863	4.818
"	3.121	2.296	.851	4.808
.02924	3.026	2.302	.946	4.774
"	3.023	2.241	.931	4.741
"	3.027	2.363	.903	4.727
.05073	2.871	2.490	1.065	4.610
"	2.860	2.485	1.047	4.596
"	2.871	2.489	1.026	4.582
0.0	3.333	1.977	.628	5.116
"	3.377	1.972	.639	5.117
"	3.384	1.928	.649	5.091
.01534	3.174	2.189	.824	4.920
"	3.170	2.206	.789	4.904
"	3.176	2.190	.785	4.866
.02237	3.064	2.293	.833	4.786
"	3.059	2.278	.870	4.825
"	3.068	2.271	.894	4.836

APPENDIX C

SUMMARY OF LEAST SQUARES FIT OF EXPERIMENTAL DATA

Total Acid - T = 60 C<sup>0</sup>

## L E A S T - S Q U A R E S   P O L Y N O M I A L S

NUMBER OF POINTS = 40  
 MEAN VALUE OF X = .020023  
 MEAN VALUE OF Y = 3.7109  
 STD ERROR OF Y = .15629

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .962455

TERM	COEFFICIENT
------	-------------

0	3.92538
1	-10.7118

WHAT NEXT?3

POLYFIT OF DEGREE 2      INDEX OF DETERM = .977005

TERM	COEFFICIENT
------	-------------

0	3.95445
1	-14.618
2	81.8023

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
.00379	3.919	3.90023	1.87726E-02	.481321
.00379	3.938	3.90023	3.77727E-02	.968473
.00379	3.935	3.90023	3.47724E-02	.891548
.00379	3.94	3.90023	3.97725E-02	1.01975

Total Acid - T = 60<sup>o</sup> C, Cont'd.

•01305	3.797	3.77762	1.93796E-02	•513011
•01305	3.801	3.77762	2.33798E-02	•618903
•01305	3.809	3.77762	3.13797E-02	•830674
•01305	3.798	3.77762	2.03795E-02	•539481
•0221	3.648	3.67135	-2.33493E-02	-•635987
•0221	3.66	3.67135	-1.13492E-02	-•309129
•0221	3.673	3.67135	1.65081E-03	4.49647E-02
•0221	3.664	3.67135	-7.34901E-03	-•200172
•01523	3.709	3.7508	-4.17962E-02	-1.11433
•01523	3.721	3.7508	-2.97961E-02	-•794395
•01523	3.698	3.7508	-5.27964E-02	-1.4076
•01523	3.718	3.7508	-3.27964E-02	-•874385
•01007	3.8	3.81555	-1.55463E-02	-•407447
•01007	3.793	3.81555	-2.25468E-02	-•590918
•01007	3.798	3.81555	-1.75467E-02	-•459873
•01007	3.802	3.81555	-1.35465E-02	-•355033
0	3.946	3.95445	-8.45480E-03	-•213804
0	3.943	3.95445	-1.14551E-02	-•289675
0	3.945	3.95445	-9.45473E-03	-•239091
0	3.941	3.95445	-1.34549E-02	-•340247
•04929	3.424	3.43267	-8.67033E-03	-•252583
•04929	3.419	3.43267	-•01367	-•398231
•04929	3.421	3.43267	-1.16701E-02	-•339972
•04929	3.42	3.43267	-•01267	-•369102
•03549	3.562	3.53869	2.33064E-02	•658615

Total Acid - T = 60 C, Cont'd.

.03549	3.565	3.53869	2.63066E-02	.7434
.03549	3.563	3.53869	2.43068E-02	.686886
.03549	3.578	3.53869	3.93066E-02	1.11077
.0263	3.641	3.62658	1.44176E-02	.397555
.0263	3.65	3.62658	2.34179E-02	.645731
.0263	3.644	3.62658	1.74179E-02	.480284
.0263	3.644	3.62658	1.74179E-02	.480284
.02491	3.625	3.64108	-1.60785E-02	-.441585
.02491	3.627	3.64108	-1.40786E-02	-.386661
.02491	3.63	3.64108	-1.10784E-02	-.30426
.02491	3.627	3.64108	-1.40786E-02	-.386661

STD ERROR OF ESTIMATE FOR Y = 2.43321E-02

WHAT NEXT?3

POLYFIT OF DEGREE 3 INDEX OF DETERM = .979866

TERM	COEFFICIENT
0	3.96619
1	-18.5899
2	303.045
3	-3018.73

WHAT NEXT?0

DONE

# SUMMARY OF LEAST SQUARES FIT OF EXPERIMENTAL DATA

O  
Total Ester - T = 60 C

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 40  
 MEAN VALUE OF X = .019998  
 MEAN VALUE OF Y = 1.64728  
 STD ERROR OF Y = .156544

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .962205

TERM	COEFFICIENT
------	-------------

0	1.43273
1	10.7282

WHAT NEXT?3

POLYFIT OF DEGREE 2      INDEX OF DETERM = .976901

TERM	COEFFICIENT
------	-------------

0	1.40342
1	14.6646
2	-82.3866

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
.00379	1.438	1.45781	-1.98138E-02	-1.35914
.00379	1.422	1.45781	-3.58138E-02	-2.45668
.00379	1.424	1.45781	-3.38137E-02	-2.31948
.00379	1.416	1.45781	-4.18139E-02	-2.86826
.01305	1.559	1.58076	-2.17609E-02	-1.37661

Total Ester - T = 60<sup>0</sup> C, Cont'd.

•01305	1.556	1.58076	-•024761	-1.5664
•01305	1.55	1.58076	-•030761	-1.94596
•01305	1.562	1.58076	-1.87609E-02	-1.18683
•0221	1.711	1.68727	2.37319E-02	1.40653
•0221	1.697	1.68727	9.73201E-03	.576791
•0211	1.687	1.67616	1.08376E-02	.646569
•0221	1.692	1.68727	4.73189E-03	.280447
•01523	1.647	1.60765	3.93493E-02	2.44763
•01523	1.639	1.60765	3.13492E-02	1.95
•01523	1.659	1.60765	5.13492E-02	3.19405
•01523	1.641	1.60765	3.33493E-02	2.07441
•01007	1.559	1.54274	1.62632E-02	1.05418
•01007	1.563	1.54274	2.02632E-02	1.31346
•01007	1.562	1.54274	1.92633E-02	1.24864
•01007	1.555	1.54274	1.22633E-02	.794905
0	1.413	1.40342	9.58180E-03	.682748
0	1.417	1.40342	1.35818E-02	.967762
0	1.41	1.40342	6.58178E-03	.468982
0	1.417	1.40342	1.35818E-02	.967762
•04929	1.934	1.92608	7.92074E-03	.411237
•04929	1.941	1.92608	1.49207E-02	.774668
•04929	1.939	1.92608	1.29206E-02	.670825
•04929	1.938	1.92608	1.19207E-02	.61891
•03549	1.798	1.8201	-2.20966E-02	-1.21404
•03549	1.79	1.8201	-3.00968E-02	-1.65358



Total Ester - T = 60<sup>0</sup> C, Cont'd.

.03549	1.794	1.8201	-2.60968E-02	-1.43381
.03549	1.782	1.8201	-3.80967E-02	-2.09311
.0263	1.721	1.73211	-.011112	-.641528
.0263	1.704	1.73211	-2.81119E-02	-1.62299
.0263	1.719	1.73211	-1.31118E-02	-.756985
.0263	1.712	1.73211	-.020112	-1.16113
.02491	1.73	1.71759	1.24075E-02	.72238
.02491	1.735	1.71759	1.74074E-02	1.01348
.02491	1.726	1.71759	8.40759E-03	.489499
.02491	1.732	1.71759	1.44074E-02	.838813

STD ERROR OF ESTIMATE FOR Y = 2.44267E-02

WHAT NEXT?3

POLYFIT OF DEGREE 3      INDEX OF DETERM = .979827

TERM	COEFFICIENT
0	1.39156
1	18.6783
2	-306.194
3	3055.59

WHAT NEXT?0

DONE

# SUMMARY OF LEAST SQUARES FIT OF EXPERIMENTAL DATA

Butyl Lactate - T = 60 C

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 30  
 MEAN VALUE OF X = .02002  
 MEAN VALUE OF Y = .355  
 STD ERROR OF Y = .1264

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .971115

TERM	COEFFICIENT
0	.181608
1	8.66096

WHAT NEXT?3

POLYFIT OF DEGREE 2      INDEX OF DETERM = .986904

TERM	COEFFICIENT
0	.157258
1	11.9354
2	-68.5898

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
.0037	.215	.20048	1.45203E-02	7.24279
.00379	.21	.201508	8.49235E-03	4.21441
.00379	.19	.201508	-1.15077E-02	-5.71078
.01305	.315	.301334	1.36659E-02	4.53514
.01305	.309	.301334	7.66593E-03	2.544

Butyl Lactate - T = 60<sup>o</sup> C, Cont'd.

..01305	..329	..301334	2.76659E-02	9.18114
..0221	..352	..387531	-3.55309E-02	-9.16854
..0221	..405	..387531	..017469	4.50778
..0221	..394	..387531	6.46907E-03	1.6693
..01523	..328	..323125	4.87524E-03	1.50878
..01523	..309	..323125	-1.41248E-02	-4.3713
..01523	..315	..323125	-8.12477E-03	-2.51444
..01007	..284	..270492	1.35078E-02	4.9938
..01007	..268	..270492	-2.49213E-03	-.921332
..01007	..256	..270492	-1.44922E-02	-5.3577
0	..164	..157258	6.74245E-03	4.28752
0	..149	..157258	-8.25757E-03	-5.25098
0	..14	..157258	-1.72576E-02	-10.9741
..04929	..595	..578916	1.60836E-02	2.77822
..04929	..575	..578916	-3.91638E-03	-.676502
..04929	..569	..578916	-9.91642E-03	-1.71293
..03549	..509	..494455	1.45451E-02	2.94164
..03549	..496	..494455	1.54513E-03	..312492
..03549	..485	..494455	-9.45485E-03	-1.91218
..0263	..444	..423717	2.02832E-02	4.78698
..0263	..413	..423717	-1.07168E-02	-2.52924
..0263	..4	..423717	-2.37168E-02	-5.59733
..02491	..42	..412009	7.99108E-03	1.93954
..02491	..41	..412009	-2.00891E-03	-.48759
..02491	..402	..412009	-1.00089E-02	-2.4293

Butyl Lactate - T = 60<sup>o</sup> C, Cont'd.

STD ERROR OF ESTIMATE FOR Y = .014991

WHAT NEXT?3

POLYFIT OF DEGREE 3      INDEX OF DETERM = .98717

TERM	COEFFICIENT
0	.154387
1	12.9089
2	-122.834
3	740.224

WHAT NEXT?0

DONE

# SUMMARY OF LEAST SQUARES FIT OF EXPERIMENTAL DATA

Butanol - T = 60 C

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 30  
 MEAN VALUE OF X = .020023  
 MEAN VALUE OF Y = 5.43307  
 STD ERROR OF Y = .153152

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = .951782

TERM	COEFFICIENT
0	5.64115
1	-10.392

WHAT NEXT?3

POLYFIT OF DEGREE 2 INDEX OF DETERM = .965935

TERM	COEFFICIENT
0	5.66912
1	-14.151
2	78.719

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
.00379	5.644	5.61662	.02738	.487482
.00379	5.602	5.61662	-1.46198E-02	-.260296
.00379	5.622	5.61662	5.37968E-03	9.57814E-02
.01305	5.52	5.49786	2.21424E-02	.402746
.01305	5.541	5.49786	4.31433E-02	.784729

Butanol - T = 60<sup>0</sup> C, Cont'd.

01305	5.477	5.49786	-2.08569E-02	-.379363
0221	5.399	5.39483	4.16946E-03	7.72863E-0
0221	5.406	5.39483	1.11694E-02	.20704
0221	5.392	5.39483	-2.83051E-03	-.052467
01523	5.485	5.47186	1.31397E-02	.240133
01523	5.475	5.47186	3.14045E-03	5.73927E-02
01523	5.464	5.47186	-7.86018E-03	-.143647
01007	5.554	5.5346	1.93968E-02	.350464
01007	5.41	5.5346	-.124603	-2.25135
01007	5.526	5.5346	-8.60310E-03	-.155442
0	5.657	5.66912	-1.21222E-02	-.213828
0	5.684	5.66912	1.48783E-02	.262444
0	5.688	5.66912	.018878	.332997
04929	5.176	5.16286	.013135	.254412
04929	5.156	5.16286	-6.86455E-03	-.13296
04929	5.15	5.16286	-1.28651E-02	-.249185
03549	5.277	5.26605	1.09501E-02	.207937
03549	5.268	5.26605	1.94931E-03	3.70166E-02
03549	5.256	5.26605	-1.00508E-02	-.19086
0263	5.37	5.3514	1.86014E-02	.347599
0263	5.332	5.3514	-1.93987E-02	-.362498
0263	5.357	5.3514	5.60188E-03	.104681
02491	5.392	5.36547	.026535	.494552
02491	5.361	5.36547	-4.46510E-03	-8.32193E-02
02491	5.351	5.36547	-1.44653E-02	-.269601

Butanol - T = 60<sup>o</sup> C, Cont'd.

STD ERROR OF ESTIMATE FOR Y = 2.92949E-02

WHAT NEXT?3

POLYFIT OF DEGREE 3      INDEX OF DETERM = .966553

DONE

# SUMMARY OF LEAST SQUARES FIT OF EXPERIMENTAL DATA

Total Acid - T = 70 C

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 18  
 MEAN VALUE OF X = 2.51133E-02  
 MEAN VALUE OF Y = 3.38994  
 STD ERROR OF Y = .170275

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .978006

TERM	COEFFICIENT
0	3.65622
1	-10.6028

WHAT NEXT?3

POLYFIT OF DEGREE 2      INDEX OF DETERM = .982921

TERM	COEFFICIENT
0	3.67204
1	-13.3045
2	59.8682

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	3.658	3.67204	-1.40443E-02	-.382465
0	3.683	3.67204	1.09558E-02	.298357
0	3.678	3.67204	5.95570E-03	.16219
.01258	3.56	3.51415	4.58512E-02	1.30476
.01258	3.524	3.51415	9.85146E-03	.280337
.01258	3.454	3.51415	-6.01487E-02	-1.71162



Total Acid - T = 70<sup>0</sup> C, Cont'd.

.02218	3.42	3.4064	1.35961E-02	.399132
.02218	3.383	3.4064	-2.34041E-02	-.687062
.02218	3.409	3.4064	2.59590E-03	7.62065E-01
.04151	3.228	3.22293	5.06592E-03	.157183
.04151	3.213	3.22293	-9.93443E-03	-.308242
.04151	3.226	3.22293	3.06559E-03	9.51179E-02
.04319	3.222	3.2091	1.28984E-02	.401933
.04319	3.193	3.2091	-1.61018E-02	-.501755
.04319	3.209	3.2091	-1.01566E-04	-3.16495E-03
.03122	3.34	3.31503	2.49681E-02	.75318
.03122	3.321	3.31503	5.96809E-03	.180031
.03122	3.298	3.31503	-1.70321E-02	-.513785

STD ERROR OF ESTIMATE FOR Y = 2.36895E-02

WHAT NEXT?3

POLYFIT OF DEGREE 3 INDEX OF DETERM = .98304

TERM	COEFFICIENT
0	3.67325
1	-14.2624
2	122.186
3	-960.924

WHAT NEXT?0

DONE

# SUMMARY OF LEAST SQUARES FIT OF EXPERIMENTAL DATA

Total Ester - T = 70 C

## LEAST SQUARES POLYNOMIALS

NUMBER OF POINTS = 18  
 MEAN VALUE OF X = 2.51133E-02  
 MEAN VALUE OF Y = 1.96833  
 STD ERROR OF Y = .173749

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .981045

TERM	COEFFICIENT
------	-------------

0	1.69621
1	10.8359

WHAT NEXT?3

POLYFIT OF DEGREE 2      INDEX OF DETERM = .987893

TERM	COEFFICIENT
------	-------------

0	1.67714
1	14.0901
2	-72.1122

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	1.685	1.67714	7.85851E-03	.468566
0	1.672	1.67714	-5.14150E-03	-.306563
0	1.678	1.67714	8.58545E-04	.051191
.01258	1.849	1.84298	6.01721E-03	.326493
.01258	1.832	1.84298	-1.09828E-02	-.595923
.01258	1.838	1.84298	-4.98271E-03	-.270361

Total Ester - T = 70<sup>o</sup> C, Cont'd.

02218	1.998	1.95418	4.38156E-02	2.24214
02218	1.936	1.95418	-1.81842E-02	-.930526
02218	1.933	1.95418	-2.11842E-02	-1.08404
04151	2.172	2.13777	3.42331E-02	1.60135
04151	2.109	2.13777	-2.87666E-02	-1.34564
04151	2.132	2.13777	-5.76687E-03	-.269761
04319	2.137	2.15118	-1.41768E-02	-.659027
04319	2.152	2.15118	8.23021E-04	3.82591E-02
04319	2.162	2.15118	1.08232E-02	.503132
03122	2.028	2.04675	-1.87478E-02	-.91598
03122	2.047	2.04675	2.52247E-04	1.23243E-02
03122	2.07	2.04675	2.32525E-02	1.13607

STD ERROR OF ESTIMATE FOR Y = 2.03528E-02

WHAT NEXT?3

POLYFIT OF DEGREE 3 INDEX OF DETERM = .987977

TERM	COEFFICIENT
0	1.67818
1	13.2656
2	-18.4752
3	-827.067

WHAT NEXT?0

DONE

# SUMMARY OF LEAST SQUARES FIT OF EXPERIMENTAL DATA

Butyl Lactate - T = 70 °C

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 18  
 MEAN VALUE OF X = 2.51133E-02  
 MEAN VALUE OF Y = .615556  
 STD ERROR OF Y = .139374

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1

TERM	COEFFICIENT	INDEX OF DETER
0	.397477	= 0.979177
1	8.68377	

WHAT NEXT?3

POLYFIT OF DEGREE 2 INDEX OF DETERM = .986098

TERM	COEFFICIENT
------	-------------

0	.382067
1	11.3141
2	-58.2879

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	.399	.382067	.016933	4.43195
0	.371	.382067	-.011067	-2.89661
0	.378	.382067	-4.06694E-03	-1.06446
.01258	.502	.515174	-1.31738E-02	-2.55716
.01258	.516	.515174	8.26240E-04	.160381
.01258	.526	.515174	1.08262E-02	2.10147
.02218	.625	.604339	2.06615E-02	3.41886

Butyl Lactate - T = 70<sup>o</sup> C, Cont'd.

..02218	..594	..604339	..-1.03385E-02	..-1.71072
..02218	..588	..604339	..-1.63386E-02	..-2.70355
..04151	..773	..75128	..2.17199E-02	..2.89106
..04151	..769	..75128	..01772	..2.35864
..04151	..736	..75128	..-1.52801E-02	..-2.03388
..04319	..78	..761994	..1.80063E-02	..2.36305
..04319	..761	..761994	..-9.93609E-04	..-.130396
..04319	..722	..761994	..-3.99936E-02	..-5.24855
..03122	..689	..67848	..1.05197E-02	..1.55049
..03122	..675	..67848	..-3.48032E-03	..-.512957
..03122	..676	..67848	..-2.48027E-03	..-.365562

STD ERROR OF ESTIMATE FOR Y = 1.74944E-02

WHAT NEXT?3

POLYFIT OF DEGREE 3 INDEX OF DETERM = .986235

TERM	COEFFICIENT
0	..38313
1	Y0.4707
2	..-3.42463
3	..-845.975

WHAT NEXT?0

DONE

# SUMMARY OF LEAST SQUARES FIT OF EXPERIMENTAL DATA

Butanol - T = 70 C

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 18  
 MEAN VALUE OF X = 2.51133E-02  
 MEAN VALUE OF Y = 5.11739  
 STD ERROR OF Y = .170809

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .986171      WHAT NEXT?1

TERM	COEFFICIENT
0	5.38561
1	-10.6803

WHAT NEXT? 3

POLYFIT OF DEGREE 2      INDEX OF DETERM = .990036      WHAT NEXT?2

TERM	COEFFICIENT
0	5.39968
1	-13.0834
2	53.2539

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	5.425	5.39968	2.53153E-02	.468829
0	5.386	5.39968	-1.36852E-02	-.253445
0	5.391	5.39968	-8.68511E-03	-.160845
.01258	5.25	5.24352	6.47640E-03	.123512

Butanol - T = 70<sup>o</sup> C, Cont'd.

.01258	5.231	5.24352	-1.25237E-02	-.23884
.01258	5.241	5.24352	-2.52342E-03	-4.81246E-03
.02218	5.16	5.13569	2.43073E-02	.4733
.02218	5.125	5.13569	-1.06926E-02	-.208202
.02218	5.126	5.13569	-9.69219E-03	-.188722
.04151	4.975	4.94835	2.66476E-02	.538514
.04151	4.925	4.94835	-2.33526E-02	-.471927
.04151	4.936	4.94835	-1.23529E-02	-.249637
.04319	4.954	4.93395	2.00491E-02	.40635
.04319	4.916	4.93395	-1.79501E-02	-.363807
.04319	4.937	4.93395	3.04985E-03	6.18136E-02
.03122	5.06	5.04313	1.68743E-02	.3346
.03122	5.054	5.04313	1.08738E-02	.215616
.03122	5.021	5.04313	-2.21262E-02	-.43874

STD ERROR OF ESTIMATE FOR Y = .018151

WHAT NEXT?3

POLYFIT OF DEGREE 3

INDEX OF DETERM = .990083

WHAT NEXT?1

TERM	COEFFICIENT
0	5.40044
1	-13.6858
2	.9274426
3	-604.279

WHAT NEXT?0

DONE

# SUMMARY OF LEAST SQUARES FIT OF EXPERIMENTAL DATA

Total Acid - T = 80 C

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 24  
 MEAN VALUE OF X = .01902  
 MEAN VALUE OF Y = 3.14446  
 STD ERROR OF Y = .160809

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = .960588 WHAT NEXT?1

TERM	COEFFICIENT
------	-------------

0	3.33426
1	-9.97917

WHAT NEXT?3

POLYFIT OF DEGREE 2 INDEX OF DETERM = .984936 WHAT NEXT?2

TERM	COEFFICIENT
------	-------------

0	3.36121
1	-14.1355
2	86.7209

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	3.35	3.36121	-1.12109E-02	-.333538
0	3.36	3.36121	-1.21069E-03	-3.60194E-02
0	3.361	3.36121	-2.10762E-04	-6.27042E-03
.01234	3.21	3.19998	.010016	.313
.01234	3.156	3.19998	-4.39839E-02	-1.3745
.01234	3.227	3.19998	2.70157E-02	.844244



Total Acid - T = 80<sup>0</sup> C, Cont'd.

.02214	3.124	3.09076	3.32403E-02	1.07547
.02214	3.075	3.09076	-1.57599E-02	-.509905
.02214	3.121	3.09076	3.02401E-02	.978402
.02924	3.026	3.02203	3.96681E-03	.131263
.02924	3.023	3.02203	9.66549E-04	3.19834E-02
.02924	3.027	3.02203	4.96674E-03	.164351
.05073	2.871	2.8673	3.70359E-03	.129167
.05073	2.86	2.8673	-7.29609E-03	-.254459
.05073	2.871	2.8673	3.70359E-03	.129167
0	3.333	3.36121	-2.82106E-02	-.8393
0	3.377	3.36121	.015789	.469742
0	3.384	3.36121	.022789	.678
.01534	3.174	3.16478	9.22060E-03	.29135
.01534	3.17	3.16478	5.22089E-03	.164969
.01534	3.176	3.16478	1.12209E-02	.354557
.02237	3.064	3.0884	-2.43964E-02	-.789938
.02237	3.059	3.0884	-2.93965E-02	-.951838
.02237	3.068	3.0884	-2.03967E-02	-.66043

STD ERROR OF ESTIMATE FOR Y = 2.06556E-02

WHAT NEXT?3

POLYFIT OF DEGREE 3

INDEX OF DETERM = .984945

WHAT NEXT?1

TERM	COEFFICIENT
0	3.36096
1	-13.9068
2	72.3612
3	197.926

SUMMARY OF LEAST SQUARES FIT OF EXPERIMENTAL DATA

Total Ester - T = 80 C

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 24  
 MEAN VALUE OF X = .01902  
 MEAN VALUE OF Y = 2.20392  
 STD ERROR OF Y = .167462

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .940567      WHAT NEXT?1

TERM	COEFFICIENT
0	2.00833
1	10.2835

WHAT NEXT?3

POLYFIT OF DEGREE 2      INDEX OF DETERM = .974089      WHAT NEXT?2

TERM	COEFFICIENT
0	1.9754
1	15.3621
2	-105.964

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	1.983	1.9754	7.60245E-03	.384857
0	1.989	1.9754	1.36025E-02	.688595
0	1.975	1.9754	-3.97682E-04	-2.01318E-02

°  
Total Ester - T = 80 C, Cont'd.

.01234	2.158	2.14883	9.17006E-03	.426746
.01234	2.163	2.14883	1.41702E-02	.659437
.01234	2.155	2.14883	6.17027E-03	.287146
.02214	2.234	2.26357	-2.95725E-02	-1.30645
.02214	2.267	2.26357	3.42751E-03	.15142
.02214	2.296	2.26357	3.24273E-02	1.43257
.02924	2.302	2.33399	-3.19881E-02	-1.37054
.02924	2.241	2.33399	-.092988	-3.98408
.02924	2.363	2.33399	2.90117E-02	1.24301
.05073	2.49	2.48201	7.98559E-03	.321738
.05073	2.485	2.48201	2.98595E-03	.120304
.05073	2.489	2.48201	6.98566E-03	.281451
0	1.977	1.9754	1.60241E-03	8.11184E-02
0	1.972	1.9754	-3.39770E-03	-.172001
0	1.928	1.9754	-4.73976E-02	-2.3994
.01534	2.189	2.18612	2.88296E-03	.131876
.01534	2.206	2.18612	1.98827E-02	.909497
.01534	2.19	2.18612	3.88288E-03	.177616
.02237	2.293	2.26602	.026979	1.19059
.02237	2.278	2.26602	1.19786E-02	.528619
.02237	2.271	2.26602	4.97866E-03	.219709

STD ERROR OF ESTIMATE FOR Y = 2.82105E-02

WHAT NEXT?3

Total Ester - T = 80<sup>0</sup> C, Cont'd.

POLYFIT OF DEGREE 3      INDEX OF DETERM = .978643      WHAT NEXT?1

TERM	COEFFICIENT
0	1.96973
1	20.5257
2	-430.237
3	4469.59

WHAT NEXT?0

DONE

# SUMMARY OF LEAST SQUARES FIT OF EXPERIMENTAL DATA

Butyl Lactate - T = 80 C

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 24  
 MEAN VALUE OF X = .01902  
 MEAN VALUE OF Y = .816  
 STD ERROR OF Y = .137288

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .953336      WHAT NEXT?1

TERM	COEFFICIENT
------	-------------

0	.65458
1	8.48686

WHAT NEXT?3

POLYFIT OF DEGREE 2      INDEX OF DETERM = .985327      WHAT NEXT?2

TERM	COEFFICIENT
------	-------------

0	.628209
1	12.5541
2	-84.8627

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	.61	.628209	-1.82091E-02	-2.89857
0	.621	.628209	-7.20906E-03	-1.14756
0	.625	.628209	-3.20911E-03	-.510835

Butyl Lactate - T = 80<sup>o</sup> C, Cont'd.

.01234	.789	.770205	1.87954E-02	2.44031
.01234	.76	.770205	-1.02047E-02	-1.32493
.01234	.761	.770205	-9.20463E-03	-1.19509
.02214	.875	.86456	1.04403E-02	1.20759
.02214	.863	.86456	-1.55962E-03	-.180394
.02214	.851	.86456	-1.35597E-02	-1.56839
.02924	.946	.922736	2.32637E-02	2.52116
.02924	.931	.922736	8.26371E-03	.895565
.02924	.903	.922736	-1.97363E-02	-2.13889
.05073	1.065	1.04668	1.83167E-02	1.74998
.05073	1.047	1.04668	3.16620E-04	3.02498E-02
.05073	1.026	1.04668	-2.06833E-02	-1.97608
0	.628	.628209	-2.09093E-04	-.033284
0	.639	.628209	1.07909E-02	1.71773
0	.649	.628209	2.07909E-02	3.30956
.01534	.824	.80082	.02318	2.89453
.01534	.789	.80082	-.01182	-1.47598
.01534	.785	.80082	-.01582	-1.97548
.02237	.833	.866578	-3.35784E-02	-3.87482
.02237	.87	.866578	3.42166E-03	.394848
.02237	.894	.866578	2.74217E-02	3.16437

STD ERROR OF ESTIMATE FOR Y = .017404

WHAT NEXT?3

Butyl Lactate - T = 80<sup>o</sup> C, Cont'd.

POLYFIT OF DEGREE 3

INDEX OF DETERM = .985407

WHAT NEXT?1

TERM	COEFFICIENT
0	.628826
1	11.9921
2	-49.5689
3	-486.469

WHAT NEXT?0

DONE

SUMMARY OF LEAST SQUARES FIT OF EXPERIMENTAL DATA

Butanol - T = 80 °C

LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 24  
 MEAN VALUE OF X = .01902  
 MEAN VALUE OF Y = 4.87904  
 STD ERROR OF Y = .16947

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .953992      WHAT NEXT?1

TERM	COEFFICIENT
0	5.07833
1	-10.4781

WHAT NEXT?3

POLYFIT OF DEGREE 2      INDEX OF DETERM = .989027      WHAT NEXT?2

TERM	COEFFICIENT
0	5.1124
1	-15.7324
2	109.631

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	5.13	5.1124	1.75982E-02	.344225
0	5.124	5.1124	1.15976E-02	.226853
0	5.1	5.1124	-1.24016E-02	-.242578
.01234	4.961	4.93496	.026042	.527704
.01234	4.926	4.93496	-8.95882E-03	-.181538



Butanol - T = 80<sup>o</sup> C, Cont'd.

01234	4.909	4.93496	-2.59581E-02	-.526004
02214	4.83	4.81783	1.21746E-02	.252699
02214	4.818	4.81783	1.74522E-04	3.62243E-03
02214	4.808	4.81783	-9.82571E-03	-.203945
02924	4.774	4.74612	2.78826E-02	.587482
02924	4.741	4.74612	-5.11742E-03	-.107823
02924	4.727	4.74612	-1.91174E-02	-.4028
05073	4.61	4.59643	1.35651E-02	.295121
05073	4.596	4.59643	-4.34875E-04	-9.46115E-03
05073	4.582	4.59643	-1.44348E-02	-.314044
0	5.116	5.1124	3.59821E-03	.070382
0	5.117	5.1124	4.59766E-03	8.99316E-02
0	5.091	5.1124	-2.14024E-02	-.418636
01534	4.92	4.89686	2.31352E-02	.472449
01534	4.904	4.89686	7.13539E-03	.145713
01534	4.866	4.89686	-3.08647E-02	-.630295
02237	4.786	4.81533	-2.93283E-02	-.609062
02237	4.825	4.81533	9.67121E-03	.200842
02237	4.836	4.81533	2.06718E-02	.429292

STD ERROR OF ESTIMATE FOR Y = 1.85789E-02

WHAT NEXT?3

Butanol - T = 80<sup>o</sup> C, Cont'd.

POLYFIT OF DEGREE 3      INDEX OF DETERM = .989063      WHAT NEXT?1

TERM	COEFFICIENT
0	5.11292
1	-16.2026
2	139.157
3	-406.971

WHAT NEXT?0

DONE

APPENDIX D

SUMMARY OF COMPONENT MATERIAL BALANCES

$$T = \overset{0}{60} \text{ C}$$

Cat	M	D	E <sub>1</sub>	E <sub>2</sub>
0	2.77753	1.17692	.157258	3.46222E-02
.005	2.71484	1.16857	.21522	4.54466E-02
.01	2.65591	1.16054	.269753	5.57656E-02
.015	2.60075	1.15283	.320856	6.55773E-02
.02	2.54936	1.14545	.36853	7.48827E-02
.025	2.50174	1.13839	.412774	8.36818E-02
.03	2.45788	1.13166	.453589	9.19736E-02
.035	2.41779	1.12524	.490974	.09976
.04	2.38146	1.11915	.52493	.107039
.045	2.34891	1.11338	.555457	.113813
.05	2.32012	1.10794	.582554	.120079
.055	2.29509	1.10282	.606221	.125839
.06	2.27384	1.09802	.626459	.131093

Cat	M	B	W
0	2.77753	5.66912	6.00515
.005	2.71484	5.60033	6.0762
.01	2.65591	5.53548	6.14315
.015	2.60075	5.47457	6.20602
.02	2.54936	5.41759	6.26479
.025	2.50174	5.36454	6.31947
.03	2.45788	5.31544	6.37007
.035	2.41779	5.27027	6.41657
.04	2.38146	5.22903	6.45899
.045	2.34891	5.19173	6.49731
.05	2.32012	5.15837	6.53154
.055	2.29509	5.12894	6.56169
.06	2.27384	5.10345	6.58774

DONE

SUMMARY OF COMPONENT MATERIAL BALANCES

$$T = 70^{\circ}C$$

Cat	M	D	E <sub>1</sub>	E <sub>2</sub>
0	2.53547	1.13657	.382067	7.92529E-02
.005	2.47486	1.13216	.43718	8.82255E-02
.01	2.41843	1.12655	.489379	.097449
.015	2.36619	1.11975	.538664	.106925
.02	2.31814	1.11176	.585034	.116653
.025	2.27428	1.10257	.62849	.126632
.03	2.2346	1.09219	.669031	.136862
.035	2.19911	1.08061	.706658	.147345
.04	2.16781	1.06783	.74137	.15808
.045	2.1407	1.05387	.773169	.169065
.05	2.11778	1.03871	.802052	.180303
.055	2.09905	1.02235	.828022	.191793
.06	2.0845	1.0048	.851077	.203533

DONE

Cat	M	B	W
0	2.53547	5.39968	6.28756
.005	2.47486	5.33559	6.35259
.01	2.41843	5.27417	6.41462
.015	2.36619	5.21541	6.47366
.02	2.31814	5.15931	6.5297
.025	2.27428	5.10588	6.58276
.03	2.2346	5.05511	6.63281
.035	2.19911	5.007	6.67988
.04	2.16781	4.96155	6.72395
.045	2.1407	4.91877	6.76503
.05	2.11778	4.87864	6.80311
.055	2.09905	4.84119	6.83821
.06	2.0845	4.80639	6.87031

SUMMARY OF COMPONENT MATERIAL BALANCES

$$T = 80^{\circ}C$$

Cat	M	D	E <sub>1</sub>	E <sub>2</sub>
0	2.2548	1.10641	.628209	.120391
.005	2.20332	1.08938	.688858	.135663
.01	2.15476	1.07377	.745264	.149697
.015	2.10911	1.05958	.797426	.162493
.02	2.06638	1.04681	.845346	.174049
.025	2.02656	1.03547	.889022	.184368
.03	1.98965	1.02554	.928456	.193448
.035	1.95566	1.01704	.963646	.20129
.04	1.92458	1.00996	.994593	.207894
.045	1.89642	1.0043	1.0213	.213259
.05	1.87117	1.00007	1.04376	.217385
.055	1.84884	.997252	1.06197	.220274
.06	1.82942	.99586	1.07595	.221923

Cat	M	B	W
0	2.2548	5.1124	6.59839
.005	2.20332	5.03648	6.6669
.01	2.15476	4.96604	6.73107
.015	2.10911	4.90108	6.79091
.02	2.06638	4.84161	6.84641
.025	2.02656	4.78761	6.89758
.03	1.98965	4.7391	6.94441
.035	1.95566	4.69606	6.9869
.04	1.92458	4.65851	7.02506
.045	1.89642	4.62644	7.05888
.05	1.87117	4.59986	7.08836
.055	1.84884	4.57875	7.11351
.06	1.82942	4.56313	7.13433

APPENDIX E

REACTION RATE CONSTANTS

$$T = 60^{\circ} \text{C}$$

Butyl Lactate

CAAT 0	CONST 6.99336E-06
CAAT 4.51138	CONST 9.98758E-06
CAAT 9.01433	CONST 1.30485E-05
CAAT 13.5093	CONST 1.61570E-05
CAAT 17.9967	CONST 1.92908E-05
CAAT 22.4773	CONST 2.24236E-05
CAAT 26.9517	CONST 2.55259E-05
CAAT 31.4208	CONST 2.85645E-05
CAAT 35.8853	CONST 3.15034E-05
CAAT 40.3464	CONST 3.43042E-05
CAAT 44.8049	CONST 3.69267E-05
CAAT 49.262	CONST 3.93304E-05
CAAT 53.7188	CONST 4.14753E-05

Butyllactyllactate

CAAT 0	CONST 3.60435E-06
CAAT 4.51138	CONST 4.83839E-06
CAAT 9.01433	CONST 6.06702E-06
CAAT 13.5093	CONST 7.28536E-06
CAAT 17.9967	CONST 8.48825E-06
CAAT 22.4773	CONST 9.67022E-06
CAAT 26.9517	CONST 1.08256E-05
CAAT 31.4208	CONST 1.19485E-05
CAAT 35.8853	CONST 1.30328E-05
CAAT 40.3464	CONST 1.40726E-05
CAAT 44.8049	CONST 1.50616E-05
CAAT 49.262	CONST 1.59938E-05
CAAT 53.7188	CONST 1.68634E-05



REACTION RATE CONSTANTS

$$T = 70^{\circ} \text{C}$$

Butyl lactate

CAAT 0	CONST 2.06660E-05
CAAT 4.46823	CONST 2.47824E-05
CAAT 8.92697	CONST 2.90454E-05
CAAT 13.3772	CONST 3.34353E-05
CAAT 17.8202	CONST 3.79270E-05
CAAT 22.2572	CONST 4.24890E-05
CAAT 26.6897	CONST 4.70839E-05
CAAT 31.1192	CONST 5.16674E-05
CAAT 35.5474	CONST 5.61892E-05
CAAT 39.9762	CONST 6.05930E-05
CAAT 44.4072	CONST 6.48179E-05
CAAT 48.8426	CONST 6.87992E-05
CAAT 53.2841	CONST 7.24710E-05

Butyllactyllactate

CAAT 0	CONST 9.29782E-06
CAAT 4.46823	CONST 1.05490E-05
CAAT 8.92697	CONST 1.18887E-05
CAAT 13.3772	CONST 1.33252E-05
CAAT 17.8202	CONST 1.48676E-05
CAAT 22.2572	CONST 1.65264E-05
CAAT 26.6897	CONST 1.83134E-05
CAAT 31.1192	CONST 2.02421E-05
CAAT 35.5474	CONST 2.23279E-05
CAAT 39.9762	CONST 2.45886E-05
CAAT 44.4072	CONST 2.70446E-05
CAAT 48.8426	CONST 2.97198E-05
CAAT 53.2841	CONST 3.26422E-05

REACTION RATE CONSTANTS

$$T = 80^{\circ} \text{C}$$

Butyl Lactate

CAAT 0	CONST 4.37848E-05
CAAT 4.41895	CONST 5.08336E-05
CAAT 8.83107	CONST 5.81679E-05
CAAT 13.2363	CONST 6.57421E-05
CAAT 17.6346	CONST 7.34949E-05
CAAT 22.0261	CONST 8.13475E-05
CAAT 26.4108	CONST 8.92020E-05
CAAT 30.7889	CONST 9.69410E-05
CAAT 35.1607	CONST 1.04428E-04
CAAT 39.5264	CONST 1.11512E-04
CAAT 43.8864	CONST 1.18028E-04
CAAT 48.241	CONST 1.23805E-04
CAAT 52.5909	CONST 1.28679E-04

Butyllactyllactate

CAAT 0	CONST 1.59385E-05
CAAT 4.41895	CONST 1.86748E-05
CAAT 8.83107	CONST 2.13837E-05
CAAT 13.2363	CONST 2.40340E-05
CAAT 17.6346	CONST 2.65913E-05
CAAT 22.0261	CONST 2.90195E-05
CAAT 26.4108	CONST 3.12807E-05
CAAT 30.7889	CONST 3.33367E-05
CAAT 35.1607	CONST 3.51504E-05
CAAT 39.5264	CONST 3.66867E-05
CAAT 43.8864	CONST 3.79143E-05
CAAT 48.241	CONST 3.88070E-05
CAAT 52.5909	CONST 3.93446E-05

APPENDIX F

LEAST SQUARES FIT OF OBSERVED RATE CONSTANTS

$$T = 60^{\circ} \text{C}$$

Butyl Lactate

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 6  
 MEAN VALUE OF X = 22.4422  
 MEAN VALUE OF Y = 22.2148  
 STD ERROR OF Y = 11.2955

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .999556      WHAT NEXT?2

TERM	COEFFICIENT			
0	7.09512			
1	.673717			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	6.99336	7.09512	-.101762	-1.43425
9.01433	13.0485	13.1682	-.119728	-.909219
17.9967	19.2908	19.2198	7.09953E-02	.369386
26.9517	25.5259	25.2529	.272964	1.08092
35.8853	31.5034	31.2717	.231747	.741076
44.8049	36.9267	37.2809	-.35424	-.950192

STD ERROR OF ESTIMATE FOR Y = .266192

WHAT NEXT?0

DONE

LEAST SQUARES FIT OF OBSERVED RATE CONSTANTSButyl LactateT = 70 C

## L E A S T - S Q U A R E S   P O L Y N O M I A L S

NUMBER OF POINTS = 6  
 MEAN VALUE OF X = 22.2319  
 MEAN VALUE OF Y = 42.6216  
 STD ERROR OF Y = 16.6437

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .999791      WHAT NEXT?2

TERM	COEFFICIENT			
0	20.3485			
1	1.00185			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	20.666	20.3485	.317535	1.56049
8.92697	29.0454	29.292	-.246578	-.841794
17.8202	37.927	38.2017	-.274681	-.719029
26.6897	47.0839	47.0876	-3.72314E-03	-7.90684E-03
35.5474	56.1892	55.9617	.227463	.406461
44.4072	64.8179	64.838	-.02005	-3.09233E-02

STD ERROR OF ESTIMATE FOR Y = .268903

WHAT NEXT?0

DONE

LEAST SQUARES FIT OF OBSERVED RATE CONSTANTSButyl Lactate          <sup>o</sup>  
T = 80 C

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 6  
 MEAN VALUE OF X = 21.9873  
 MEAN VALUE OF Y = 81.1843  
 STD ERROR OF Y = 28.1056

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .999632      WHAT NEXT?2

TERM	COEFFICIENT			
0	43.5573			
1	1.71131			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	43.7848	43.5573	.227509	.52232
8.83107	58.1679	58.67	-.502068	-.855749
17.6346	73.4949	73.7355	-.240616	-.326323
26.4108	89.202	88.7543	.447693	.504418
35.1607	104.428	103.728	.699921	.674765
43.8864	118.028	118.66	-.632446	-.532988

STD ERROR OF ESTIMATE FOR Y = .602502

WHAT NEXT?0

DONE

LEAST SQUARES FIT OF OBSERVED RATE CONSTANTSButyllactyllactate

$$T = 60^{\circ}C$$

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 6  
 MEAN VALUE OF X = 22.4422  
 MEAN VALUE OF Y = 9.51327  
 STD ERROR OF Y = 4.30664

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .998911      WHAT NEXT?2

TERM	COEFFICIENT
0	3.75046
1	.256785

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	3.60435	3.75046	-.146108	-3.89573
9.01433	6.06702	6.0652	1.81675E-03	2.99536E-02
17.9967	8.48825	8.37174	.116508	1.39169
26.9517	10.8256	10.6713	.154346	1.44638
35.8853	13.0328	12.9653	6.75335E-02	.52088
44.8049	15.0616	15.2557	-.194088	-1.27223

STD ERROR OF ESTIMATE FOR Y = .158886

WHAT NEXT?0

DONE

LEAST SQUARES FIT OF OBSERVED RATE CONSTANTSButyllactyllactateT = 70 ° C

## L E A S T - S Q U A R E S   P O L Y N O M I A L S

NUMBER OF POINTS = 6  
 MEAN VALUE OF X = 22.2319  
 MEAN VALUE OF Y = 17.29  
 STD ERROR OF Y = 6.64074

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .987833      WHAT NEXT?2

TERM	COEFFICIENT			
0	8.45648			
1	.397335			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	9.29782	8.45648	.841335	9.949
8.92697	11.8887	12.0035	-.114782	-.956242
17.8202	14.8676	15.5371	-.669476	-4.30889
26.6897	18.3134	19.0612	-.747841	-3.92336
35.5474	22.3279	22.5807	-.252819	-1.11962
44.4072	27.0446	26.101	.943573	3.61508

STD ERROR OF ESTIMATE FOR Y = .818952

WHAT NEXT?0

DONE



LEAST SQUARES FIT OF OBSERVED RATE CONSTANTSButyllactyllactateT = 80 C

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 6  
 MEAN VALUE OF X = 21.9873  
 MEAN VALUE OF Y = 28.0432  
 STD ERROR OF Y = 8.38347

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .988117      WHAT NEXT?2

TERM	COEFFICIENT			
0	16.8844			
1	.507509			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
0	15.9385	16.8844	-.945923	-5.60234
8.83107	21.3837	21.3663	1.74332E-02	.081592
17.6346	26.5913	25.8341	.75716	2.93085
26.4108	31.2807	30.2881	.992561	3.27706
35.1607	35.1504	34.7288	.421608	1.214
43.8864	37.9143	39.1572	-1.24286	-3.17403

STD ERROR OF ESTIMATE FOR Y = 1.02176

WHAT NEXT?0

DONE

APPENDIX G

LEAST SQUARE FIT FOR ARRHENIUS PARAMETERSk UncatalyzedButyl Lactate

DONE  
 SCR  
 GET-\$POLFT  
 1 DATA 3,1  
 10 DATA .003003,1.95941,.00291545,3.01301,.00283286,3.77408  
 RUN  
 POLFT

LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 2.91710E-03  
 MEAN VALUE OF Y = 2.9155  
 STD ERROR OF Y = .911257

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .994239      WHAT NEXT?2

TERM	COEFFICIENT				
0	34.069				
1	-10679.6				
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF	
.003003	1.95941	1.99816	-3.87514E-02	-1.93935	
2.91545E-03	3.01301	2.93316	.079855	2.72249	
2.83286E-03	3.77408	3.81519	-4.11057E-02	-1.07742	

STD ERROR OF ESTIMATE FOR Y = .097817

WHAT NEXT?0

DONE

LEAST SQUARE FIT FOR ARRHENIUS PARAMETERSk CatalyzedButyl Lactate

10 DATA .003003, -.394945, .00291545, .00184809, .00283286, .537259  
 RUN  
 POLFT

## L E A S T - S Q U A R E S P O L Y N O M I A L S

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 2.91710E-03  
 MEAN VALUE OF Y = .048054  
 STD ERROR OF Y = .467817

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = .989537 WHAT NEXT?2

TERM	COEFFICIENT			
0	16.0034			
1	-5469.58			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
.003003	-.394945	-.421761	2.68155E-02	-6.358
2.91545E-03	1.84809E-03	5.71003E-02	-5.52522E-02	-96.7634
2.83286E-03	.537259	.508833	2.84261E-02	5.58652

STD ERROR OF ESTIMATE FOR Y = 6.76751E-02

WHAT NEXT?0

DONE

LEAST SQUARE FIT FOR ARRHENIUS PARAMETERSk UncatalyzedButyllactyllactate

10 DATA .003003,1.32188,.00291545,2.13493,.00283286,2.82639  
 RUN  
 POLFT

L E A S T - S Q U A R E S   P O L Y N O M I A L S

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 2.91710E-03  
 MEAN VALUE OF Y = 2.0944  
 STD ERROR OF Y = .753073

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1      INDEX OF DETERM = .999112      WHAT NEXT?2

TERM	COEFFICIENT			
0	27.903			
1	-8847.34			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
.003003	1.32188	1.33444	-.012562	-.94137
2.91545E-03	2.13493	2.10903	2.59023E-02	1.22816
2.83286E-03	2.82639	2.83973	-1.33395E-02	-.469746

STD ERROR OF ESTIMATE FOR Y = 3.17281E-02

WHAT NEXT?0

DONE

LEAST SQUARE FIT FOR ARRHENIUS PARAMETERSk CatalyzedButyllactyllactate

10 DATA .003003, -1.35952, .00291545, -.922976, .00283286, -.678241  
 RUN  
 POLFT

## L E A S T - S Q U A R E S P O L Y N O M I A L S

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 2.91710E-03  
 MEAN VALUE OF Y = -.986912  
 STD ERROR OF Y = .34511

NOTE: CODE FOR 'WHAT NEXT?' IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = .979318 WHAT NEXT?2

TERM	COEFFICIENT			
0	10.7223			
1	-4013.98			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
.003003	-1.35952	-1.3317	-2.78225E-02	2.08925
2.91545E-03	-.922976	-.980274	5.72982E-02	-5.84512
2.83286E-03	-.678241	-.648758	-2.94831E-02	4.54454

STD ERROR OF ESTIMATE FOR Y = 7.01885E-02

WHAT NEXT?0

DONE

APPENDIX H

COMPUTER PROGRAM OF SOLUTION OF THE BATCH REACTOR  
DESIGN EQUATION FOR A SECOND ORDER REVERSIBLE SYSTEM

The following computer program solves for the conversion of a reactant as a function of time in a batch reactor for a second order reversible reaction. The program is a solution of equations (85) and (86). The program given below is for the formation of butyllactyllactate as a function of time.

```

5  LET T=0
10  LET I=2.21E-05
20  LET Q=2.75
30  LET V=1.1187
40  LET A=.124
50  LET B=6.897
60  LET R=0
70  LET S=4.321
80  LET J=Q*A*B-R*S
90  LET K=-Q*B-Q*A-R-S
100 LET L=Q-1
110 LET M=4*J*L-K*K
120 LET N=(T*I*SQR(-M))/(V*Q)
130 LET X=(K*K+M)*(1-EXP(N))
140 LET Y=(2*L)*((K*EXP(N))-(SQR(-M)*EXP(N))-K-SQR(-M))
150 LET Z=X/Y
160 PRINT T,Z
170 LET T=T+100
180 IF T>10000 THEN 9999
190 GOTO 120
9999 END

```



BUTYL LACTATE FORMATION AS A FUNCTION OF TIME IN A  
BATCH REACTOR

<u>Time</u> <u>Sec</u>	<u>Butyl Lactate</u> <u>Conc., moles/kg</u>
0	0
100	.149455
200	.289182
300	.419951
400	.542455
500	.657323
600	.765122
700	.866371
800	.961538
900	1.05105
1000	1.13531
1100	1.21466
1200	1.28945
1300	1.35996
1400	1.42649
1500	1.48928
1600	1.54857
1700	1.6046
1800	1.65754
1900	1.70761
2000	1.75496
2100	1.79977
2200	1.84218
2300	1.88234
2400	1.92037
2500	1.9564
2600	1.99055
2700	2.02291
2800	2.0536
2900	2.0827
3000	2.1103
3100	2.13649
3200	2.16134
3300	2.18493
3400	2.20731
3500	2.22857
3600	2.24876
3700	2.26793
3800	2.28613
3900	2.30343
4000	2.31987

Butyl Lactate Formation...Cont'd.

<u>Time Sec</u>	<u>Butyl Lactate Conc., moles/kg</u>
4100	2.33548
4200	2.35032
4300	2.36443
4400	2.37784
4500	2.39058
4600	2.4027
4700	2.41422
4800	2.42518
4900	2.4356
5000	2.44551

BUTYLLACTYLACTATE FORMATION AS A FUNCTION OF  
TIME IN A BATCH REACTOR

<u>Time</u> <u>Sec</u>	<u>Butyllactyl-</u> <u>lactate, Conc.,</u> <u>moles/kg</u>
0	0
100	1.67526E-03
200	3.32231E-03
300	4.94167E-03
400	6.53380E-03
500	8.09914E-03
600	9.63817E-03
700	1.11513E-02
800	1.26391E-02
900	1.41018E-02
1000	.01554
1100	.016954
1200	1.83443E-02
1300	1.97113E-02
1400	2.10553E-02
1500	2.23767E-02
1600	2.36761E-02
1700	2.49535E-02
1800	2.62096E-02
1900	2.74446E-02
2000	.028659
2100	2.98529E-02
2200	3.10269E-02
2300	3.21812E-02
2400	3.33161E-02
2500	.034432
2600	3.55293E-02
2700	3.66082E-02
2800	.037669
2900	3.87121E-02
3000	3.97377E-02
3100	4.07461E-02
3200	4.17377E-02
3300	4.27127E-02
3400	4.36714E-02
3500	.044614
3600	4.55409E-02
3700	4.64524E-02
3800	4.73485E-02
3900	4.82297E-02
4000	4.90962E-02
4100	4.99481E-02

Butyllactyllactate Formation...Cont'd.

Time <u>Sec</u>	Butyllactyl- lactate, Conc., <u>Moles/kg</u>
4200	5.07859E-02
4300	5.16096E-02
4400	5.24196E-02
4500	.053216
4600	5.39992E-02
4700	5.47693E-02
4800	5.55265E-02
4900	5.62711E-02
5000	5.70033E-02

APPENDIX I

# COMPUTER PROGRAM FOR LEAST SQUARES POLYNOMIALS

```

100 READ M,N
110 DIM A[15],B[15],S[15],G[15],U[15]
120 DIM Q[200],P[200],X[200],Y[200],C[200]
130 LET Z=0
140 LET O=1
150 LET K=12
160 LET N=N+1
170 IF N>12 THEN 9999
180 IF M<N THEN 1640
190 IF M>200 THEN 1590
200 LET T7=Z
210 LET T8=Z
220 LET W7=Z
230 FOR I=1 TO M
240 READ X[I],Y[I]
250 LET W7=W7+X[I]
260 LET T7=T7+Y[I]
270 LET T8=T8+Y[I]2
280 NEXT I
290 LET T9=(M*T8-T72)/(M-1)
300 PRINT
310 PRINT "L E A S T - S Q U A R E S   P O L Y N O M I A L S"
320 PRINT
330 PRINT "          NUMBER OF POINTS =" ; M
340 PRINT "          MEAN VALUE OF X =" ; W7/M
350 PRINT "          MEAN VALUE OF Y =" ; T7/M
360 PRINT "          STD ERROR OF Y =" ; SQR(T9)
370 PRINT
380 PRINT "    NOTE:  CODE FOR 'WHAT NEXT?' IS:"
390 PRINT
400 PRINT "          0 = STOP PROGRAM"
410 PRINT "          1 = COEFFICIENTS ONLY"
420 PRINT "          2 = ENTIRE SUMMARY"
430 PRINT "          3 = FIT NEXT HIGHER DEGREE"
440 PRINT
450 PRINT
460 FOR I=1 TO M
470 LET P[I]=Z
480 LET Q[I]=0
490 NEXT I
500 FOR I=1 TO 11
510 LET A[I]=Z
520 LET B[I]=Z
530 LET S[I]=Z
540 NEXT I
550 LET E1=Z
560 LET F1=Z
570 LET W1=M
580 LET N4=K
590 LET I=1

```

Least Squares Polynomials,..Cont'd.

```

600 LET K1=2
610 IF N=0 THEN 9999
620 LET K1=N4
630 LET W=Z
640 FOR L=1 TO M
650 LET W=W+Y[L]*Q[L]
660 NEXT L
670 LET S[I]=W/W1
680 IF I-N4 >= 0 THEN 880
690 IF I-M >= 0 THEN 880
700 LET E1=Z
710 FOR L=1 TO M
720 LET E1=E1+X[L]*Q[L]*Q[L]
730 NEXT L
740 LET E1=E1/W1
750 LET A[I+1]=E1
760 LET W=Z
770 FOR L=1 TO M
780 LET V=(X[L]-E1)*Q[L]-F1*P[L]
790 LET P[L]=Q[L]
800 LET Q[L]=V
810 LET W=W+V*V
820 NEXT L
830 LET F1=W/W1
840 LET B[I+2]=F1
850 LET W1=W
860 LET I=I+1
870 GOTO 630
880 FOR L=1 TO 13
890 LET G[L]=Z
900 NEXT L
910 LET G[2]=0
920 FOR J=1 TO N
930 LET S1=Z
940 FOR L=1 TO N
950 IF L=1 THEN 970
960 LET G[L+1]=G[L+1]-A[L]*G[L]-B[L]*G[L-1]
970 LET S1=S1+S[L]*G[L+1]
980 NEXT L
990 LET U[J]=S1
1000 LET L=N
1010 FOR I2=2 TO N
1020 LET G[L+1]=G[L]
1030 LET L=L-1
1040 NEXT I2
1050 LET G[2]=Z
1060 NEXT J
1070 PRINT
1080 LET T=Z
1090 FOR L=1 TO M

```

Least Squares Polynomials...Cont'd.

```

1100 LET C[L]=Z
1110 LET J=N
1120 FOR I2=1 TO N
1130 LET C[L]=C[L]*X[L]+U[J]
1140 LET J=J-1
1150 NEXT I2
1160 LET T3=Y[L]-C[L]
1170 LET T=T+T3*2
1180 NEXT L
1190 IF M <> N THEN 1220
1200 LET T5=0
1210 GOTO 1230
1220 LET T5=T/(M-N)
1230 LET Q7=1-T/(T9*(M-1))
1240 PRINT
1250 PRINT "POLYFIT OF DEGREE";N-1;
1260 PRINT "INDEX OF DETERM =" ;Q7;
1270 GOSUB 1670
1280 PRINT
1290 PRINT
1300 IF R=0 THEN 9999
1310 IF R=3 THEN 1560
1320 PRINT "TERM","COEFFICIENT"
1330 PRINT
1340 FOR J=1 TO N
1350 LET I2=J-1
1360 PRINT I2,U[J]
1370 NEXT J
1380 IF R=1 THEN 1530
1390 PRINT
1400 PRINT "X-ACTUAL","Y-ACTUAL","Y-CALC","DIFF","PCT-DIFF"
1410 PRINT
1420 FOR L=1 TO M
1430 LET Q8=Y[L]-C[L]
1440 PRINT X[L],Y[L],C[L],Q8,
1450 IF C[L]=0 THEN 1480
1460 PRINT 100*Q8/C[L]
1470 GOTO 1490
1480 PRINT "INFINITE"
1490 NEXT L
1500 PRINT
1510 PRINT "          STD ERROR OF ESTIMATE FOR Y =" ;SQR(T5)
1520 IF K=N THEN 9999
1530 PRINT
1540 GOSUB 1670
1550 GOTO 1300

```



Least Squares Polynomials...Cont'd.

```
1560 LET N=N+1
1570 IF M<N THEN 1640
1580 GOTO 880
1590 PRINT
1600 PRINT "PROGRAM SIZE LIMIT IS 200 DATA POINTS"
1610 GOTO 9999
1620 PRINT "ELEVENTH DEGREE IS THE LIMIT."
1630 GOTO 9999
1640 PRINT
1650 PRINT "TOO FEW POINTS FOR FITTING DEGREE";N-1
1660 GOTO 9999
1670 PRINT "    WHAT NEXT";
1680 INPUT R
1690 RETURN
9999 END
```

# BIBLIOGRAPHY

- (1) Anonymous, "First U.S. Synthetic Lactic Acid Unit Goes on Stream," Oil and Gas Journal 62, 94 F3, 1964.
- (2) Anonymous, "Synthetic Lactic Acid," Ind. & Eng. Chem. 56, 55F, 1964.
- (3) Backhaus, A.A., U.S. Patents: 1,400, 849-51 (1921); 1,403, 224-5, 1,425, 624-5 (1922); 1,454, 462-3 (1923).
- (4) Bass, S.L., U.S. Patent 2,092,494 (1937).
- (5) Beilstein, 4th ed., Vol. III, pp 261-95; 1st Suppl., Vol. III, pp 99-112; 2nd Suppl., Vol III, pp 182-212.
- (6) Berman, S., Isbejian, H., Sedoff, A. and Othmer, D.F., Ind. & Eng., Chem., 40, 2139 (1948).
- (7) Bezzi, S., Riccoboni, L., and Sullam, C., Mem. accad. Italia, Classe sci. fis, mat. mat., 8, 127 (1937); C.A., 32, 5379.
- (8) Blumenthal, F. and Chain, M., Ger. Pat. 169,992 (Nov. 9, 1904).
- (9) Borsook, H., Huffman, H.M., and Lin, Y.P., Biol. Chem., 102,449 (1933).
- (10) Braun, G., U.S. Pat. 2,024,565 (1936).
- (11) Bruson, H.A., U.S. Pat. 2,400,973 (May 28, 1946).
- (12) Burns, R., Jones, D.T., and Ritchie, P.D., J. Chem. Soc., 1935, 400.
- (13) Burton, L.U., Food Ind., 9, 634-6 (1937).
- (14) Chem. & Eng. News, "Monsanto Starts New Lactic Acid Plant," 41, 44-6 D9, 1963.
- (15) Claborn, H.U., U.S. Pat. 2,371,281 (March 13, 1945).
- (16) Datta, S.C.; Day, J.N.E.; and Ingold, C.K., J. Chem. Soc., 1939, 838; Hughes, E.D., Ingod, C.K., and Masterman, S., ibid, p 840.

- (17) Day, J.N.E., and Ingold, C.K., Trans. Faraday Soc., 1941, 37, 686.
- (18) Dix, R. Continuous Esterification of Lactic Acid, Newark College of Engineering, Thesis, June, 1966.
- (19) Eder, R., and Kutter, F., Helv. Chim. Acta, 9 (1926) 557-578.
- (20) Fein, M.L., and Fisher, C.H., J. Org. Chem., 15, 530 (1950).
- (21) Filachione, E.M., and Fisher, C.H., Ind. Eng. Chem 36, 223 (1944).
- (22) Filachione, E. M., and Fisher, C.H., Ind. Eng. Chem., 38, 228 (1946).
- (23) Filachione, E.M., Lengel, J.H., and Fisher, C.H., Ind. & Eng. Chem., 37, 388 (1945).
- (24) Fisher, C.H. and Filachione, E.N., U.S. Dept. Agr., Bur. Agr. Ind. Chem., AIC-178, 22pp (May 1948).
- (25) Fisher, C.N., and Filachione, E.M., U.S. Dept. Agr., Bur. Agr. Ind. Chem., AIC-279, 32pp (Oct 1950).
- (26) Glasstone, S., Textbook of Physical Chemistry, p.1127, Van Nostrand Co., 1946.
- (27) Haag, I.L., U.S. Pat. 2,013,099 ( Sept. 3, 1935).
- (28) Structure and Mechanism in Organic Chemistry, C.K. Ingold, Cornell University Press, Ithaca, N.Y. 1953, Chap XIV.
- (29) Jenemann, J.A., U.S. Pat. 1,906068 (April 25, 1933).
- (30) Kaplan, J., Kinetics of the Lactic Acid-Butyl Alcohol Esterification Reaction, Newark College of Engineering, Thesis, June, 1966.
- (31) Keyes, C.E., Ind. Eng. Chem., 24, 1096 (1932).
- (32) Kolosovskii, N.A., Kulikov, F.S. and Becturoy, A., Bull. S oc. Chim. (5) 2; 460-79 (1935).
- (33) Landau, M., U.S. Patent 1,157,402 (Oct 19, 1915).

- (34) Lawrie, J.W., U.S. Pat. 1,157,402 (Oct 19, 1915).
- (35) Levenspiel, O., Chemical Reaction Engineering, John Wiley & Sons: New York; 1962.
- (36) Leyes, C.E., and Othmer, D.F., Trans. Am. Inst. Chem. Engrs. 41, 157 (1945).
- (37) Loder, D .S., U.S. Pat. 2,365,945 (1942).
- (38) Macallum, A.D., U.S. Pat. 2,013,104 (Sept. 3, 1935).
- (39) Macallum, A.D., U.S. Pat. 2,125,383 (Aug. 2, 1938).
- (40) Muller, J., U.S. Pat. 2,232,554 (Feb. 18, 1941).
- (41) Noerdinger, H ., Caroselli, A., and Berg, L., U.S. Pat. 924. 924,494 (June 8, 1909).
- (42) Olive, T.R., Chem. & Met. Eng. 43, 480 (1936).
- (43) Olson, E.T., U.S. Pat. 1,240,766 (Sept. 19, 1917).
- (44) Peckham, G.T., Jr., Chem. Eng News, 22, 440 (1944).
- (45) Prescott, S.C., and Dunn, C.G., Industrial Microbiology, New York, McGraw-Hill Book Co. 1940.
- (46) Rehberg, C.E., and Dixon, M.B., "Plasticizers from Lactic Acid," Abstracts of Papers, 116th Meeting, Am. Chem. Soc. (Atlantic City), Sept. 1949, p.23N.
- (47) Rehberg, C.E., Dixon, M.B., Dietz, T.J., and Meis, P.E., Ind. Eng. Chem., 42, 2374 (1950).
- (48) Rozhdestrenskii, A.A., Soviet Sakhar 1933, No. 3-4, 37.
- (49) Rozhdestrenskii, A.A., Trans. VI Mendeleev Congr. Theoret. App. Chem. 1932, 2, Pt. 2, 166-8 (1935).
- (50) Smith, L.T., and Claborn, H.J., Ind. Eng. Chem. News Ed. 17, 641 (1939).
- (51) Smith, L.T., Fisher, C.H., Ratchford, W.P. and Fein, N.L., Ind. Eng. Chem., 34, 473 (1942).
- (52) Sokoloff, B ., and Professional Drug Products, Inc., Brit. Pat. 516,518 (Jan 8, 1942).

- (53) Stearn, J.T., Makower, B., and Groggins, P.H.,  
Ind. Eng. Chem. 32, 1335 (1940).
- (54) Tindall, J.B., U.S. Pat. 2,223,797 (Dec. 3, 1940).
- (55) Troupe, R.A., Aspy, W.L., and Schrodtt, P.R., Ind.  
Eng. Chem., 43, 1143 (1951).
- (56) Troupe, R.A. and DiMilla, E., Ind. & Eng. Chem.,  
49, No. 5, 847-855, May 1957.
- (57) Troupe, R.A., and Kobe, K.A., Ind. & Eng. Chem.,  
42, No. 5, 801-810, May 1950.
- (58) Troupe, R.A., and Kobe, K.A., Ind. & Eng. Chem.,  
42, No. 7, 1403-09, July 1950.
- (59) "Industrial Fermentations", Ed. by L.A. under  
Kofler and R.J. Hickey, Chemical Publishing  
Co., N.Y., N.Y., Vol. I, Chap 12 pg 391. (1954).
- (60) Waite, C.N., Ger. Pat. 140,319 (July 9, 1901).
- (61) Ward, G.E., & Tabenkin, B., U.S. Pat. 2,331,948  
(Oct. 19, 1943).
- (62) "Composition of Lactic Acid" Paul D. Watson,  
Ind. & Eng. Chemistry, Vol 32, No. 3, 1940.
- (63) Watson, P.D., Ind. Eng. Chem., 40, 1393 (1948).
- (64) Weisberg, S.M., Chappell, F.L., Stringer, W.E.,  
and Stevens, S., U.S. Pat. 2,290,926 (July  
28, 1942).
- (65) Wenker, H., U.S. Pat. 2,334,524 (Nov. 16, 1943).
- (66) Woodward, C. F., Chemurgic Digest, 9, No. 6,  
9 (1950).