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INSTITUTE OF TECHNOLOGY

DEPARTMENT OF CHEMICAL ENGINEERING

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DIFFUSION IN CATALYTIC HETEROGENEOUS SYSTEMS

Studies in Vapor Phase Esterification

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INTRODUCTION

An ester can be defined as the compound formed when an acyl group $(-\overset{=O}{C}-R)$ replaces the active hydrogen of an alcohol. In organic chemistry esters are usually classified as derivatives of carboxylic acids. They are regarded as the organic equivalent of an inorganic salt, since the ester can be derived by elimination of water from an acid and a hydroxy compound; however, the resemblance is in form only, as the mechanisms are probably far different.

Esters form a group of very important and useful compounds. The lower esters are noted for their volatility and solvent properties and can be recognized by their definite fruity odors. Besides their use as solvents, the lower esters are also used in the production of artificial flavorings. Many plastics and intermediates for the production of plastics are esters.

The number of reactions by which esters are produced is long. They can be divided into two groups - those in which two compounds react to give an ester and another compound, and those in which two compounds react to give an ester alone. The first group are all replacement reactions such as: 1) direct esterification, in which an alcohol reacts with an acid, either organic or inorganic, and 2) alcoholysis and acidolysis, in which an alcohol or an acid replaces its like part in an ester molecule. The second group are addition reactions in which a compound is added to an unsaturate; the formation of ethyl sulfate from ethylene and sulfuric acid is an example of this.

Esters are usually prepared in the liquid phase under various conditions of temperature and pressure. The esterification of primary alcohols with organic acids is best known and has been studied extensively. The reaction is slow, equilibrium is attained only after refluxing for several days, and the limit of conversion to ester for the lower alcohols and acids is about 60 to 70 percent. The speed of the reaction is increased enormously by the addition of a catalyst; acid catalysts are the most common with hydrochloric and sulfuric acid being generally used; however, the list of esterification catalysts is legend. The limit of conversion is increased by removing one or both of the products of the reaction so as to discourage the reverse reaction from occurring.

Some lower esters have been prepared by vapor phase esterification. A catalyst is necessary because the homogeneous reaction is negligible as high as 300°C. Silica gel has been most widely used as a catalyst but is not the only one. The conversions are much higher in the vapor than in the liquid phase. No commercial units have been described.

This work is an experimental and theoretical investigation of the vapor phase esterification of ethyl, n-propyl, and n-butyl alcohol with acetic acid. The reactions have been carried out in a flow system using a bench scale apparatus of stainless steel. The catalyst, tungstic oxide, is carried by uniform porous cylinders of alumina in the form of a packed bed. Equations which correlate the data have been obtained from a study of the kinetics of the reaction. Actually, this research is a continuation of the work of Michael Stusiak (20) who constructed the apparatus and made a kinetic study of the vapor phase esterification of ethyl alcohol with acetic acid at 160°C.

LITERATURE SURVEY

In his study of the esterification of ethyl alcohol with acetic acid, Stusiak (20) included a very extensive and thorough search of the literature. He did not limit himself just to ethyl acetate, but rather included the whole field of vapor phase esterification. No new papers on the subject have appeared since he finished, and rather than repeat his work here, the reader is referred to Stusiak's literature survey.

This literature survey shows that the work done so far on vapor phase esterification can be lumped into three groups. The first group contains about fifteen papers all devoted to the determination of an equilibrium constant for the formation of ethyl acetate from ethyl alcohol and acetic acid. Essex and Clark (6) finally solved this problem; they give the equilibrium constant as a function of temperature and the standard free energy change for the vapor phase reaction of ethyl alcohol and acetic acid to ethyl acetate. The second group has six papers which are concerned with suitable catalysts for vapor phase esterifications. These catalysts are mostly metal oxides on carriers and they have been used to esterify most of the low molecular weight alcohols and organic acids. The third group contains two papers on the kinetics of vapor phase esterification of ethyl acetate.

These last two papers are the most interesting. The first was by Hoerig, Hanson, and Kowalke (10) who measured the rates of esterification of acetic acid and ethyl alcohol vapors at 150, 190, 230, and 270°C. and one atmosphere in a flow system using silica gel catalyst and an equimolar mixture of the reactants. The authors made an attempt to determine the rate-controlling step at 230°C. and came to the conclusion that mass transfer through a gas film on the external surface of the catalyst was not rate controlling, but that diffusion within the catalyst particles might be.

Buckley and Altpeter (3) published the second paper. Their catalyst was silica gel, the reactants were ethyl alcohol and acetic acid, and the apparatus was essentially that used by Hoerig, Hanson, and Kowalke (10). Data were obtained at 200, 230, and 260°C, under total pressures of 1 to 2.33 atmospheres and at three different molal ratios of acid to alcohol. The authors concluded that the reaction rate was limited by the rate at which acetic acid was adsorbed when the mole fraction of the acid in the feed was less than 0.7, and that the rate of adsorption depended on the water content of the catalyst. A reaction rate equation based on these conclusions was established by the methods of Hougen and Watson (11) and used to correlate the experimental data. The following assumptions had to be made before the final rate equation correlated the conversion data: (1) alcohol was not adsorbed; (2) alcohol reacted with adsorbed acid by impact only; (3) the number of active sites on the catalyst was a function of the amount of water adsorbed; (4) the equilibrium constant for adsorption of acetic acid was zero; and (5) diffusion within the catalyst was not controlling.

In his work Stusiak (20) carried out the continuous vapor phase reaction of ethyl alcohol and acetic acid to form ethyl acetate and water in the same fixed bed reactor that was used in this research. The bed contained 2170 grams of dry catalyst made up of WO_3 carried on porous alumina spheres averaging 0.523 cm. in diameter. The dried balls were impregnated with a solution of tungstic acid in concentrated ammonium hydroxide. The balls were dried and heated at 450°C. in order to decompose the tungstate compound. A catalyst particle had an apparent density of 1.6886 gm./cc., an absolute density of 3.860 gms./cc., a fractional void volume of 0.5625 and contained 7.87% WO_3 by weight.

The variables studied were temperature, rate of reactant feed, mole ratio in reactant feed, and pressure over a small range. For an equimolal feed, a pressure of one atmosphere, and 1150 gms. of catalyst per mole per hour, the fraction of acid converted at 140°C, 160°C, 180°C were 0.306, 0.395, and 0.645, respectively. Conversions, from the previous two papers, using silica gel as a catalyst, are 0.3, 0.45, and 0.6 at 200°C, 230°C, and 260°C, respectively. With the tungstic acid catalyst higher conversions at significantly lower temperatures are possible. The product was water white and there were no indications of side reactions.

Kinetic data were obtained at 140°C, 160°C, and 180°C, but only at 160°C was an attempt made to determine a rate-controlling step. Analysis of the data showed that a surface reaction is the rate-controlling step. A mechanism was postulated and a rate equation based on this mechanism was established by graphically differentiating the integral conversion curves to obtain the rate of the reaction and then using least squares as suggested by Hougen & Watson (11). At 160°C, the rate is given by:

$$r = 0.0123 \frac{p_A \, p_B - \dfrac{p_R \, p_S}{K}}{\left[1 + 3.327 \, p_A + 1.075 \, p_B\right]^2} \qquad (1)$$

where p_A, p_B, p_R, p_S are the partial pressures of acid, alcohol, ester, and water, respectively.

An investigation into the effect of intraparticle diffusion was made by referring to the paper by Smith and Amundson (19) which shows that if the overall reaction is pseudo-first order the ratio of the effluent to the influent partial pressure is given by the expression:

$$\log e \frac{p_A}{p_{A_o}} = \frac{3 \, W' \, \gamma \, D_A \, x}{R^2 \, \rho_p \, q} \left[\frac{\tanh R\sqrt{P} - R\sqrt{P}}{\tanh R\sqrt{P}}\right] \qquad (2)$$

where W' = mass of catalyst, g./cc.

γ = void fraction in the particle

D_A = diffusion coefficient of acid in the medium

x = reactor depth

R = particle radius

ρ_p = particle density

q = flow rate to reactor

P = k/D_A

k = reaction velocity constant

p_A = effluent partial pressure of acid

p_{A_o} = influent partial pressure of acid.

Experimentally it was found at a given mole ratio of reactants and at a given temperature, $\log_e \frac{p_A}{p_{A_o}}$ is a linear function of 1/q as Equation 2 predicts. From the Sutherland equation a diffusion coefficient may be computed and hence a velocity constant k may be calculated using Equation 2. If one assumes the diffusivity may vary arbitrarily it is found that the velocity constant as calculated from the above is unaffected and hence that intraparticle diffusion had a negligible effect in this reaction. Using this method the activation energy was found to be 10.3 K cal./g. mole.

EXPERIMENTAL WORK

Statement of the Problem

This problem is defined as a study of vapor phase catalytic esterification. The important variables are reactor temperature, total pressure, molar ratio of alcohol to acid, and feed rate. The objectives of the project were:

1) to ascertain a rate-controlling step from the kinetics of the reaction.
2) to establish a rate equation or a pseudo-rate equation which will correlate the conversion data.

Reactants

The reactants used in this work were four in number; glacial acetic acid, ethanol, n-propanol, and n-butanol. The acid was Du Pont C.P. glacial acetic; the ethanol was USI synthetic absolute alcohol, and the n-propanol and n-butanol were Eimer & Amend "tested purity" analytical reagent alcohols.

Both the alcohol and the acids were subjected to a series of chemical and physical tests to determine their purity and suitability as reactants. These tests were:

A. Acids

1) During every running day the total acid content was determined.
2) Determination of water content in each 5 gal. reservoir of acid.

B. Alcohols

1) Every 5 gal. reservoir of alcohol was analyzed for total alcohol content.

2) Determination of water content in each 5 gal. reservoir of alcohol.

3) Periodic checks for the contaminants: aldehydes, ketones, and unsaturates.

4) Periodic determinations of density.

5) The boiling point range and refractive index of each 5-gal. reservoir of alcohol were determined.

References as to how these tests were carried out will be found in Appendix D, "Analytical Procedures." Laboratory Data for these tests are on file with the Chemical Engineering Department, University of Minnesota.

Table I summarizes this analytical work which was done on the reactants. An examination of the table shows that the total alcohol content of the alcohols was always at least 99.7%, the water content was about 0.1%, leaving 0.2% unaccounted for. The physical tests carried out on the alcohols also establish the fact that these alcohols were very pure. Both the refractive index and the density determinations were almost identical with values reported in the literature. The boiling point range as reported in Table I is uncorrected for atmospheric pressure and was determined with an uncalibrated thermometer which explains the difference between the determined boiling point and that reported in the literature;

Table I.

	Ethanol	n-Propanol	n-Butanol	Acetic Acid
Avg. Total Alcohol or Acid Content	99.7%	99.8%	99.7%	99.7%
Avg. Total Water Content	0.12%	0.13%	0.09%	0.23%
Presence of Aldehydes, Ketones, and Unsaturates	None	None	None	
Refractive Index Experimental	$n^{D}_{20^\circ C} = 1.36140$	$n^{D}_{25^\circ C} = 1.38357$	$n^{D}_{25^\circ C} = 1.39734$	
Refractive Index Literature	$n^{D}_{20^\circ C} = 1.36140$ (16)	$n^{D}_{25^\circ C} = 1.3835$ (1)	$n^{D}_{25^\circ C} = 1.3974$ (2)	
Density Experimental	$d^{25.0^\circ C}_{4^\circ C} = 0.7853$	$d^{27.6^\circ C}_{4^\circ C} = 0.7982$	$d^{28.1^\circ C}_{4^\circ C} = 0.8031$	
Density Literature	$d^{25.0^\circ C}_{4^\circ C} = 0.7848$ (12)	$d^{27.6^\circ C}_{4^\circ C} = 0.7980$ (12)	$d^{28.1^\circ C}_{4^\circ C} = 0.8040$ (12)	
Boiling Point Range	77.2°C - 78.2°C < 1°C	96.3°C - 97.3°C < 1°C	116.7°C - 117.4°C < 1°C	
Boiling Point Literature	78.32°C (760 mm) (1)	97.209°C(760mm) (21)	117.726°C (760 mm) (21)	

( ) refers to the Bibliography.

however, the boiling point range was always less than 1°C. which is another proof of purity. Qualitative analysis indicated that no aldehydes, ketones, or unsaturates were present. With this evidence of purity and the fact that the sum of the alcohol content and water came to within 0.2 of 100%, the assumption was made that the alcohols were contaminated with water alone and no attempt was made to purify them further.

The acetic acid analysis averaged 99.7% by weight HOHC, and 0.23% water. Since the sum of the acetic acid and water contents was so close to 100%, and because the manufacturers' analysis was so complete, no attempt was made to analyze the acid further. The assumption was made that the only impurity in the acid was water.

The Catalyst

The catalyst was composed of tungsten trioxide carried on porous alumina pellets approximately 1/8" in diameter and 1/8" long. This matwrial was purchased from The Harshaw Chemical Company of Cleveland, Ohio. Their description and analysis of the catalyst follows.

Tungsten-Alumina Catalyst W-0101 T 1/8"

Use: Dehydrogenation, destructive dehydration, synthesis.

Analysis:	WO_3	10%
	Al_2O_3	88%
	Na_2O	0.4%
	L.O.I. at 600°C.	1.0%

Descriptive: Greenish-yellow 1/8" tablets weighing approximately 60 lbs./ft.^{3}. Average side crushing strength 10 lbs.

A description of tungsten trioxide will disclose the properties that might make it an important solid catalyst. It is an acidic oxide readily prepared by igniting the acid, H_2WO_4. It is insoluble in water and all acids except hydrofluoric, but is soluble in solutions of carbonates and alkali hydroxides including ammonium hydroxide. At room temperature tungsten trioxide is lemon yellow but changes to orange on heating. It is very stable to heat exerting an oxygen pressure of only 1.555×10^{-14} mm. at 800°C. and is a weak oxidizing agent. When it is heated with carbon a blue oxide forms above 1050°C.; when hydrogen is used a mixture of brown oxides is obtained between 800° and 900°C. and the metal at 1080°C.; with aluminum and zinc, reduction of the oxide is directly to metallic tungsten.

Before the catalyst was used, the particle diameter, particle length, particle density, absolute density, and fractional voids within the particle were determined. The oven-dried weight of the catalyst and the tungsten trioxide content of the catalyst were also determined.

The particle diameter, D_p, and the particle length, L_p, were determined by measurement with a micrometer. A random sample of 297 catalyst pellets was dried for 24 hours at 400°C., weighed on an analytical balance, and then the diameter and length of each pellet were measured with a micrometer to 0.001 mm. An arithmetic average of these measurements gave the values of particle diameter and length, which were:

$$D_p = 3.276 \text{ mm.}$$

$$L_p = 3.577 \text{ mm.}$$

The individual particle measurements are on file in the Chemical Engineering Department, University of Minnesota.

The particle density, ρ_p, was derived from the relationship between the weight and the volume of the 297 pellets which were measured to obtain the catalyst diameter and length.

The volume of a single pellet $= \frac{\pi}{4} D_p^2 L_p$

The volume of 297 pellets $= \frac{\pi}{4} \sum_{i=1}^{i=297} D_{p_i}^2 L_{p_i}$

The volume of 297 pellets $= (0.7854)(11.39734) = 8.95147$ cc.

The weight of 297 pellets $= 13.4218$ g.

Particle Density, ρ_p $= 13.4218/8.95147 = 1.4994 \frac{\text{g.}}{\text{cc.}}$

The computations of $\sum_{i=1}^{i=297} D_{p_i}^2 L_i$ are on file in the Chemical Engineering Department.

The absolute density, ρ_C, was obtained with a pycnometer. A sample of dried catalyst of known weight was kept under vacuum in a small flask for an hour. Distilled water was admitted until the catalyst was covered. The vacuum was broken and the pellets transferred to a pycnometer which was immediately filled with distilled water and weighed. The volume of the solid was calculated from the weight of water necessary to fill an empty pycnometer at a given temperature and the weight of water and catalyst that filled it at the same temperature. The absolute density was calculated from the weight and volume of the solid.

Temperature: 26.6°C.

Weight of dry sample of catalyst = 2.4661 g.

Density of water at 26.6°C. = 0.9966515 g./cc.

Weight of water to fill pycnometer - without catalyst

= 10.3450 g.

Volume of water = 10.3450/0.9966515 = 10.37976 cc.

Weight of water to fill pycnometer with catalyst

= 9.6758 g.

Volume of water = 9.6758/0.9966515 = 9.70831 cc.

Volume of solid = 10.37976 - 9.70831 = 0.67145 cc.

Absolute density of catalyst, ρ_C = 2.4661/0.67145 = 3.673 $\frac{g.}{cc.}$

The absolute density was determined for four different samples of the catalyst. The other three determinations are:

3.639 g./cc.

3.661

3.669

The absolute density, ρ_C = average of the four determinations

= 3.660 g./cc.

The void fraction within the particle is the ratio of the "empty" volume of the particle to the total volume of the particle.

Internal Void Fraction: $\gamma = \dfrac{\text{Total vol. cat. - solid vol. cat.}}{\text{Total vol. cat.}}$

$$\gamma = \frac{\frac{1}{\rho_P} - \frac{1}{\rho_C}}{\frac{1}{\rho_P}} = \frac{\rho_C - \rho_P}{\rho_C} = 1 - \frac{\rho_P}{\rho_C}$$

$$\gamma = 1 - \frac{1.4994}{3.660} = 1 - 0.4097 = 0.5903$$

The oven-dried weight of the catalyst was determined by taking 9 random samples of the catalyst of about 10 g. each and heating to constant weight in an oven at 400°C. The weight loss of the samples was averaged and this value was used to determine the weight of the catalyst on an oven-dried basis: The average loss on heating at 400°C. was 2.03% on an oven-dried basis. Pertinent data on this procedure is on file in the Chemical Engineering Department.

The tungsten trioxide content of the catalyst was determined by a gravimetric method suggested by The Harshaw Chemical Company, manufacturers of the catalyst. Their method is almost identical to that of Kolthoff and Sandell (13) for analyzing tungsten in steel. Two random samples of the catalyst of about 1 gram each were analyzed simultaneously and the results averaged to give a tungsten trioxide content of 9.89%; this is based on the original sample being dried to constant weight at 600°C. Pertinent data on the procedure and results are on file in the Chemical Engineering Department, University of Minnesota.

One batch of tungsten trioxide catalyst of the Harshaw Chemical Company was used for all esterification experiments. A quantity of the air-dried catalyst weighing 2272.0 g. was poured into a 2" stainless steel pipe, which acted as the reactor in this research, to make up a randomly packed catalyst bed. The catalyst was weighed on a semi-analytical balance capable of loads up to 5000 g. with a precision of 0.5g.; caligrated weights were used and corrections were made for air buoyancy in order to know the bed weight with some accuracy. Inside calipers were used to determine the bed diameter while a meter stick was used for bed length; these two measurements gave the bed volume. The bulk density of the bed, ρ_b, was simply the air-dried weight of the bed divided by bed volume. The loss on heating at 400°C. for the catalyst was the method used to determine the oven-dried weight of the bed. Table II summarizes the properties of the bed along with those of the catalyst.

Table II.

Properties of the Catalyst:

Particle Diameter, D_p = 3.276 mm.

Particle Length, L_p = 3.577 mm.

Particle Density, ρ_p = 1.4994 g./cc.

Absolute Density, ρ_C = 3.660 g./cc.

Internal Void Fraction, γ = 0.5903

Composition:

Loss on Heating at 400°C.: 2.03%

Tungsten Trioxide Content: 9.89%

Properties of the Bed:

Diameter, D = 5.25 cm.

Depth, h = 100.0 cm.

Volume of bed, V = 2165 cc.

Air-dried weight of bed: 2270.0 g.

Oven-dried weight of bed: W = 2225.9 g.

Bulk Density, ρ_b = 1.0494 g./cc.

External Void Fraction, α = 0.3001.

The Apparatus

The apparatus consisted of a reactants pumping section, vaporizer-superheaters for the alcohol and acid, an isothermal reactor, a product condenser, and a Dowtherm circulating heater. A flow diagram is given in Figure 1 and photographs are presented in Stusiak's work (20).

The pumping section comprised containers (A, B, Figure 1) for the alcohol and acid, pumps and flowrators (C, Figure 1). The reservoirs for the alcohol and acid were constructed from Type 316 stainless steel and had a capacity of five gallons. Drying tubes at the top of the tanks kept cut moisture. Two Model PPI-M Low Volume (Precision) multi-purpose gearless pumps manufactured by Eco Engineering Company delivered the reactants to the preheaters. The pumps were made from Type 316 stainless steel and were close coupled to Model 20EM Graham variable speed transmissions. Liquid reactants were metered with Fischer & Porter precision flowrators calibrated at room temperatures between 26.1°C. to 29.6°C. The calibration is on file in the Chemical Engineering Department, University of Minnesota. Type 316 stainless steel semi-needle valves were installed in the liquid lines between the flowrators and the pumps; these valves were manipulated by means of a gear train for fine adjustment of flow rate. Between the flowrators and preheaters another Type 316 stainless steel semi-needle valve was installed; the purpose of this valve was to damp out any float fluctuations in the flowrators caused by small pressure fluctua-

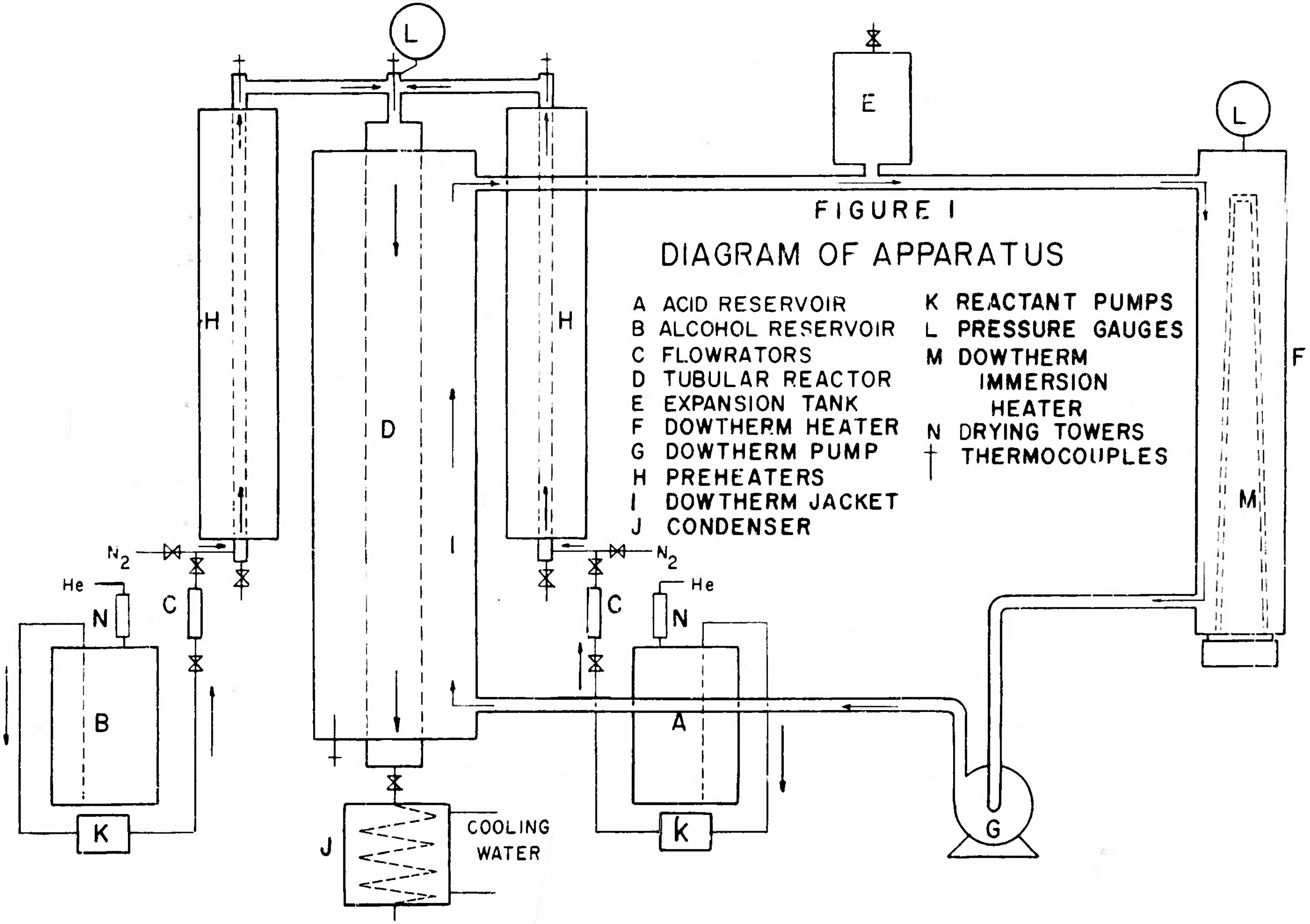

FIGURE I

DIAGRAM OF APPARATUS

A ACID RESERVOIR
B ALCOHOL RESERVOIR
C FLOWRATORS
D TUBULAR REACTOR
E EXPANSION TANK
F DOWTHERM HEATER
G DOWTHERM PUMP
H PREHEATERS
I DOWTHERM JACKET
J CONDENSER
K REACTANT PUMPS
L PRESSURE GAUGES
M DOWTHERM IMMERSION HEATER
N DRYING TOWERS
† THERMOCOUPLES

tions in the reactor and preheaters which in turn were caused by slug flow in the product condenser. Provision was made in the pumping section for passing nitrogen through the system before and after a run.

The vaporizer-superheaters (H, Figure 1) were electrically heated and built identically. Each was constructed from a 44-1/2" length of 3/4" N.P.S. Type 316 stainless steel pipe. Sheet asbestos (1/8") was wrapped twice around the pipe. Two heaters, each made of twenty-nine feet of No. 18 Nichrome IV wire delivering 1060 watts at 115 volts, were wound over the asbestos on each preheater. One heater which covered the lower half of the preheater acted as a liquid vaporizer; the other heater which covered the top half of the preheater acted as a superheater. The heaters were mounted vertically inside 6" sheet metal cylinders capped with 3/8" transite plate and filled with vermiculite.

The tubular reactor (D, Figure 1) was built from a four-foot length of 2", Type 316 stainless steel pipe. Heat was added by circulating Dowtherm A through a jacket (I, Figure 1) electrically welded to the pipe. The jacket was 5" standard black pipe 45" long and was insulated with magnesia pipe covering. The ends of the reactor were sealed with stainless steel threaded caps which increased the length of the reactor by 2-1/2". A satisfactory seal was obtained by silver soldering the original threads and recutting with a sharp die. The top cap of the reactor had a 3/4" connection for the preheaters, whereas the bottom cap had a 1/8" connection for the product condenser. The inside diameter, D, of the reactor was measured carefully at both ends with calipers; a value of 5.25 cm. was obtained. A stainless steel plate perforated with 3/32" holes was placed about 4.25 in. from the bottom cap to act as a catalyst support. For a description of the properties of the catalyst bed, the reader is referred to the catalyst section.

A product condenser, (J, Figure 1) was made from 13 feet of 3/8" O.D., 20 gage stainless steel tubing. This tubing was wound into a coil of 11 turns, the coil was 10" long and 4" in diameter. This coil was enclosed in a can about 7" in diameter and 1' deep; water at about 4°C. circulating through this can acted as the cooling medium. Between the reactor and the condenser a stainless steel valve was placed to be used both for sealing the reactor when it was not in operation and for throttling for runs above atmospheric pressure.

A brief description of the Dowtherm circulation heater will be given in order to explain its construction and the various parts. Three feet of 3" standard black pipe and two 3" T's were connected. A 2000 watt, 115 volt Type MO Chromalox immersion heater was screwed into the bottom T and a pressure gauge into the top T. An auxiliary heater supplying 1060 watts at 115 volts was made from 29 feet of No. 18 Nichrome IV wire wound round the 3" pipe which had been previously coated with No. 1 Sauereisen cement. A second auxiliary heater also supplying 1060 watts at 115 volts also was made from 29 feet of Nichrome IV wire. This heater was wound around the 3/4" inlet pipe to the Dowtherm pump. Dowtherm A was circulated with a heavy duty, single suction centrifugal pump (G, Figure 1) manufactured by Dean Brothers Pumps, Inc. The hot liquid entered the jacket of the reactor at the bottom and left at the top. The capacity of the circulating system was about four gallons. An expansion tank (E, Figure 1) fabricated from 20" of 5" pipe was installed between the outlet of the jacket and the inlet of the heater.

Temperature Measurement and Control

Four temperatures were measured during any experimental run. These temperatures were observed with iron-constantan thermocouples in Type 316 stainless steel pressure-tight wells located as shown in Figure 1. The couples were Type 3D35S "Midgets" produced by Brown Instrument Company. Temperatures at the outlets of the two vaporizer-superheaters and at the inlet to the Dowtherm jacket were recorded separately with Leeds & Northrup Micromax recorder-controllers. Inasmuch as these instruments lacked cold junction compensation, an ice-water mixture in a Dewar flask was used as a reference junction. The leads from the thermocuples to the cold junction were rubber-covered iron constantan wire and those from the cold junction to the recorder-controller were rubber-covered copper wire. The temperature at the inlet to the reactor was measured carefully at short intervals during a run with a Leeds & Northrup No. 8657-C double range potentiometer-indicator. During the experimental work, the recorders were checked periodically against this same instrument.

The four temperatures mentioned above were influenced by a total of 8 heaters. These were three in the Dowtherm section (a 2000 watt immersion heater, and two 1000 watt auxiliary heaters); four in the preheater section (two 1000 watt vaporizer and two 1000 watt superheaters); and a 600 watt cone heater between the preheater and the reactor. Of these eight heaters, the immersion heater, the two superheaters and the cone heater were capable of automatic operation while the remainder were manually operated.

The Dowtherm temperature and the superheater temperatures were regulated in the following manner. The recorder-controllers were connected to Leeds & Northrup No. 10764 M.E.C. control units and the M.E.C. units were connected to Leeds & Northrup No. 10224-25 driving mechanisms which operated three variacs that supplied power to the Dowtherm immersion heater and to the two superheaters. The superheaters were easily supplied by Type V-10M Variacs, but a Type V-20M Variac was required by the immersion heater. Temperatures at the locations previously mentioned were regulated by controlling the power delivered by the Variacs. For all runs, power to each superheater and to the Dowtherm immersion heater was controlled manually with the "manual setter" on each respective M.E.C. unit until the recorder-controller indicated that the temperature was at the control point. When such was the case, the control unit was switched to automatic operation and kept there until a run was completed.

The four manually controlled heaters had much simpler reasons for existence. The auxiliary Dowtherm heater wrapped around the inlet pipe to the Dowtherm pump, which was supplied by a Type V-10M Variac, was designed to shorten the time necessary to get the Dowtherm to operating temperature at which time it was shut off; while the other Dowtherm auxiliary heater, which was plugged into a 115 volt wall outlet and operated continuously during a run, was made to take some of the heating load off the Dowtherm immersion heater. The vaporizer heaters, as their name connotes, were there to vaporize the feed streams; Type V-10M Variacs were used to regulate their power input. These variacs were adjusted before a run to give enough power to the vaporizers so that the feed would be vaporized and slightly superheated; the final superheat temperature being controlled by the superheaters.

When the apparatus was tested with nitrogen, the temperature at the inlet to the reactor was 10-15°C. lower than the temperature at the outlet. This difference was eliminated by enclosing the tops of the preheaters and the connecting lines to the reactor in an aluminum box heated with a 600 watt cone element. The temperature of the box was controlled with a Fenwal thermal switch connected in series with the element.

Temperatures at other points were checked by Stusiak (20). A thermocouple well made out of 1/4" copper tubing was located near the outlet of the Dowtherm jacket. The Dowtherm was heated and the inlet and outlet temperatures of the jacket were measured simultaneously. The difference between them was at no time greater than 1°C. The temperature at the perforated plate, that is, at the bottom of the catalyst bed, was measured by inserting a thermocouple through the hole in the bottom cap of the reactor. This temperature and the inlet temperature of the jacket checked within 1°C., when nitrogen was passed through and the system was at a steady state. Temperatures within the bed were not measured, but were assumed to be equal to the temperature of the Dowtherm in the jacket.

Pressure Measurement and Control

Pressures were measured with a 4-1/2" Type 101 Mastergauge with tube, tip, and socket of Type 316 stainless steel produced by the Jas. P. Marsh Corporation. The gauge was inserted in the line between the tops of the preheaters. Pressure could be controlled with the valve between the reactor and the product condenser.

Operating Procedure

The following procedure was adopted for operating the reactor. Nitrogen was passed thru the catalyst bed while the reactor and vaporizer-superheaters were being heated. When the Dowtherm reached its operating temperature, the M.E.C. unit controlling the power to the immersion heater was switched to automatic operation. By this time the vaporizer-superheaters were near their control points so the nitrogen was shut off and the feeding of reactants begun. Preliminary investigation had shown that with a reasonable amount of power input to the vaporizers, the liquid holdup in the vaporizers never exceeded approximately 150 ml.; therefore, the initial feed rates were adjusted just as high as possible in order to very quickly obtain a liquid holdup of over 150 ml. When this state had been obtained, the feeds were cut back to the values desired for the particular run and the superheaters were switched to automatic control. With this method of operation the liquid level in the vaporizer quickly fell to a steady state value and correspondingly the superheater temperature came to the control point rapidly. The alternate method of adjusting the feeds to the values desired right from the start was found very unsatisfactory; the time necessary to obtain the needed liquid holdup in this method is very long thereby causing a very slow attainment of steady state in the preheaters. Temperatures and feed rates were checked frequently during a run. About one hour after the feed streams were turned on, sampling of the product was begun. This was continued at 1/2 hour intervals until at least 5 samples gave the same results. These results were considered to be the steady state value for that run. The feeds were then adjusted to new operating conditions and another run started. Within an hour the reactor would again be at the steady state.

When a running day was completed the feeds were stopped and the preheaters were drained. Power was left on while nitrogen was passed through the bed for about one hour or until material no longer formed in the consenser. Finally, the power was turned off and the valve between the reactor and product condenser was closed.

Analysis of the Product

By far the most common method used to determine the conversion to ester was to analyze the product for acetic acid. This consisted in titrating a weighed sample of reactor product with sodium hydroxide to a phenolphthalein endpoint. At least 5 steady state samples, taken at 1/2 hr. intervals, were used to calculate ester conversion.

In order to be sure that the acetic acid analysis is a valid measure of ester conversion and to check for side reactions, the product was periodically subjected to a complete material balance and mass flow rate balance. The material balance consisted of analyzing the product for alcohol and water by methods based on the use of Karl Fischer reagent, and for acid and ester by saponifying and neutralizing with sodium hydroxide. During every run a mass balance was determined by weighing a timed quantity of product in order to obtain the product flow rate.

EXPERIMENTAL RESULTS

Laboratory Data and Sample Calculations

This research included a study of the vapor phase esterification of three esters: ethyl acetate, n-propyl acetate, and n-butyl acetate. For each ester three different operating temperatures, T, were considered and at each temperature the mole ratio of alcohol to acid, R, was varied. Finally, at a constant temperature and mole ratio of alcohol to acid, the acid feed rate in moles per hour, F_{A_o}, was varied. The three variables, T, R, and F_{A_o}, were the only independent variables considered; no attempt was made to vary the total operating pressure or to introduce water and ester as feeds.

Since the weight of the catalyst, W, was a constant for all experiments, the quantity W/F_{A_o} varied as F_{A_o} varied; and as W/F_{A_o} varied, the conversion in moles of ester formed per mole of acid fed, X, also varied. Therefore, the laboratory data can be grouped into a series of runs; any one series will be for one ester at a constant temperature, a constant mole ratio of alcohol to acid, and at varying values of W/F_{A_o}. The values of W/F_{A_o} for each series of runs varied between 235 and 1300. Table III shows how temperature, T, and mole ratio, R, varied for each ester, while Tables IV, V, and VI have the laboratory data arranged into their respective groups. Under each series designation are listed the run numbers, the operating temperature, T, the operating pressure, P, the mole ratio of alcohol to acid, R, the values of W/F_{A_o}, the mass velocity, G, and the conversion, X. Because the values of R were so nearly a constant for any series of runs, only an arithmetic average value is reported for the series; this same line of reasoning was followed for the values of P. Under "Laboratory Data" in Appendix A, all pertinent information concerning the runs is listed.

The fraction of the acid converted or the moles ester formed per mole acid fed, X, was calculated from the composition of the feed, the gravimetric feed rate, and the analysis of the product for acid content. A detailed explanation of the method used to determine the acid content of the product will be found in Appendix D, Analytical Procedures, under the heading, "Analysis of the Product." A sample calculation for the conversion, X, based on one hour of operation, follows:

Sample Calculation: Ethyl Acetate: Run #58.

Temperature of reactor (T°C.)	160
Pressure of reactor (atm.)	0.9643
Rate of flow of acid (g./hr.)	131.0
Rate of flow of alcohol (g./hr.)	100.5
Mass rate of flow (g./hr)	231.5
Normality of sodium hydroxide solution	0.4792
Composition of acid (wt. %)	99.78%
Composition of alcohol (wt.%)	99.8%

Molecular weight of acetic acid	60.052
Molecular weight of ethyl alcohol	46.068
Cross-sectional area of reactor (sq.ft.)	0.0233
Mass of Catalyst (g.)	2225.9

For one hour of operation:

g. moles of acid fed, $F_{A_o} = \frac{(131.0)(0.9978)}{60.052} =$ 2.1766

g. moles of alcohol fed, $F_{B_o} = \frac{(100.5)(0.998)}{46.068} =$ 2.1772

g. catalyst / g. mole acid fed, $\frac{W}{F_{A_o}} = \frac{2225.9}{2.1766} =$ 1022.7

moles of alcohol / moles of acid, $R = \frac{2.1772}{2.1766} =$ 1.0003

mass velocity, $G, \frac{\text{lb.}}{(\text{hr.})(\text{sq.ft.})} = \frac{(231.5)}{(453.6)(0.0233)} =$ 21.9

total volume of base used (ml.) 145.25

total weight of product samples (gm.) 11.4671

g.moles of unreacted acid: $\frac{(145.25)(0.4792)(231.5)}{(1000)(11.4671)} =$ 1.4052

Fractional conversion of acid, $X = \frac{2.1766 - 1.4052}{2.17766} =$ 0.355

Figures 2, 3 and 4 are derived from the data in Tables IV, V, and VI. In the figures, X is plotted against W/F_{A_o}; they show the effect of W/F_{A_o} on X for the various operating temperatures and molar ratios of alcohol to acid for each ester.

Table III.

Ester	Operating Temperature	Mole Ratio Alcohol to Acid R
Ethyl Acetate	180°C.	1.4992
		1.0007
		0.7502
	160°C.	1.5008
		1.0005
		0.7502
	140°C.	1.5005
		1.0001
n-Propyl Acetate	180°C.	1.5001
		1.0000
		0.7495
	160°C.	1.5009
		0.9997
		0.7501
	140°C.	1.5008
		1.0006
n-Butyl Acetate	180°C.	1.0000
		0.7506
		0.4998
	160°C.	1.0001
		0.7498
		0.5003
	150°C.	0.9999
		0.7501

Table IV.

Ethyl Acetate

Series I; T = 180°C.; R = 1.4992; P = 0.9841 atm.

Run No.	W/F_{A_o}	G	X
30	1312.8	20.8	0.841
31	1154.4	23.8	0.795
32	1022.8	26.6	0.760
33	861.7	31.6	0.684
34	730.8	37.4	0.634
35	580.4	47.0	0.540
36	468.7	58.2	0.472
37	324.3	84.1	0.341

Series II; T = 180°C.; R = 1.0007; P = 0.9621 atm.

Run No.	W/F_{A_o}	G	X
17	1313.0	17.0	0.708
18	1154.5	19.4	0.673
10	1021.8	21.9	0.646
11	860.8	26.0	0.589
12	730.8	30.7	0.532
13	580.9	38.6	0.444
14	469.2	47.8	0.399
15	324.6	69.0	0.299
16	237.2	94.4	0.223

Series III; T = 180°C.; R = 0.7502; P = 0.9673 atm.

Run No.	W/F_{A_o}	G	X
49	1313.8	15.2	0.532
50	1155.2	17.3	0.507
51	1022.9	19.5	0.488
52	861.8	23.2	0.455
53	730.5	27.4	0.422
54	580.6	34.4	0.358
55	469.1	42.6	0.311
56	324.1	61.6	0.256
57	236.7	84.3	0.196

Table IV. (continued)

Ethyl Acetate

Series IV; T = 160°C.; R = 1.5008; P = 0.9729 atm.

Run No.	W/F_{A_o}	G	X
23	1314.1	20.8	0.497
24	1155.5	23.6	0.455
22	1022.9	26.6	0.413
25	861.7	31.6	0.360
26	729.8	37.3	0.316
27	580.8	47.0	0.272
28	469.3	58.2	0.220
29	324.7	84.0	0.154

Series V; T = 160°C.; R = 1.0005; P = 0.9663 atm.

Run No.	W/F_{A_o}	G	X
7	1316.6	17.0	0.444
8	1157.6	19.4	0.396
1	1024.1	21.9	0.364
2	862.7	26.0	0.306
3	730.0	30.7	0.277
4	580.2	38.6	0.226
5	468.8	47.8	0.190
6	324.1	69.0	0.137

Series Va; T = 160°C.; R = 1.0005; P = 0.9663 atm.
Repeat Runs

Run No.	W/F_{A_o}	G	X
9	1025.1	21.9	0.358
19	1022.4	21.9	0.365
20	1023.0	21.9	0.362
21	1022.9	21.9	0.364
39	1021.9	21.9	0.371
58	1022.7	21.9	0.355
59	1022.7	21.9	0.372
72	1023.1	21.9	0.377
73	1023.4	21.9	0.365

Table IV. (continued)

Ethyl Acetate

Series VI; T = 160°C.; R = 0.7502; P = 0.9730 atm.

Run No.	W/F_{A_o}	G	X
40	1312.8	15.2	0.340
41	1154.4	17.3	0.315
47	1154.6	17.3	0.312
38	1021.9	19.5	0.310
48	1022.4	19.5	0.297
42	861.1	23.2	0.264
43	730.3	27.4	0.239
44	580.5	34.4	0.202
45	468.7	42.6	0.176
46	324.3	61.6	0.139

Series VII; T = 140°C.;,R = 1.5005; P = 0.9734 atm.

Run No.	W/F_{A_o}	G	X
66	1313.5	20.8	0.299
67	1089.3	25.1	0.256
68	861.6	31.7	0.214
69	650.4	42.0	0.173
70	468.6	58.2	0.132
71	324.2	84.2	0.098

Series VIII; T = 140°C; R = 1.0001; P = 0.9724 atm.

Run No.	W/F_{A_o}	G	X
60	1313.5	17.1	0.244
61	1089.3	20.6	0.217
62	862.0	26.0	0.190
63	650.6	34.5	0.148
64	468.4	47.9	0.120
65	324.1	69.2	0.091

Table V.

n-Propyl Acetate

Series I; T = 180°C.; R = 1.5001; P = 0.9696 atm.

Run No.	W/F_{A_o}	G	X
44	1300.8	24.4	0.806
45	1151.2	27.6	0.769
46	1031.7	30.8	0.717
47	882.3	36.0	0.658
48	758.1	41.8	0.606
49	599.1	53.2	0.529
50	485.3	65.3	0.444
51	328.8	96.5	0.366

Series II; T = 180°C.; R = 1.0000; P = 0.9682 atm.

Run No.	W/F_{A_o}	G	X
16	1300.3	19.5	0.685
17	1150.6	22.0	0.661
9	1030.6	24.6	0.645
10	881.4	28.8	0.601
11	759.3	33.4	0.563
12	600.0	42.3	0.492
13	485.6	52.2	0.431
14	328.9	77.1	0.323
15	232.7	109.0	0.230

Series III; T = 180°C.; R = 0.7495; P = 0.9629 atm.

Run No.	W/F_{A_o}	G	X
36	1298.8	17.1	0.574
37	1149.4	19.3	0.559
38	1030.1	21.5	0.529
39	881.5	25.2	0.486
40	758.3	29.3	0.461
41	599.2	37.0	0.404
42	485.4	45.7	0.349
43	328.7	67.5	0.264

Table V. (continued)

n-Propyl Acetate

Series IV; T = 160°C.; R = 1.5009; P = 0.9663 atm.

Run No.	W/F_{A_o}	G	X
27	1299.1	24.4	0.488
28	1149.7	27.6	0.441
29	1032.7	30.7	0.405
30	883.2	35.9	0.356
31	759.7	41.8	0.325
35	599.2	52.9	0.266
32	485.6	65.3	0.227
33	328.9	96.4	0.164

Series V; T = 160°C.; R = 0.9997; P = 0.9702 atm.

Run No.	W/F_{A_o}	G	X
7	1299.1	19.5	0.430
8	1150.0	22.1	0.398
18	1030.3	24.6	0.366
2	880.9	28.7	0.329
3	758.8	33.4	0.298
4	599.6	42.3	0.252
5	485.5	52.2	0.220
6	328.8	77.1	0.160

Series Va; T = 160°C.; R = 0.9995; P = 0.9716
Repeat Runs

Run No.	W/F_{A_o}	G	X
1	1030.0	24.6	0.377
34	1030.6	24.6	0.371
52	1030.8	24.6	0.371
53	1030.7	24.6	0.372
68	1029.9	24.6	0.374

Table V. (continued)

n-Propyl Acetate

Series VI; T = 160°C; R = 0.7501; P = 0.9614 atm.

Run No.	W/F_{A_o}	G	X
25	1299.3	17.1	0.371
26	1149.8	19.3	0.348
19	1030.3	21.5	0.314
20	881.0	25.2	0.285
21	757.8	29.7	0.263
22	598.9	37.0	0.229
23	485.9	45.7	0.198
24	329.1	67.5	0.140

Series VII; T = 140°C.; R = 1.5008; P = 0.9760 atm.

Run No.	W/F_{A_o}	G	X
60	1298.7	24.4	0.269
61	1088.6	29.1	0.237
67	881.8	36.0	0.198
63	670.0	47.3	0.165
64	485.5	65.3	0.125
65	328.8	96.4	0.090

Series VIII; T = 140°C.; R = 1.0006; P = 0.9641 atm.

Run No.	W/F_{A_o}	G	X
54	1299.1	19.5	0.252
55	1088.9	23.3	0.213
56	881.2	28.8	0.179
57	669.8	37.9	0.148
58	485.4	52.2	0.114
59	328.7	77.1	0.075

Table VI.

n-Butyl Acetate

Series I; T = 180°C.; R = 1.0000; P = 0.9726 atm.

Run No.	W/F_{A_o}	G	X
15	1299.3	21.8	0.778
16	1150.0	24.6	0.746
9	1030.7	27.5	0.727
10	881.5	32.1	0.683
11	758.8	37.3	0.643
12	600.0	47.3	0.578
13	485.7	58.4	0.514
17	397.6	71.3	0.433
14	328.9	86.2	0.360
18	275.1	103.0	0.333

Series II; T = 180°C.; R = 0.7506; P = 0.9800

Run No.	W/F_{A_o}	G	X
37	1301.5	18.8	0.631
38	1151.8	21.2	0.611
39	1032.1	23.7	0.589
40	882.8	27.7	0.560
41	757.9	32.2	0.532
42	599.8	40.7	0.485
43	485.9	50.3	0.432
44	329.1	74.2	0.349
53	232.5	104.9	0.262

Series III; T = 180°C.; R = 0.4998; P = 0.9660 atm.

Run No.	W/F_{A_o}	G	X
45	1300.0	15.8	0.480
46	1150.5	17.8	0.452
47	1030.2	19.9	0.444
48	881.1	23.3	0.417
49	758.5	27.0	0.405
50	599.4	34.2	0.373
51	485.4	42.2	0.343
52	328.8	62.3	0.273
54	232.5	88.1	0.219

Table VI. (continued)

n-Butyl Acetate

Series IV; T = 160°C.; R = 1.0001; P = 0.9663 atm.

Run No.	W/F_{A_o}	G	X
7	1299.5	21.8	0.516
8	1150.0	24.6	0.483
19	1031.3	27.5	0.447
2	881.1	32.1	0.388
3	757.9	37.3	0.370
4	599.4	47.3	0.321
5	485.6	58.3	0.280
6	328.9	86.1	0.206

Series IVa; T = 160°C.; R = 0.9998; P = 0.9671 atm.
Repeat Runs

Run No.	W/F_{A_o}	G	X
1	1030.2	27.5	0.436
36	1030.2	27.5	0.441
55	1030.3	27.5	0.448
56	1030.0	27.5	0.447
69	1029.9	27.5	0.449

Series V; T = 160°C.; R = 0.7498; P = 0.9658 atm.

Run No.	W/F_{A_o}	G	X
20	1298.6	18.8	0.448
21	1149.2	21.3	0.416
22	1029.9	23.7	0.387
23	881.6	27.8	0.343
24	758.4	32.3	0.317
25	599.3	40.8	0.269
26	485.1	50.4	0.232
27	328.6	74.4	0.171

Table VI. (continued)

n-Butyl Acetate

Series VI; T = 160°C.; R = 0.5003; P = 0.9657 atm.

Run No.	W/F_{A_o}	G	X
28	1298.4	15.8	0.383
29	1149.0	17.9	0.349
30	1029.7	19.9	0.321
31	881.3	23.3	0.298
32	758.1	27.1	0.270
33	599.1	34.3	0.234
34	485.6	42.2	0.206
35	328.9	62.3	0.149

Series VII; T = 150°C.; R = 0.9999; P = 0.9561 atm.

Run No.	W/F_{A_o}	G	X
57	1299.7	21.8	0.385
58	1089.4	26.0	0.336
59	881.6	32.2	0.282
60	670.1	42.3	0.242
61	485.6	58.4	0.184
62	328.9	86.2	0.134

Series VIII; T = 150°C.; R = 0.7501; P = 0.9665

Run No.	W/F_{A_o}	G	X
63	1299.6	18.8	0.356
64	1089.4	22.4	0.312
65	881.1	27.7	0.265
66	669.6	36.5	0.228
67	486.0	50.3	0.176
68	329.1	74.3	0.124

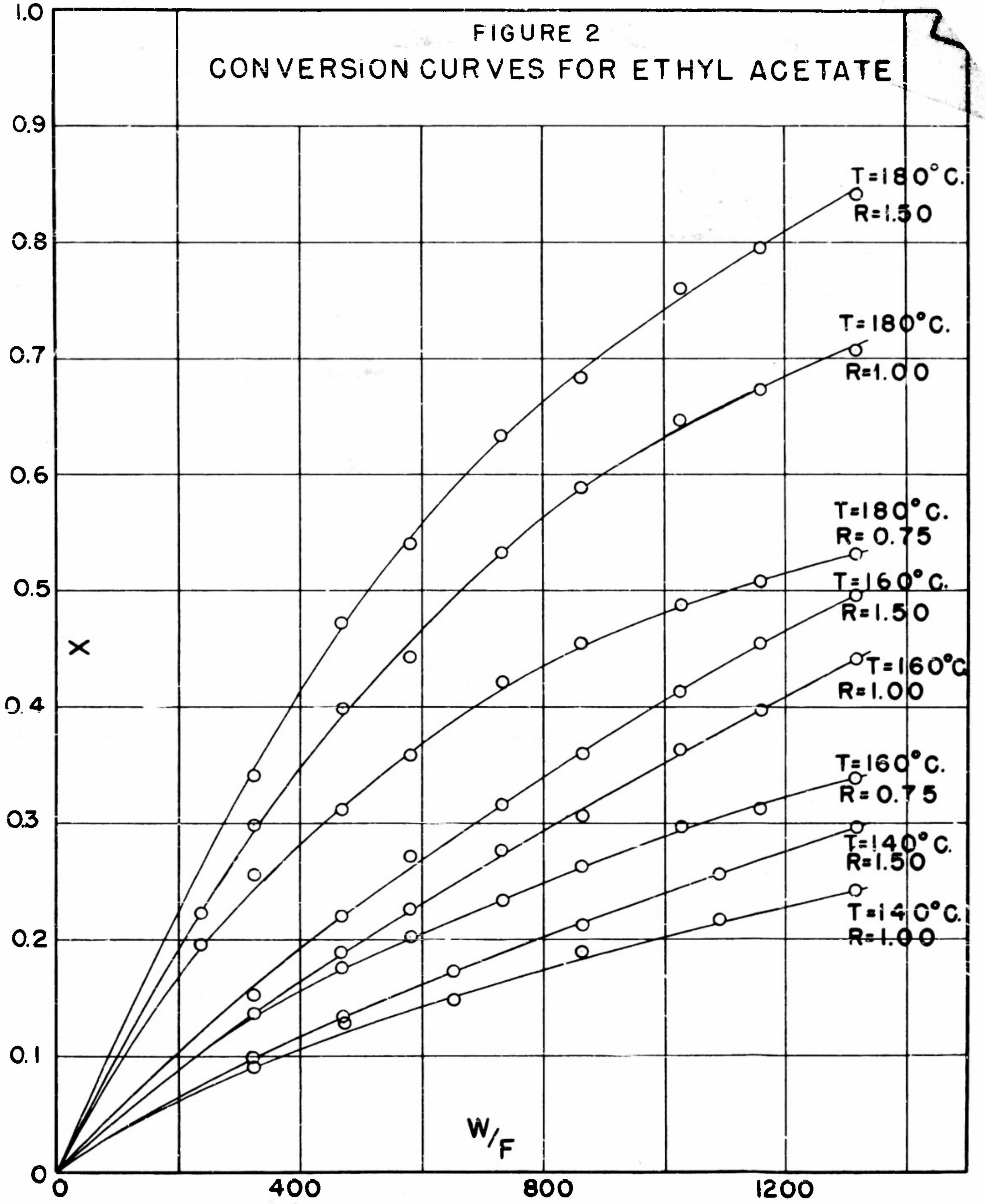

FIGURE 2

CONVERSION CURVES FOR ETHYL ACETATE

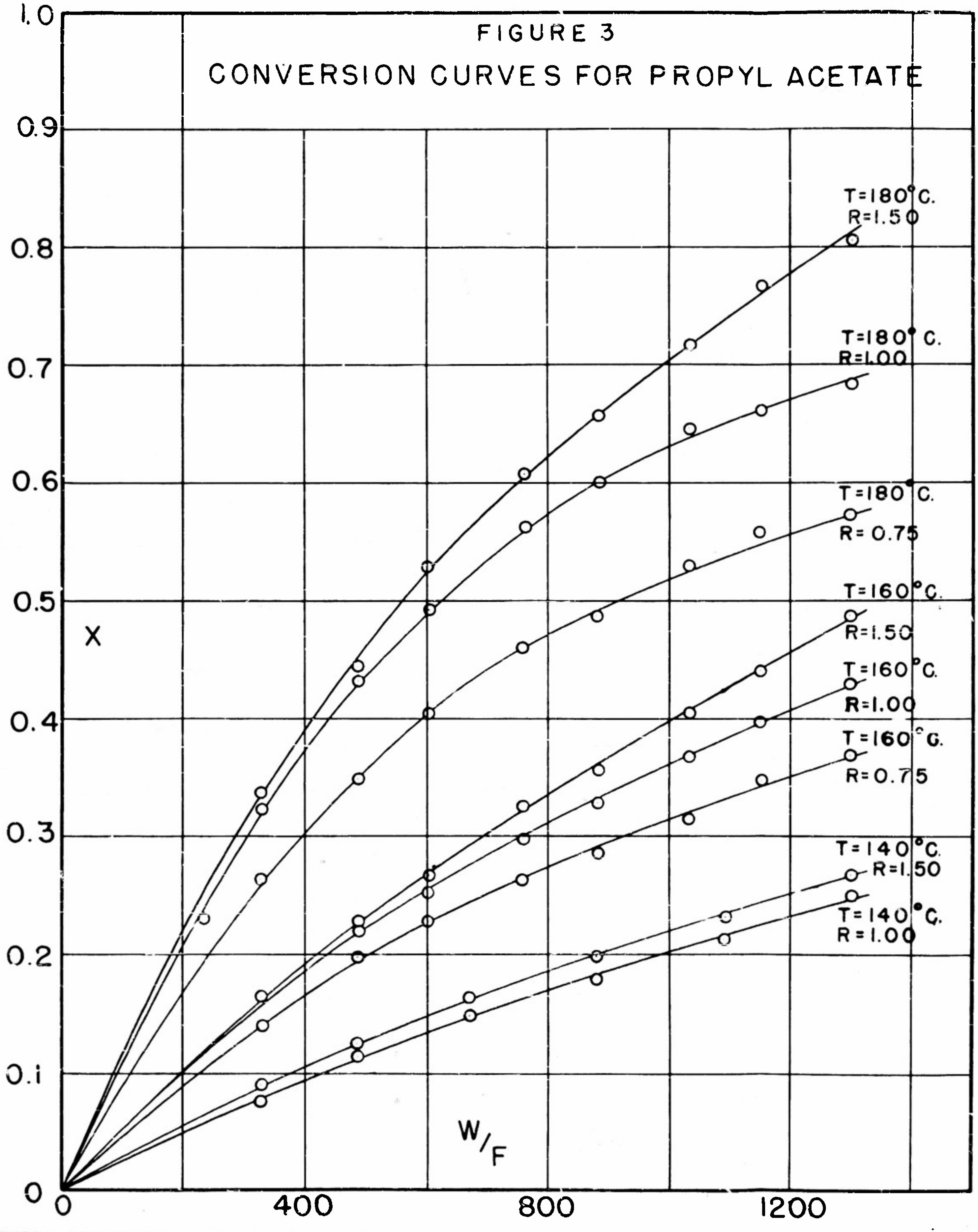
FIGURE 3
CONVERSION CURVES FOR PROPYL ACETATE
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
X
W/F
0
400
800
1200
T=180°C.
R=1.50
T=180°C.
R=1.00
T=180°C.
R=0.75
T=160°C.
R=1.50
T=160°C.
R=1.00
T=160°C.
R=0.75
T=140°C.
R=1.50
T=140°C.
R=1.00

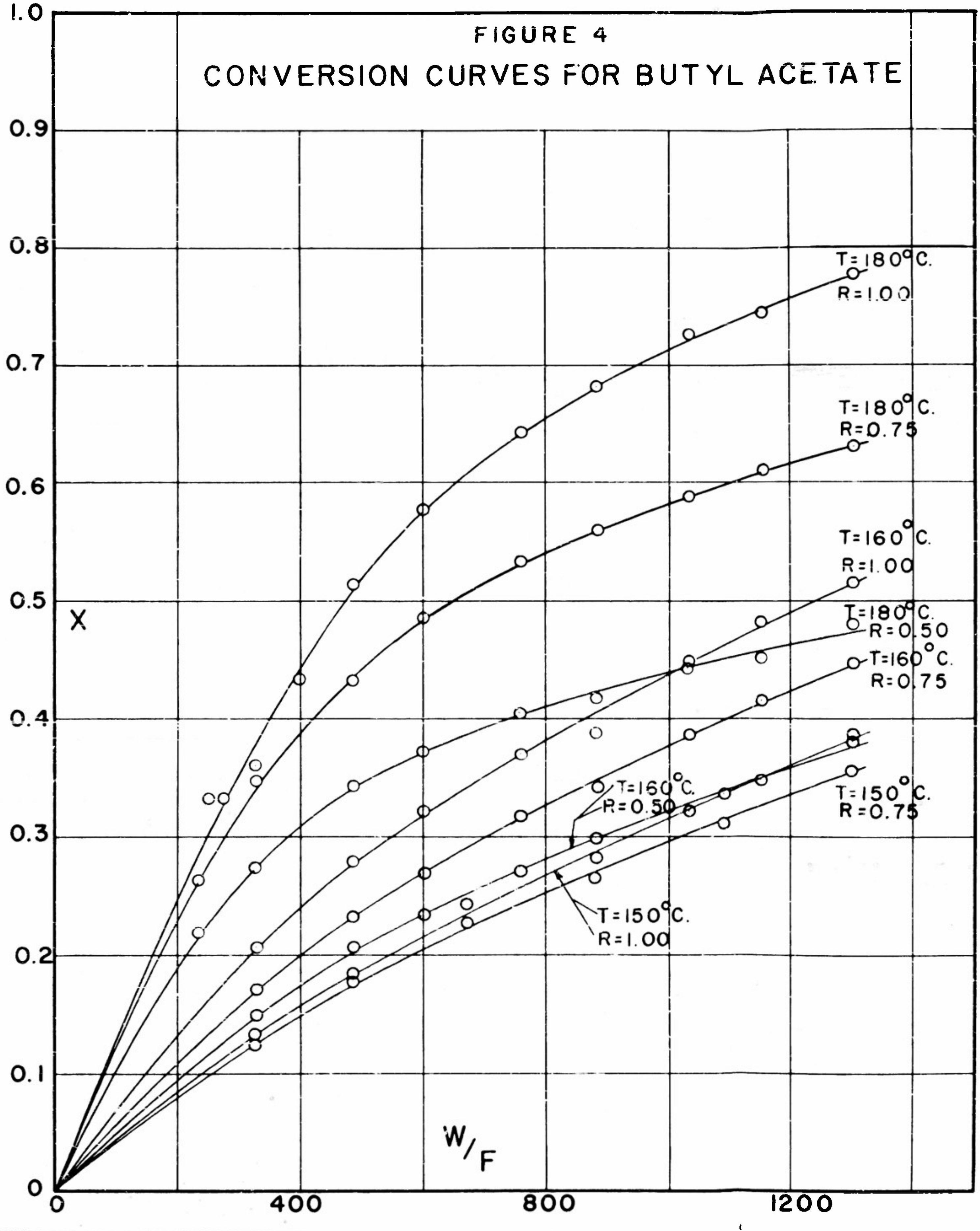

FIGURE 4

CONVERSION CURVES FOR BUTYL ACETATE

Material Balances

Under "Analysis of the Product" in the preceding chapter, the fact was mentioned that the product was periodically subjected to a complete material balance in order to check for side reactions. The material balance consisted in analyzing the product: 1) for water by using Karl Fischer reagent, 2) for alcohol, by first driving all alcohol in the product to water by using Borontrifluoride-Glacial Acetic Acid Esterification Catalyst, and then analyzing for the water by using Karl Fischer reagent; 3) for acid by neutralizing the product with sodium hydroxide; and 4) for ester, by first saponifying the neutralized product, and analyzing for the acid formed with sodium hydroxide.

The water balance on the product consisted of determining the product's total water content; since the water content of the feeds was known, the water content of the product brought about by chemical reaction is then determined. This water content can then be converted into moles/hr. of water leaving the reactor which should be equal to the moles/hr. of ester or H_2O leaving the reactor as determined by titrating the product for acid. The moles/hr. of water leaving the reactor as determined by titrating the product for acid was labeled the theoretical water content of the product; the results of the water balance were reported as the percentage of this theoretical water in the product.

The alcohol balance on the product consisted in converting all alcohol in the product to ester and water by using a Borontrifluoride Glacial Acetic Acid reagent. Karl Fischer Reagent was then used to determine the amount of water in this treated product; this water came from three sources: 1) the water formed by regular reactor conversion, 2) the water formed by reaction of the alcohol in the product with Boron-trifluoride Glacial Acetic Acid Esterification catalyst, and 3) the water that was originally present in the feeds. By subtracting away the known water content of the feeds, the moles/hr. of water formed by chemical reaction is determined. If there are no side reactions the moles/hr. of water formed by chemical reaction should be equal to the moles/hr. of alcohol feed to the reactor as determined by the alcohol flowrator. These results were reported as % alcohol recovery by esterification which is the ratio of the moles/hr. of alcohol fed as determined by Karl Fischer analysis to the moles/hr. of alcohol feed as determined by the alcohol flowrator.

The ester balance on the product consisted of saponifying with an excess of sodium hydroxide a sample of the product which had been previously analyzed for acetic acid. After the saponification was complete, the amount of base still left in the sample was determined by first making the sample acid with standard hydrochloric acid and then back titrating with standard sodium hydroxide. For a balance the moles of base used up in the saponification plus the moles of base used to analyze the sample for acetic acid should equal the moles of acetic acid in the sample based on no conversion in the reactor. These results were reported as percent acid recovery through saponification which is the ratio of the moles of base used up in saponification and neutralization of the product sample to the moles of acid in the product sample based on no reactor conversion.

Sample calculations and detailed analytical procedures for these analyses of the product are given in Appendix D, Analytical Procedures, under the heading "Analysis of the Product." Laboratory data and results are on file in the Chemical Engineering Department. Table VII summarizes the results of the material balance to which the product was subjected. Satisfactory balances were obtained in all cases. A glance at the table will show that the results are all about 100%, the ideal value; there was some scattering - a deviation of ± 2% - but this is to be expected since the reactor cycles a bit about a steady state, and along with the errors inherent in the analytical procedures, a 2% error is quite possible. The results of the material balances on the product seem to indicate that no side reactions were occurring.

At least once during every run a timed quantity of the product was weighed to obtain the product flow rate. This product flow rate was then compared with the feed rate; the results are listed in Appendix A under the heading $w_{observed}$. The agreement between feed rate and product flow rate is entirely satisfactory, being within 2%. This excellent agreement shows that all the product was being condensed, that no non-condensable compounds resulting from cracking or dehydrogenation were being produced, and that the flowrators were on calibration throughout the experimental work.

Table VII.

Material Balance

Ethyl Acetate

T	160		160				160	
R	1.00		1.50				0.75	
Run #	20	58	22	23	25	27	41	42
% Acid Rec. Thru Sapon.		99.91%		100.4%	100.5%	99.25%	101.4%	100.5%
% Alc. Rec. Thru Ester		100.0%		100.2%		99.6%		98.1%
% Theo. H_2O in Prod.	101.9%	100.8%	99.5%	99.0%		102.1%		101.0%

T	160		180				180		
R	0.75		1.00				1.50		
Run #	43	45	13	14	16	17	32	34	36
% Acid Rec. Thru Sapon.	99.91%	99.34%	99.44%	98.55%	99.50%	97.52%	99.23%	98.34%	98.38%
% Alc. Rec. Thru Ester		100.1%					100.0%		99.50%
% Theo. H_2O in Prod.		101.0%					102.4%		99.81%

Table VII. (continued)

Material Balance

Ethyl Acetate

T	180		140	140
R	0.75		1.00	1.50
Run#	50	53	62	70
% Acid Rec. Thru Sapon.	101.1%	99.50%	98.79%	97.57%
% Alc. Rec. Thru Ester.	100.0%	99.82%	100.0%	100.2%
% Theo. H_2O in Prod.	99.5%	101.0%	101.1%	100.0%

Propyl Acetate

T	160							
R	1.00							
Run #	1	3	4	5	6	7	8	34
% Acid Rec. Thru Sapon.	98.12%	98.69%	98.80%	98.03%		100.5%		100.0%
% Alc. Rec. Thru Ester.								100.1%
% Theo. H_2O in Prod.					99.9%		101.0%	100.0%

Table VII. (continued)

Material Balance

Propyl Acetate

T	160		160			180				
R	1.50		0 0.75			1.00				
Run #	27	32	21	23	25	10	11	12	13	17
% Acid Rec. Thru Sapon.	98.51%	98.38%	99.32%	98.43%	99.33%		97.52%		96.21%	
% Alc. Rec. Thru Ester.	99.9%	100.6%		103.1%	101.2%					
% Theo. H_2O in Prod.	100.1%	95.75%		97.8%	99.0%	101.6%		100.3%		99.9%

T	180	180	140	140
R	1.50	0.75	1.00	1.50
Run #	44	36	57	63
% Acid Rec. Thru Sapon.	99.09%	93.13%	99.10%	97.49%
% Alc. Rec. Thru Ester	99.8%	99.7%	99.3%	99.6%
% Theo H_2O in Prod.	99.6%	102.1%	102.5%	100.0%

Table VII. (continued)

Material Balance

Butyl Acetate

T	160					160		150
R	1.00					0.75		0.50
Run #	1	4	6	7	8	20	26	28
% Acid Rec. Thru Sapon.	100.2%	97.55%		100.3%	99.99%	100.1%	99.7%	98.40%
% Alc. Rec. Thru Ester.					99.6%	99.1%	99.0%	98.3%
% Theo. H_2O in Prod.			99.8%		101.5%	99.6%	99.3%	97.8%

T	180					180	180	150	150
R	1.00					0.75	0.50	1.00	0.75
Run #	9	11	12	15	16	41	49	60	65
% Acid Rec. Thru Sapon.	101.6%	98.54%		101.61%	100.0%	98.98%	99.57%	100.0%	99.8%
% Alc. Rec. Thru Ester.					99.9%	100.2%	101.6%	99.7%	98.8%
% Theo. H_2O in Prod.			99.6%		100.0%	100.8%	102.0%	99.9%	99.8%

Catalyst Activity

In order to prove that the catalyst did not change activity during the laboratory work, a series of repeat or check runs were made. The first run ever made with the catalyst (Ethyl Acetate, Run #1) was defined as the primary standard run, and all subsequent check runs were referred back to it. Two secondary standard runs were set up; one for n-propyl acetate (Run #1), and one for n-butyl acetate (Run #1) by making propyl acetate: run #1, and butyl acetate: run #1, and then checking the catalyst against the primary standard, ethyl acetate: run #1. These secondary standard runs allowed for a catalyst check during a series of propyl or butyl acetate runs without changing the reactor over to ethyl acetate. However, it should be made clear that all during the experimental work the catalyst was checked against the primary standard; after a series of propyl or butyl acetate runs, during which there would be checks against the secondary standards, the catalyst was always compared with the primary standard run. Table VIII summarizes these check runs; it lists the conversion for the primary standard run, the two secondary standard runs and the check runs, along with the number and kind of runs made between check runs. Examination of the table shows that the runs could be checked and that the catalyst maintained a constant activity. During the total of 210 runs which were made, the catalyst was checked 9 times times against ethyl acetate: run #1; the conversions for these runs varied from 0.355 to 0.377, a spread of 6%; also the conversion for

Table VIII.

Ester	Run No.	Date Performed	Conv. Stand. Run	Conv. Check Run	Remarks	Exp. Work Between Check Runs
Ethyl Acetate	1	11-23-53	0.364	0.364	Primary Standard	
"	9	11-30	0.364	0.358	Check	9 runs Ethyl Acetate
"	19	12-6	0.364	0.364	Check	10 runs Ethyl Acetate
"	20	12-22	0.364	0.362	Check	1 run Ethyl Acetate
						17 runs Propyl Acetate
"	21	1-14-54	0.364	0.364	Check	1 run Ethyl Acetate
						18 runs Butyl Acetate
"	39	1-27	0.364	0.371	Check	18 runs Ethyl Acetate
"	58	2-8	0.364	0.355	Check	19 runs Ethyl Acetate
"	59	3-25	0.364	0.372	Check	35 runs Propyl Acetate
						37 runs Butyl Acetate
"	72	4-1	0.364	0.377	Check	14 runs Ethyl Acetate
"	73	4-22	0.364	0.365	Check	16 runs Propyl Acetate
						14 runs Butyl Acetate
						1 run Ethyl Acetate
						210 runs Total
Propyl Acetate	1	12-9-53	0.370	0.377	Secondary Standard	
"	18	2-13-54	0.370	0.366	Check	
"	34	2-24	0.370	0.371	Check	17 runs Propyl Acetate
"	52	3-3	0.370	0.371	Check	18 runs Propyl Acetate
"	53	4-5	0.370	0.372	Check	
"	68	4-12	0.370	0.374	Check	16 runs Propyl Acetate

Table VIII. (continued)

Ester	Run No.	Date Performed	Conv. Stand. Run	Conv. Check Run	Remarks	Exp. Work Between Check Runs
Butyl Acetate	1	1-2-53	0.445	0.436	Secondary Standard	
"	19	3-5	0.445	0.447	Check	
"	36	3-14	0.445	0.441	Check	18 runs Butyl Acetate
"	55	3-24	0.445	0.448	Check	19 runs Butyl Acetate
"	56	4-13	0.445	0.447	Check	
"	69	4-21	0.445	0.449	Check	14 runs Butyl Acetate

the first run made (Ethyl Acetate, run #1) was 0.364 while that of the 210th run (Ethyl Acetate, run #73, a check run) was 0.365. The agreement between the 5 secondary check runs for propyl acetate and the 5 secondary check runs for butyl acetate is just as good.

Homogeneous Reaction, Liquid Phase Reaction, and Inertness of the Carrier

No runs were made without catalyst in the reactor because it has been established that the rate of the homogeneous reaction is negligible (3, 8, 10). Moreover, no effort was made to determine the extent of conversion during sampling and analysis. Buckley and Altpeter (3) have shown that it is very small and can be disregarded. However, the catalytic properties of the activated alumina catalyst carrier were tested; the reactor was loaded with 2602 g. of oven-dried 1/4" spheres of porous activated alumina of quality XF-101 bought from Aluminum Ore Company by M. Stusiak (20) for his esterification studies with this reactor. Ethyl alcohol and acetic acid were fed to the reactor and the conversion checked by titrating for acid in the usual manner. The reactor was run at 6 hour intervals for a total of 48 hours; the results of these runs follow:

Total Hours Running	Conversion
0	0.775
6	0.596
12	0.191
18	0.168
24	0.124
30	0.068
36	0.069
42	0.029
48	0.010

The conversion after 48 hours is practically negligible so that the tungsten oxide is the catalyst and the alumina is only acting as a carrier. The high conversions obtained initially were probably due to the fact that the catalyst was oven-dried; therefore, acting as a dehydrating agent, and causing the homogeneous reaction to proceed more rapidly since the water formed would be removed. The Harshaw catalyst used in this research did not show any initial fluctuations in conversions; most likely, because it was loaded in the air dried state. Of course, the catalyst used in this research was carried on 1/8" pellets of activated alumina rather than 1/4" balls; however, it is difficult to believe that this would make much difference.

Product Appearance

Finally, something should be said about the appearance of the product. During all the runs the product remained water-white; on occasion the first few milliliters of product stream were faintly brown, but this quickly cleared up.

In summary, the following assumptions seem justified as the kinetic analysis of the data is approached.

1) Esterification is the only reaction occurring; side reactions are improbable.
2) All product was being condensed and the mass flow rates could be checked.
3) The catalyst activity remained a constant.

4) The homogeneous reaction is negligible along with the reaction in the liquid phase.

5) The tungsten trioxide is a necessary part of the catalyst.

6) The reactor is isothermal in operation.

KINETIC ANALYSIS

Rate Steps in Heterogeneous Catalysis

When a gaseous reaction is catalyzed by porous particles the following physical and chemical rate steps are always present (11).

1) The transfer of reactants from the gas stream to the exterior surface of the catalyst and of the products from the exterior surface to the gas stream.
2) The diffusion of reactants and products in the pores of the catalyst.
3) The activated desorption of product.
4) The chemisorption of reactants on the surface of the catalyst.
5) The surface reaction of adsorbed reactants.

A mechanism that defines the rate of reaction exactly requires quantitative expressions for the rate of every step that contributes to the mechanism. However, it is well known that the relative importance of each step in determining the overall rate of a reaction varies widely. For many reactions only the slowest single step of the five types listed need be considered. If the remaining steps are chemical, they are assumed to be at equilibrium. The slowest single step is termed the rate-determining or rate-controlling step.

The five steps will be considered separately to see if a rate-controlling step can be found. The selection or exclusion of steps will be determined by the results of this research and by reference to the paper by Yang and Hougen (22).

Step 1: Diffusion

It is evident from Figures 2, 3, and 4 that the rate of reaction is quite sensitive to temperature. On the other hand, the rate of mass transfer through an external film on the catalyst particles is affected only slightly by temperature. From Figures 2, 3, and 4, therefore, one might suppose that mass transfer is not the rate-controlling step.

When surface reactions proceed slowly, film resistances are small and can be neglected. When the experimental accuracy is not greater than 5% the film resistance can be neglected if for a given component $\Delta p/p$ is less than or equal to 0.05. For this research the slowest and fastest experimental rates, determined by graphical differentiation were as follows:

Ester	Rate $\frac{\text{g. moles}}{(\text{g.catalyst})(\text{hr.})}$	Mass Velocity G $\frac{\text{lbs.}}{(\text{hr.})(\text{sq.ft.})}$
Ethyl Acetate	0.000913 (180°C.)	84.1
	0.000128 (140°C.)	17.1
Propyl Acetate	0.000833 (180°C.)	96.5
	0.000155 (140°C.)	19.5
Butyl Acetate	0.001000 (180°C.)	103.0
	0.000200 (150°C.)	18.8

Because these rates are low they also tend to reject mass transfer as the rate-controlling step.

Equations for mass and heat transfer can be used to estimate film resistances for each component of a reaction. Graphs from the paper by Yang and Hougen (22) were used instead. In their paper the authors plotted the reaction rate number,

$$\left(\frac{\sqrt{a_p}\ r\ M_m\ p_f}{p_A\ \mu\ a_M}\right)\left(\frac{\mu}{\rho\ D_{A_m}}\right)^{2/3}$$

against the modified Reynolds number $\sqrt{a_p}\,G/\mu$ for various values of $\Delta p/p$. In this work, the ratio, $\Delta p/p$, was evaluated for acetic acid for the six rates and mass velocities mentioned previously. Calculations of the six cases follow:

where:

1) a_p = surface area / single catalyst pellet, (cm.^{2})

$= \frac{\pi}{2} D_p^2 + \pi D_p L_p$

2) a_M = surface area of pellets / unit mass, $\left(\frac{\text{cm.}^2}{\text{g. of cat.}}\right)$

$= \frac{2}{L_p \rho_p} + \frac{4}{D_p \rho_p}$

3) M_m = mean molecular weight of gas mixture, $\left(\frac{\text{g.}}{\text{mole}}\right)$

= (Mol.wt.Acid) y_A + (Mol.wt.Alc.)(y_B) + (Mol.wt.Ester) y_S

+ (Mol.wt.H_2O) y_R

y_A, y_B, y_S, y_R = mole fraction of acid, alcohol, ester, and water, respectively.

4) p_f = pressure factor (atm.) = total operating pressure.

5) r = rate of reaction, $\frac{\text{moles}}{\text{(g.cat.)(sec.)}}$

6) p_A = partial pressure of acetic acid in gas mixture

$$= \frac{(\text{moles acetic acid})(1 \text{ atm.})}{(\text{total moles})}$$

7) G = mass flow rate: $\frac{g.}{(sec.)(cm.^2)}$ based on an empty column.

8) μ = viscosity in poises for gas mixture - calculated by a method suggested by Hougen & Watson (11, page 874) based on the Theory of Corresponding States.

10) ρ = density of gas mixture$\left(\frac{g.}{c.c.}\right)$; density of individual gases from ideal gas laws, $\rho = \frac{pM}{RT}$; density of gas mixture $= y_A\,\rho_A + y_B\,\rho_B + y_R\,\rho_R + y_S\,\rho_S$.

11) D_{A_m} = mean diffusivity $\left(\frac{cm.^2}{sec.}\right)$ of acetic acid in gas mixture. Diffusivity of acetic acid in each component of the mixture estimated by Gilliland Equation (15). Diffusivity of acetic acid in the gas mixture estimated by a method suggested by Curtis & Hirschfelder (5) where:

$$\frac{1 - y_A}{D_{A_m}} = \frac{y_B}{D_{AB}} + \frac{y_R}{D_{AR}} + \frac{y_S}{D_{AS}}$$

D_{AB}, D_{AR}, D_{AS} = diffusivity of acetic acid in the individual components of the mixture.

For the six cases the value of $\Delta p_A / p_A$ was less than 0.005 which shows that not only is diffusion not the rate-controlling step, but also that the film resistance can be neglected without incurring an error of more than 0.5%.

Table IX.

	Ethyl Acetate		Propyl Acetate		Butyl Acetate	
	Slowest Rate	Fastest Rate	Slowest Rate	Fastest Rate	Slowest Rate	Fastest Rate
$\sqrt{a_p}$ (cm.)	0.7326	0.7326	0.7326	0.7326	0.7326	0.7326
$a_m \frac{(cm.^2)}{(g.cat.)}$	11.8723	11.8723	11.8723	11.8723	11.8723	11.8723
$M_m (\frac{g.}{mole})$	53	53	60	60	66	66
p_f (atm.)	1	1	1	1	1	1
$r \frac{(moles)}{(g.cat.)(sec.)}$	$3.33x10^{-8}$	$25.36x10^{-8}$	$4.31x10^{-8}$	$23.14x10^{-8}$	$5.56x10^{-8}$	$27.78x10^{-8}$
p_A (atm.)	0.3073	0.2244	0.2418	0.2229	0.2612	0.2754
$G (\frac{g.}{sec.cm.^2})$	$23.2x10^{-4}$	$113.9x10^{-4}$	$26.4x10^{-4}$	$130.7x10^{-4}$	$25.5x10^{-4}$	$139.5x10^{-4}$
μ (c.p.)	0.0137	0.0130	0.0111	0.0119	0.0105	0.0109
$\rho (\frac{g.}{cm.^3})$	0.00157	0.00138	0.00177	0.00162	0.00190	0.00181
$D_{A_m} (\frac{cm.^2}{sec.})$	0.0611	0.0700	0.0562	0.0652	0.0450	0.0540
$\frac{\mu}{\rho D_{A_m}}$	1.27	1.22	1.07	1.09	1.15	1.08
Modified Reynolds No.	12.4	64.2	17.4	85.6	17.8	93.8
Reaction Rate No.	0.00329	0.0347	0.00630	0.0374	0.00950	0.0407
$\Delta p/p$	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005

Step 2: Intraparticle Diffusion

If the interior surface of a catalyst particle is readily available to all components of a reaction, then diffusion in the pores and capillaries will not be the rate-controlling step. This means that the interior surface of the catalyst is very effective and that the reaction proceeds at the same rate at the internal surface as it does at the external surface. The effectiveness will be high if the particle is small, the pores are large and interconnected within the particle and connected to the external surface, the diffusion coefficients of the reactants and products are high, and the rate of the reaction is low.

The particles which were used had a diameter of 0.3276 cm., a length of 0.3577 cm., and an internal void fraction of 0.5903. They had been formed by pelleting and the pores were well connected with the external surface. For pelleted particles, the effective pore radius is supposed to be approximately proportional to the square root of the internal void fraction; for an internal void fraction of 0.5903, the pore radius should be quite large. In Table IX the estimated diffusivity of acetic acid in the various gas mixtures was about 0.055 cm.^{2}/sec. while the reaction rates varied around 0.000500 moles/g.cat.hr.; these values answer the criterion of high diffusion coefficients and low reaction rates. Since the requirements for high effectiveness of the interior surface have been met reasonably well, diffusion in the pores of the catalyst is probably not the rate-controlling step. Experimental results bear out this assumption, since the increase in conversion with temperature as shown in Figures 2, 3, and 4, cannot be explained by diffusion in the pores alone.

Step 3: Desorption of Product

Figures 2, 3, and 4 eliminate desorption of water or ester as the rate-controlling step. If desorption of one of the products were rate-controlling, the conversion at a given temperature would be almost independent of the composition of the feed. The results show that this was certainly not the case.

Step 4: Adsorption of Reactants

The data show that the rate of adsorption of acetic acid can not be the rate-controlling step. If the adsorption of acid were rate-controlling the order of the curves in Figures 2, 3, and 4 would necessarily be reversed; the curves for the lowest value of R would be at the top. However, the rate of adsorption of alcohol as the rate-controlling step is a possibility. In order to determine whether or not alcohol adsorption is rate-controlling, a rate equation based on this mechanism must be derived and calculations made to see how well the laboratory data fits the hypothesized mechanism. The rate equation for an alcohol adsorption mechanism is completely described by Hougen and Watson (11) and will not be derived here. The reaction will be represented by the expression

$$A + B \rightleftharpoons R + S$$

where A, B, R, and S refer to the acetic acid, alcohol, ester, and water, respectively. The final rate equation for alcohol adsorption is:

$$r = \frac{k_B \, L \, (a_B - \frac{a_R \, a_S}{a_A \, K}}{1 + K_A \, a_A + K_R \, a_R + K_S + a_S + \frac{a_R \, a_S \, K_B}{a_A \, K}} \qquad (3)$$

where: r = reaction rate, moles ester formed/(hr.)(g.catalyst)

k_B = forward adsorption velocity constant for alcohol

L = total moles of active centers per unit mass of catalyst-g.moles/g. of catalyst.

K = overall equilibrium constant.

K_A, K_B, K_R, K_S = adsorption equilibrium constants for acetic acid, alcohol, water, and ester, respectively.

a_A, a_B, a_R, a_S = activities in concentration units of acid, alcohol, water, and ester, respectively.

This is the equation that the laboratory data must fit in order for alcohol adsorption to be rate-controlling. The calculations concerning this mechanism are in the next chapter where all possible mechanisms will be proved together.

Step 5: Surface Reaction

The laboratory data as it exists in Figures 2, 3 and 4 gives no information on whether or not the surface reaction of adsorbed reactants is the rate controlling step; therefore, this step must be considered as a possibility. The same line of reasoning is followed as in the case of adsorption; a rate equation is derived and calculations made in order to see how well the data fits.

The derivation of the rate equation for the surface reaction controlling will be found in the book by Hougen and Watson (11). Again the reaction will be represented by:

$$A + B \rightleftharpoons R + S$$

and the final rate equation for the surface reaction is

$$r = \frac{k\ s\ L\ K_A\ K_B\ (a_A\ a_B - \frac{a_R\ a_S}{K})}{(1 + K_A\ a_A + K_B\ a_B + K_R\ a_R + K_S\ a_S)^2} \qquad (4)$$

where: r = rate of the reaction; moles ester formed/(hr.)(g.cat.)

k = forward velocity constant.

s = number of neighboring sites when surface is bare.

L, K_A, K_B, K_R, K_S, a_A, a_B, a_R, a_S = the same as for adsorption.

As in the case of adsorption the laboratory data must fit Equation (4) for the surface reaction to be rate-controlling. Again the calculations for the proof of this mechanism are in the next chapter.

CORRELATION OF THE CONVERSION DATA

The Rate Equations as a Function of the Conversion

In order to correlate the laboratory data the rate equations or simplifications of them were integrated over the length of the catalyst bed. The resulting integrated rate equations were compared with the experimental reaction measurements and conclusions were drawn regarding the correctness of the assumed rate mechanism.

In a steady-state flow system, the relationship between space velocity or its reciprocal, the time factor W/F_{A_o}, and conversion is obtained by consideration of an elementary section of reactor containing a mass of catalyst dW in which a conversion dX is produced. Then a material balance gives

$$r dW = d(N_T \, y_S) = d(N_T \frac{F_{A_o} X}{N_T}) = F_{A_o} dX \qquad (5)$$

where: r = reaction rate, moles ester formed/(mass of catalyst)(hour)

W = mass of catalyst in reactor

N_T = total moles/(hour) of gas flowing in reactor at any point

y_S = mole fraction of ester in gas phase

F_{A_o} = moles/hour of acid fed to the reactor

X = moles ester formed/moles acid fed.

Integration yields

$$\int_0^{W/F_{A_o}} \frac{d\,W}{F_{A_o}} = \frac{W}{F_{A_o}} = \frac{1}{S_V}\frac{\rho_B}{\rho_A} = \int_0^X \frac{dX}{r} \qquad (6)$$

where S_V = space velocity of acid fed, volume of acid/(volume of catalyst bed)(hour)

ρ_B = bulb density of catalyst, mass/volume

ρ_A = density of acid fed, mass/volume.

The integration of equation (6) can be completed by expressing r as a function of X.

The rate equations in the previous section have been written in terms of the activities of the components of the reaction. The activity, a, may be defined as the ratio of the fugacity, f, in any given state to the fugacity, f°, in some standard state generally taken at the same temperature. For gases the activity is referred to the standard state, at any fixed temperature, in which the gas has a fugacity of one atmosphere. Consequently, the activity and fugacity of a gas are identical numerically. Therefore, in the rate equations activities may be replaced by fugacities.

The fugacity and pressure are identical for an ideal gas. It has been shown (4), (6), (7), that the alcohol, water, and ester vapors behave like ideal gases at pressures less than one atmosphere in the range of temperature used in this research. Therefore, the partial pressure of these components can be substituted for their fugacities in the rate equations. Acetic acid vapor, on the other hand, shows exceptional behavior. Even as high as

300°C. the association of the acid to the dimer is significant and must be taken into account.

The equilibrium constant, K_X, for the association of acetic acid vapor as a function of temperature has been determined by Essex and Clarke (6). Stusiak (20) showed that the fugacity of the acetic acid vapor was equal numerically to the partial pressure of the acetic acid monomer; therefore, wherever the activity of the acetic acid vapor appears in a rate expression the partial pressure of the monomer may be substituted for it. The assumption can also be made that the acetic acid monomer behaves like an ideal gas.

By expressing the partial pressures of the reaction components as functions of X, equation (5) can be integrated since the rate expressions will now be a function of X alone. From the stoichiometry of the reaction and values of K_X the number of moles of each component and the total number of moles of gas mixture can be calculated for any conversion, X. Dalton's Law of Partial Pressures can then be used to determine the partial pressure of each component. The derivation of the partial pressures as functions of X follows:

Let F_{A_o} = moles/hour acid fed

F_{B_o} = moles/hour alcohol fed

$R = F_{B_o}/F_{A_o}$

At any point in the reactor:

N_A = moles/hour acid monomer

N_{A_2} = moles/hour acid dimer

N_B = moles/hour alcohol

N_S = moles/hour ester

N_R = moles/hour water

N_T = total moles/hour flowing

C = moles water fed/mole acid fed

π = total operating pressure

X = moles ester formed/mole acid fed.

Then from the above definitions and stoichiometry

$$X = \frac{F_{A_o} - N_A - 2\,N_{A_2}}{F_{A_o}} \tag{7}$$

and

$$N_A = N_A \tag{8}$$

$$N_{A_2} = \frac{F_{A_o}\,(1-X) - N_A}{2} \tag{9}$$

$$N_B = F_{B_o} - F_{A_o} X = F_{A_o}(R-X) \tag{10}$$

$$N_S = F_{A_o}\,X \tag{11}$$

$$N_R = F_{A_o} X + F_{A_o} C \tag{12}$$

$$N_T = \frac{N_A + F_{A_o}\left[1+X+2(R+C)\right]}{2} \tag{13}$$

Now the association reaction of acetic acid is

$$2HAc \rightleftharpoons (HAc)_2$$

therefore,

$$K_X = \frac{p_{A_2}}{p_A^2} = \frac{N_{A_2}\ N_T}{N_A^2\ \pi} \tag{14}$$

or

$$N_{A_2} = \frac{K_X\ \pi\ N_A^2}{N_T} \tag{15}$$

Substituting equation (9) for N_{A_2}, equation (13) for N_T and solving for N_A gives:

$$\frac{N_A}{F_{A_o}} = \left[\frac{-(X+R+C) + \left[(4K_X\pi+1)(1+R+C)^2 - 4K\pi(X+R+C)^2\right]^{1/2}}{4K\pi+1}\right] \tag{16}$$

Equation (16) was found to be much too complicated algebraically for integration so it was simplified. Analytic geometry and a plot of $\frac{N_A}{F_{A_o}} = f(X)$ showed the fact that equation (16) is an askew ellipse with very little curvature in the range of X encountered in the laboratory experiments; therefore, $\frac{N_A}{F_{A_o}}$ could be expressed as a linear function of X. In order to determine the constants a and b in the equation:

$$\frac{N_A}{F_{A_o}} = a + bX \tag{17}$$

the Method of Least Squares was applied to values of $\frac{N_A}{F_{A_o}}$ calculated from equation (16). Different constants were determined for each series of runs. In each series of runs the maximum value of X was rounded off to the next 0.05 and values of $\frac{N_A}{F_{A_o}}$ were calculated from equation (16) at intervals of 0.05 of a conversion unit from X=0 to the maximum value of X for the series. These were the values of $\frac{N_A}{F_{A_o}}$ which were used to fit the monomer concentration to a linear variation with X. The values of $\frac{N_A}{F_{A_o}}$ calculated from the equation $\frac{N_A}{F_{A_o}} = a+bX$ were close enough to those calculated from equation (16). The average percent deviation was about ±2%. As a check on the accuracy and suitability of $\frac{N_A}{F_{A_o}} = a+bX$, the monomer concentration was fit to a quadratic equation of the form $\frac{N_A}{F_{A_o}} = a+bX+cX^2$ for the ethyl acetate series at R = 1.50 and 1.00 and T = 180 and 160°C. The equation $\frac{N_A}{F_{A_o}} = a+bX+cX^2$ fit equation (16) to four decimal places. When the two different equations for the monomer concentration were used in the integrated rate expressions for Ethyl Acetate, no significant differences were obtained in the results; therefore, the equation $\frac{N_A}{F_{A_o}} = a+bX$ was assumed to give a satisfactory expression for the monomer and was adopted because of its greater simplicity. Calculations and results for the determination of the constants a and b will be found in the appendix under the heading, "Monomer Concentration," Appendix C.

With the moles of each component expressed as a function of X, the partial pressure of each component becomes a function of X through Dalton's Law. The equations are:

$$N_T = \frac{N_A + F_{A_o}\left[1+X+2(R+C)\right]}{2} = \frac{F_{A_o}\left[1+a+2(R+C) + (b+1)\ X\right]}{2} \qquad (18)$$

$$p_A = \frac{F_{A_o}\left[a+bX\right]\pi}{N_T} \qquad (19)$$

$$p_B = \frac{F_{A_o} \left[R - X \right] \pi}{N_T} \tag{20}$$

$$p_R = p_S = \frac{F_{A_o} \, X \, \pi}{N_T} \tag{21}$$

The Adsorption Mechanism

With the rate expressions as functions of X a correlation of the laboratory data could be attempted. The rate mechanism in which the adsorption of alcohol controls was tried; the rate expression for this is given by equation (3):

$$r = \frac{k_B \, L \, (a_B - \frac{a_R \, a_S}{a_A \, K})}{1 + K_A \, a_A + K_R \, a_R + K_S \, a_S + \frac{a_R \, a_S \, K_B}{a_A \, K}} \tag{3}$$

If alcohol adsorption is controlling the value of the alcohol adsorption constant, K_B, is very small; while the overall equilibrium constant for the reaction, K, is 30 for ethyl acetate at 160°C; therefore, the assumption was made that the two terms, $\frac{a_R \, a_S}{a_A \, K}$ and $\frac{a_R \, a_S \, K_B}{a_A \, K}$, could be neglected without introducing any large error. Also, since the amount of water in the reactant feeds is of the order of 0.01 mole of water/mole acid fed, $a_R = a_S$ and the expressions $K_R \, a_R$ and $K_S \, a_S$ can be grouped under one constant. The simplified rate expression is:

$$r = \frac{k_B \, a_B}{1 + K_A \, a_A + K_R \, a_R} \tag{22}$$

Substitution of partial pressures for activities and then equations (19), (20) and (21) for the partial pressure one obtains:

$$r = \frac{k_B\ \pi(R-X)}{N_T + K_A\ \pi(a+bX) + K_R\ \pi\ X} \tag{23}$$

Equation (18) gives N_T in terms of X; the final equation for r in terms of X is

$$r = \frac{k_B\ \pi(R-X)}{\dfrac{\left[1 + 2(R+C) + a + (b+1)\ X\right]}{2} + K_A\ \pi(a+bX) + K_R\ \pi\ X} \tag{24}$$

Equation (24) can be substituted into equation (5) and the whole integrated to obtain:

$$\frac{W}{F_{A_o}} = \int_o^X \frac{\frac{1}{2}\left[1 + 2(R+C) + a + (b+1)\ X\right] + K_A\ \pi(a+bX) + K_R\pi X}{k_B\ \pi(R-X)}\ dX \tag{25}$$

Integration of the right side of equation (25) leads to

$$\frac{W}{F_{A_o}} = -\frac{1}{k_B}\left[\frac{1 + 2(R+C) + a + R(b+1)}{2\pi}\right] \ln\frac{R-X}{R} - \frac{(b+1)\ X}{k_B\ (2\pi)}$$

$$-\frac{K_A}{k_B}\left[(bR+a)\ \ln\frac{R-X}{R} + bX\right] - \frac{K_R}{k_B}\left[X + R\ \ln\frac{R-X}{R}\right] \tag{26}$$

Substitution of letters for the expressions in equation (26)

$$\frac{W}{F_{A_o}} = \frac{1}{k_B}\ Y + \frac{K_A}{k_B}\ Z + \frac{K_R}{k_B}\ T \tag{27}$$

Values of $\frac{W}{F_{A_o}}$, Y, Z, and T, are either known or can be calculated from each experimental value of the conversion to give a series of observed values, $(\frac{W}{F_{A_{o_i}}}, Y_i, Z_i, T_i)$, $(i=1,2---n)$, where the n refers to the laboratory values of X for any ester at any one temperature. The most probable values of the constants, $\frac{1}{k_B}$, $\frac{K_A}{k_B}$ and $\frac{K_R}{k_B}$, can then be evaluated by the Method of Least Squares in the same manner as the monomer concentration equation was determined.

Table X gives the values of the constants k_B, K_A, and K_R as determined from the procedure above. The only point that need be made concerning this table is the fact that for every ester and for every temperature there is at least one of the three constants that is negative. Since k_B, K_A, and K_R are physical constants, a negative value is impossible. Therefore, the adsorption of alcohol as a rate-controlling mechanism is improbable, and by a process of elimination this leaves only a surface reaction as the rate-controlling step.

The simplifying assumptions made in deriving equation (22), neglecting the two terms $\frac{a_R\ a_S}{a_A\ K}$ and $\frac{a_R\ a_S\ K_B}{a_A\ k}$, were checked by considering the reverse reaction in equation (22) for ethyl acetate at 180°C. for all three mole ratios (R = 1.5, 1.0, and 0.75). This made the rate equation for the adsorption of alcohol:

$$r = \frac{k_B\ (a_B - \frac{a_R\ a_S}{a_A\ K})}{1 + K_A\ a_A + K_R\ a_S} \qquad (28)$$

Integration of equation (28) gives an equation of the same type as equation (27)

TABLE X.

Values of the Constants k_B, K_A and K_R

Ester	Temp. °C.	k_B	K_A	K_R
Ethyl Acetate	180	0.001900	-0.3888	0.7753
	160	0.004281	-11.4466	6.0541
	140	0.0004659	-0.7472	5.1377
Propyl Acetate	180	0.001236	-1.3603	0.3513
	160	0.0008203	0.1322	-0.2565
	140	0.0002571	-1.6885	1.8680
Butyl Acetate	180	0.001678	-1.10549	-26.0076
	160	0.0008012	-0.7923	-0.1693
	150	0.0001979	-1.7682	-1.7395

$$\frac{W}{F_{A_o}} = \frac{1}{k_B} Y + \frac{K_A}{K_B} Z + \frac{K_R}{k} T \qquad (29)$$

only in this case Y, Z, and T contain the reverse reaction. The values of Y, Z, and T containing the reverse reaction were only slightly different from those without the reverse reaction; the difference was not enough to cause a sign change in the constants, k_B, K_A, and K_R. In both cases, with or without the reverse reaction, the values of Y, Z, and T, remain in the same order with respect to R; in order for the constants to be positive the order of Y, Z, and T with respect to R must change. Since the addition of the term $\frac{a_R\, a_S}{a_A K}$ made so little difference, the addition of the even smaller term $\frac{a_R\, a_S\, K_B}{a_A\, k}$ will have little influence. The use of a simplified rate equation for the adsorption of alcohol controlling seemed justified at least for ethyl acetate at 180°C. The use of a simplified rate equation for ethyl acetate at lower temperatures follows from the fact that the equilibrium constant increases thereby making $\frac{a_R\, a_S}{a_A\, K}$ smaller. For the other two esters the equilibrium constants are unknown; they would be slightly less than the ethyl acetate value, but could not possibly be small enough to cause a change in the order of Y, Z, and T; therefore, a simplified rate equation is justified for all three esters.

Surface Reactions

The only rate-controlling step that is left to be considered is the surface reaction. The rate expression for the surface reaction as the rate-controlling step is given by equation (4):

$$r = \frac{k\, s\, L\, K_A\, K_B \left(a_A\, a_B - \frac{a_R\, a_S}{K}\right)}{\left[1 + K_A a_A + K_B\, a_B + K_R\, a_R + K_S\, a_S\right]^2} \tag{4}$$

Again some preliminary simplifications were made; $\frac{a_R\, a_S}{K}$ was neglected because it was so small, and $K_R\, a_R$ and $K_S\, a_S$ were grouped under one constant since a_R is essentially equal to a_S. The simplified rate equation becomes:

$$r = \frac{k\, a_A\, a_B}{\left[1 + K_A\, a_A + K_B\, a_B + K_R\, a_R\right]^2} \tag{30}$$

Substitution of partial pressure for activities and then equations (18), (19), (20), and (21) for the partial pressure, one obtains r as a function of X.

$$r = \frac{k\,[a+bX]\,[R-X]\,\pi^2}{\left[\frac{1 + a + 2(R+C) + (b+1)X}{2} + K_A(a+bX)\,\pi + K_B(R-X)\,\pi + K_R\,\pi\, X\right]^2} \tag{31}$$

Equation (31) can be substituted into equation (5) and the whole integrated to obtain:

$$\frac{W}{F_{A_o}} = \frac{-\left[1+2(R+C)+a+R(b+1) + 2\pi\, K_A(a+bR) + 2\pi\, K_R\, R\right]^2 \ln \frac{R-X}{R}}{4\pi^2\, k(a+bR)}$$

$$+ \frac{\left[1+2(R+C) + a - \frac{a}{b}(b+1) + 2\pi\, K_B \frac{(a+bR)}{b} - 2\pi\, K_R \frac{a}{b}\right]^2 \ln \frac{a+bX}{a}}{4\pi^2\, k(a+bR)}$$

$$= \frac{\left[b+1+2K_A\, \pi\, b - 2\pi\, K_B + 2\pi\, K_R\right]^2}{4\pi^2\, k}\; \frac{X}{b} \tag{32}$$

In order to evaluate the constants in equation (32) by the Method of Least Squares the squared terms must be eliminated; squaring and expanding the brackets leads to the constants, the constants squared, and cross-products of the constants - a total of nine in all. So far as Least Squares are concerned these nine constants are independent, and each must be evaluated; this leads ultimately to the solution of nine simultaneous algebraic equations for these nine constants. Rather than attempt the impossible task of solving for the nine constants, it was decided to try simpler rate expressions based on equation (30) which would not contain so many constants. It was hoped that these simpler rate equations would correlate the laboratory data even though they would not give the absolute values of the constants.

The first simplified rate expression considered was obtained by neglecting the denominator of equation (30) altogether; this assumes that the reaction is second-order, irreversible, and homogeneous. The rate expression is:

$$r = k\, a_A\, a_B \tag{33}$$

Expressing equation (33) as a function of X and integrating by use of equation (5):

$$\frac{W}{F_{A_o}} = - \frac{\left[1+2(R+C)+a+R(b+1)\right]^2}{4\pi^2(a+bR)\,k} \ln \frac{R-X}{R} + \frac{\left[1+2(R+C)+a - \frac{a}{b}(b+1)\right]^2}{4\pi^2(a+bR)\,k} \ln \frac{a+bX}{a} - \frac{(b+1)^2}{4\pi^2\,k}\,\frac{X}{b} \tag{34}$$

Substitution of a letter for the right side of equation (34):

$$\frac{W}{F_{A_o}} = \frac{1}{k} Y \tag{35}$$

If equation (34) correlates the data, a plot of Y vs. $\frac{W}{F_{A_o}}$ should give one straight line for all values of X and R at any one temperature and for any ester. Values of Y were calculated for the esters at the various operating conditions; a different line was obtained for every value of R at any one temperature. This means that the constant $\frac{1}{k}$ was a function of R which is not true; therefore, this rate equation did not correlate the data.

If the denominator of equation (30) is squared two of the terms that are obtained are $K_A^2 \; a_A^2$ and 1. Neglecting all other terms in the denominator leads to the following expression for the rate:

$$r = \frac{k \; a_A \; a_B}{\left[1 + m \; a_A^{2}\right]} \tag{36}$$

Equation (36) can be expressed in terms of X in the usual manner:

$$r = \frac{k \; \pi^2 (a+bX)(R-X)}{\frac{\left[1 + 2(R+C) + a + (b+1) \; X\right]}{4}^{2} + m \; \pi^2 (a+bX)^2} \tag{37}$$

Substitution of equation (37) into equation (5) and integration leads to:

$$\frac{W}{F_{A_o}} = \frac{-\left[1+2(R+C)+a+R(b+1)\right]^2}{4\,\pi^2(a+bR)\,k} \ln\frac{R-X}{R} + \frac{\left[1+2(R+C)+a-\frac{a}{b}(b+1)\right]^2}{} \ln\frac{a+bX}{a}$$

$$-\frac{(b+1)^2}{4\,\pi^2\,k}\,\frac{X}{b} - \frac{m}{k}\left[(bR+a)\ln\frac{R-X}{R} + bX\right] \qquad (38)$$

Substitution of letters for the expression in equation (38)

$$\frac{W}{F_{A_o}} = \frac{1}{k}\,Y + \frac{m}{k}\,Z \qquad (39)$$

Once again values of $\frac{W}{F_{A_o}}$, Y, and Z are either known or can be calculated from each experimental value of the conversion to give a series of observed values, $(\frac{W}{F_{A_{o_i}}}, Y_i, Z_i)$, (i=1,2---n), where the n refers to the laboratory values of X for any ester at any one temperature. The most probable values of the constants, $\frac{1}{k}$ and $\frac{m}{k}$, can then be evaluated by the Method of Least Squares.

Table XI gives the values of the constants k and m as determined from the procedure above. Table XII compares the calculated values of $\frac{W}{F_{A_o}}$ to the experimental values of $\frac{W}{F_{A_o}}$. The calculated values of $\frac{W}{F_{A_o}}$ in Table XII were obtained by plugging the constants from Table XI and the experimental values of X from Tables IV, V, and VI back into equation (38) and solving for $\frac{W}{F_{A_o}}$. The experimental values of $\frac{W}{F_{A_o}}$ in Table XII come from Tables IV, V, and VI. The third column in Table XII is the percentage difference between the calculated and experimental values of $\frac{W}{F_{A_o}}$. Figures 5, 6, and 7 give a visual comparison of the two values of $\frac{W}{F_{A_o}}$; the solid lines are a plot of calculated $\frac{W}{F_{A_o}}$ vs. the experimental values of X while the circled points are the experimental data.

TABLE XI.

Values of the Constants k and m

Ester	Temp. °C.	k	m
Ethyl Acetate	180	0.015195	14.6519
	160	0.0050628	9.3603
	140	0.0028334	10.4120
Propyl Acetate	180	0.011039	5.9874
	160	0.0039321	3.6602
	140	0.0019528	3.7266
Butyl Acetate	180	0.0146368	5.4771
	160	0.0047139	1.9637
	150	0.0029284	1.1377

TABLE XII.

Calculated Values of W/F_{A_o} from equation (36)

Ethyl Acetate

T = 180°C; R = 1.50

Run No.	W/F_{A_o} Exp.	W/F_{A_o} Calc.	% Diff.
30	1312.8	1292.7	-1.54
31	1154.4	1120.6	
32	1022.8	1015.8	-0.68
33	861.7	831.3	
34	730.8	732.5	+0.23
35	580.4	577.5	
36	468.7	482.7	+2.98
37	324.3	325.8	+0.46
T = 180°C.; R = 1.00			
17	1313.0	1344.3	+2.38
18	1154.5	1202.4	
10	1021.8	1087.0	+6.38
11	860.8	905.5	
12	730.8	763.1	+4.41
13	580.9	591.3	
14	469.2	515.8	+9.93
15	324.6	348.0	
16	237.2	252.1	5.91
T = 180°C.; R = 0.75			
49	1313.8	1180.5	-10.14
50	1155.2	1062.1	
51	1022.9	964.2	-5.73
52	861.8	857.7	
53	730.5	762.9	+4.43
54	580.6	603.4	
55	469.1	501.6	+6.92
56	324.1	354.6	
57	236.7	264.3	+11.66
T = 160°C; R = 1.50			
23	1314.1	1294.4	-1.49
24	1155.5	1144.4	
22	1022.9	1005.1	-1.74
25	861.7	843.3	
26	729.8	718.8	-1.50
27	580.8	611.1	
28	469.3	472.3	+0.63
29	324.7	319.1	+1.72

TABLE XII. (continued)

Ethyl Acetate

T = 160°C.; R = 1.00

Run No.	W/F_{A_0} Exp.	W/F_{A_0} Calc.	% Diff.
7	1316.6	1396.0	+6.03
8	1157.6	1185.2	
1	1024.1	1056.6	+3.17
2	862.7	843.7	
3	730.0	746.4	+2.24
4	580.2	585.6	
5	468.8	480.1	+2.41
6	324.1	334.2	+3.08
T = 160°C.; R = 0.75			
40	1312.8	1204.2	-8.27
41	1154.4	1083.1	
48	1022.4	1000.7	-2.12
42	861.1	858.7	
43	730.3	758.1	+3.80
44	580.5	608.8	
45	468.7	506.8	+8.12
46	324.3	383.3	+18.19
T = 140°C.; R = 1.50			
66	1313.5	1296.6	-1.28
67	1089.3	1079.9	
68	861.6	880.0	+2.13
69	650.4	694.5	
70	468.6	517.9	+10.52
71	324.2	377.7	+16.50
T = 140°C.; R = 1.00			
60	1313.5	1211.4	-7.77
61	1089.3	1054.6	
62	862.0	866.8	+0.55
63	650.6	683.6	
64	468.4	543.6	+16.05
65	324.1	404.4	+24.77

TABLE XII. (continued)

Propyl Acetate

T = 180°C.; R = 1.50

Run No.	W/F_{A_0} Exp.	W/F_{A_0} Calc.	% Diff.
44	1300.8	1337.5	+2.44
45	1151.2	1179.1	
46	1031.7	1002.4	-2.84
47	882.3	840.8	
48	758.1	722.7	+4.67
49	599.1	577.4	
50	485.3	446.1	-8.08
51	328.8	309.0	-6.02
	T = 180°C.; R = 1.00		
16	1300.3	1254.1	-3.55
17	1150.6	1149.1	
9	1030.6	1085.7	+5.34
10	881.4	923.8	
11	759.3	821.1	+8.13
12	600.0	648.6	
13	485.6	527.6	+8.65
14	328.9	354.3	
15	232.7	233.4	+0.29
	T = 180°C.; R = 0.75		
36	1298.8	1232.0	-5.14
37	1149.4	1152.0	
38	1030.1	1013.0	-1.66
39	881.5	849.6	
40	758.3	769.0	+1.40
41	599.2	613.4	
42	485.4	490.5	+1.04
43	328.7	335.5	2.05
	T = 160°C.; R = 1.50		
27	1299.1	1342.1	3.30
28	1149.7	1154.2	
29	1032.7	1022.8	-0.96
30	883.2	858.6	
31	759.7	762.5	+0.36
35	599.2	593.9	
32	485.6	491.3	+1.17
33	328.9	338.6	+2.95

TABLE XII. (continued)

Propyl Acetate

T = 160°C.; R = 1.00

Run No.	W/F_{A_o} Exp.	W/F_{A_o} Calc.	% Diff.
7	1299.1	1283.2	-1.22
8	1150.0	1139.9	
18	1030.3	1008.3	-2.13
2	880.9	868.7	
3	758.8	760.8	+0.25
4	599.6	613.7	
5	485.5	499.4	+2.86
6	328.8	337.7	+2.70
	T = 160°C.; R = 0.75		
25	1299.3	1274.1	-1.94
26	1149.8	1152.3	
19	1030.3	988.4	-4.06
20	881.0	861.6	
21	757.8	772.2	+1.89
22	598.9	624.2	
23	485.9	506.8	+4.30
24	329.1	346.1	+5.15
	T = 140°C.; R = 1.50		
60	1298.7	1265.7	-2.53
61	1088.6	1086.3	-0.21
62	881.8	880.1	
63	670.0	715.4	+6.78
64	485.5	497.0	
65	328.8	341.0	+3.70
	T = 140°C.; R = 1.00		
54	1299.1	1302.1	+0.22
55	1088.9	1056.3	
56	881.2	857.9	-2.64
57	669.8	688.3	
58	485.4	513.6	+5.80
59	328.7	326.2	-0.75

TABLE XII. (Continued)

Butyl Acetate

T = 180°C.; R = 1.50

Run No.	W/F_{A_o} Exp.	W/F_{A_o} Calc.	% Diff.
15	1299.3	1360.1	+4.68
16	1150.0	1179.4	+2.55
9	1030.7	1089.8	
10	881.5	917.1	+4.04
11	758.8	791.9	
12	600.0	631.6	+5.26
13	485.7	509.0	
17	397.6	386.2	-2.86
14	328.9	296.6	
18	275.1	267.2	-2.89

T = 180°C.; R = 1.00

Run No.	W/F_{A_o} Exp.	W/F_{A_o} Calc.	% Diff.
37	1301.5	1168.6	-10.21
38	1151.8	1051.2	
39	1032.1	943.5	-8.58
40	882.8	826.0	
41	757.9	731.6	-3.46
42	599.8	602.8	
43	485.9	487.8	+0.38
44	329.1	348.4	
53	232.5	235.6	+1.33

T = 180°C.; R = 0.75

Run No.	W/F_{A_o} Exp.	W/F_{A_o} Calc.	% Diff.
45	1300.0	1282.1	-1.38
46	1150.5	1146.3	-0.36
47	1030.2	1066.8	
48	881.1	861.0	-2.28
49	758.5	797.9	
50	599.4	623.2	+3.96
51	485.4	518.9	
52	328.8	340.9	+3.67
54	232.5	239.6	+3.04

T = 160°C.; R.= 1.50

Run No.	W/F_{A_o} Exp.	W/F_{A_o} Calc.	% Diff.
7	1299.5	1336.6	+2.85
8	1150.0	1186.0	
19	1031.3	1039.0	+0.73
2	881.1	829.7	
3	757.9	772.5	+1.92
4	599.4	619.9	
5	485.6	503.3	+3.64
6	328.9	334.9	+1.81

TABLE XII. (continued)

Butyl Acetate

T = 160°C.; R = 1.00

Run No.	W/F_{A_o} Exp.	W/F_{A_o} Calc.	% Diff.
20	1298.6	1290.0	+0.65
21	1149.2	1121.2	
22	1029.9	986.6	-4.20
23	881.6	829.0	
24	758.4	736.5	-2.89
25	599.3	584.9	
26	485.1	482.3	-0.56
27	328.6	324.7	-1.18
T = 160°C.; R = 0.75			
28	1298.4	1370.6	+5.56
29	1149.0	1193.4	
30	1029.7	1051.7	+2.13
31	881.3	915.4	
32	758.1	772.3	+1.87
33	599.1	606.5	
34	485.6	492.1	+1.34
35	328.9	333.2	+1.31
T = 150°C.; R = 1.50			
57	1299.7	1317.4	+1.34
58	1089.4	1074.0	
59	881.6	840.5	-4.65
60	670.1	686.9	
61	485.6	488.5	+0.60
62	328.9	334.2	+1.62
T = 150°C.; R = 1.00			
63	1299.6	1327.6	+2.15
64	1089.4	1077.1	
65	881.1	848.0	-3.76
66	669.6	690.0	
67	486.0	495.0	+1.85
68	329.1	325.8	-0.99

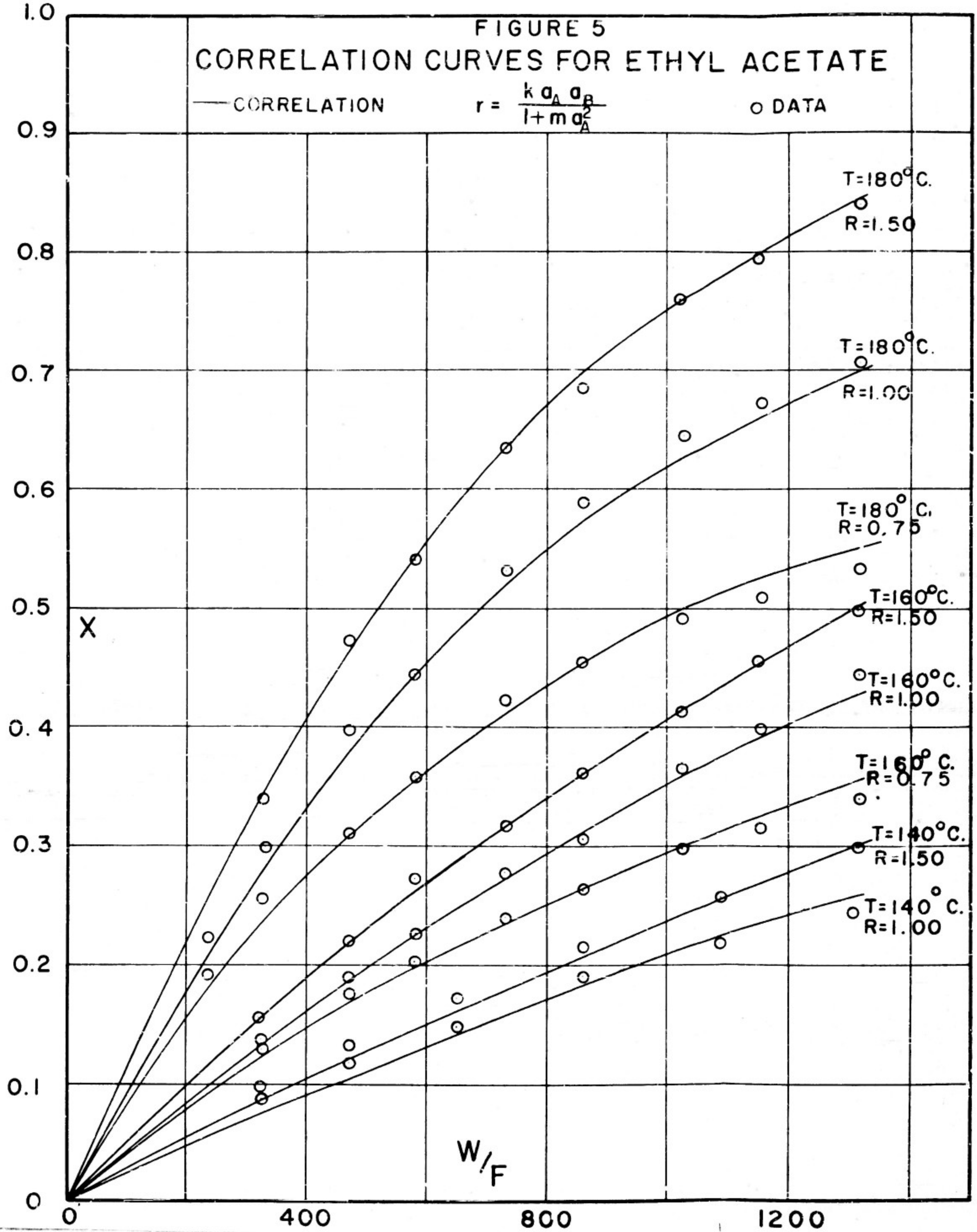

FIGURE 5

CORRELATION CURVES FOR ETHYL ACETATE

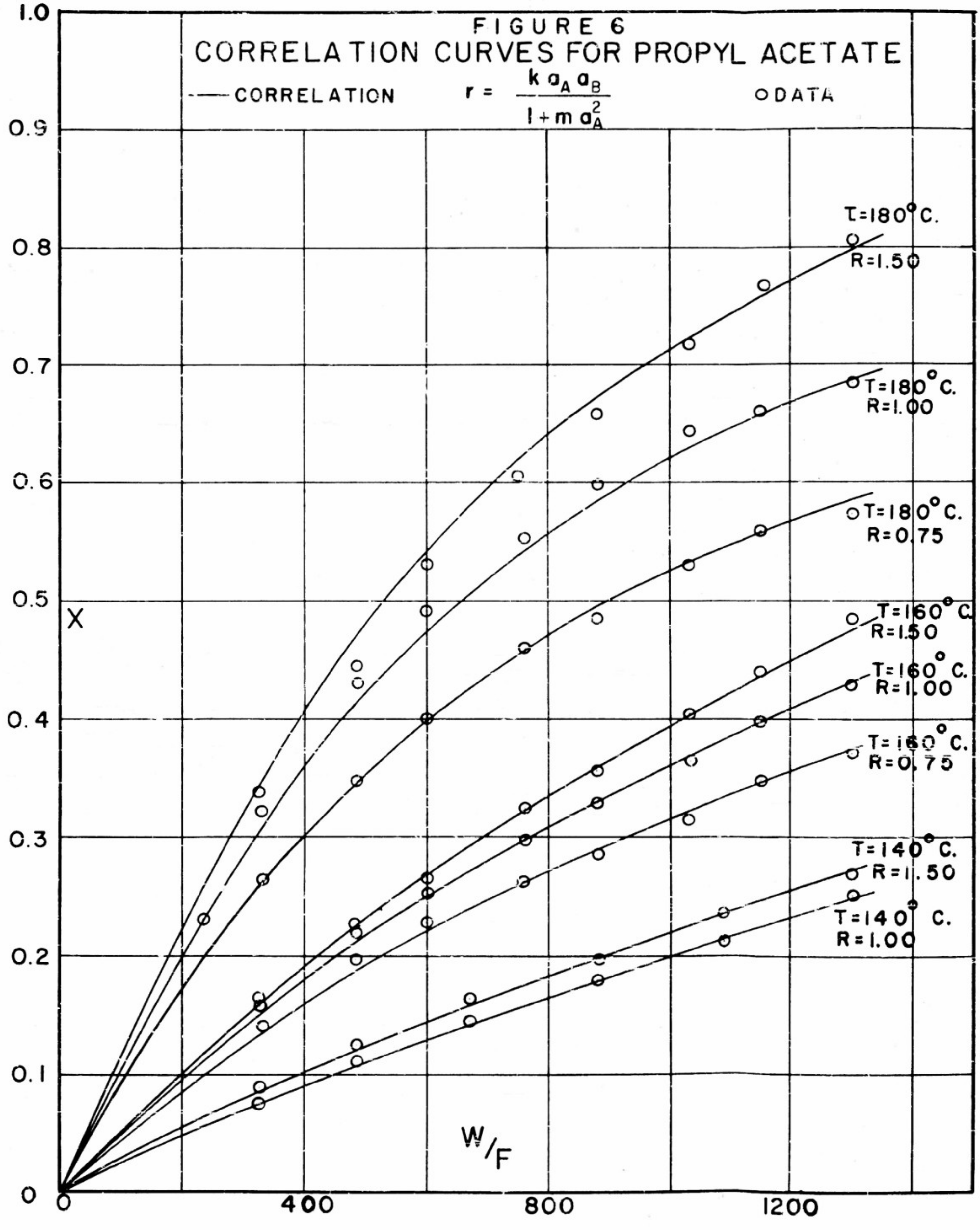

FIGURE 6

CORRELATION CURVES FOR PROPYL ACETATE

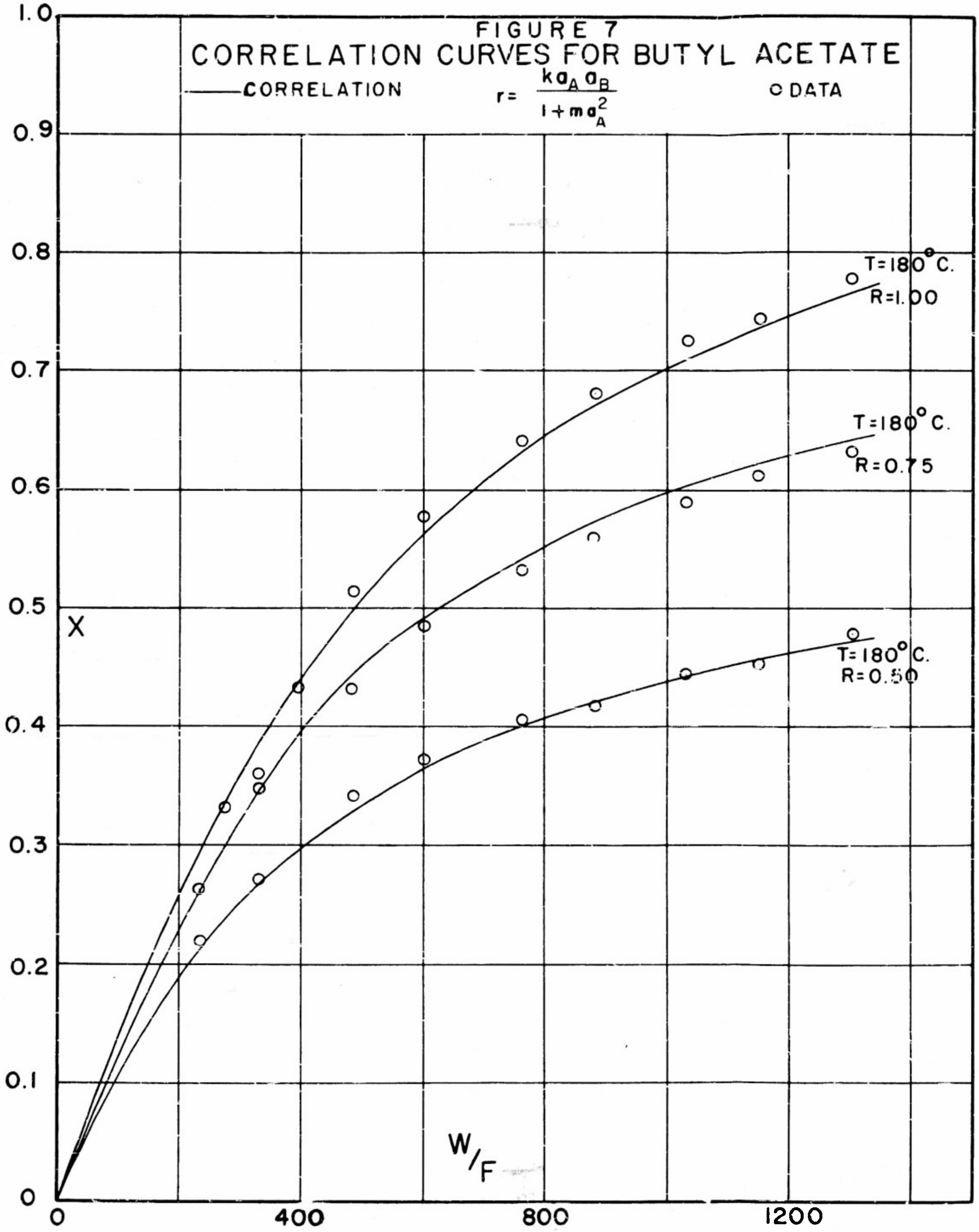

FIGURE 7

CORRELATION CURVES FOR BUTYL ACETATE

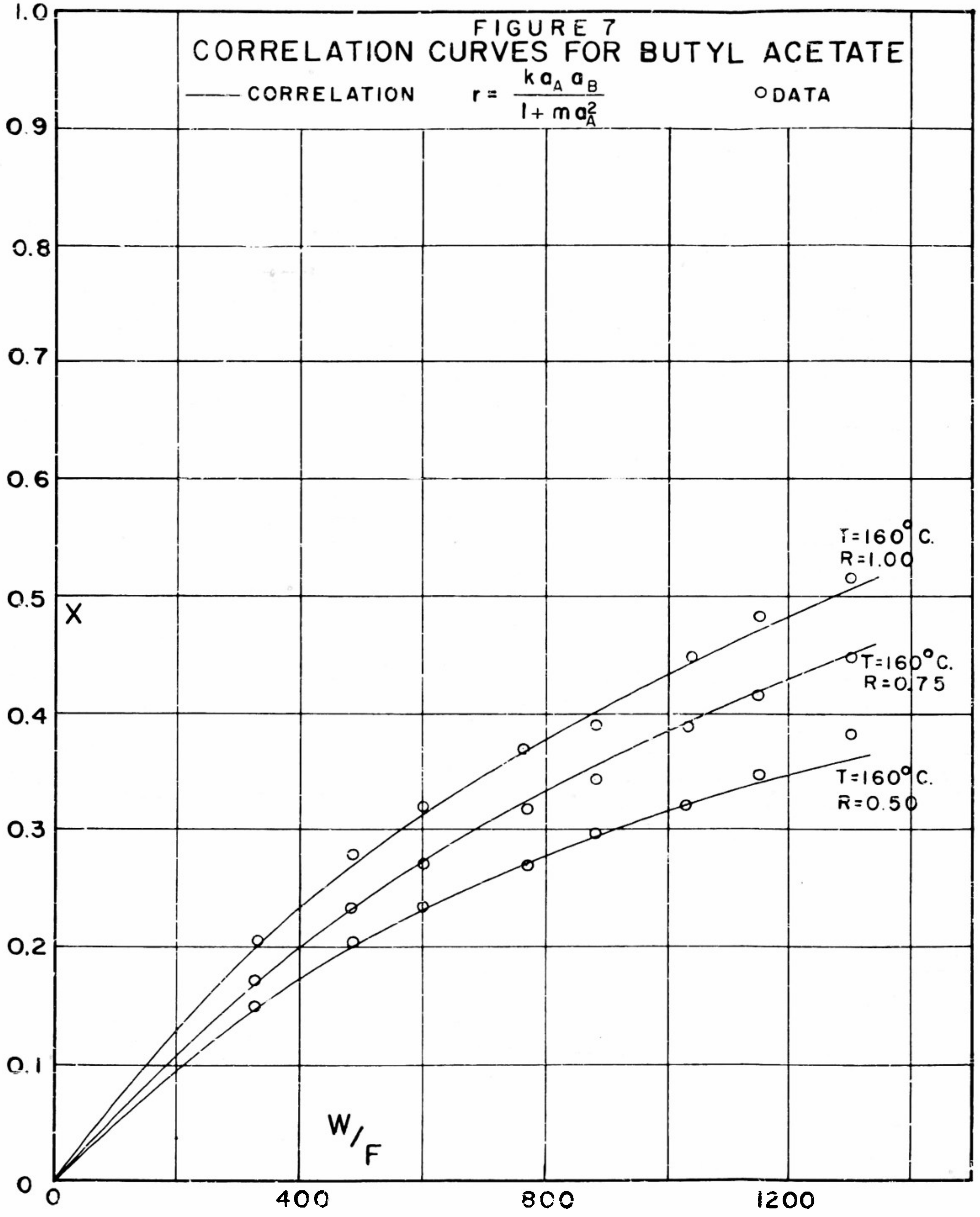

FIGURE 7

CORRELATION CURVES FOR BUTYL ACETATE

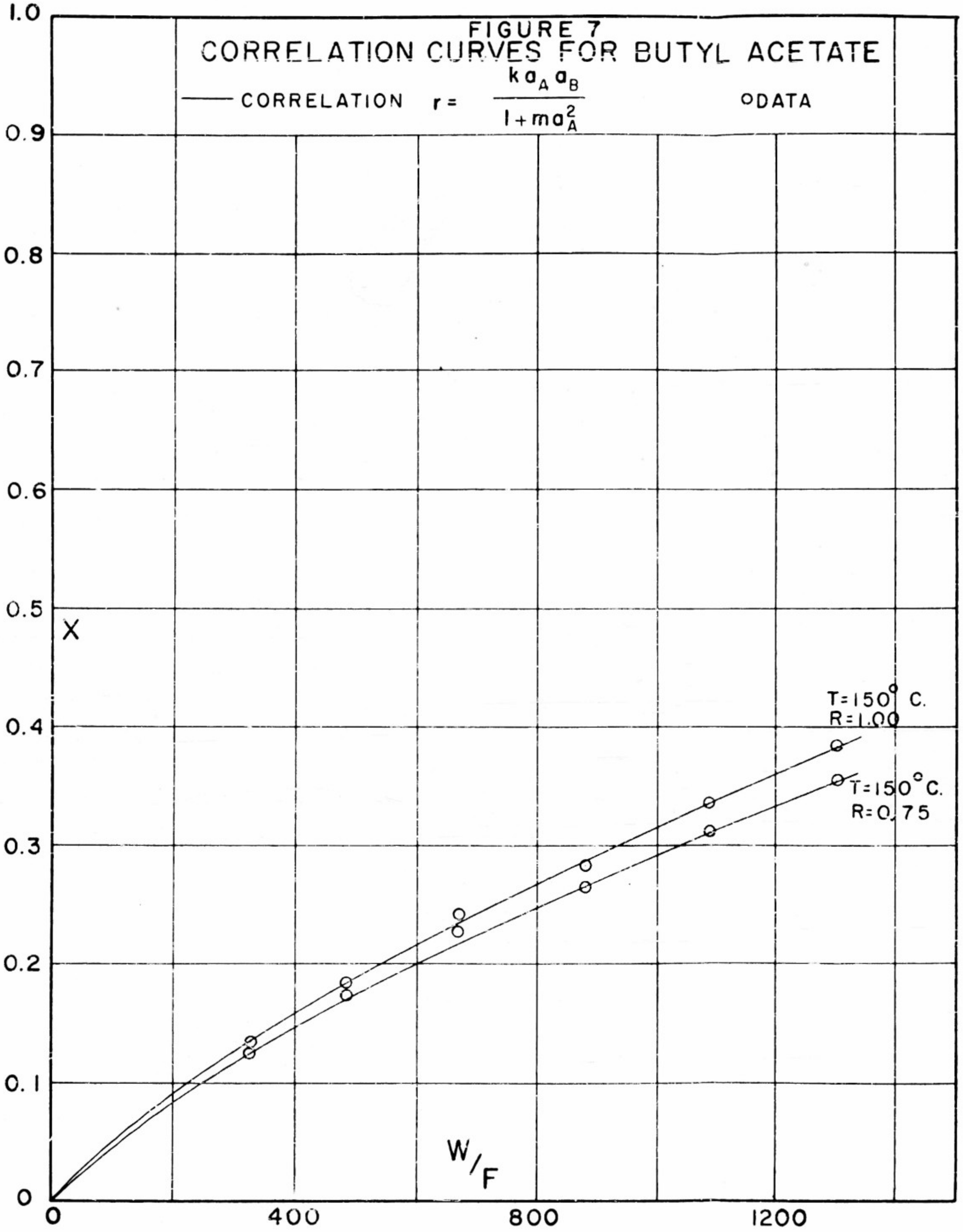

FIGURE 7
CORRELATION CURVES FOR BUTYL ACETATE

An examination of Table XII and Figures 5, 6, and 7 will show that the rate expression $r = k\, a_A\, a_B/1 + m\, a_A^2$ correlates the laboratory data quite well. The difference between the calculated and experimental values of $\frac{W}{F_{A_o}}$ for the esters propyl acetate and butyl acetate is less than 10% with an average difference of ±5%. Ethyl acetate did not correlate as well; for several values of $\frac{W}{F_{A_o}}$ the percentage difference was greater than 10%; in fact, for the high flow rates at 140°C. the difference reached 25%. Still, the average difference remained less than 10% so the correlation is certainly usable.

The question arises as to just how precise we can expect $\frac{W}{F_{A_o}}$ to be in the light of experimental error. The total differential of $\frac{W}{F_{A_o}}$ in equation (38) should give an estimation of the probable error in $\frac{W}{F_{A_o}}$. Rather than differentiate equation (38) with respect to every variable, it was decided to differentiate with respect to X alone since the errors in the other variables would be small and since the major source of error in $\frac{W}{F_{A_o}}$ is in the ratio of logarithmic terms. Rearranging and differentiating equation (38) and then dividing by $\frac{W}{F_{A_o}}$ gives:

$$\frac{d\left(\frac{W}{F_{A_o}}\right)}{\frac{W}{F_{A_o}}} = \frac{1}{(k)\left(\frac{W}{F_{A_o}}\right)} \left[\left\{ \frac{\left[1+2(R+C)+a+R(b+1)\right]^2}{4\pi^2(a+bR)} + m(bR+a) \right\} \frac{dX}{R-X} \right.$$

$$\left. + \frac{\left[1+2(R+C)+a-\frac{a}{b}(b+1)\right]^2}{4\pi^2(a+bR)} \frac{bdX}{a+bX} - \left\{ \frac{(b+1)^2}{4\pi^2 b} + bm \right\} dX \right] \tag{40}$$

Reference to the section on catalyst check runs will show that these runs had a maximum spread of about 6%. This fact can be used as an estimation of the probable error in X, and the probable value of dX can then be estimated by the following equation:

$$dX = 0.06X \qquad (41)$$

The values of $d(W/F_{A_o})/W/F_{A_o}$ were determined for ethyl acetate at the high and low end of each integral curve; the results of these calculations are listed in Table XIII. The values of $d(W/F_{A_o})/W/F_{A_o}$ for propyl and butyl acetate would be similar to those of ethyl acetate. Table XIII shows that the error in the calculated value of W/F_{A_o} could go as high as 15.8% and as low as 5.4% with an average error of about 10%. With this fact in mind the average difference of 5% between calculated W/F_{A_o} and experimental W/F_{A_o} for the correlation based on $r = \dfrac{k\, a_A\, a_B}{1+m\, a_A^{\,2}}$ is about as good as could be expected.

Table XIII brings up another point; the probable error in W/F_{A_o} is not a constant; rather it is a function of temperature, mole ratio, and flow rate. Now the Principle of Least Squares is based on the assumption that the observed values are of equal precision which is not the case in this work. However, for lack of anything better, Least Squares was used. Scarborough (19) is of the opinion that the use of Least Squares when the observed values are not of equal precision is all right. He compared the results of fitting data, which did not have equal precision, to

TABLE XIII.

Error in the Calculated Value of W/F_{A_o}

Ethyl Acetate

Run No.	Temp. °C.	R	G. $\frac{lb.}{hr.ft.^2}$	$d(W/F_{A_o})/W/F_{A_o} \times 100$
30	180	1.4992	20.8	15.8%
37	180	1.4992	84.1	6.9
17	180	1.007	17.0	14.2
16	180	1.007	94.4	7.5
49	180	0.7502	15.2	8.5
57	180	0.7502	84.3	5.4
23	160	1.5008	20.8	8.6
29	160	1.5008	84.0	6.5
7	160	1.0005	17.0	9.6
6	160	1.005	69.0	6.9
40	160	0.7502	15.2	8.0
46	160	0.7502	61.6	8.6
66	140	1.5005	20.8	7.1
71	140	1.5005	84.2	7.3
60	140	1.0001	17.1	6.8
65	140	1.0001	69.2	8.1

various types of applicable equations by ordinary Least Squares and by using a "Weighted" Least Squares. No significant improvement was noted when "Weighted" residuals were used; therefore, he concluded that the use of any method more complicated than the ordinary Least Squares is not worth the effort. It should be mentioned that in computing the values of the constants by the Method of Least Squares all data and derived data were treated as exact numbers, and all computations were carried to seven significant figures in order to be sure that no significant figures were eliminated by subtraction.

Finally a correlation of the data was attempted in which the reverse reaction was put into equation (36). This made the rate equation:

$$r = \frac{k \left[a_A \, a_B - \frac{a_R \, a_S}{K} \right]}{1 + m \, a_A^2} \tag{42}$$

Computations were carried out only for ethyl acetate at 180°C. No significant change was noted in the values of the integrals, in the values of the constants, and in the correlation. Therefore, it was assumed that the contribution of the term $\frac{a_R \, a_S}{K}$ is negligible and can be neglected.

The rate equation $r = \frac{k \, a_A \, a_B}{\left[1 + m \, a_A^2 \right]}$ was varied and made more complicated in the hope that the correlation might be improved. When the denominator of equation (30) is squared, another term that arises is $K_R \, a_R$; this term was added to the denominator of equation (36) to give

$$r = \frac{k\ a_A\ a_B}{\left[1 + m\ a_A^{\ 2} + n\ a_R\right]} \tag{43}$$

Equation (43) is expressed in terms of X as usual:

$$r = \frac{k\ \pi^2(a+bX)(R-X)}{\dfrac{\left[1+2(R+C)+a+(b+1)X\right]^2}{4} + m\pi^2(a+bX)^2 + n\pi\,\dfrac{\left[1+2(R+C)+a+(b+1)X\right]\ X}{2}} \tag{44}$$

Substitution of equation (44) into equation (5) and integration leads to:

$$\begin{aligned} \frac{W}{F_{A_o}} = {} & -\frac{\left[1+2(R+C)+a+R(b+1)\right]^2}{4\ \pi^2(a+bR)\ k}\ \ln\frac{R-X}{R} + \frac{\left[1+2(R+C)+a - \frac{a}{b}(b+1)\right]^2}{4\ \pi^2(a+bR)\ k}\ \ln\frac{a+bX}{a} \\ & - \frac{(b+1)^2}{4\ \pi^2\ k}\ \frac{X}{b} - \frac{m}{k}\left[(bR+a)\ \ln\frac{R-X}{R} + bX)\right] \\ & - \frac{n}{k}\left[\frac{R\left[1+2(R+C)+a+R(b+1)\right]}{2\ \pi(a+bR)}\ \ln\frac{R-X}{R} + \frac{a\left[1+2(R+C)+a - \frac{a}{b}(b+1)\right]}{2\ \pi\ b(a+bR)}\ \ln\frac{a+bX}{a}\right. \\ & \left. + \frac{b+1}{2\pi}\ \frac{X}{b}\right] \end{aligned} \tag{45}$$

Substitution of letters for the expressions in equation (45):

$$\frac{W}{F_{A_o}} = \frac{1}{k}\ Y + \frac{m}{k}\ Z + \frac{n}{k}\ X \tag{46}$$

The constants were determined by the Method of Least Squares and are listed in Table XIV.

TABLE XIV.

Values of the Constants k, m, and n

Ester	Temp. °C.	k	m	n
Ethyl Acetate	180	0.021201	21.6914	1.6419
	160	0.0053753	10.0136	0.5344
	140	0.0051742	20.5842	12.9257
Propyl Acetate	180	0.011174	6.0816	0.05748
	160	0.0041181	3.8309	0.47060
	140	0.0021973	4.1237	2.3046
Butyl Acetate	180	0.019634	8.2576	1.1728
	160	0.0045924	1.8506	-0.14848
	150	0.0028019	0.9400	-0.3032

A comparison of Table XI and XIV will show that there was very little change in the values of the constants with the addition of the terms, n a_R, except for ethyl acetate at 140°C.; this same behavior was followed for the values of calculated W/F_{A_o}. Table XV gives the values of calculated W/F_{A_o} and Figure 8 gives a visual comparison of experimental and calculated W/F_{A_o} for ethyl acetate at 140°C. for this new rate expression. The correlation results for propyl and butyl acetate and for ethyl acetate at 180°C. and 160°C. for this new mechanism are not listed; they are almost identical with those in Table XI. The percentage differences in Table XIV are now less than 10% and the correlation of ethyl acetate at 140°C. is more in line with those in Table XII.

Before leaving this rate-expression one more fact should be pointed out. The constant n for butyl acetate at 160°C. and 150°C. is negative; this does not disprove the surface mechanism as it did in the case of alcohol adsorption. It must be remembered that these are simplified rate expressions and the constants, k, m, and n are now mathematical groupings of physical constants. The possibility of a large positive physical constant subtracting from a smaller positive physical constant to make the correlation constant, n, negative is not improbable. Actually one should divorce himself from the idea of a physical constant and treat k, m, and n as pure empirical constants.

Other rate expressions were tried, all based on a surface reaction, in the hope that there would be some improvement in the correlation. The following equations were considered:

TABLE XV.

Calculated Values of W/F_{A_o} for Ethyl Acetate at 140°C. from Equation (45)

T = 140°C.; R = 1.50

Run No.	W/F_{A_o} Exp.	W/F_{A_o} Calc.	% Diff.
66	1313.5	1352.9	3.99
67	1089.3	1077.4	-1.09
68	861.6	839.8	-2.64
69	650.4	635.5	-2.30
70	468.6	454.3	-3.05
71	324.2	320.2	-1.25
T = 140°C.; R = 1.00			
60	1313.5	1287.1	-2.01
61	1089.3	1087.0	-0.21
62	862.0	860.3	-0.20
63	650.6	652.6	+0.31
64	468.4	503.5	+7.49
65	324.1	353.0	8.91

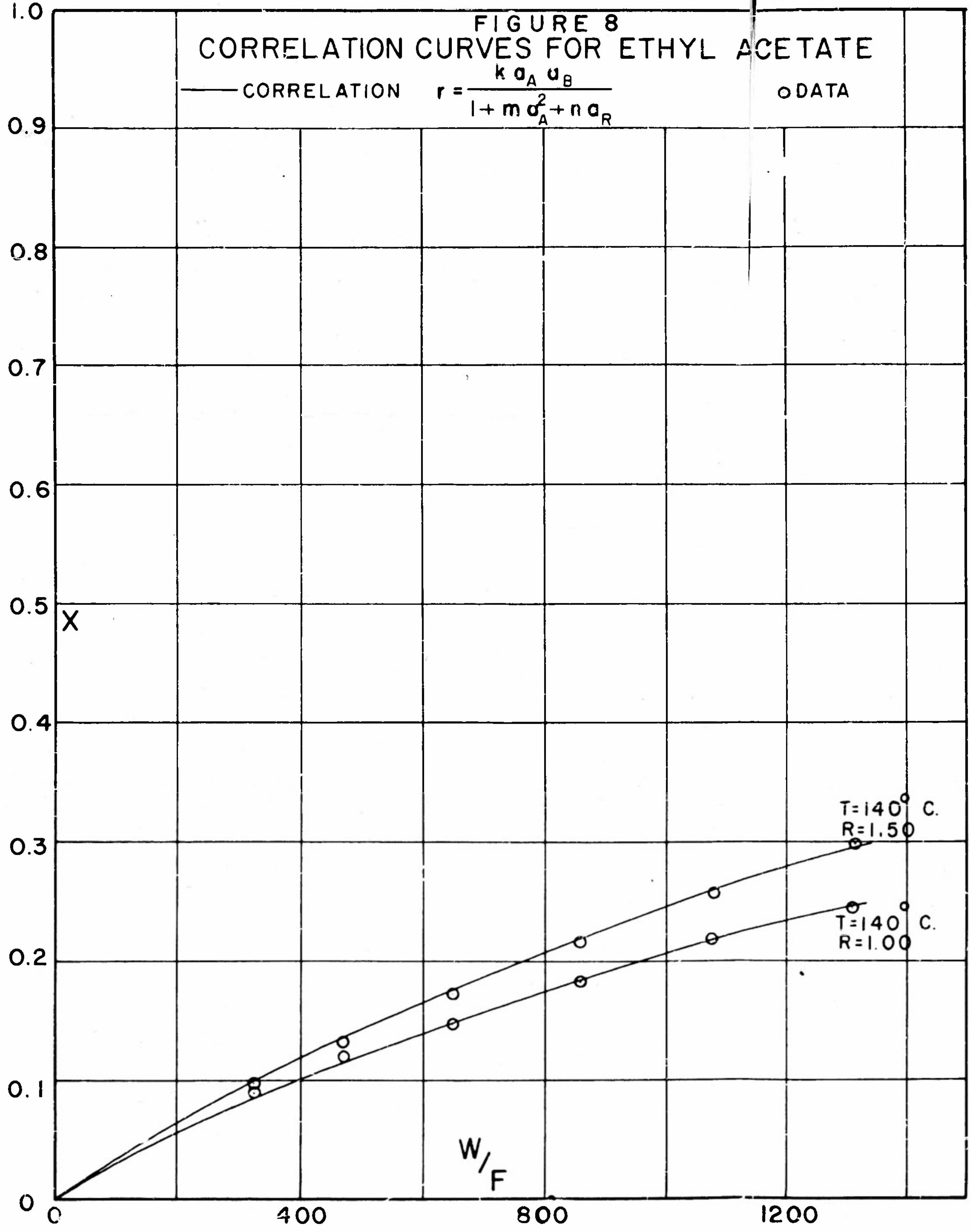

FIGURE 8
CORRELATION CURVES FOR ETHYL ACETATE

$$r = \frac{k\, a_A\, a_B}{[1 + m\, a_A^2 + n\, a_B]} \tag{47}$$

$$r = \frac{k\, a_A\, a_B}{[1 + m\, a_A^2 + n\, a_A]} \tag{48}$$

$$r = \frac{k\, a_A\, a_B}{[1 + m\, a_A^2 + n\, a_A + o\, a_R]} \tag{49}$$

$$r = \frac{k\, a_A\, a_B}{[1 + m\, a_A^2 + n\, a_A + o\, a_R + s\, a_B]} \tag{50}$$

Equations (47), (48), and (50) were applied only to ethyl acetate at 180°C.; Equation (49) was applied to ethyl acetate at all temperatures and to propyl acetate at 180°C. and 140°C. Table XVI lists these constants according to equation number and operating conditions. Values of calculated W/F_{A_o} were determined for equations (47), (48) and (49); there was no improvement in the correlations. No attempt was made to calculate W/F_{A_o} for equation (50) since the constants had such improbable values. These calculations indicated that no further improvement could be expected in the correlations by adding terms to equation (36); therefore, it appears that the rate expression $r = k\, a_A\, a_B / 1 + m\, a_A^2$ correlates the data as well as any more complicated expression.

In Figure 9 the values of k from Table XI, those based on the equation $r = k\, a_A\, a_B / 1 + m\, a_A^2$, are plotted as ln k vs. $\frac{1}{T} \times 1000$. The three points for any one ester do not lie on a straight line; this is not too surprising because the rate equation

FIGURE 9

EFFECT OF TEMPERATURE ON k IN THE EQUATION

$$r = \frac{k a_A a_B}{1 + m a_A^2}$$

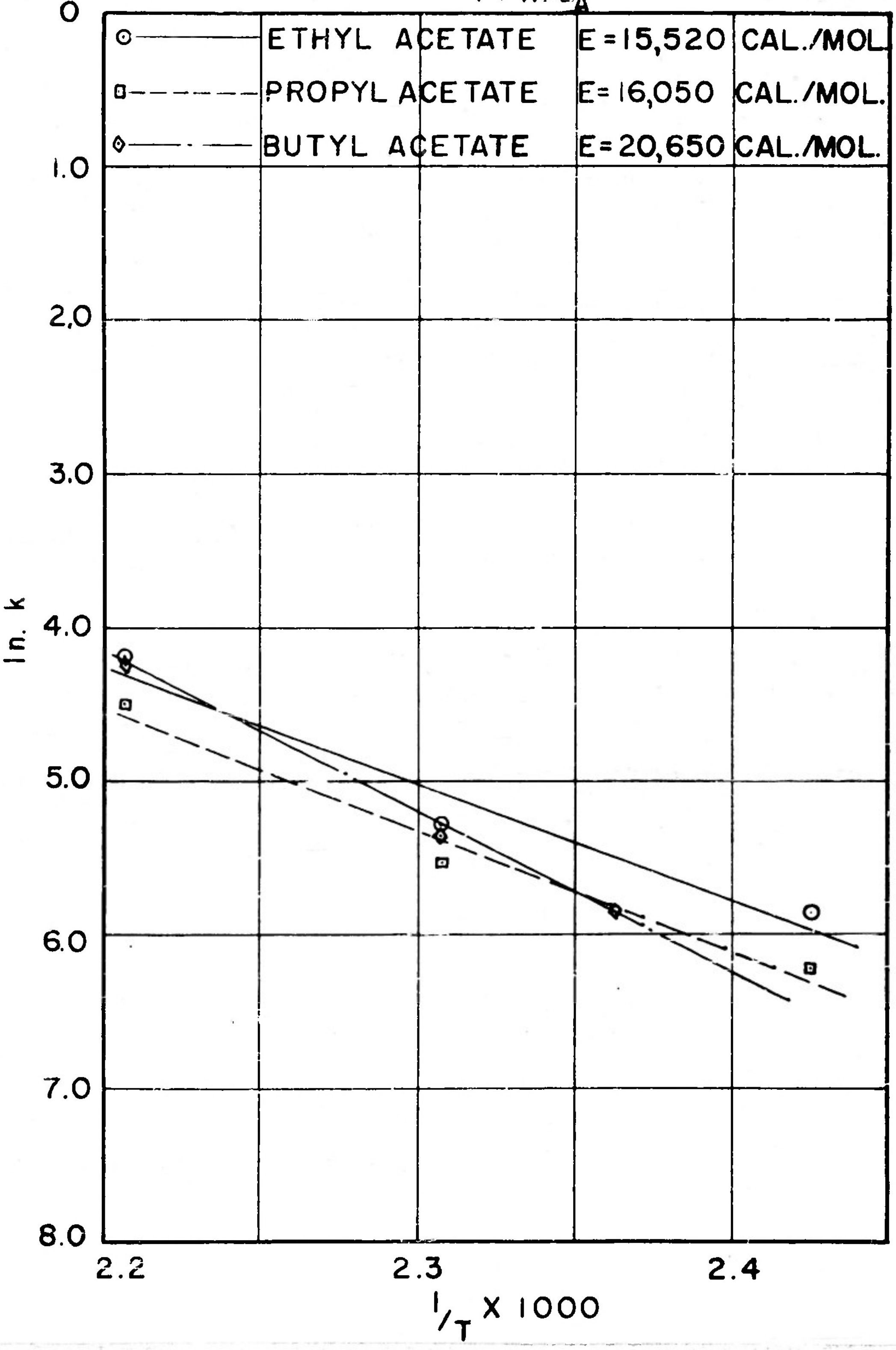

TABLE XVI.

Constants in Equations (47), (48), (49), (50)

Eq. No.	Ester	Temp. °C.	k	m	n	o	s
47	Ethyl Acetate	180°C.	0.012511	11.5380	-0.4420		
48	"	180°C.	0.011890	17.1327	-2.4342		
50	"	180°C.	-0.0004779	-0.08942	-3.2249	59.0517	-100.90
49	"	180°C.	0.015654	21.0278	-2.4022	1.1384	
49	"	160°C.	0.0045895	2.5796	1.4306	-0.3951	
49	"	140°C.	0.028735	38.2189	37.1503	72.8532	
49	Propyl Acetate	180°C.	-0.0029922	3.5050	-3.4126	-4.2980	
49	"	160°C.	0.0028953	3.5829	-0.7522	-1.3402	

used is a simplification and the constant k is not a true velocity constant. Even so, the slopes of the best straight lines which can be drawn (by Least Squares) yield an activation energy of 15,520 cal./mole for ethyl acetate, 16,053 cal./mole for n-propyl acetate, and 20,650 cal./mole for n-butyl acetate. No attempt was made to find a relationship between m and $\frac{1}{T}$ for the equation $r = \frac{k\, a_A\, a_B}{1 + m\, a_A^2}$; a glance at Table XI will show that the relationship is certainly not exponential. Also nothing was done about the constants in Table XII; the values of k are about the same as those for Table XI and the values of m and n have no apparent relationship with $\frac{1}{T}$. Finally, it is interesting to note the similiarity in the numerical values of k in Table XI for the various esters at any one operating temperature. It appears that any differences between the esters is taken care of by the constant m, while k remains essentially the same for the three esters.

In summary, then, it can be said that diffusion through a gas film on the catalyst, intraparticle diffusion, desorption of products, and adsorption of reactants appear not to be the rate-controlling step; this leaves a surface reaction as the only possible mechanism. Because of the complexity of the equation for a surface reaction, it was impossible to obtain positive proof that a surface reaction controls; however, the data correlates well within 10% with equations which are simplifications of the surface reaction. This, in itself, points to a surface reaction as a rate-controlling step. Perhaps even more important than pointing to the rate-controlling step, these simplified equations show that kinetic data can be correlated by much simpler expressions than those derived from theory.

METHYL ACETATE

Prior to obtaining the laboratory data for the ethyl acetate, propyl acetate, and butyl acetate the reactor was used to make a series of runs in which methyl acetate was formed from methyl alcohol and acetic acid.

The acetic acid used for the methyl acetate was the same as that used for the other esters. The methyl alcohol was Du Pont C.P. methanol; according to the manufacturer's specifications it assayed 99.85% by weight methanol. Unfortunately, the Karl Fischer methods for analyzing for alcohol and water content had not been set up when the methyl alcohol was run so no quantitative chemical data is available on this alcohol. However, the methanol was subjected to the same physical tests as the other alcohols. The results of these physical tests were as follows: 1. boiling point range was less than 0.8°C.; 2. negative test for aldehydes, ketones, and unsaturates; 3. $d^{26.8°C.}_{4°C.} = 0.7851$ compared to a literature value of $d^{26.8°C.}_{4°C.} = 0.7849$ (12); and, 4. $n^{D}_{20°C.} = 1.3288$ compared to a literature value of $n^{D}_{20°C.} = 1.3288$. These physical tests indicated a high degree of purity; for lack of anything better the alcohol was assumed to be 99.85% by weight methanol as claimed by the manufacturer.

For the methyl acetate the reactor was used exactly as it had been left by Stusiak (20); for the other esters both the reactor and the operating procedures were remodeled. Stusiak's (20) catalyst bed was also used for the methyl acetate; for a description of the physical and chemical properties of this bed the reader is referred to Stusiak's work (20) and the literature survey of this report. The catalyst was tungstic oxide carried on activated alumina spheres; the bed had an oven dried weight of 2170 g.

As for the other esters, the only variables considered in the case of methyl acetate were T, R, and F_{A_o} ; no attempt was made to vary the total operating pressure or to introduce water and ester as feeds. Table XVII has the data for methyl acetate arranged into groups according to operating conditions, while Figure 10 is the usual plot of X vs. W/F_{A_o} . Calculations for the methyl acetate runs were the same as for the other esters; pertinent information on these runs is listed in Appendix A.

The only material balances obtained for the methyl acetate series were a mass flow rate balance and an ester balance; the Karl Fischer methods had not been set up yet. The mass flow rate balances are listed in Appendix A under the heading $w_{OBSERVED}$; the agreement between feed rate and product flow rate is entirely satisfactory. Table XVIII contains the ester balances; the results are not as good as those for the other esters, but still good enough to show that if any side reactions are occurring they are very slight and can be neglected. Finally a sample of reactor product was carefully fractionated at nearly total reflux in a packed column. The initial boiling point war 54.0°C.; now the system's lowest boiling point is an azeotrope of methanol and methyl acetate which boils at 54°C. (15); therefore, the product contained no low

TABLE XVII.

Methyl Acetate

Series I; T = 180°C. R = 0.9999 P = 0.9612 atm.

Run No.	W/F_{A_o}	G	X
22	1280.4	14.8	0.603
21	1125.9	16.8	0.552
20	995.5	19.0	0.504
19	840.0	22.5	0.446
18	711.5	26.6	0.403
17	456.5	41.5	0.286
23	315.7	59.9	0.205

Series II: T = 160°C. R = 1.4995 P = 0.9667 atm.

16	1280.2	17.4	0.479
11	1124.9	19.8	0.438
13	997.1	22.3	0.393
12	839.2	26.5	0.341
15	711.2	31.3	0.297
14	564.9	39.3	0.239
9	456.1	48.3	0.207
10	316.3	70.3	0.145

Series III: T = 160°C. R = 1.0000 P = 0.9662 atm.

1	1284.8	14.8	0.400
6	1126.4	16.6	0.364
7	995.3	19.0	0.333
2	797.4	23.8	0.279
8	710.8	26.6	0.252
3	566.7	33.5	0.214
4	457.4	41.4	0.177
5	316.2	59.9	0.128

Series IV: T = 140°C. R = 0.9999 P = 0.9677 atm.

29	1280.7	14.8	0.213
28	1128.3	16.8	0.194
27	997.2	19.0	0.180
26	839.9	22.5	0.164
25	710.8	26.6	0.142
24	457.2	41.4	0.103
30	316.2	59.9	0.076

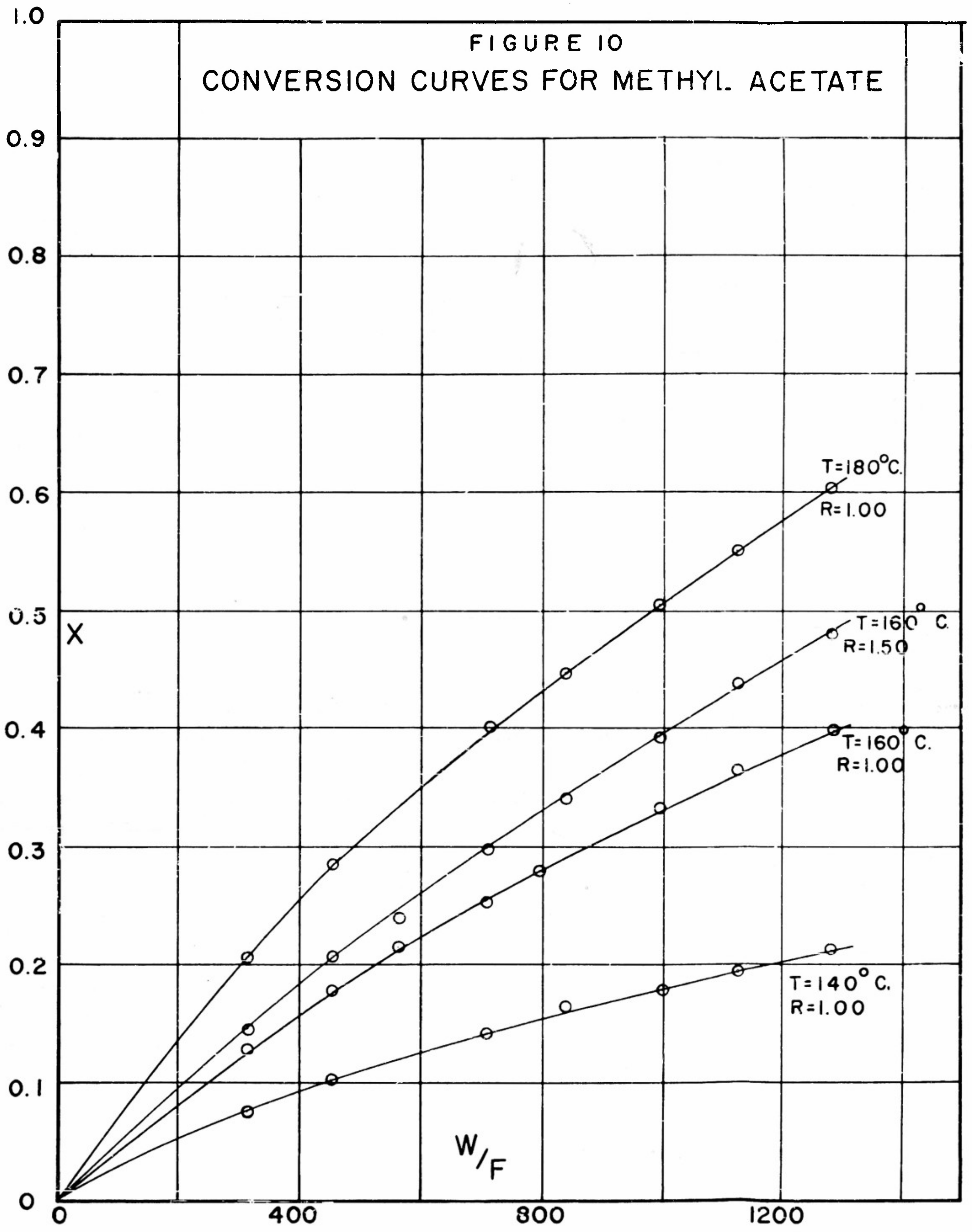

FIGURE 10

CONVERSION CURVES FOR METHYL ACETATE

boilers. In spite of the fact that a complete material balance was not made on the methyl acetate, the above information strongly indicates that side reactions could be neglected; this, then, was the assumption which was made.

A very poor method was set up to check catalyst activity during the methyl acetate runs. For each series of runs in Table XVII the last run in numerical sequence was considered a check run; if it fell on the integral curve in Figure 10 drawn through the other points in its series, the assumption was made that the catalyst had not lost any activity. This was always the case; unfortunately, when some of the first methyl acetate runs were repeated as a further check, the data could not be reproduced. Finally ethyl alcohol and acetic acid were fed to the reactor in an attempt to reproduce Stusiak's data; the conversions came out to be about one-half of Stusiak's values. Table XIX lists these repeat runs for both methyl and ethyl acetate; a glance at the table will show that the catalyst had been poisoned, just exactly when and how it was poisoned was impossible to determine. It was at this point that the reactor and operating procedures were remodeled and a new catalyst bed made from the Harshaw catalyst. Therefore, the methyl acetate data is presented for what it is worth; it is unreliable since the catalyst activity changed during the performance of the experiments. However, it does give some idea of the magnitude of the conversions obtained in the vapor phase esterification of methanol and acetic acid to form methyl acetate using a tungstic oxide catalyst.

TABLE XVIII.

Material Balance

Methyl Acetate

Run No.	T	R	% Acid Recovery Thru Saponification
12	160	1.5009	96.0%
13	160	1.5000	91.4
17	180	1.000	99.2
18	180	1.000	94.7
23	180	1.0001	105.2
24	140	1.0002	101.0
25	140	0.9994	99.5
35	160	1.0000	99.2

Ethyl Acetate

Run No.	T	R	% Acid Recovery Thru Saponification
1	160	1.0001	98.4

TABLE XIX.

Repeat Runs

Methyl Acetate

Date	Run No.	T	W/F_{A_o}	R	X
3/24/53	7	160	995.3	0.9975	0.333
5/26/53	32	160	997.3	0.9996	0.281
5/28/53	33	160	995.6	1.0000	0.250
6/1/53	34	160	997.2	1.0000	0.250
6/2/53	35	160	997.7	1.0000	0.260
4/7/53	13	160	997.1	1.5000	0.393
5/25/53	31	160	996.4	1.5003	0.341
5/12/53	29	140	1280.7	0.9994	0.213
6/9/53	36	140	1281.1	0.9998	0.196

Ethyl Acetate

Date	Run No.	T	W/F_{A_o}	R	X
6/4/53	1	160	998.8	1.0001	0.174
6/5/53	2	160	996.1	1.0005	0.168
M. Stusiak		160	998.0	1.003	0.360

A kinetic analysis was made of the methyl acetate data even though it was unreliable. The same procedures were followed as in the case of the other esters. Diffusion through a gas film on the surface of the catalyst, diffusion inside the catalyst particle, desorption of the product, and adsorption of acetic acid can all be eliminated as rate controlling steps for the same reasons that they were eliminated in the case of the esters previously considered. Only adsorption of methanol and a surface reaction are left as possible mechanisms. The constants, k_B, K_A, and K_R, for adsorption of methanol controlling are listed in Table XX; they are negative which eliminates this mechanism. Therefore, only a surface reaction is possible.

As in the case of ethyl acetate, propyl acetate, and butyl acetate, an attempt was made to fit the methyl acetate data to the rate equation: $r = \frac{k\, a_A\, a_B}{1 + m\, a_A^2}$ rather than trying to solve the complete equation for a surface reaction. Table XX lists the constants k and m for this simplified rate expression while Table XXI compares the calculated values of W/F_{A_o} to the experimental values of W/F_{A_o} for the methyl acetate. Figure 11 gives a visual comparison of the two values of W/F_{A_o}. Examination of Tables XX and XXI and Figure 11 will show that the methyl acetate data correlated as well as the other esters. Note that the constant m at 140°C is negative which is a radical change in behavior from the other esters. This negative constant and the

TABLE XX.

Constants for Methyl Acetate

Mechanism	Temp. °C.	k_B	K_A	K_R
Adsorption of Alcohol	180	0.001250	-0.29739	-0.04443
	160	0.0006877	-0.50364	0.68661
	140	0.003161	-0.001489	151.59
Surface Reaction		k	m	
	180	0.011658	15.4036	
	160	0.006094	16.0153	
	140	0.0005209	-6.6689	

TABLE XXI.

Calculated Values of W/F_{A_o} from Equation (36)

Methyl Acetate

T = 180°C.; R = 1.00

Run No.	W/F_{A_o} Exp.	W/F_{A_o} Calc.	% Diff.
22	1280.4	1297.3	+1.32
21	1125.9	1120.5	
20	995.5	975.8	-1.98
19	840.0	822.1	
18	711.5	719.3	+1.10
17	456.5	474.8	
23	315.7	326.8	+3.52
T = 160°C.; R = 1.50			
16	1280.2	1275.9	-0.33
11	1124.9	1137.5	
13	997.1	994.8	-0.23
12	839.2	840.0	
15	711.2	716.5	+0.74
14	564.9	562.1	
9	456.1	481.2	+5.50
10	316.3	328.8	+3.95

TABLE XXI. (continued)

T = 160°C.; R = 1.00

Run No.	W/F_{A_o} Exp.	W/F_{A_o} Calc.	% Diff.
1	1284.8	1250.9	-2.63
6	1126.4	1108.0	
7	995.3	991.8	-0.35
2	797.4	802.6	
8	710.8	713.3	+0.35
3	566.7	593.0	
4	457.4	481.0	+5.15
5	316.2	339.7	+7.43

T = 140°C.; R = 1.00

29	1280.7	1286.0	+0.41
28	1128.3	1112.1	
27	997.2	992.9	-0.43
26	839.9	865.3	
25	710.8	704.3	-0.91
24	457.2	456.7	
30	316.2	311.2	-1.58

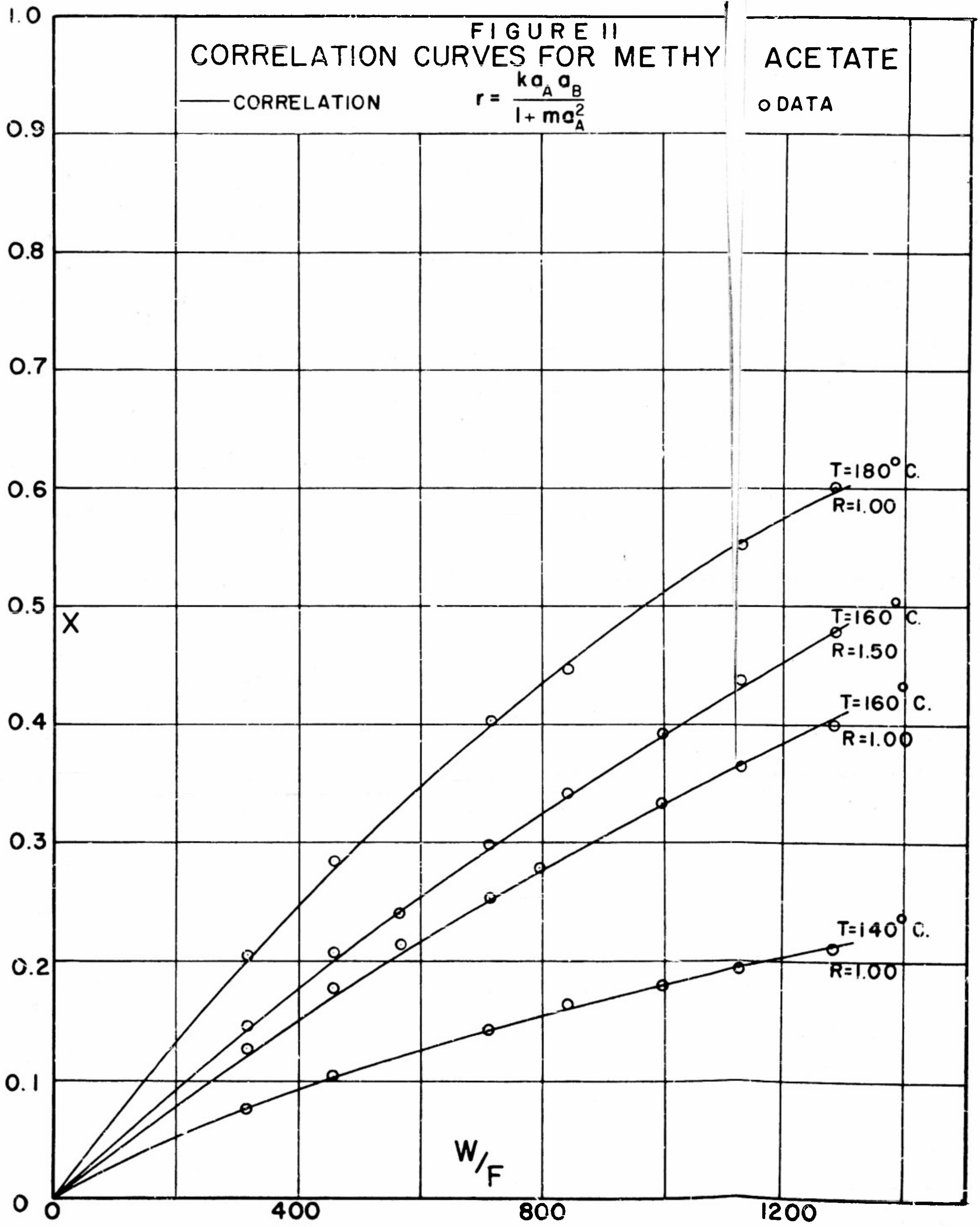

FIGURE 11
CORRELATION CURVES FOR METHY ACETATE

very low values for the conversions at 140°C. strongly hint that the catalyst began to be poisoned during the 140°C. runs, which were the last of the methyl acetate series, and not during any of the previous runs. However, it was felt that this behavior was not strong enough proof to justify assuming a constant catalyst activity for the 180°C. and 160°C. runs, and then trying to correct the 140°C. runs for loss in catalyst activity. Therefore, the methyl acetate data and correlation are presented just as they were observed.

It appears that a surface reaction controls; any other mechanism can be disproved. The simplified surface reaction equation $r = \frac{k\, a_A\, a_B}{1 + m\, a_A^2}$ correlates the data within 10% which points to the surface reaction and again shows that kinetic data can be correlated with simple expressions. Finally, the relationship among the constants still holds; the values of k for methyl acetate are similar to those for the other esters except at 140°C. where the methyl acetate data may be unreliable.

SUMMARY

1) Tungstic oxide carried on porous alumina cylinders was used to esterify acetic acid and methyl, ethyl, n-propyl, and n-butyl alcohol in the vapor phase.

2) A bench-scale apparatus was used for carrying out the reactions. A continuous-flow, packed tubular reactor was employed.

3) Kinetic data were obtained at 140°C., 150°C., 160°C., and 180°C. and with mole ratios of alcohol to acid of 1.50, 1.00, 0.75 and 0.50.

4) From analysis of the data it appears that a surface reaction is the rate-controlling step.

5) A pseudo-rate equation was determined that reproduced the data. This equation was

$$r = \frac{k\, a_A\, a_B}{1 + m\, a_A^2}$$

The rate equation was a simplification of the true surface reaction rate equation; any more complicated equation than the one above did not improve the correlation. The pseudo-rate equation also showed that kinetic data can be correlated by simpler expressions than those predicted by theory.

NOMENCLATURE

a = activity.

a, b, c = empirical constants.

A = composition of acid; wt. % acid.

B = composition of acid; wt. % alcohol.

C = water feed rate; g. moles water/g. mole acid feed.

d = density of alcohols; g./cc.

D = diameter, cm.

D = deviation in least squares.

F = feed rate; g.moles/hr.

f = fugacity.

G = mass velocity; lbs./(hr.)(sq.ft.).

h = depth of bed; cm.

K = overall equilibrium constant.

K_A, K_B, K_R, K_S = adsorption equilibrium constants for acetic acid, alcohol, water, and ester, respectively.

K_X = equilibrium constant for association of HOAc into $(HOAc)_2$.

k = empirical correlation constant.

k = reaction velocity constant

L = length, mm.

L = total number of active centers, g.moles/g.catalyst.

m = empirical correlation constant.

N = number of g.moles/hr.

N = normality.

n = empirical correlation constant.
n^D = refractive index; sodium D line.
o = empirical correlation constant.
P = total pressure, atm.
p = partial pressure, atm.
r = rate of reaction, g.moles/(g.catalyst)(hr.)
R = molal ratio of alcohol to acid in feed.
s = number of neighboring sites when surface is bare.
s = empirical correlation constant.
S_V = space velocity of acid feed, vol. of acid/(vol. of cat. bed)(hr.).
T = temperature, °C, °A.
T = symbol for mathematical grouping of terms in a flow equation.
V = volume of packed bed, cc.
w = mass flow rate, gr./hr.
W = mass of oven dried catalyst, g.
X = fraction of acid in feed converted, g.moles acid converted÷g. mole acid fed.
y = mole fraction
Y = symbol for mathematical grouping of terms in a flow equation.
Z = symbol for mathematical grouping of terms in a flow equation.

α = external void fraction.
γ = internal void fraction
ρ = density, g./cc.
π = total pressure.

Subscripts:

A = acetic acid.

A_2 = acetic acid dimer.

B = alcohol

R = water

S = ester

b = bulk

c = solid

i = any one value in a set

o = initial conditions

OBS. = observed - timed product flow rate

p = particle

T = total

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APPENDIX A

Conversion Based on Analysis of Product for Acid

Ethyl Acetate

Run #	1	2	3	4	5	6
Date	11-23-53	11-23-53	11-25-53	11-25-53	11-25-53	11-27-53
T	160	160	160	160	160	160
P	0.9472	0.9472	0.9613	0.9613	0.9613	0.9759
w_{A_o}	131.0	155.5	183.6	231.0	285.9	413.2
w_{B_o}	100.3	119.0	140.7	177.0	219.2	315.6
w	231.3	274.5	324.3	408.0	505.1	728.8
$w_{OBS.}$	232.5	270.2	325.2	392.7	497.5	710.7
Error	+0.52%	-1.57%	+0.28%	-3.75%	-1.50%	-2.48%
N	0.4871	0.4871	0.4735	0.4735	0.4735	0.4851
A	99.64%	99.64%	99.73%	99.73%	99.73%	99.81%
B	100%	100%	100%	100%	100%	100%
F_{A_o}	2.1736	2.5801	3.0491	3.8363	4.7480	6.8676
F_{B_o}	2.1772	2.5831	3.0542	3.8421	4.7582	6.8507
R	1.0017	1.0011	1.0017	1.0015	1.0021	0.9975
W/F_{A_o}	1024.1	862.7	730.0	580.2	468.8	324.1
G	21.88	25.97	30.68	38.60	47.79	68.96
Conv.	0.364	0.306	0.277	0.226	0.190	0.137

Ethyl Acetate

Run #	7	8	9	10	11	12
Date	11-30-53	11-30-53	11-30-53	12-1-53	12-1-53	12-2-53
T	160	160	160	180	180	180
P	0.9762	0.9762	0.9762	0.9666	0.9666	0.9667
w_{A_o}	102.0	116.0	131.0	131.0	155.5	183.6
w_{B_o}	77.9	88.6	100.1	100.4	119.1	140.7
w	179.9	204.6	231.1	231.4	274.6	324.3
$w_{OBS.}$	178.2	204.4	227.0	228.0	273.0	320.6
Error	-0.94%	-0.10%	-1.77%	-1.26%	-0.58%	-1.14%
N	0.4883	0.4883	0.4883	0.4733	0.4733	0.4713
A	99.54%	99.54%	99.54%	99.86%	99.86%	99.62%
B	100%	100%	100%	100%	100%	100%
F_{A_o}	1.6907	1.9228	2.1714	2.1784	2.5858	3.0457
F_{B_o}	1.6914	1.9232	2.1729	2.1794	2.5853	3.0542
R	1.0004	1.0002	1.0007	1.0005	0.9998	1.0028
W/F_{A_o}	1316.6	1157.6	1025.1	1021.8	860.8	730.8
G	17.02	19.36	21.87	21.89	25.98	30.68
Conv.	0.444	0.396	0.358	0.646	0.589	0.532

Ethyl Acetate

Run #	13	14	15	16	17	18
Date	12-2-53	12-3-53	12-3-53	12-4-53	12-5-53	12-5-53
T	180	180	180	180	180	180
P	0.9667	0.9557	0.9557	0.9457	0.9676	0.9676
w_{A_o}	231.0	285.9	413.2	565.8	102.0	116.0
w_{B_o}	177.0	218.6	315.9	432.2	78.1	88.8
w	408.0	504.5	729.1	998.0	180.1	204.8
$w_{OBS.}$	401.3	510.3	724.5		176.7	203.4
Error	-1.64%	+1.03%	-0.63%		-1.89%	-0.39%
N	0.4713	0.4606	0.4606	0.4975	0.4803	0.4803
A	99.62%	99.65%	99.65%	99.58%	99.81%	99.81%
B	100%	100%	100%	100%	100%	100%
F_{A_o}	3.8320	4.7442	6.8566	9.3823	1.6953	1.9280
F_{B_o}	3.8421	4.7452	6.8573	9.3818	1.6953	1.9280
R	1.0026	1.0002	1.0001	0.9999	1.0000	1.0000
W/F_{A_o}	580.9	469.2	324.6	237.2	1313.0	1154.5
G	38.60	47.79	68.98	94.43	17.04	19.38
Conv.	0.444	0.399	0.299	0.223	0.708	0.673

Ethyl Acetate

Run #	19	20	21	22	23	24
Date	12-6-53	12-22-53	1-14-54	1-14-54	1-16-54	1-16-54
T	160	160	160	160	160	160
P	0.9597	0.9824	0.9650	0.9650	0.9800	0.9800
w_{A_o}	131.0	131.0	131.0	131.0	102.0	116.0
w_{B_o}	100.3	100.3	100.4	150.5	117.3	133.3
w	231.3	231.3	231.4	281.5	219.3	249.3
$w_{OBS.}$	230.4	228.9	231.4	280.2	217.8	251.8
Error	-0.30%	-1.04%	0%	-0.50%	-0.68%	+1.00%
N	0.4801	0.4624	0.4822	0.4822	0.4828	0.4828
A	99.80%	99.74%	99.75%	99.75%	99.72%	99.72%
B	100%	99.9%	99.9%	99.9%	99.9%	99.9%
F_{A_o}	2.1771	2.1758	2.1760	2.1760	1.6938	1.9263
F_{B_o}	2.1772	2.1757	2.1772	3.2636	2.5437	2.8907
R	1.0000	1.0000	1.0006	1.4998	1.5018	1.5006
W/F_{A_o}	1022.4	1023.0	1022.9	1022.9	1314.1	1155.5
G	21.88	21.88	21.89	26.63	20.75	23.59
Conv.	0.365	0.362	0.364	0.413	0.497	0.455

Ethyl Acetate

Run #	25	26	27	28	29	30
Date	1-17-54	1-17-54	1-18-54	1-18-54	1-18-54	1-20-54
T	160	160	160	160	160	180
P	0.9834	0.9834	0.9638	0.9638	0.9638	0.9779
w_{A_o}	155.5	183.6	231.0	285.9	413.2	102.0
w_{B_o}	178.6	211.0	265.4	328.5	474.4	117.3
w	334.1	394.6	496.4	614.4	887.6	219.3
$w_{OBS.}$	333.3	399.2	501.4	614.8	896.5	217.7
Error	-0.24%	+1.17%	+1.01%	+0.07%	+1.03%	-0.73%
N	0.4853	0.4853	0.4670	0.4670	0.4670	0.4675
A	99.76%	99.76%	99.63%	99.63%	99.63%	99.82%
B	99.9%	99.9%	99.9%	99.9%	99.9%	99.8%
F_{A_o}	2.5832	3.0500	3.8324	4.7433	6.8552	1.6955
F_{B_o}	3.8733	4.5756	5.7553	7.1236	10.2875	2.5411
R	1.4994	1.5002	1.5017	1.5018	1.5007	1.4987
W/F_{A_o}	861.7	729.8	580.8	469.3	324.7	1312.8
G	31.61	37.34	46.97	58.17	83.96	20.75
Conv.	0.360	0.316	0.272	0.220	0.154	0.841

Ethyl Acetate

Run #	31	32	33	34	35	36
Date	1-20-54	1-21-54	1-21-54	1-22-54	1-22-54	1-26-54
T	180	180	180	180	180	180
P	0.9779	0.9939	0.9939	0.9839	0.9839	0.9805
w_{A_o}	116.0	131.0	155.5	183.6	231.0	285.9
w_{B_o}	133.3	150.6	178.7	211.1	265.6	328.8
w	249.3	281.6	334.2	394.7	496.6	614.7
$w_{OBS.}$	248.9	284.3	336.4	396.7	493.0	621.7
Error	-0.16%	+0.96%	+0.66%	+0.51%	-0.72%	+1.14%
N	0.4675	0.4804	0.4804	0.5037	0.5037	0.4487
A	99.82%	99.76%	99.76%	99.71%	99.71%	99.75%
B	99.8%	99.8%	99.8%	99.8%	99.8%	99.8%
F_{A_o}	1.9282	2.1762	2.5832	3.0485	3.8350	4.7490
F_{B_o}	2.8878	3.2625	3.8713	4.5710	5.7539	7.1230
R	1.4977	1.4992	1.4986	1.4994	1.5004	1.4999
W/F_{A_o}	1154.4	1022.8	861.7	730.2	580.4	468.7
G	23.59	26.64	31.62	37.35	46.99	58.16
Conv.	0.795	0.760	0.684	0.634	0.540	0.472

Ethyl Acetate

Run #	37	38	39	40	41	42
Date	1-26-54	1-27-54	1-27-54	1-28-54	1-28-54	1-29-54
T	180	160	160	160	160	160
P	0.9805	0.9804	0.9804	0.9782	0.9782	0.9709
w_{A_o}	413.2	131.0	131.0	102.0	116.0	155.5
w_{B_o}	475.2	75.4	100.5	58.7	66.7	89.5
w	888.4	206.4	231.5	160.7	182.7	245.0
$w_{OBS.}$	898.6	207.8	229.0	158.3	181.9	248.1
Error	+1.15%	+0.68%	-1.08%	-1.49%	-0.44%	+1.26%
N	0.4487	0.4767	0.4767	0.4714	0.4714	0.4833
A	99.75%	99.85%	99.85%	99.82%	99.82%	99.82%
B	99.8%	99.8%	99.8%	99.8%	99.8%	99.8%
F_{A_o}	6.8635	2.1782	2.1782	1.6955	1.9282	2.5848
F_{B_o}	10.2946	1.6334	2.1772	1.2717	1.4450	1.9389
R	1.4999	0.7499	0.9995	0.7500	0.7494	0.7501
W/F_{A_o}	324.3	1021.9	1021.9	1312.8	1154.4	861.1
G	84.06	19.53	21.90	15.20	17.29	23.18
Conv.	0.341	0.310	0.371	0.340	0.315	0.264

Ethyl Acetate

Run #	43	44	45	46	47	48
Date	1-31-54	1-31-54	2-1-54	2-1-54	2-2-54	2-2-54
T	160	160	160	160	160	160
P	0,9796	0.9796	0.9680	0.9680	0.9634	0.9634
w_{A_o}	183.6	231.0	285.9	413.2	116.0	131.0
w_{B_o}	105.7	132.9	164.5	237.7	66.7	75.4
w	289.3	363.9	450.4	650.9	182.7	206.4
$w_{OBS.}$	293.0	366.8	456.1	659.1	181.4	209.5
Error	+1.28%	+0.77%	+1.27%	+1.26%	-0.71%	+1.50%
N	0.4848	0.4848	0.4728	0.4728	0.4803	0.4803
A	99.69%	99.69%	99.75%	99.75%	99.80%	99.80%
B	99.8%	99.8%	99.8%	99.8%	99.8%	99.8%
F_{A_o}	3.0479	3.8347	4.7490	6.8635	1.9278	2.1771
F_{B_o}	2.2898	2.8791	3.5637	5.1494	1.4450	1.6334
R	0.7513	0.7508	0.7504	0.7503	0.7496	0.7503
W/F_{A_o}	730.3	580.5	468.7	324.3	1154.6	1022.4
G	27.37	34.43	42.62	61.59	17.29	19.53
Conv.	0.239	0.202	0.176	0.139	0.312	0.297

Ethyl Acetate

Run #	49	50	51	52	53	54
Date	2-3-54	2-3-54	12-3-54	2-3-54	2-4-54	2-4-54
T	180	180	180	180	180	180
P	0.9657	0.9657	0.9657	0.9657	0.9670	0.9670
w_{A_o}	102.0	116.0	131.0	155.5	183.6	231.0
w_{B_o}	58.7	66.7	75.4	89.5	105.5	132.7
w	160.7	182.7	206.4	245.0	289.1	363.7
$w_{OBS.}$	160.2	182.3	204.3	247.0	289.3	363.6
Error	-0.31%	-0.22%	-1.02%	+0.82%	+0.07%	-0.03%
N	0.4610	0.4610	0.4610	0.4610	0.4886	0.4886
A	99.75%	99.75%	99.75%	99.75%	99.66%	99.66%
B	99.8%	99.8%	99.8%	99.8%	99.8%	99.8%
F_{A_o}	1.6943	1.9268	2.1760	2.5829	3.0470	3.8336
F_{B_o}	1.2717	1.4450	1.6334	1.9389	2.2855	2.8748
R	0.7506	0.7499	0.7506	0.7507	0.7501	0.7499
W/F_{A_o}	1313.8	1155.2	1022.9	861.8	730.5	580.6
G	15.20	17.29	19.53	23.18	27.35	34.41
Conv.	0.532	0.507	0.488	0.455	0.422	0.358

Ethyl Acetate

Run #	55	56	57	58	59	60
Date	2-4-54	2-5-54	2-5-54	2-8-54	3-25-54	3-26-54
T	180	180	180	160	160	140
P	0.9670	0.9708	0.9708	0.9643	0.9441	0.9759
w_{A_o}	285.9	413.2	565.8	131.0	131.0	102.0
w_{B_o}	164.4	237.6	325.4	100.5	100.5	78.4
w	450.3	650.8	891.2	231.5	231.5	180.4
$w_{OBS.}$	450.7	657.1	902.1	232.0	231.7	179.5
Error	+0.09%	+0.96%	+1.22%	+0.22%	+0.09%	-0.39%
N	0.4886	0.5346	0.5346	0.4792	0.4722	0.4828
A	99.66%	99.80%	99.80%	99.78%	99.77%	99.77%
B	99.8%	99.8%	99.8%	99.8%	99.8%	99.6%
F_{A_o}	4.7447	6.8669	9.4030	2.1766	2.1764	1.6946
F_{B_o}	3.5615	5.1473	7.0493	2.1772	2.1772	1.6950
R	0.7506	0.7496	0.7497	1.0003	1.0004	1.0002
W/F_{A_o}	469.1	324.1	236.7	1022.7	1022.7	1313.5
G	42.61	61.58	84.32	21.90	21.90	17.07
Conv.	0.311	0.256	0.196	0.355	0.372	0.244

Ethyl Acetate

Run #	61	62	63	64	65	66
Date	3-26-54	3-27-54	3-27-54	3-27-54	3-29-54	3-30-54
T	140	140	140	140	140	140
P	0.9759	0.9679	0.9679	0.9734	0.9734	0.9726
w_{A_o}	123.0	155.5	206.0	285.9	413.2	102.0
w_{B_o}	94.5	119.5	158.3	219.8	317.6	117.7
w	217.5	275.0	364.3	505.7	730.8	219.7
$w_{OBS.}$	215.5	274.9	363.2	509.3	727.1	216.9
Error	-0.92%	-0.04%	-0.30%	+0.85%	-0.43%	-1.27%
N	0.4828	0.4786	0.4786	0.4950	0.4950	0.4685
A	99.77%	99.73%	99.73%	99.81%	99.81%	99.77%
B	99.6%	99.6%	99.6%	99.6%	99.6%	99.6%
F_{A_o}	2.0435	2.5824	3.4211	4.7518	6.8676	1.6946
F_{B_o}	2.0431	2.5836	3.4225	4.7521	6.8665	2.5447
R	0.9998	1.0005	1.0004	1.0001	0.9998	1.5017
W/F_{A_o}	1089.3	862.0	650.6	468.4	324.1	1313.5
G	20.58	26.02	34.47	47.85	69.15	20.79
Conv.	0.217	0.190	0.148	0.131	0.091	0.299

Ethyl Acetate

Run #	67	68	69	70	71	72
Date	3-30-54	3-30-54	3-30-54	3-31-54	3-31-54	4-1-54
T	140	140	140	140	140	160
P	0.9726	0.9726	0.9726	0.9751	0.9751	0.9695
w_{A_o}	123.0	155.5	206.0	285.9	413.2	131.0
w_{B_o}	141.9	179.4	237.6	329.1	476.2	100.6
w	264.9	334.9	443.6	615.0	889.4	231.6
$w_{OBS.}$	263.7	334.2	443.7	619.3	888.2	227.9
Error	-0.45%	-0.21%	+0.02%	+0.70%	-0.07%	-1.60%
N	0.4685	0.4685	0.4685	0.4908	0.4908	0.4852
A	99.77%	99.77%	99.77%	99.77%	99.77%	99.73%
B	99.6%	99.6%	99.6%	99.6%	99.6%	99.6%
F_{A_o}	2.0435	2.5835	3.4225	4.7499	6.8649	2.1756
F_{B_o}	3.0679	3.8787	5.1370	7.1152	10.2955	2.1750
R	1.5013	1.5013	1.5009	1.4980	1.4997	0.9997
W/F_{A_o}	1089.3	861.6	650.4	468.6	324.2	1023.1
G	25.06	31.69	41.97	58.19	84.15	21.91
Conv.	0.256	0.214	0.173	0.132	0.098	0.377

Conversion Based on Analysis of Product for Acid

Propyl Acetate

Run #	1	2	3	4	5	6
Date	12-9-53	12-9-53	12-10-53	12-10-53	12-14-53	12-14-53
T	160	160	160	160	160	160
P	0.9694	0.9694	0.9576	0.9576	0.9716	0.9716
w_{A_o}	130.0	152.0	176.7	223.6	276.0	407.5
w_{B_o}	129.7	151.6	176.5	223.4	275.8	407.2
w	259.7	303.6	353.2	447.0	551.8	814.7
$w_{CBS.}$	259.8	304.9	350.7	444.0	550.2	
Error	+0.04%	+0.43%	-0.71%	-0.67%	-0.24%	
N	0.4784	0.4784	0.4683	0.4683	0.4821	0.4821
A	99.83%	99.83%	99.70%	99.70%	99.75%	99.75%
B	99.80%	99.80%	99.86%	99.86%	99.88%	99.88%
F_{A_o}	2.1611	2.5268	2.9336	3.7123	4.5845	6.7688
F_{B_o}	2.1540	2.5177	2.9330	3.7123	4.5849	6.7693
R	0.9967	0.9964	0.9998	1.0000	1.0001	1.0001
W/F_{A_o}	1030.0	880.9	758.8	599.6	485.5	328.8
G	24.57	28.73	33.42	42.29	52.21	77.08
Conv.	0.377	0.329	0.298	0.252	0.220	0.160

Propyl Acetate

Run #	7	8	9	10	11	12
Date	12-15-53	12-15-53	12-16-53	12-16-53	12-18-53	12-18-53
T	160	160	180	180	180	180
P	0.9879	0.9879	0.9872	0.9872	0.9655	0.9655
w_{A_o}	103.1	116.5	130.0	152.0	176.7	223.6
w_{B_o}	103.2	116.5	129.9	151.9	176.4	223.2
w	206.3	233.0	259.9	303.9	353.1	446.8
$w_{OBS.}$	206.0	230.4	258.9	305.6	352.4	447.4
Error	-0.15%	-1.12%	-0.38%	+0.56%	-0.20%	+0.13%
N	0.4536	0.4536	0.4682	0.4682	0.4650	0.4650
A	99.80%	99.80%	99.77%	99.77%	99.63%	99.63%
B	99.89%	99.89%	99.89%	99.89%	99.9%	99.9%
F_{A_o}	1.7134	1.9361	2.1598	2.5253	2.9316	3.7097
F_{B_o}	1.7154	1.9365	2.1592	2.5249	2.9325	3.7105
R	1.0012	1.0002	0.9997	0.9998	1.0003	1.0002
W/F_{A_o}	1299.1	1150	1030.6	881.4	759.3	600.0
G	19.52	22.05	24.59	28.75	33.41	42.28
Conv.	0.430	0.398	0.645	0.601	0.563	0.492

Propyl Acetate

Run #	13	1114	15	16	17	18
Date	12-19-53	12-19-53	12-19-53	12-20-53	12-20-53	2-13-54
T	180	180	180	180	180	160
P	0.9649	0.9649	0.9649	0.9568	0.9568	0.9579
w_{A_o}	276.0	407.5	576.1	103.1	116.5	130.0
w_{B_o}	275.8	407.2	575.6	103.0	116.4	130.1
w	551.8	814.7	1151.7	206.1	237.9	260.1
$w_{OBS.}$	551.9	814.0		205.4	229.9	261.1
Error	0%	-0.09%		-0.34%	-1.29%	+0.38%
N	0.4813	0.4813	0.4813	0.4900	0.4900	0.4721
A	99.74%	99.74%	99.74%	99.71%	99.71%	99.80%
B	99.9%	99.9%	99.9%	99.9%	99.9%	99.8%
F_{A_o}	4.5841	6.7681	9.5675	1.7119	1.9344	2.1605
F_{B_o}	4.5849	6.7693	9.5678	1.7118	1.9344	2.1606
R	1.0002	1.0002	1.0000	0.9999	1.0000	1.0000
W/F_{A_o}	485.6	328.9	232.7	1300.3	1150.6	1030.3
G	52.21	77.08	109.0	19.50	22.04	24.61
Conv.	0.431	0.323	0.230	0.685	0.661	0.366

Propyl Acetate

Run #	19	20	21	22	23	24
Date	2-13-54	2-14-54	2-14-54	2-14-54	2-15-54	2-15-54
T	160	160	160	160	160	160
P	0.9579	0.9562	0.9562	0.9562	0.9622	0.9622
w_{A_o}	130.0	152.0	176.7	223.6	276.0	407.5
w_{B_o}	97.6	114.0	132.6	167.8	207.1	305.8
w	227.6	266.0	309.3	391.4	483.1	713.3
$w_{OBS.}$	227.0	266.4	304.1	390.0	482.1	719.7
Error	-0.26%	+0.15%	-1.68%	+0.36%	-0.21%	+0.89%
N	0.4721	0.4932	0.4932	0.4932	0.4827	0.4827
A	99.80%	99.82%	99.82%	99.82%	99.68%	99.68%
B	99.8%	99.8%	99.8%	99.8%	99.8%	99.8%
F_{A_o}	2.1605	2.5266	2.9372	3.7167	4.5813	6.7641
F_{B_o}	1.6204	1.8932	2.2021	2.7867	3.4394	5.0785
R	0.7500	0.7493	0.7497	0.7498	0.7507	0.7508
W/F_{A_o}	1030.3	881.0	757.8	598.9	485.9	329.1
G	21.53	25.17	29.65	37.03	45.71	67.49
Conv.	0.314	0.285	0.263	0.229	0.198	0.140

Propyl Acatate

Run #	25	26	27	28	29	30
Date	2-18-54	2-18-54	2-19-54	2-19-54	2-22-54	2-22-54
T	160	160	160	160	160	160
P	0.9701	0.9701	0.9676	0.9676	0.9691	0.9691
w_{A_o}	103.1	116.5	103.1	116.5	130.0	152.0
w_{B_o}	77.4	87.4	154.8	174.9	195.2	227.7
w	180.5	203.9	257.9	291.4	325.2	379.7
$w_{OBS.}$	180.0	204.5	256.4	293.9	323.8	380.0
Error	-0.28%	+0.29%	-0.58%	+0.86%	-0.43%	-0.05%
N	0.4720	0.4720	0.4765	0.4765	0.4836	0.4836
A	99.79%	99.79%	99.80%	99.80%	99.57%	99.57%
B	99.8%	99.8%	99.8%	99.8%	99.8%	99.8%
F_{A_o}	1.7132	1.9359	1.7134	1.9361	2.1555	2.5203
F_{B_o}	1.2851	1.4521	2.5708	2.9046	3.2417	3.7815
R	0.7501	0.7501	1.5004	1.5002	1.5039	1.5004
W/F_{A_o}	1229.3	1149.8	1299.1	1149.7	1032.7	883.2
G	17.08	19.29	24.40	27.57	30.77	35.93
Conv.	0.371	0.348	0.488	0.441	0.405	0.356

Propyl Acetate

Run #	31	32	33	34	35	36
Date	2-22-54	2-23-54	2-23-54	2-24-54	2-24-54	2-25-54
T	160	160	160	160	160	180
P	0.9691	0.9655	0.9655	0.9570	0.9570	0.9630
w_{A_o}	176.7	276.0	407.5	130.0	223.6	103.1
w_{B_o}	264.7	414.2	611.6	130.1	335.6	77.4
w	441.4	690.2	1019.1	260.1	559.2	180.5
$w_{OBS.}$	436.1	686.5	1037.7	260.1	562.5	180.7
Error	-1.24%	-0.54%	+1.83%	0%	+0.59%	+0.11%
N	0.4836	0.4909	0.4909	0.4773	0.4773	0.4752
A	99.57%	99.74%	99.74%	99.77%	99.77%	99.82%
B	99.8%	99.8%	99.8%	99.8%	99.8%	99.8%
F_{A_o}	2.9298	4.5841	6.7681	2.1598	3.7149	1.7138
F_{B_o}	4.3960	6.8787	10.1570	2.1606	5.5734	1.2851
R	1.5004	1.5006	1.5007	1.0004	1.5003	0.7499
W/F_{A_o}	759.7	485.6	328.9	1030.6	599.2	1298.8
G	41.76	65.30	96.42	24.61	52.91	17.08
Conv.	0.325	0.227	0.164	0.371	0.266	0.574

Propyl Acetate

Run #	37	38	39	40	41	42
Date	2-25-54	2-25-54	2-27-54	2-27-54	2-27-54	2-28-54
T	180	180	180	180	180	180
P	0.9630	0.9630	0.9608	0.9608	0.9608	0.9657
w_{A_o}	116.5	130.0	152.0	176.7	223.6	276.0
w_{B_o}	87.4	97.6	114.0	132.6	167.8	207.1
w	203.9	227.6	266.0	309.3	391.4	483.1
$w_{OBS.}$	204.7	225.8	267.3	307.0	390.3	484.4
Error	+0.39%	+0.79%	+0.49%	-0.74%	-0.28%	+0.27%
N	0.4752	0.4752	0.4617	0.4617	0.4617	0.4750
A	99.82%	99.82%	99.76%	99.76%	99.76%	99.78%
B	99.8%	99.8%	99.7%	99.7%	99.7%	99.7%
F_{A_o}	1.9365	2.1609	2.5251	2.9354	3.7145	4.5859
F_{B_o}	1.4515	1.6209	1.8913	2.1999	2.7839	3.4359
R	0.7495	0.7501	0.7490	0.7494	0.7495	0.7492
W/F_{A_o}	1149.4	1030.1	881.5	758.3	599.2	485.4
G	19.29	21.53	25.17	29.27	37.03	45.71
Conv.	0.559	0.529	0.486	0.461	0.404	0.349

Propyl Acetate

Run #	43	44	45	46	47	48
Date	2-28-54	3-1-54	3-1-54	3-1-54	3-1-54	3-2-54
T	180	180	180	180	180	180
P	0.9657	0.9654	0.9654	0.9654	0.9654	0.9727
w_{A_o}	407.5	103.1	116.5	130.0	152.0	176.7
w_{B_o}	305.8	154.8	174.9	195.2	228.1	265.5
w	713.3	257.9	291.4	325.2	380.1	442.2
$w_{OBS.}$	709.7	255.5	290.8	326.9	380.0	446.9
Error	-0.50%	-0.93%	-0.21%	+0.53%	+0.08%	+1.25%
N	0.4750	0.4644	0.4644	0.4644	0.4644	0.4035
A	99.78%	99.67%	99.67%	99.67%	99.67%	99.79%
B	99.7%	99.7%	99.7%	99.7%	99.7%	99.7%
F_{A_o}	6.7709	1.7112	1.9336	2.1576	2.5228	2.9363
F_{B_o}	5.0734	2.5682	2.9017	3.2385	3.7777	4.4048
R	0.7493	1.5008	1.5007	1.5010	1.5000	1.5001
W/F_{A_o}	328.7	1300.8	1151.2	1031.7	882.3	758.1
G	67.49	24.40	27.56	30.77	35.96	41.84
Conv.	0.264	0.806	0.769	0.717	0.658	0.606

Propyl Acetate

Run #	49	50	51	52	53	54
Date	3-2-54	3-2-54	3-3-54	3-3-54	4-5-54	4-6-54
T	180	180	180	160	160	140
P	0.9726	0.9726	0.9776	0.9776	0.9682	0.9643
w_{A_o}	223.6	276.0	407.5	130.0	130.0	103.1
w_{B_o}	335.9	414.2	612.0	130.1	130.0	103.2
w	562.5	690.2	1019.5	260.1	260.0	206.3
$w_{OBS.}$	568.8	692.4		260.4	262.0	206.1
Error	+1.12%	+0.32%		+0.12%	+0.69%	-0.10%
N	0.4035	0.4035	0.4533	0.4533	0.4774	0.4812
A	99.79%	99.79%	99.75%	99.75%	99.76%	99.80%
B	99.7%	99.7%	99.7%	99.7%	99.9%	99.9%
F_{A_o}	3.7156	4.5864	6.7688	2.1594	2.1596	1.7134
F_{B_o}	5.5728	6.8719	10.1535	2.1584	2.1611	1.7156
R	1.4998	1.4983	1.5000	0.9995	1.0007	1.0013
W/F_{A_o}	599.1	485.3	328.8	1030.8	1030.7	1299.1
G	53.22	65.30	96.46	24.61	24.60	19.52
Conv.	0.529	0.444	0.336	0.371	0.372	0.252

Propyl Acetate

Run #	55	56	57	58	59	60
Date	4-6-54	4-6-54	4-7-54	4-7-54	4-7-54	4-8-54
T	140	140	140	140	140	140
P	0.9643	0.9643	0.9639	0.9639	0.9639	0.9855
w_{A_o}	123.0	152.0	200.0	276.0	407.5	103.1
w_{B_o}	123.1	152.0	200.0	275.9	407.4	154.6
w	246.1	304.0	400.0	551.9	814.9	257.7
$w_{OBS.}$	246.7	303.3	399.1	549.4	812.8	257.4
Error	+0.24%	-0.23%	-0.23%	-0.45%	-0.26%	-0.11%
N	0.4812	0.4812	0.5247	0.5247	0.5247	0.4785
A	99.80%	99.80%	99.78%	99.78%	99.78%	99.83%
B	99.9%	99.9%	99.9%	99.9%	99.9%	99.9%
F_{A_o}	2.0441	2.5261	3.3231	4.5859	6.7709	1.7139
F_{B_o}	2.0464	2.5268	3.3248	4.5865	6.7726	2.5701
R	1.0011	1.0003	1.0005	1.0001	1.0003	1.4996
W/F_{A_o}	1088.9	881.2	669.8	485.4	328.7	1298.7
G	23.29	28.76	37.85	52.22	77.10	24.38
Conv.	0.213	0.179	0.148	0.114	0.075	0.269

Propyl Acetate

Run #	61	62	63	64	65	66
Date	4-8-54	4-8-54	4-9-54	4-9-54	4-9-54	4-10-54
T	140	140	140	140	140	140
P	0.9855	0.9855	0.9717	0.9717	0.9717	0.9700
w_{A_o}	123.0	152.0	200.0	276.0	407.5	123.0
w_{B_o}	184.4	227.9	300.1	414.1	611.4	184.4
w	307.4	379.9	500.1	690.1	1018.9	307.4
$w_{OBS.}$	308.2	379.3	498.3	689.0	1018.3	306.1
Error	+0.26%	-0.16%	-0.36%	-0.16%	-0.06%	-0.42%
N	0.4785	0.4785	0.4867	0.4867	0.4867	0.4799
A	99.83%	99.83%	99.75%	99.75%	99.75%	99.73%
B	99.9%	99.9%	99.9%	99.9%	99.9%	99.9%
F_{A_o}	2.0447	2.5268	3.3221	4.5845	6.7688	2.0427
F_{B_o}	3.0655	3.7886	4.9888	6.8840	10.1639	3.0655
R	1.4992	1.4994	1.5016	1.5016	1.5016	1.5007
W/F_{A_o}	1088.6	880.9	670.0	485.5	328.8	1089.7
G	29.09	35.95	47.32	65.30	96.41	29.09
Conv.	0.237	0.193	0.165	0.125	0.090	0.231

Propyl Acetate

Run #	67	68
Date	4-10-54	4-12-54
T	140	160
P	0.9700	0.9859
w_{A_o}	152.0	130.0
w_{B_o}	227.9	130.0
w	379.9	260.0
$w_{OBS.}$	379.2	258.9
Error	-0.18%	-0.42%
N	0.4799	0.5130
A	99.73%	99.84%
B	99.9%	99.9%
F_{A_o}	2.5243	2.1613
F_{B_o}	3.7886	2.1611
R	1.5009	1.0001
W/F_{A_o}	881.8	1029.9
G	35.95	24.60
Conv.	0.198	0.374

Conversion Based on Analysis of Product for Acid

Butyl Acetate

Run #	1	2	3	4	5	6
Date	1-2-54	1-2-54	1-2-54	1-4-53	1-4-53	1-4-53
T	160	160	160	160	160	160
P	0.9572	0.9572	0.9572	0.9697	0.9697	0.9697
w_{A_o}	130.0	152.0	176.7	223.6	276.0	407.5
w_{B_o}	160.2	187.3	217.7	275.9	340.4	502.6
w	290.2	339.3	394.4	499.5	616.4	910.1
$w_{OBS.}$	389.1	339.0	394.5	498.7	633.2	890.6
Error	-0.38%	-0.09%	+0.03%	-0.16%	+1.44%	+0.60%
N	0.4825	0.4825	0.4825	0.4751	0.4751	0.4751
A	99.81%	99.86%	99.81%	99.73%	99.73%	99.73%
B	99.8%	99.8%	99.8%	99.8%	99.8%	99.8%
F_{A_o}	2.1607	2.5263	2.9369	3.7134	4.5836	6.7675
F_{B_o}	2.1613	2.5270	2.9371	3.7134	4.5834	6.7673
R	1.0003	1.0003	1.0000	1.0000	1.0000	1.0000
W/F_{A_o}	1030.2	881.1	757.9	599.4	485.6	328.9
G	27.46	32.10	37.32	47.76	58.32	86.11
Conv.	0.436	0.388	0.370	0.321	0.280	0.206

Butyl Acetate

Run #	7	8	9	10	11	12
Date	1-5-53	1-5-53	1-6-54	1-6-54	1-7-54	1-7-54
T	160	160	180	180	180	180
P	0.9646	0.9646	0.9746	0.9746	0.9632	0.9632
w_{A_o}	103.1	116.5	130.0	152.0	176.7	223.6
w_{B_o}	127.2	143.8	160.5	187.7	218.1	275.9
w	230.3	260.3	290.5	339.7	394.8	499.5
$w_{OBS.}$	230.2	260.3	292.2	339.5	397.7	502.4
Error	-0.04%	0%	+0.65%	+0.03%	+0.79%	+0.58%
N	0.4857	0.4857	0.4708	0.4708	0.4756	0.4756
A	99.77%	99.77%	99.76%	99.76%	99.69%	99.69%
B	99.8%	99.8%	99.7%	99.7%	99.7%	99.7%
F_{A_o}	1.7129	1.9355	2.1596	2.5251	2.9336	3.7119
F_{B_o}	1.7120	1.9354	2.1589	2.5248	2.9337	3.7112
R	0.9994	1.0000	0.9997	0.9999	1.0000	0.9998
W/F_{A_o}	1299.5	1150.0	1030.7	881.5	758.8	600.0
G	21.79	24.63	27.49	32.14	37.34	47.26
Conv.	0.516	0.483	0.727	0.683	0.643	0.578

Butyl Acetate

Run #	13	14	15	16	17	18
Date	1-8-54	1-8-54	1-11-54	1-11-54	1-12-54	1-12-54
T	180	180	180	180	180	180
P	0.9622	0.9622	0.9770	0.9770	0.9861	0.9861
w_{A_o}	276.0	407.5	103.1	116.5	337.2	487.3
w_{B_o}	340.7	503.1	127.4	143.9	416.3	601.6
w	616.7	910.6	230.5	260.4	753.5	1088.9
$w_{OBS.}$	632.2	885.5	234.5	261.8	756.4	
Error	+1.27%		+1.74%	+0.54%	+0.38%	
N	0.4603	0.4603	0.4737	0.4737	0.4728	0.4728
A	99.72%	99.72%	99.78%	99.78%	99.68%	99.68%
B	99.7%	99.7%	99.7%	99.7%	99.7%	99.7%
F_{A_o}	4.5831	6.7668	1.7131	1.9357	5.5983	8.0903
F_{B_o}	4.5828	6.7673	1.7137	1.9356	5.5986	8.0906
R	0.9999	1.0001	1.0004	1.0000	1.0001	1.0000
W/F_{A_o}	485.7	328.9	1299.3	1150.0	397.6	275.1
G	58.35	86.16	21.81	24.64	71.30	103.03
Conv.	0.514	0.360	0.778	0.746	0.433	0.333

Butyl Acetate

Run #	19	20	21	22	23	24
Date	3-5-54	3-8-54	3-8-54	3-8-54	3-9-54	3-9-54
T	160	160	160	160	160	160
P	0.9780	0.9717	0.9717	0.9717	0.9629	0.9629
w_{A_o}	130.0	103.1	116.5	130.0	152.0	176.7
w_{B_o}	161.1	95.8	108.3	120.8	141.3	164.2
w	291.1	198.9	224.8	250.8	293.3	340.9
$w_{OBS.}$	294.1	198.8	221.8	250.7	290.8	339.9
Error	+1.03%	-0.05%	-1.30%	-0.04%	-0.85%	-0.29%
N	0.4840	0.4690	0.4690	0.4690	0.4637	0.4637
A	99.70%	99.84%	99.84%	99.84%	99.75%	99.75%
B	99.4%	99.4%	99.4%	99.4%	99.4%	99.4%
F_{A_o}	2.1583	1.7141	1.9369	2.1613	2.5248	2.9351
F_{B_o}	2.1605	1.2847	1.4524	1.6200	1.8949	2.2020
R	1.0010	0.7495	0.7499	0.7495	0.7505	0.7502
W/F_{A_o}	1031.3	1298.6	1149.2	1029.9	881.6	758.4
G	27.54	18.82	21.27	23.73	27.75	32.26
Conv.	0.447	0.448	0.416	0.387	0.343	0.317

Butyl Acetate

Run #	25	26	27	28	29	30
Date	3-9-54	3-10-54	3-10-54	3-11-54	3-11-54	3-11-54
T	160	160	160	160	160	160
P	0.9629	0.9613	0.9613	0.9641	0.9641	0.9641
w_{A_o}	223.6	276.0	407.5	103.1	116.5	130.0
w_{B_o}	207.8	256.3	378.4	63.9	72.2	80.6
w	431.4	532.3	785.9	167.0	188.7	210.6
$w_{OBS.}$	428.9	526.7	781.1	166.7	187.6	210.6
Error	-0.60%	-1.05%	-0.61%	-0.18%	-0.58%	0%
N	0.4637	0.4787	0.4787	0.4729	0.4729	0.4729
A	99.75%	99.83%	99.83%	99.86%	99.86%	99.86%
B	99.4%	99.4%	99.4%	99.4%	99.4%	99.4%
F_{A_o}	3.7141	4.5882	6.7742	1.7144	1.9373	2.1618
F_{B_o}	2.7867	3.4372	5.0746	0.8569	0.9683	1.0809
R	0.7503	0.7491	0.7491	0.4998	0.4998	0.5000
W/F_{A_o}	599.3	485.1	328.6	1298.4	1149.0	1029.7
G	40.82	50.36	74.36	15.80	17.85	19.93
Conv.	0.269	0.232	0.171	0.383	0.349	0.321

Butyl Acetate

Run #	31	32	33	34	35	36
Date	3-12-54	3-12-54	3-12-54	3-13-54	3-13-54	3-14-54
T	160	160	160	160	160	160
P	0.9658	0.9658	0.9658	0.9678	0.9678	0.9738
w_{A_o}	152.0	176.7	223.6	276.0	407.5	130.0
w_{B_o}	94.1	109.4	138.4	170.3	251.4	160.6
w	246.1	286.1	362.0	446.3	658.9	290.6
$w_{OBS.}$	244.6	285.1	361.4	443.5	659.2	
Error	-0.61%	-0.35%	-0.17%	-0.63%	+0.05%	
N	0.4987	0.4987	0.4987	0.4929	0.4929	0.4713
A	99.79%	99.79%	99.79%	99.74%	99.74%	99.81%
B	99.7%	99.7%	99.7%	99.7%	99.7%	99.7%
F_{A_o}	2.5258	2.9363	3.7156	4.5841	6.7681	2.1607
F_{B_o}	1.2658	1.4716	1.8616	2.2907	3.3816	2.1603
R	0.5011	0.5012	0.5010	0.4997	0.4996	0.9998
W/F_{A_o}	881.3	758.1	599.1	485.6	328.9	1030.2
G	23.29	27.07	34.25	42.23	62.34	27.50
Conv.	0.298	0.270	0.234	0.206	0.149	0.441

Butyl Acetate

Run #	37	38	39	40	41	42
Date	3-15-54	3-15-54	3-15-54	3-15-54	3-16-54	3-17-54
T	180	180	180	180	180	180
P	0.9845	0.9845	0.9845	0.9845	0.9864	0.9745
w_{A_o}	103.1	116.5	130.0	152.0	176.7	223.6
w_{B_o}	95.5	108.0	120.5	140.6	163.8	207.0
w	198.9	224.5	250.5	292.6	340.5	430.6
$w_{OBS.}$	199.0	224.4	249.8	292.8	339.7	433.2
Error	-0.05%	-0.04%	-0.28%	-0.17%	-0.23%	+0.53%
N	0.4560	0.4560	0.4560	0.4560	0.4449	0.4679
A	99.62%	99.62%	99.62%	99.62%	99.81%	99.67%
B	99.7%	99.7%	99.7%	99.7%	99.7%	99.7%
F_{A_o}	1.7103	1.9326	2.1566	2.5215	2.9369	3.7112
F_{B_o}	1.2846	1.4527	1.6209	1.8912	2.2033	2.7844
R	0.7511	0.7517	0.7516	0.7500	0.7502	0.7503
W/F_{A_o}	1301.5	1151.8	1032.1	882.8	757.9	599.8
G	18.82	21.24	23.70	27.69	32.22	40.74
Conv.	0.631	0.611	0.589	0.560	0.532	0.485

Butyl Acetate

Run #	43	44	45	46	47	48
Date	3-17-54	3-17-54	3-18-54	3-18-54	3-22-54	3-22-54
T	180	180	180	180	180	180
P	0.9745	0.9745	0.9617	0.9617	0.9639	0.9639
w_{A_o}	276.0	407.5	103.1	116.5	130.0	152.0
w_{B_o}	255.6	377.0	63.6	71.8	80.3	93.8
w	531.6	784.5	166.7	188.3	210.3	245.8
$w_{OBS.}$	536.3	796.4	166.8	187.8	209.0	245.0
Error	+0.88%	+1.49%	+0.06%	-0.27%	-0.62%	-0.33%
N	0.4679	0.4679	0.4528	0.4528	0.4753	0.4753
A	99.67%	99.67%	99.73%	99.73%	99.81%	99.81%
B	99.7%	99.7%	99.8%	99.8%	99.8%	99.8%
F_{A_o}	4.5808	6.7634	1.7122	1.9347	2.1607	2.5263
F_{B_o}	3.4381	5.0711	0.8564	0.9668	1.0812	1.2630
R	0.7505	0.7498	0.5002	0.4997	0.5004	0.4999
W/F_{A_o}	485.9	329.1	1300.0	1150.0	1030.2	881.1
G	50.30	74.23	15.77	17.82	19.90	23.26
Conv.	0.432	0.349	0.480	0.452	0.444	0.417

Butyl Acetate

Run #	49	50	51	52	53	54
Date	3-19-54	3-19-54	3-20-54	3-20-54	3-23-54	3-23-54
T	180	180	180	180	180	180
P	0.9600	0.9600	0.9755	0.9755	0.9718	0.9718
w_{A_o}	176.7	223.6	276.0	407.5	576.1	576.1
w_{B_o}	108.9	137.8	170.3	251.4	533.1	355.4
w	285.6	361.4	446.3	658.9	1109.2	931.5
$w_{OBS.}$	282.6	361.9	443.3	650.6		
Error	-1.05%	+0.14%	-0.67%	-1.26%		
N	0.4754	0.4754	0.4806	0.4806	0.4941	0.4941
A	99.74%	99.74%	99.77%	99.77%	99.78%	99.78%
B	99.8%	99.8%	99.8%	99.8%	99.8%	99.8%
F_{A_o}	2.9348	3.7138	4.5854	6.7702	9.5722	9.5722
F_{B_o}	1.4633	1.8554	2.2930	3.3850	7.1780	4.7853
R	0.4986	0.4996	0.5001	0.5000	0.7499	0.4999
W/F_{A_o}	758.5	599.4	485.4	328.8	232.5	232.5
G	27.02	34.19	42.23	62.34	104.9	88.14
Conv.	0.405	0.373	0.343	0.273	0.262	0.219

Butyl Acetate

Run #	55	56	57	58	59	60
Date	3-24-54	4-13-54	4-14-54	4-14-54	4-14-54	4-15-54
T	160	160	150	150	150	150
P	0.9683	0.9676	0.9593	0.9593	0.9593	0.9529
w_{A_o}	130.0	130.0	103.1	123.0	152.0	200.0
w_{B_o}	160.4	161.0	127.6	152.2	188.1	247.4
w	290.4	291.0	230.7	275.2	340.1	447.4
$w_{OBS.}$	287.6	289.6	228.6	278.6	338.4	449.2
Error	-0.96%	-0.41%	-0.91%	+1.24%	-0.50%	+0.40%
N	0.4867	0.4788	0.4602	0.4602	0.4602	0.4803
A	99.80%	99.83%	99.75%	99.75%	99.75%	99.73%
B	99.8%	99.5%	99.5%	99.5%	99.5%	99.5%
F_{A_o}	2.1605	2.1611	1.7126	2.0431	2.5248	3.3215
F_{B_o}	2.1597	2.1613	1.7129	2.0432	2.5251	3.3211
R	0.9996	1.0001	1.0002	1.0000	1.0001	0.9999
W/F_{A_o}	1030.3	1030.0	1299.7	1089.4	881.6	670.1
G	27.48	27.53	21.83	26.04	32.18	42.33
Conv.	0.448	0.447	0.385	0.336	0.282	0.242

Butyl Acetate

Run #	61	62	63	64	65	66
Date	4-15-54	4-15-54	4-16-54	4-16-54	4-17-54	4-17-54
T	150	150	150	150	150	150
P	0.9529	0.9529	0.9667	0.9667	0.9549	0.9549
w_{A_o}	276.0	407.5	103.1	123.0	152.0	200.0
w_{B_o}	341.3	504.0	95.7	114.2	141.1	185.7
w	617.3	911.5	198.8	237.2	293.1	385.7
$w_{OBS.}$	612.4	907.0	196.7	237.0	292.1	386.2
Error	-0.79%	-0.49%	-1.06%	-0.08%	-0.34%	+0.13%
N	0.4803	0.4803	0.4820	0.4820	0.4803	0.4803
A	99.73%	99.73%	99.76%	99.76%	99.81%	99.81%
B	99.5%	99.5%	99.5%	99.5%	99.5%	99.5%
F_{A_o}	4.5836	6.7675	1.7127	2.0433	2.5263	3.3241
F_{B_o}	4.5817	6.7658	1.2847	1.5330	1.8942	2.4929
R	0.9996	0.9997	0.7501	0.7503	0.7498	0.7499
W/F_{A_o}	485.6	328.9	1299.6	1089.4	881.1	669.6
G	58.41	86.24	18.81	22.44	27.73	36.49
Conv.	0.184	0.134	0.356	0.312	0.265	0.228

Butyl Acetate

Run #	67	68	69
Date	4-20-54	4-20-54	4-21-54
T	150	150	160
P	0.9779	0.9779	0.9687
w_{A_o}	276.0	407.5	130.0
w_{B_o}	256.0	378.0	160.9
w	532.0	785.5	290.9
$w_{OBS.}$	530.8	786.4	289.9
Error	-0.23%	+0.11%	-1.03%
N	0.4654	0.4654	0.4990
A	99.66%	99.66%	99.84%
B	99.5%	99.5%	99.5%
F_{A_o}	4.5804	6.7627	2.1613
F_{B_o}	3.4366	5.0743	2.1600
R	0.7503	0.7503	0.9994
W/F_{A_o}	486.0	329.1	1029.9
G	50.34	74.32	27.52
Conv.	0.176	0.124	0.449

Conversion Based on Analysis of Product for Acid

Methyl Acetate

Run #	1	2	3	4	5	6
Date	3-2-53	3-5-53	3-18-53	3-19-53	3-20-53	3-23-53
T	160	160	160	160	160	160
P	0.9631	0.9735	0.9571	0.9687	0.9611	0.9614
w_{A_o}	102.0	164.0	231.0	285.9	413.2	116.0
w_{B_o}	54.3	87.2	122.9	152.1	219.8	61.7
w	156.3	251.2	353.9	438.0	633.0	177.7
$w_{OBS.}$			355.2	440.6	633.5	177.0
Error			+0.37	+0.59	+0.08	-0.39
N	0.4552	0.4642	0.4470	0.4646	0.4600	0.4635
A	99.44%	99.65%	99.54%	99.65%	99.75%	99.73%
F_{A_o}	1.6890	2.7214	3.8290	4.7442	6.8636	1.9265
F_{B_o}	1.6934	2.7227	3.8356	4.7469	6.8597	1.9259
R	1.0030	1.0005	1.002	1.001	0.9994	0.9997
W/F_{A_o}	1284.8	797.4	566.7	457.4	316.2	1126.4
G	14.8	23.8	33.5	41.4	59.9	16.8
Conv.	0.400	0.279	0.214	0.177	0.128	0.364

Methyl Acetate

Run #	7	8	9	10	11	12
Date	3-24-53	3-25-53	3-28-53	4-2-53	4-1-53	4-6-53
T	160	160	160	160	160	160
P	0.9679	0.9771	0.9713	0.9651	0.9687	0.9629
w_{A_o}	131.0	183.6	285.9	413.2	116.0	155.5
w_{B_o}	69.7	97.7	228.1	329.7	92.8	124.1
w	200.7	281.3	514.0	742.9	208.8	279.6
$w_{OBS.}$	199.0	279.1			208.8	275.2
Error	-0.86	-0.79			0	-1.57
N	0.4593	0.4586	0.4532	0.4573	0.4720	0.4639
A	99.95%	99.86%	99.93%	99.70%	99.86%	99.86%
F_{A_o}	2.1803	3.0530	4.7575	6.8601	1.9290	2.5858
F_{B_o}	2.1749	3.0482	7.1188	10.2896	2.8953	3.8730
R	0.9975	0.9984	1.4963	1.4999	1.5009	1.4978
W/F_{A_o}	995.3	710.8	456.1	316.3	1124.9	839.2
G	19.0	26.6	48.3	70.3	19.8	26.5
Conv.	0.333	0.252	0.207	0.145	0.436	0.341

Methyl Acetate

Run #	13	14	15	16	17	18
Date	4-7-53	4-8-53	4-11-53	4-13-53	4-15-53	4-21-53
T	160	160	160	160	180	180
P	0.9658	0.9625	0.9683	0.9687	0.9603	0.9566
w_{A_o}	131.0	231.0	183.6	102.0	285.9	183.6
w_{B_o}	104.6	184.7	146.7	81.5	152.3	97.7
w	235.6	415.7	330.3	183.5	438.2	281.3
$w_{OBS.}$	234.0	412.6	328.1	181.5	434.0	280.7
Error	-0.68%	-0.75%	-0.67%	-1.08%	-0.96%	-0.21%
N	0.4561	0.4606	0.4511	0.4606	0.4600	0.4537
A	99.76%	99.86%	99.79%	99.80%	99.84%	99.75%
F_{A_o}	2.1763	3.8413	3.0509	1.6951	4.7533	3.0497
F_{B_o}	3.2645	5.7643	4.5784	2.5426	4.7531	3.0497
R	1.5000	1.5006	1.5007	1.5000	1.0000	1.0000
W/F_{A_o}	997.1	564.9	711.2	1260.2	456.5	711.5
G	22.3	39.3	31.3	17.4	41.5	26.6
Conv.	0.393	0.239	0.297	0.479	0.286	0.403

Methyl Acetate

Run #	19	20	21	22	23	24
Date	4-23-53	4-24-53	4-27-53	4-27-53	4-29-53	4-30-53
T	180	180	180	180	180	140
P	0.9671	0.9571	0.9633	0.9633	0.9608	0.9514
w_{A_o}	155.5	131.0	116.0	102.0	413.2	285.9
w_{B_o}	82.7	69.9	61.7	54.3	220.3	152.1
w	238.2	200.9	177.7	156.3	633.5	438.0
$w_{OBS.}$		201.1			636.8	434.9
Error		+0.13			+0.52	-0.71
N	0.4610	0.4632	0.4524	0.4524	0.4624	0.4679
A	99.76%	99.33%	99.78%	99.78%	99.91%	99.69%
F_{A_o}	2.5832	2.1799	1.9274	1.6948	6.8745	4.7461
F_{B_o}	2.5819	2.1800	1.9268	1.6934	6.8754	4.7469
R	1.0005	1.0000	0.9997	0.9992	1.0001	1.0002
W/F_{A_o}	840.0	995.5	1125.9	1280.4	315.7	457.2
G	22.5	19.0	16.8	14.8	59.9	41.4
Conv.	0.446	0.504	0.552	0.603	0.205	0.103

Methyl Acetate

Run #	25	26	27	28	29	30
Date	5-5-53	5-6-53	5-7-53	5-11-53	5-12-53	5-13-53
T	140	140	140	140	140	140
P	0.9714	0.9671	0.9659	0.9618	0.9753	0.9808
w_{A_o}	183.6	155.5	131.0	116.0	102.0	413.2
w_{B_o}	97.9	82.7	69.7	61.6	54.3	219.9
w	281.5	238.3	200.7	177.6	156.3	633.1
$w_{OBS.}$		237.1				634.9
Error		-0.49				+0.28
N	0.4731	0.4629	0.4647	0.4588	0.4575	0.4607
A	99.86%	99.77%	99.76%	99.57%	99.76%	99.75%
F_{A_o}	3.0531	2.5835	2.1762	1.9233	1.6944	6.8635
F_{B_o}	3.0544	2.5819	2.1762	1.9237	1.6934	6.8629
R	1.0004	0.9994	1.0000	1.0002	0.9994	0.9999
W/F_{A_o}	710.8	839.9	997.2	1128.3	1280.7	316.2
G	26.6	22.5	19.0	16.8	14.8	59.9
Conv.	0.142	0.164	0.180	0.194	0.213	0.076

Methyl Acetate

Run #	31	32	33	34	35	36
Date	5-25-53	5-26-53	5-28-53	6-1-53	6-2-53	6-9-53
T	160	160	160	160	160	140
P	0.9614	0.9764	0.9762	0.9770	0.9747	
w_{A_o}	131.0	131.0	131.0	131.0	131.0	102.0
w_{B_o}	104.7	69.7	69.8	69.7	69.7	54.3
w	235.7	200.7	200.8	200.7	200.7	156.3
$w_{OBS.}$	243.0			197.0	198.6	155.5
Error	+3.10			-1.87	-1.05	-0.52
N	0.4612	0.4584	0.4652	0.4608	0.4524	0.4547
A	99.84%	99.74%	99.91%	99.75%	99.70%	99.72%
F_{A_o}	2.1779	2.1758	2.1795	2.1760	2.1749	1.6938
F_{B_o}	3.2676	2.1750	2.1795	2.1759	2.1750	1.6934
R	1.5003	0.9996	1.0000	1.0000	1.0000	0.9998
W/F_{A_o}	996.4	997.3	995.6	997.2	997.7	1281.1
G	22.3	19.0	19.0	19.0	19.0	14.8
Conv.	0.341	0.281	0.250	0.250	0.260	0.196

Conversion Based on Analysis of Product for Acid

Stusiak's Catalyst

Ethyl Acetate

Run #	1	2
Date	6-4-53	6-5-53
T	160	160
P	0.9570	0.9654
w_{A_o}	131.0	131.0
w_{B_o}	100.1	100.4
w	231.1	231.4
$w_{OBS.}$	236.9	227.6
Error	+2.47	-1.64
N	0.4532	0.4595
A	99.60	99.86
F_{A_o}	2.1727	2.1784
F_{B_o}	2.1729	2.1794
R	1.0001	1.0005
W/F_{A_o}	998.8	996.1
G	21.9	21.9
Conv.	0.174	0.168

APPENDIX B.

Data on File in the Chem. Engr. Dept., Univ. of Minn.

1) Analysis of Reactants for water, alcohol, and acid.
2) Analysis of Product for Water.
3) Analysis of Product for Alcohol.
4) Analysis of Product for Ester.
5) Determination of Catalyst Diameter and Length.
6) Determination of Catalyst Particle Density
7) Determination of Catalyst Loss on Heating at 400°C.
8) Calibration of Flowrators.

APPENDIX C.

Monomer Concentration

The principle of least squares asserts that the best representative curve is that for which the sum of the squares of the residuals is a minimum. The problem becomes one of representing the set of observed values $(X_i, \frac{N_A}{F_{A_{o_i}}})$, $(i = 1,2,\ldots n)$, as calculated from equation (16), by the equation $\frac{N_A}{F_{A_{o_i}}} = a + bX$ containing the undetermined constants a and b. The deviation D_i of any observed value $\frac{N_A}{F_{A_o}}$ is:

$$D_i = \frac{N_A}{F_{A_o}} - \frac{N_A}{F_{A_{o_i}}} = a + bX_i - \frac{N_A}{F_{A_{o_i}}} .$$

the most probable values of a and b are those which result in a minimum value of $\sum_{i=1}^{n} D_i^2$ for all of the n observed values involved. Thus

$$S = \sum_{i=1}^{n} D_i^2 = \text{minimum.}$$

Since $S = f(a,b)$, it follows that necessary conditions for a minimum are:

$$\frac{\partial S}{\partial a} = 2 \sum_{i=1}^{n} D_i \frac{\partial D_i}{\partial a} = 0 \; ; \; \frac{\partial S}{\partial b} = 2 \sum_{i=1}^{n} D_i \frac{\partial D_i}{\partial b} = 0$$

and $$\frac{\partial D_i}{\partial a} = 1 \; ; \; \frac{\partial D_i}{\partial b} = X_i .$$

These equations may be written in summation form as follows:

$$n\,a + b \sum_{i=1}^{n} X_i - \sum \frac{N_A}{F_{A_{o_i}}} = 0$$

$$a \sum_{i=1}^{n} X_i + b \sum_{i=1}^{n} X_i^2 - \sum \frac{N_A}{F_{A_{o_i}}} X_i = 0$$

Each of the summations may be evaluated from the n observed values, and the 2 equations solved simultaneously for a and b.

If the equation for the monomer is a quadratic, $\frac{N_A}{F_{A_o}} = a + bX + cX^2$, the derivation is the same only there are three constants to be evaluated. The summation equations are:

$$n\,a + b \sum_{i=1}^{n} X_i + c \sum_{i=1}^{n} X_i^2 - \sum_{i=1}^{n} \frac{N_A}{F_{A_{o_i}}} = 0$$

$$a \sum_{i=1}^{n} X_i + b \sum_{i=1}^{n} X_i^2 + c \sum_{i=1}^{n} X_i^3 - \sum \frac{N_A}{F_{A_{o_i}}} X_i = 0$$

$$a \sum_{i=1}^{n} X_i^2 + b \sum_{i=1}^{n} X_i^3 + c \sum_{i=1}^{n} X_i^4 - \sum \frac{N_A}{F_{A_{o_i}}} X_i^2 = 0$$

These calculations were carried out and the constants a and b evaluated for each series of runs. The constant c was evaluated only for the ethyl acetate series at $R = 1.50$ and 1.00 and $T = 180$ and 160°C.

The results follow.

Values of the Constants a, b and c in the Monomer Equation

Ethyl Acetate

T	R	K_X	a	b	c
180°C.	1.4992	0.34005	0.8310	-0.7875	
180	1.0007	0.34005	0.7979	-0.7299	
180	0.7502	0.34005	0.7720	-0.6784	
160	1.5008	0.60842	0.7376	-0.6296	
160	1.0005	0.60842	0.6993	-0.5753	
160	0.7502	0.60842	0.6711	-0.5256	
140	1.5005	1.2288	0.6145	-0.4600	
140	1.0001	1.2288	0.5700	-0.3985	
180	1.4992	0.34005	0.8150	-0.6669	-0.1419
180	1.0007	0.34005	0.7865	-0.6237	-0.1523
160	1.5008	0.60842	0.7330	-0.5642	-0.1338
160	1.0005	0.60842	0.6935	-0.4885	-0.1929

Propyl Acetate

T	R	K_X	a	b
180	1.5001	0.34005	0.8290	-0.7799
180	1.0000	0.34005	0.7979	-0.7299
180	0.7495	0.34005	0.7735	-0.6865
160	1.5009	0.60842	0.7376	-0.6296
160	0.9997	0.60842	0.6993	-0.5753
160	0.7501	0.60842	0.6720	-0.5333
140	1.5008	1.2288	0.6145	-0.4600
140	1.0006	1.2288	0.5700	-0.3985

Butyl Acetate

T	R	K_X	a	b
180	1.0000	0.34005	0.8019	-0.7463
180	0.7506	0.34005	0.7751	-0.6945
180	0.4998	0.34005	0.7454	-0.6368
160	1.0001	0.60842	0.6914	-0.5470
160	0.7498	0.60842	0.6731	-0.5416
160	0.5003	0.60842	0.6429	-0.4955
150	0.9999	0.85049	0.6415	-0.4988
150	0.7501	0.85049	0.6123	-0.4560

APPENDIX D.

Analytical Procedures

1) Preparation of Standard Sodium Hydroxide

A 50% by weight carbonate free sodium hydroxide solution was prepared according to the procedure outlined by Kolthoff and Sandell (13) and stored in a paraffin lined bottle. An alkaline automatic buret was used for titrating; the sodium hydroxide in the buret (about 0.45N) was protected from the atmosphere by drying tubes filled with activated alumina. The normality of the standard solution was checked two or three times during each running day against potassium acid phthalate using phenolphthalein as indicator. Tests were not made for absorbed carbon dioxide because the solution was used up rapidly. A sharp color change was obtained for all the titrations.

2) Water Analysis: (Determination of Water by the Method of Karl Fischer)

All moisture was determined by using Karl Fischer reagent in a Sattler-Geyer Moisturimeter manufactured by the Scientific Glass Apparatus Company and described by Zerban and Sattler (23). Two 50 ml. burets (methanol and K.F. reagent) and a titration flask are so modified that they go together to form a unit sealed from the atmosphere so that the titration can proceed without interference from the water vapor in the air.

All titrations were carried out to an excess of Karl Fischer reagent. A known volume of methanol of known water content was added to the titration flask and then the sample, containing from 50 to 250 mg. of water, was weighed into the titration flask from a special 15 ml. Erlenmeyer flask fitted with a medicine dropper through a ground glass joint as described by Zerban and Sattler (23). The mixture was titrated directly with Karl Fischer reagent; the end point change was from chromate yellow to red-brown of iodine. When several determinations were made one after the other, the visual endpoint became progressively harder to determine because as spent K.F. reagent accumulates the original chromate yellow deepens to a dark straw making the red-brown of the iodine difficult to see. To deal with this situation a second endpoint mechanism, the dead stop endpoint method as used by Zerban and Sattler (23) was incorporated. With both the visual and dead stop methods available, the endpoint was easily reproduced.

The Karl Fischer Reagent used for water determinations was prepared according to the procedure outlined by Mitchell and Smith (14). The reagent is unstable; it changes its water-equivalence with time. Therefore, the Karl Fischer reagent was standardized against water whenever it was used, and as close to the time that the moisture determinations were made as was possible. Also, all reagent was allowed to stand for at least a week before use; Zerban and Sattler (23) claim that if the reagent is a good one, at this time a relatively stable reagent will be available.

Finally the amount of water in the methanol that is used as a diluent in the procedure was determined by titrating samples of methanol with Karl Fischer reagent.

3) Analysis of the Acetic Acid.

A. Hydrogen Ion Content.

Dupont C.P. reagent grade glacial acetic acid was used as the acid feed. During each run two portions of acid analyzed separately and each about 0.75 g. were removed from the acid reservoir and weighed in small glass stoppered weighing bottles. A bottle and its contents were quickly transferred to a beaker containing sufficient water to immerse the bottle and titrated with standard sodium hydroxide using phenolphthalein as indicator.

Sample Analysis: Ethyl Acetate: Run #58.

Sample No.	1	2
Normality of standard sodium hydroxide:	0.4792	0.4792
Weight of Acetic Acid, by difference:	0.8622 g.	0.9545 g.
Volume of base required:	29.90 ml.	33.09 ml.

Composition of acid (wt.%)

$$\frac{(\text{Vol.Base})(\text{Normality Base})(\text{Mol. wt. } CH_3COOH)(100)}{(1000)(\text{Sample wt.})}$$

$$\text{Sample 1: } \frac{(29.90)(0.4792)(60.052)(100)}{(1000)(0.8622)} = 99.79\%$$

$$\text{Sample 2: } \frac{(33.09)(0.4792)(60.052)(100)}{(1000)(0.9545)} = 99.76\%$$

Av.: 99.78%

B. Water Content

The acid feeds were analyzed for water by the method suggested by Mitchell and Smith (14). Into the Karl Fischer titration flask are measured 25 ml. of methanol; approximately 2 grams of acid are weighed out from the weighing pipette into the titration flask; and the whole titrated with Karl Fischer reagent. Two determinations are made in this manner, and since the water-equivalence of the methanol is known the water content of the acid is determined.

Sample Analysis: Ethyl Acetate: Run #42

Sample No.	1	2
Weight of the acid by difference:	1.5050 g.	1.5050 g.
mg. of H_2O/ml. K.F. reagent:	3.214	3.214
ml. of K.F. reagent for acid + methanol:	12.00 ml.	12.08 ml.
ml. of K.F. reagent/25 ml. methanol:	11.20 ml.	11.20 ml.
ml. of K.F. reagent for acid:	0.80 ml.	0.88 ml.

% H_2O in acid:

$$\frac{(\text{ml. K.F.})\left(\frac{\text{mg. H}_2\text{O}}{\text{ml. K.F.}}\right)(100)}{(\text{wt. sample})(1000)}$$

$$\text{Sample 1: } \frac{(0.80)(3.214)(100)}{(1.5050)(1000)} = 0.17\%$$

$$\text{Sample 2: } \frac{(0.88)(3.214)(100)}{(1.5175)(1000)} = 0.19\%$$

Av.: 0.18%

Smith and Mitchell (14) found in analyses of most organic acids that the absolute precision and accuracy varied from ±0.00 to ±0.1% on samples containing from 0.00 to 28% water.

4) Analysis of the Alcohols:

A. Qualitative Analysis:

Several qualitative tests were used to determine whether the alcohols contained aldehydes, ketones and unsaturates. Ketones and unsaturates were tested for by methods suggested by Shriner and Fuson (17) while the aldehyde test was that one suggested by Furman (9).

B. Physical Analysis:

A series of physical properties were determined for the alcohols and these observed values compared with values from the literature for the pure compounds as another method of checking purity. These were:

1) the boiling point range as determined by the ASTM distillation procedure outlined in Perry (50); 2) the refractive index as determined by using a Bausch & Lomb Precision Refractometer type 33-45-03; and 3) the density as determined by using a 10 ml. pycnometer of the ground glass joint thermometer and capillary sidearm type.

C. Alcohol Hydroxyl Group Content

The alcohol feeds were analyzed for the hydroxyl group by the method outlined by Mitchell and Smith (14). Their method depends on the fact that an alcohol can be quantitatively esterified in the presence of glacial acetic acid-boron trifluoride catalyst. Once the alcohol has been converted to ester and water, Karl Fischer reagent can be used to determine the water content of the sample. Since for every mole of water formed a mole of the alcohol reacted, the alcoholic hydroxyl group content is then determined.

Three determinations of the alcohol along with a blank were all made at once. Into a 250 ml. volumetric flask are transferred 20 ml. of the esterification catalyst and approximately 10 milli-equivalents of alcohol; the flask is maintained at 67°C. for 2 hours in a water bath and then allowed to cool spontaneously. Then 5 ml. of C.P. pyridine are added to destroy any excess catalyst, and 25 ml. of methanol to act as a diluent and the whole titrated with K.F. reagent. The water originally present in the alcohol sample is determined by analyzing the alcohol for water, the water content of the methanol is known, the blank gives the water content of the catalyst and pyridine; therefore the water formed by esterification is determined.

Sample Analysis: Ethyl Acetate: Run #43

Sample No.	1	2
Weight of alcohol by difference:	0.0916	0.1717 g.
% H_2O in alcohol	0.13%	0.13%
mg. of H_2O originally in sample:	0.1191 mg.	0.2232 mg.
mg. H_2O/ml. K.F. reagent:	3.123	3.123
ml. K.F. for alcohol, H_2O, and catalyst:	39.65 ml.	49.65 ml.
ml. K.F. for blank (catalyst)	28.15 ml.	28.15 ml.
ml. K.F. for alcohol + H_2O:	11.50 ml.	21.50 ml.
ml. K.F. for H_2O originally in sample:	0.37 ml.	0.70 ml.
ml. K.F. for alcohol:	11.13 ml.	20.80 ml.

% Alcohol by weight:

$$\frac{(\text{ml. K.F. for Alcohol})\left(\frac{\text{mg. } H_2O}{\text{ml. K.F.}}\right)(\text{mol.wt. of alc.})(100)}{(\text{mol. wt. } H_2O)(1000)(\text{wt. sample})}$$

$$\text{Sample 1: } \frac{(11.13)(3.123)(46.068)(100)}{(18.016)(1000)(0.0916)} = 99.9\%$$

$$\text{Sample 2: } \frac{(20.80)(3.123)(46.068)(100)}{(18.016)(1000)(0.1717)} = 99.7\%$$

Av.: 99.8%

Mitchell and Smith (14) claim a precision and accuracy for the method of ±0.3%. The analysis of the alcohols carried out in this work showed about the same precision. The alcohol determinations carried out at any one time showed some scattering; however, never more than ±0.3%. An arithmetic average of the determinations was taken as the result of the analysis and reported to 0.1%.

D. Water Content

Alcohol was analyzed for water in the same manner as the acids. Into the titration flask go 25 ml. of methanol, approximately 2 grams of alcohol, and the whole is titrated with Karl Fischer reagent. Two determinations are made in this manner, and since the water equivalence of the methanol is known, the water content of the acid is determined.

Sample Analysis: Ethyl Acetate: Run #43.

Sample No.	1	2
Weight of the alcohol by difference:	1.3628 g.	1.4659 g.
mg. H_2O/ml. K.F. reagent:	3.123	3.123
ml. of K.F. reagent/25 ml. methanol:	11.70 ml.	11.70 ml.
ml. of K.F. reagent for alcohol + methanol:	12.25 ml.	12.30 ml.
ml. of K.F. reagent for alcohol:	0.55 ml.	0.60 ml.

% H_2O in alcohol:

$$\frac{(\text{ml. K.F.})\left(\frac{\text{mg. } H_2O}{\text{ml. K.F.}}\right)(100)}{(\text{wt. sample})(1000)}$$

$$\text{Sample 1: } \frac{(0.55)(3.123)(100)}{(1.3628)(1000)} = 0.13\%$$

$$\text{Sample 2: } \frac{(0.60)(3.123)(100)}{(1.4659)(1000)} = 0.13\%$$

Av.: 0.13%

Again Smith and Mitchell (14) claim in analysis of most alcohols that the absolute precision and accuracy is of the order of ±0.1%.

5) Analysis of the Product

A. Acid Analysis:

A 1.5 to 2.0 gram sample of product was collected in a stoppered weighing bottle and quickly weighed. The bottle with its contents was immersed in approximately 100 ml. of distilled water in a 250 ml. beaker. Two drops of phenolphthalein indicator were added and the solution titrated with carbonate-free standard sodium hydroxide solution. Persistent endpoints were obtained for all titrations.

Sampling of the product was continued at 1/2 hr. intervals until at least 5 steady state samples were obtained (approximately the same conversion). The total weight of the steady state samples and the base necessary to neutralize them was used to calculate the conversion for the run concerned.

Time	Sample wt.	Ml. NaOH	$\frac{\text{cc.NaOH}}{\text{gr.sample}}$	Conversion
1:00 P.M.	1.4320 g.	18.00 ml.	12.58	0.360*
1:30	1.4230	17.95	12.62	0.357*
2:00	1.4255	17.95	12.59	0.357*
2:30	1.4255	18.00	12.62	0.357*
3:00	1.4824	19.30	13.02	0.338
3:30	1.4439	18.50	12.80	0.348
4:00	1.4400	18.40	12.78	0.351*
4:15	1.4408	18.40	12.75	0.351
4:30	1.4380	18.30	12.72	0.351*
5:00	1.4432	18.35	12.70	0.353*
5:30	1.4399	18.30	12.70	0.353*

The above table shows typical reactor behavior; the individual conversions as a function of time varied from 1 to 3% and sometimes, as happened on this particular afternoon about 3:00 P.M., the reactor slipped off the steady state. Only the conversions marked with an asterisk were considered steady state and used in calculating the conversion. The average conversion for a run was obtained by using the total volume of base and the total sample weight of the steady state conversions.

Total weight steady state samples:	11.4671 g.
Total volume of sodium hydroxide	145.25 ml.
Normality of sodium hydroxide:	0.4792
Moles/hr. acid fed:	2.1766
Mass flow rate	231.5 g./hr.

Moles/hr. acid converted:

$$\frac{(\text{ml.NaOH})(\text{Normality of base})(\text{mass flow rate})}{(\text{wt. sample})(1000)}$$

$$= \frac{(145.25)(0.4792)(231.5)}{(11.4671)(1000)} = 1.4052$$

$$\text{Conversion} = \frac{\text{mole/hr. acid fed} - \text{mole/hr. acid converted}}{\text{mole/hr. acid fed}}$$

$$= \frac{2.1766 - 1.4052}{2.1766} = 0.355$$

B. Water Analysis

The product was analyzed for water in the same manner as the alcohol and acid feeds.

Since the water content of the feeds was known, the water content of the product brought about by chemical reaction is then determined. This water content can then be converted into moles/hour of water coming out of the reactor which should be equal to the moles/hour of ester leaving the reactor as determined by titrating the product for acid.

Sample Analysis: Ethyl Acetate: Run #58

Sample No.	1	2
Weight of product by difference:	0.5076	0.4050 g.
mg. H_2O/ml. K.F. reagent:	2.887	2.887
ml. K.F. reagent/25 ml. methanol:	12.30	12.30 ml.
ml. K.F. reagent for product + methanol:	23.23	21.03 ml.
ml. K.F. reagent for product:	10.93	8.73 ml.
Mass flow rate:	231.5	231.5 g./hr.

Moles/hr. Water out:

$$\frac{(\text{ml. K.F.})\left(\frac{\text{mg. } H_2O}{\text{ml. K.F.}}\right)(\text{mass flow rate})}{(\text{mol. wt. } H_2O)(\text{sample wt.})(1000)}$$

$$1)\quad \frac{(10.93)(2.887)(231.5)}{(18.016)(0.5076)(1000)} = 0.7988$$

$$2)\quad \frac{(8.73)(2.887)(231.5)}{(18.016)(0.4050)(1000)} = 0.7996$$

Av.: 0.7992 moles/hr.

Moles/hr. Water fed:

$$\frac{(\text{Alcohol Flow rate})(\%\ H_2O \text{ in Alc.}) + (\text{Acid Flow Rate})(\%H_2O \text{in Acid})}{\text{Mol. wt. } H_2O}$$

$$= \frac{(131.0)(0.0018) + (100.5)(0.0013)}{18.016} = 0.0203$$

Conversion: $\frac{\text{moles ester}}{\text{moles acid fed}} = 0.355$

Moles/hr. Acid Fed: 2.1766

Moles/hr. Ester formed:

(Conversion)(Moles/hr. Acid fed) = (0.355)(2.1766) = 0.7727

% Theoretical Water in Product:

$$= \frac{\text{Moles/hr. } H_2O \text{ out}}{\text{Moles/hr. ester formed + moles/hr. } H_2O \text{ in}} = \frac{(0.7936)(100)}{(0.7930)}$$

= 100.8%

Moles/hr. ester formed plus moles/hr. water fed should equal moles/hr. water out.

C. Alcohol Analysis

The product was analyzed for alcohol in the same manner as the alcohol feed was analyzed for the alcoholic hydroxyl group. By subtracting away the known water content of the feeds, one should obtain from the above titration the moles/hr. of alcohol feed to the reactor as determined by the alcohol flow rator.

Sample Analysis: Ethyl Acetate: Run # 58

Sample No.	1	2	3
Weight of product by difference:	0.3033 gm.	0.2976 gm.	0.2050
Mass flow rate:	231.5 gm.	231.5	231.5
mg. H_2O/ml. K.F. reagent:	2.687	2.887	2.887
ml. K.F. reagent for Alcohol + H_2O fed + blank	48.22 ml.	47.90	42.39
ml. K.F. reagent for blank:	30.25 ml.	30.25	30.25
ml. K.F. reagent for Alcohol + H_2O fed	17.97 ml.	17.65	12.14

Alcohol Flow rate:	100.5 g./hr.	100.5	100.5
Acid Flow rate:	131.0 g./hr.	131.0 g./hr.	131.0g/hr
Alcohol H_2O Content:	0.13%	0.13%	0.13%
Acid H_2O Content:	0.18%	0.18%	0.18%
Moles/hr. H_2O fed:	0.0203	0.0203	0.0203

$$= \frac{(\text{Alc. Flow rate})(\text{Alc. } H_2O \text{ content}) + (\text{Acid Flow rate})(\text{Acid } H_2O \text{ content})}{(\text{mol. wt. } H_2O)}$$

Moles/hr. Alcohol by Karl Fischer:

$$\frac{(\text{ml. K.F.})\left(\frac{\text{mg. } H_2O}{\text{ml. K.F.}}\right)(\text{mass Flow rate})}{(\text{mol. wt. } H_2O)(\text{wt. sample})(1000)} - \text{moles/hr. } H_2O \text{ fed}$$

1) $\frac{(17.97)(2.887)(231.5)}{(18.016)(0.3033)(1000)} - 0.0203 = 2.1977 - 0.0203 = 2.1774$ moles/hr.

2) $\frac{(17.65)(2.887)(231.5)}{(18.016)(0.2976)(1000)} - 0.0203 = 2.2001 - 0.0203 = 2.1798$ moles/hr.

3) $\frac{(12.14)(2.887)(231.5)}{(18.016)(0.2050)(1000)} - 0.0203 = 2.1969 - 0.0203 = 2.1766$ moles/hr.

Ave.: 2.1779 moles/hr.

Moles/hr. Alcohol by Flow rator:

$F_{B_o} = 2.1772$ moles/hr.

% Alcohol Recovery by Esterification:

$$\frac{\text{Exp. Alcohol}}{\text{Theo. Alcohol}} = \frac{2.1779}{2.1772} = 100.0\%$$

The moles/hr. alcohol by Karl Fischer should equal moles/hr. alcohol by the alcohol flowrator for a balance.

D. Ester Analysis:

The product was analyzed for esters by saponification with an excess of carbonate-free standard sodium hydroxide solution after being analyzed for acid. When the saponification was complete (allowed to stand over night), standard hydrochloric acid was added in excess and the excess acid back-titrated with standard base. The total base should equal the total acid for a balance on the ester. Only one determination was made for any ester balance.

Sample Analysis: Ethyl Acetate: Run #58.

Normality of base for acetic acid analysis and Saponification:	0.4792
Normality of hydrochloric acid:	0.6064
Composition of Acetic Acid, % by wt.	99.76%
Composition of Alcohol, % by wt.	99.8%
Molar Ratio of Alcohol to Acid, R	1.0003
Weight of Product by difference	1.4674

Moles of acid entering:

$$\frac{\text{sample wt.}}{\dfrac{\text{mol. wt. acid}}{\text{Acid comp.}} + \dfrac{(\text{mol.wt.Alc.})(R)}{\text{Alc. comp.}}} = \frac{1.4674}{\dfrac{60.052}{0.9978} + \dfrac{(46.068)(1.0003)}{0.998}}$$

$$= 0.013796$$

Moles of base for Analysis of Sample:

$$\frac{(\text{ml. NaOH for analysis})(\text{normality of base})}{1000} = \frac{(0.4792)(18.52)}{1000}$$

$$= 0.008875$$

Moles of base for Saponification:

$$\frac{(\text{ml. NaOH for sapon.})(\text{normality of base})}{1000} = \frac{(0.4792)(50.00)}{1000}$$

$$= 0.023960$$

Normality of base for HCl back-titration: 0.4721

Moles base for excess acid:

$$\frac{(\text{ml. NaOH for excess acid})(\text{normality of base})}{1000} = \frac{(4.60)(0.4721)}{1000}$$

$$= 0.002172$$

Moles of HCl added:

$$\frac{(\text{ml. HCl added})(\text{normality of HCl})}{1000} = \frac{(35.00)(0.6064)}{1000} = 0.021224$$

Total Base added: 0.035007

Total Acid added: 0.021224

Difference 0.013783

This difference should equal the moles of acid entering (based on no conversion) for an ester balance.

$$\%\ \text{Recovery thru Saponification: } \frac{(0.013783)(100)}{(0.013796)} = 99.91\%$$