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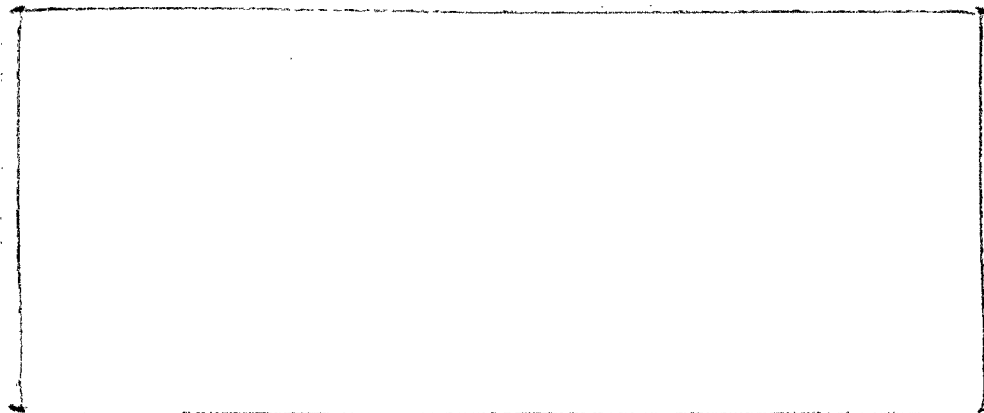
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UNIVERSITY OF MINNESOTA
INSTITUTE OF TECHNOLOGY

DEPARTMENT OF CHEMICAL ENGINEERING

MINNEAPOLIS 14, MINNESOTA



DIFFUSION IN CATALYTIC HETEROGENEOUS SYSTEMS

STUDIES IN VAPOR PHASE ESTERIFICATION

OFFICE OF NAVAL RESEARCH CONTRACT

NR 351-287

DEPARTMENT OF CHEMICAL ENGINEERING

UNIVERSITY OF MINNESOTA

MINNEAPOLIS 14, MINNESOTA

SUBMITTED NOVEMBER 3, 1952

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Abstract

The continuous vapor phase reaction of ethyl alcohol and acetic acid to form ethyl acetate and water has been carried out in a fixed bed reactor. The reactor was of stainless steel four feet in length and two inches in diameter, heated by circulating Dowtherm A enclosed in a jacket. The bed contained 2170 grams of dry catalyst. The catalyst was 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 gms./cc., an absolute density of 3.860 gms./cc., and a fractional void volume of 0.5625. The balls contained 7.87% WO_3 by weight.

The liquid reactants were pumped through flowmeters and thence into the electrical preheaters. The vaporized reactants entered the reactor at the top, passed through the catalyst bed, and then to the condenser. The product from the condenser was immediately analyzed. The apparatus is automatically controlled with respect to temperature. It is possible to operate at pressures slightly above atmospheric.

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. catalyst per (mole of acid 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 literature, 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 oxide catalyst higher conversions at significantly lower temperatures are possible than with other catalysts. The product is water white and indications are that there are no side reactions of importance.

Kinetic data were obtained at 140°C., 160°C., and 180°C., with the bulk of the data at 160°C. 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. At 160°C. the rate is given by

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

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

In order to investigate in some detail the effect of intraparticle diffusion, reference to the paper of Smith and Amundson shows that if the overall reaction is pseudo-first order the ratio of effluent to influent partial pressures is given by the expression

$$\log_e \frac{p_A}{p_{A_0}} = \frac{3W'\tau D_A x}{R^2 \rho_p q} \left[\frac{\tanh R\sqrt{P} - R\sqrt{P}}{\tanh R\sqrt{P}} \right] \quad (2)$$

where

- W' = mass of catalyst, g./cc.
- τ = void fraction in the particle
- D_A = diffusion coefficient of acid in the medium
- x = reactor depth
- R^2 = particle radius
- ρ_p = particle density
- q = flow rate to reactor
- $P = \frac{k}{D_A}$
- k = reaction velocity constant
- p_A = effluent partial pressure of acid
- p_{A_0} = influent partial pressure of acid

Experimentally it is found at a given mol ratio of reactants and at a given temperature, $\log \frac{p_A}{p_{A_0}}$ is a linear function of $1/q$ as Equation 2 might predict. 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 has a negligible effect in this reaction.

Using this method the activation energy is 10.3 K cal./g.mole.



Fig. 1. Apparatus - Control Panel.

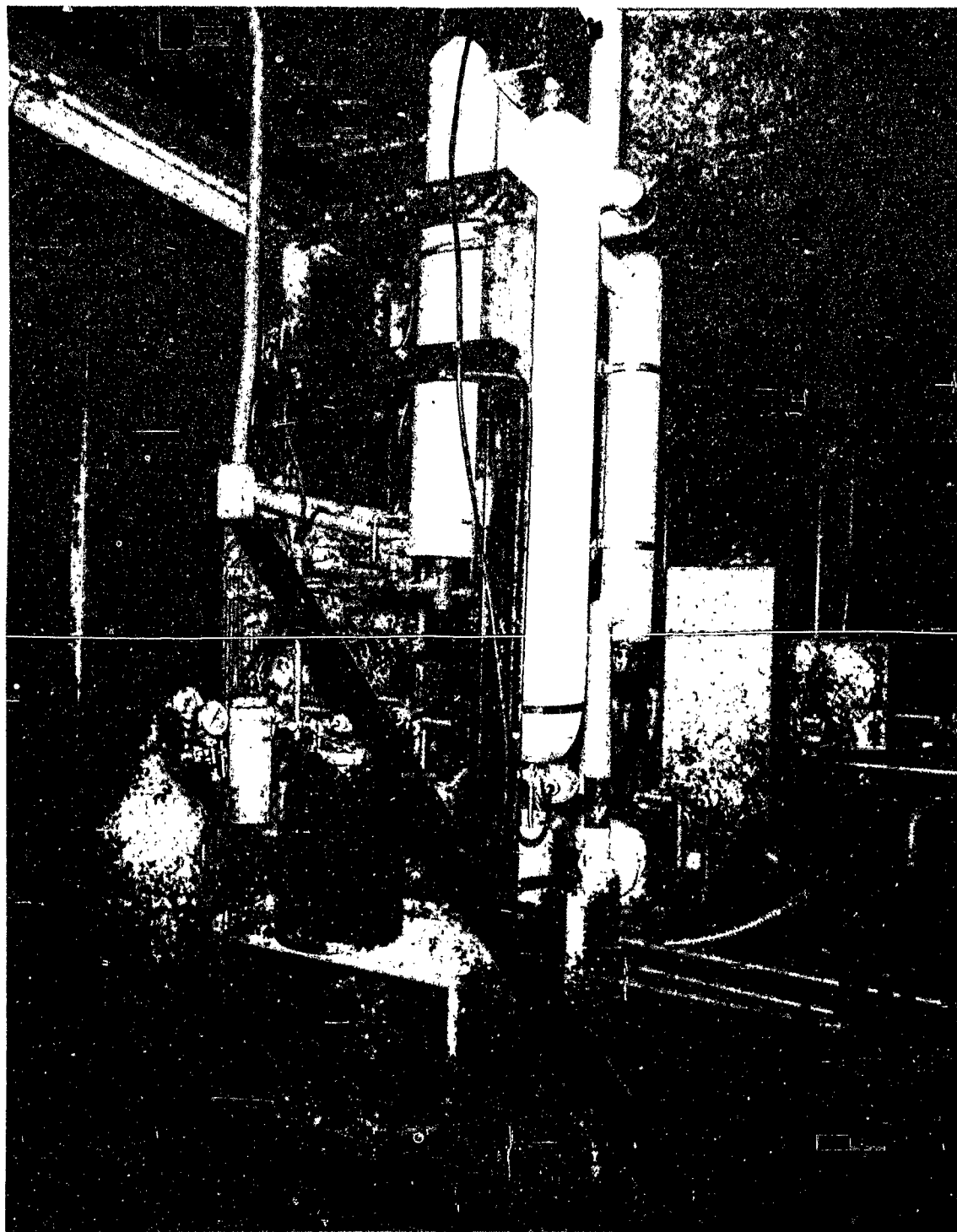


Fig. 2. Apparatus

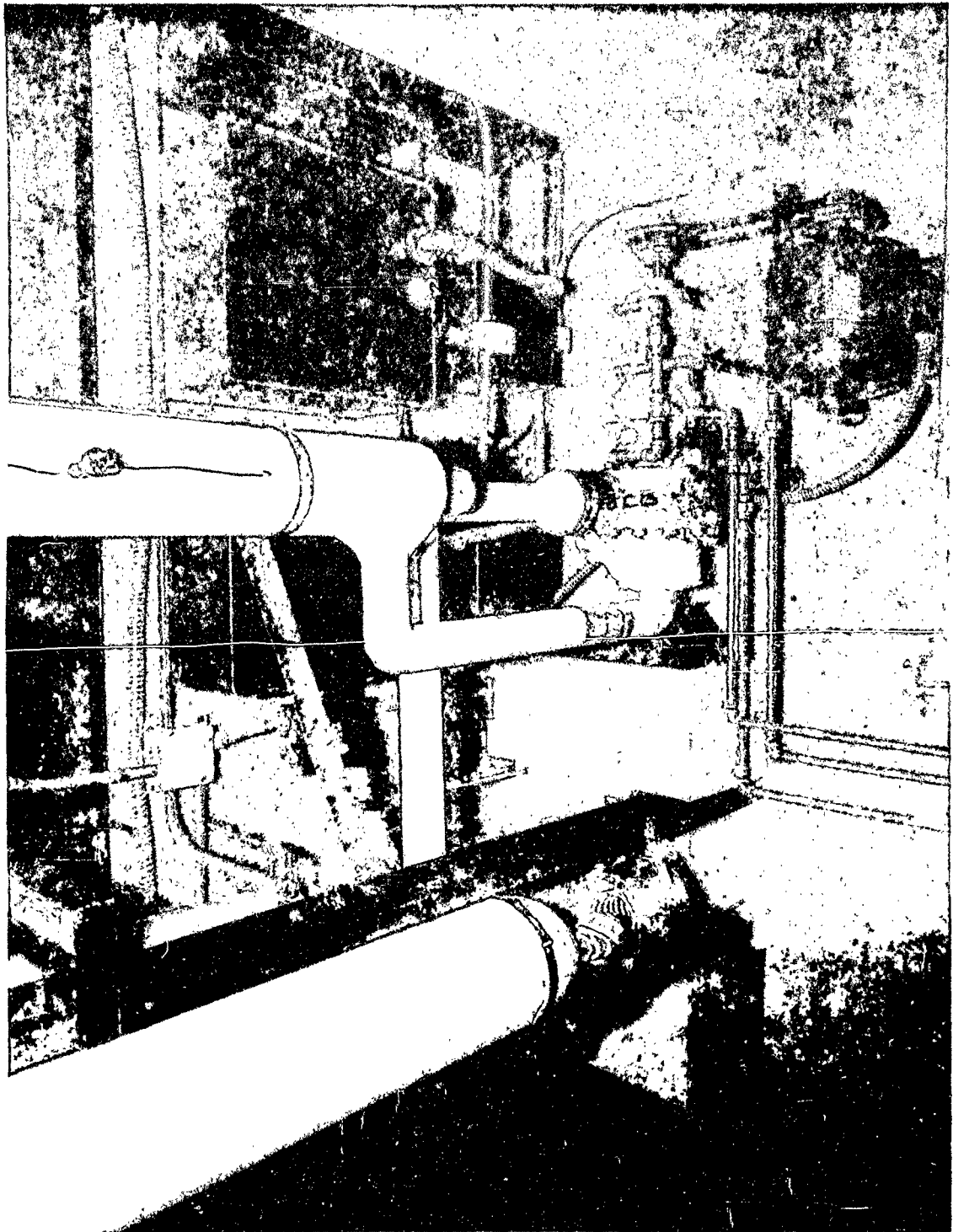


Fig. 3. Apparatus - Dowtherm Pump and Heater

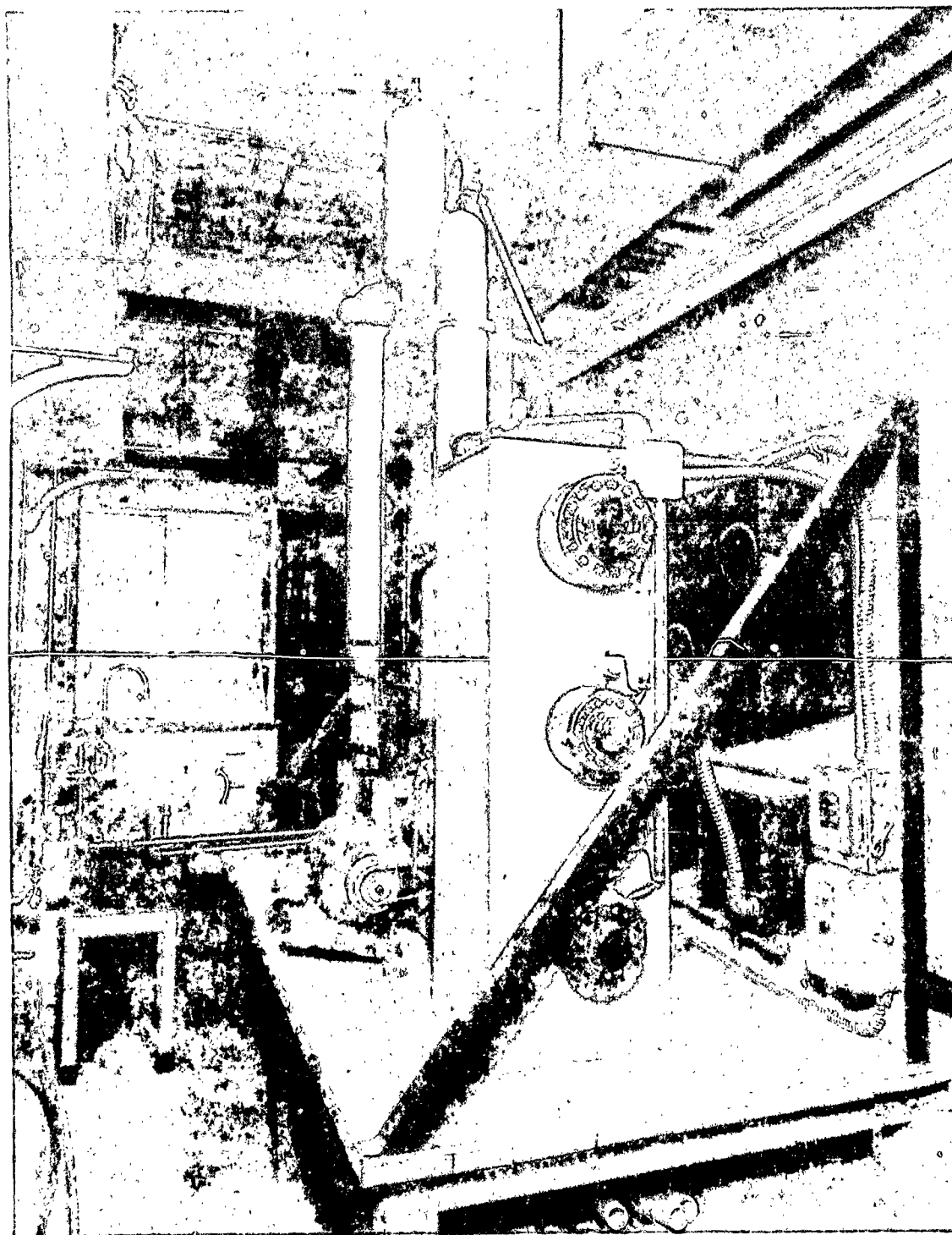


Fig. 4. Apparatus - Variacs.

INTRODUCTION

In organic chemistry esters are classified as derivatives of carboxylic acids. Very frequently they are regarded as alcohols of which the hydroxyl hydrogen has been replaced by the acyl group $-C(=O)-R$. In actuality they constitute 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. The fragrance of many fruits and flowers can be attributed to mixtures of esters. Artificial flavoring liquids are mixtures of synthetic esters blended to reproduce the taste and smell of a natural extract or fruit.

In general, liquid esters are less dense than water and with the exception of those with low molecular weight are practically insoluble in water. The lower esters are more stable to heat than are the acids and esters of solid acids melt at lower temperatures than do the acids. Methyl and ethyl esters boil at temperatures considerably below the boiling points of the respective acids.

The process of forming esters is known as esterification. The reaction of esterification, although many, can be divided into two types: those in which two compounds react to give an ester only, and those in which two compounds react to give an ester and another compound. An example of the first

type is the reaction of ethyl alcohol with ketene and of the second is the reaction of ethyl alcohol with acetic acid.

For the most part, esters are prepared in the liquid phase under various conditions of temperature and pressure. Esterification of primary alcohols with organic acids is best known and has been studied extensively. The pure components react very slowly even when heated. With an equimolar mixture of acetic acid and ethyl alcohol equilibrium is attained only after refluxing for several days. The limit of conversion to ester of lower alcohols and acids is about 60 to 70 percent.

The rate of attainment of equilibrium is greatly increased by the addition of a catalyst. Acid catalysts are the most common and in practice hydrochloric and sulfuric acids are generally used. Over certain ranges of concentration the rate of esterification is proportional to the hydrogen ion concentration.

The list of esterification catalysts is long. Perchloric acid, phosphoric acid, mono-sodium sulfate, aluminum sulfate, zinc chloride, anhydrous nickel sulfate have been used - many others could be mentioned. Recently tungstic acid and tungstic oxide (1, 27, 38) have been tried as esterification catalysts. At 65°, 80°, and 95° C., tungstic acid was more active for esterification of propyl alcohol with acetic acid than was tungstic oxide.

Lower esters like ethyl acetate have been prepared by vapor phase esterification. A catalyst is necessary because the homogeneous reaction does not occur to any measurable extent at temperatures as high as 300°C. Silica gel has been most widely used but has not been accepted as the most suitable. However, agreement is general that conversions are 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 alcohol with acetic acid under a variety of conditions. The reaction has been carried out in a flow system using a bench scale apparatus of stainless steel. The catalyst, tungstic oxide, is carried by uniform porous spheres of alumina in the form of a packed bed. A rate equation which correlates the data has been obtained from a study of the kinetics of the reaction. It is hoped that the work outlined here shall contribute, in a small way perhaps, to the large field of applied kinetics and prove useful in the design of reactors of large capacity.

LITERATURE SURVEY

The history of esterification in the vapor-phase dates back to the work of Berthelot and Pean de St. Gilles (2) in the middle of the last century. They showed that the limit of the reaction went up when the volume of the system was increased.

In 1911 Sabatier and Mailhe (31) published a paper on direct esterification of primary alcohols and aliphatic acids by catalysis. Equivalent amounts of reactants were passed over titanium dioxide at 280° - 300°C . Gaseous products resulting from the decomposition of the acid or alcohol were negligible. Esterification was rapid, reaching limits equal to more than 75 percent conversion. Thorium dioxide was also used but was less satisfactory than titanium dioxide.

About ten years later Milligan and Reid (25) reacted equivalent amounts of acetic acid and ethyl alcohol on silica gel at 150° , 250° and 350°C . At 150°C . the limit of esterification was 75-80 percent. These workers contended that silica gel as a catalyst was more than twice as active as titanium dioxide. About a year later Milligan, Chappell and Reid (24) while working with the same catalyst and materials discovered that the percentage conversion depended on the temperature and rate of passage of the vapors over the catalyst. At 150°C and low rates of flow conversions as high as 90 percent were attained.

Edgar and Schuyler (7) investigated esterification equilibria in the gaseous phase for the same system using a distillation method. Like Berthelot and Pean de St. Gilles, they observed that the yield of ester increased with the amount of vapor space after equivalent mixtures had been heated in tubes a sufficient length of time. Their data indicated that the equilibrium constant was higher for the vapor-phase reaction than it was for the liquid-phase reaction. At 75°C the constant varied between 347 and 559, the wide range being caused by experimental and analytical difficulties. At 150°C, equilibrium corresponded to about 95 percent conversion.

It is evident that general agreement was lacking on equilibria governing the vapor-phase reaction between ethyl alcohol and acetic acid. Swientoslawski and Posnanski (34)(35) obtained with an ebullioscope a mean value of 59 for the equilibrium constant from ten determinations with a possible error of $\pm 10\%$, and maintained that it was independent of the temperature. Gajendragad (11) esterified methyl and ethyl alcohols with acetic acid at 230°C. over potassium-alum and silica gel catalysts, but did not record the equilibrium constant. He did state that the equilibrium constant was not far from that obtained by other observers in the liquid phase at lower temperatures.

In 1930 Frolich, Carpenter and Knox (9) published

a paper that was to clarify any inconsistencies in the values of the equilibrium constant for the vapor-phase esterification of ethyl alcohol and acetic acid. A flow system was used, zirconium dioxide was the catalyst, the temperature range was 250°-300°C., and the equilibrium was to be approached from both the acid-alcohol and ester-water sides using equimolar mixtures. At 250°C. the reaction proceeded too slowly for equilibrium to be reached; at 300°C. equilibrium was approached from the acid-alcohol side only; and at 280°C. equilibrium was approached from both sides. The equilibrium constants and conversions for 280° and 300°C. were 49 ± 4 and 63 and 87.5 percent and 88.8 percent, respectively. The authors concluded that the equilibrium constant changed only slightly with temperature and that in the absence of a catalyst no appreciable amount of ester was formed. It is evident that they did not achieve their purpose.

Tidwell and Reid (37) carried out essentially the same research but with more success. They used silica gel as a catalyst, approached equilibrium from both sides and worked in the temperature range 150° -300°C. Their results reproduced below in condensed form, show that the equilibrium constant varied with the temperature in such a way that the highest conversion was obtained at the lowest temperature.

Results of Tidwell and Reid

<u>Temperature, °C.</u>	<u>Average Conversion, %</u>	<u>K.</u>
150°	84.7	30.9
200	83.7	24.9
250	78.1	12.7
300	74.9	8.9

The excellent paper by Essex and Clark (8) demonstrated conclusively how the equilibrium constant for the esterification of ethyl alcohol with acetic acid varied with temperature. The reactants were passed over silica gel until the concentration of the acid in the product was constant. Runs were made over considerable ranges of flow and equilibrium was approached from both sides. Equilibrium constants based on the fugacity rather than the partial pressure of acetic acid, and taking into account the association of the acetic acid, were determined. At 150°, 165° and 200°C the values were 33.62, 26.38 and 16.07, respectively. Expressions were developed for the association constant and the fugacity of acetic acid, and for the standard free energy change of the gaseous reaction.

Other researches dealing with equilibria of vapor-phase esterification have been reported. With a distillation method, Swientoslawski and Solcewicz (36) got 40.8 at 75.9°C. for

an equimolar mixture of ethyl alcohol and acetic acid and 39.3 at 73.7°C for a three to one alcohol to acid mixture for the equilibrium constant.

Jatkar and Gajendragad (19) reacted different mixtures of acetic acid and ethyl alcohol vapors at 230° and 260°C by passing them very slowly over silica gel and potassium-alum catalysts. For equimolar mixtures, equilibrium conversions of 77 and 75 percent were reported. Potassium alum was a more active catalyst than silica gel but catalyzed the ether reaction. This side-reaction was eliminated (20) by using methyl alcohol. With alum catalyst the limit of conversion of an equimolar mixture at 230°C was 75.8 percent.

An interesting research using a unique experimental method was published by Halford and Brundage (16). Acetic acid and ethyl acetate were treated as solutes in a large excess of solvent containing 1.2237 moles of water per mole of alcohol. The liquid phase equilibrium constant at 40°C was obtained from measurements made at 40°, 60°, 79° and 99°C and transferred to the vapor-phase with the aid of vapor compositions measured separately by an air-saturation method. For vapor-phase esterification at 40°C the constant was 122 ± 3 . The equilibrium data of Jatkar and Gajendragad (19) were combined with the results of this work to develop the expression $\Delta F^\circ = -3970 + 3.1 T$ for the standard free energy of the gaseous reaction.

Knox and Burbridge (22) devised a static method using zirconium oxide as catalyst to study esterification equilibria in the vapor phase. With equimolar mixtures of acetic acid and ethyl alcohol, and ester and water, the limits of esterification at 125°, 150° and 200°C were 85.77, 84.51 and 81.38 percent, respectively. The corresponding equilibrium constants calculated by the method of Essex and Clark (8) and corrected for association of acetic acid were 45.7 ± 1.4 , 33.3 ± 1.0 and 19.8 ± 0.4 . The data extrapolated to 40°C gave 191 for the constant as compared to the value 122 obtained by Halford and Brundage (16). A plot of the data yielded $\Delta F^\circ = -4175.6 + 2.88 T$.

Vapor phase esterification over NaHSO_4 was investigated by Brundage and Black (3). The catalyst was suspended on glass beads contained in a continuous coil constructed of Pyrex glass. Samples of dilute solutions of acetic acid and ethyl acetate in an alcohol-water solution were vaporized and circulated until the acid content of the mixture became constant, whereupon equilibrium was assumed. From the analysis of the final mixture equilibrium constants were calculated to be 74.5 ± 3.3 at 100° and 48.2 ± 1.3 at 125°C. Sodium acid sulphate was more active at low temperatures than was silica gel.

Goldanskii and workers (12, 13, 14, 15) obtained

some very interesting results on vapor phase esterification from their studies on heterogeneous catalysis in multimolecular adsorption layers. They showed that the reaction between acetic acid and ethyl alcohol vapors was completely heterogeneous; that is, it took place in the liquid adsorption layer. This reaction was immeasurably slow at 75°C in a glass vessel but was accelerated by the addition of hydrogen chloride (0.6 - 0.18%). In the presence of this catalyst equilibrium between equimolar amounts of acid and alcohol was at 92 mole percent of ethyl acetate. The rate up to 40 percent transformation was of zero order and was proportional to the surface area of the glass, which was varied by inserting glass tubing. The velocity increased rapidly with p/p_0 where p was the total pressure and p_0 the pressure at which droplets appeared on the wall. The temperature coefficient was negative if the velocities for constant p were compared at temperatures in the range 45-82°C. If the comparison were made at constant p/p_0 , the coefficient was positive and corresponded to an activation energy of 15,000 cal./mole, which is around the value for the liquid phase reaction. The thickness of the adsorption layer was calculated from the velocity of the reaction; for $p/p_0 = 0.7$ the thickness was 10^{-7} cm. and for $p/p_0 = 0.8$ it was 10^{-6} cm. The equilibrium constants were 305 at 45°C and 196 at 75°C.

Catalysts other than the ones mentioned have been employed for vapor phase esterification. Eleven different metallic oxides were tried by De Sandor (5) at 100°, 125°, 150° and 200°C for the formation of esters and the catalytic oxidation of ethyl alcohol. Silica gel and cerium oxide, CeO, proved satisfactory for esterification. The effects of several anhydrous salts on the extent of conversion in the vapor phase esterification of ethyl alcohol and acetic acid were studied by Dolian and Briscoe (6). $\text{Al}_2(\text{SO}_4)_3$ and $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$ had little if any effect on the conversion; $\text{Cr}_2(\text{SO}_4)_3$ increased it slightly, and $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3$ markedly. MgSO_4 induced esterification at a temperature higher than that at which the hydrate lost all of its water and CaCl_2 exhibited a minimum of esterification. The catalytic activity of other salts increased in the following order: Na_2SO_4 , NaOAc , NaPO_3 , CdSO_4 , ZnSO_4 , MnSO_4 , ZnCl_2 , NiSO_4 .

The data of Jatkar and Valvekar (21) on the activity of various catalysts was more meaningful. With equal rates of flow of an equimolar mixture of acetic acid and ethyl alcohol at 150°C they obtained the following results:

<u>Catalyst</u>	<u>Conversion, %</u>
Silica Gel	Very low
Ferric Alum	5
10% ZrO_2 on Silica Gel	38
NaHSO_4	40
Phosphoric Acid	70
Activated Charcoal	75
KHSO_4	80

Equilibrium conversion was about 85 percent.

Spangenberg (33) attempted to esterify acetic acid in the vapor phase with five primary, one primary unsaturated, two secondary and three tertiary alcohols on twelve salts and metal oxides. An oxide catalyst was prepared by saturating pumice with a solution of the acetate or nitrate of a metal and heating until the oxide formed, whereas a salt catalyst was prepared by saturating the pumice and heating to a temperature lower than the decomposition temperature. Rates of flow of the liquid ranged from 40 to 100 ml./hr. and the temperature measured at the catalyst varied between 245° and 410° . The results of this work are best presented in the form of a table.

<u>Alcohol</u>	<u>Composition of Catalyst wt. %</u>	<u>Maximum Conversion Obtained, %</u>
Ethyl	AgVO ₃ 92.6, Ag 7.4	58.7
Propyl	ThO ₂	86.9
Propyl	TiO ₂	95.2
iso-Butyl	ThO ₂	87.1
Amyl	ThO ₂	94.3
Amyl	BeO	37.9
Amyl	CdO	30.2
Amyl	Ce ₂ O ₃	40.4
iso-Propyl	ThO ₂	17.2
iso-Propyl	ZrO ₂	9.9
iso-Propyl	TiO ₂	39.8
sec-Butyl	ThO ₂	13.9
sec-Butyl	TiO ₂	34.9
tert-Butyl	ThO ₂	14.7
tert-Butyl	TiO ₂	15.9
tert-Amyl	BeO	5.2
tert-Amyl	TiO ₂	23.7

The table shows clearly that the best results were obtained with ThO₂ and TiO₂.

Several examples of vapor phase esterification have been specified and in each case the ester was formed from an acid and an alcohol. Mukherji and Goswami (26) achieved some success in converting vaporized ethyl alcohol into ethyl acetate using various materials as catalyst. In a characteristic run, ethyl alcohol when passed over $\text{Cu-Al}_2\text{O}_3\text{-CrO}_3$ at 275° gave six percent ethyl acetate and four percent acetic acid. CeO_2 , $\text{Ce}(\text{SO}_4)_2$, $\text{CuO-CeO}_2(1:1)$, $\text{Cu-CeO}_2(1:1)$, $\text{Cu-Ce}(\text{SO}_4)_2(3:1)$, ThO_2 were also used.

Thus far reference has been made mainly to work dealing with equilibria of, or catalysts used in, vapor phase esterification. Within the last ten years two papers have appeared in the literature on the kinetics of vapor phase esterification. The first was by Hoerig, Hanson and Kowalke (17) 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.

An attempt was made to determine the rate-controlling step. The differential equation for the second order reversible reaction was expanded for application to a flow system and integrated graphically using the data at 230°C . The rate constants that were estimated varied with the mass velocity proving that the actual rate of reaction was not the rate-

controlling step. The authors were able to demonstrate with graphs 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. The graphs showed that mass transfer coefficients were independent of mass velocity and increased linearly with temperature. Activation energies of 550, 1,280, 1820 and 3420 calories at 270°, 230°, 190° and 150°C., respectively, were obtained by plotting the logarithm of the mass transfer coefficient against the reciprocal of the absolute temperature.

Buckley and Altpeter (4) 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 (17). 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 from their results 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 (18) and used to correlate the experimental conversion data.

It is interesting that 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.

EXPERIMENTAL WORK

Statement of the Problem

The work to be outlined is defined as studies in vapor phase esterification. The important variables are reactor temperature, total pressure, molar ratio of alcohol to acid and feed rate. The several objectives of this research are best stated separately:

1. to find a catalyst for the vapor phase esterification of ethyl alcohol with acetic acid and to contrive a method for making the catalyst.
2. to construct a bench-scale apparatus for carrying out the reaction.
3. to study the kinetics of the reaction and from the kinetics to ascertain the rate-controlling step.
4. to establish a rate equation based on the rate-controlling step that will correlate the conversion data.
5. to use the rate equation to relate chemical reaction and diffusion within a particle of catalyst.

Materials Used

The reactants were synthetic absolute alcohol and glacial acetic acid. These were chosen because they were readily available, easy to handle and pertinent information about them

could be obtained. The reactant acid was between 99.50 and 100 percent HOAc by weight for all analyses and like the product was analyzed volumetrically by titration with carbonate-free standard sodium hydroxide solution using phenolphthalein indicator. The hydroxide was standardized against reagent grade potassium-acid-phthalate. Alkaline silver nitrate reagent (10) with alcohol gave a negative test for aldehydes. Consequently, water was assumed as the only possible impurity. However, the reactant alcohol was assumed to be 100% $\text{CH}_3\text{CH}_2\text{OH}$ by weight because density measurements indicated that water was present in negligible amounts.

Higher alcohols and acids are being considered for future work.

The Catalyst

The catalyst was composed by tungsten trioxide carried on porous alumina and prepared from J. T. Baker C.P. grade powdered tungstic acid, concentrated ammonium hydroxide and alumina balls of quality XF-101 bought from Aluminum Ore Company.

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 between 650 and 850°C . whereas the metal 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° . With aluminum and zinc, reduction of the oxide is directly to metallic tungsten.

Alumina balls smaller than 4-6 mesh were not available. The balls that were bought were marked 4-6 mesh but nearly all were larger than 4 mesh. The quality was poor and many were broken. After careful sorting and inspection, a batch weighing 2597.7 g. remained which contained balls that were nearly perfect spheres, smaller than 0.2035 in. but larger than 0.1875 in. The catalyst was prepared from this batch.

The carefully graded alumina balls were placed in a cold muffle furnace and the temperature was raised very slowly to 450° - 460°C . When the balls ceased to lose weight at this temperature, they were cooled slowly to 300°C ., quickly removed and placed in large desiccators, cooled to room temperature and weighed. The dry weight was recorded and the percent loss in weight calculated.

The solution with which the oven-dried alumina was

impregnated was prepared in the following manner. To 3400 ml. of concentrated ammonium hydroxide solution were slowly added 985.0 g. of tungstic acid. The mixture was left to stand overnight before being filtered to remove any residue. It was then analyzed for tungsten trioxide. The quantities of acid and ammonium hydroxide used are the results of a series of tests on small samples of the carrier.

The dried balls were transferred from the desiccators to a large heavy-walled flask and the whole evacuated for three hours. Impregnating solution was admitted while the flask and contents were under vacuum. When the balls were covered with solution the vacuum was broken. After an hour the excess solution was decanted, and the balls were discharged into a large evaporating dish which was then placed in a cold drying oven. The temperature of the oven was raised slowly to 105°C. When the balls were dry they were conveyed to a muffle furnace set at 100-110°C. The temperature of the furnace was raised very slowly to 450-460°C. and was maintained at that level until ammonia could no longer be detected. During the ignition a slow stream of nitrogen was passed through the oven. When ignition was complete, the temperature of the furnace was lowered slowly to 300°C. At this temperature the catalyst was quickly removed and deposited in large desiccators, cooled to room temperature and weighed.

Before the catalyst was used, the particle diameter, bulk density, particle or apparent density, absolute density and fractional voids within the particle were determined. The particle diameter, D_p , is an average of measurements made with a micrometer on 300 balls. The bulk density, ρ_p , was obtained in the usual manner. A straightforward but tedious method was used to get the particle density, ρ_p . A random sample of 63 oven-dried particles was quickly weighed. The diameters of the particles were measured with a micrometer and the volume of the sample calculated. The particle density was derived from the relationship between the weight and the volume. The absolute density 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 balls 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. The void fraction within the particle was given by the relation, $\tau = 1 - \rho_p/\rho_c$, between the apparent and absolute densities of the catalyst.

The calculations and quantities that were pertinent to the preparation of the catalyst follow:

Alumina balls

Weight of air-dried balls	2597.7 gm.
Weight of oven-dried balls	2319.7 gm.
Loss in weight	278.0 gm.
Percent loss in weight $\frac{(278.0)(100)}{2597.7} =$	10.70

Composition of impregnating solution

8.2569 gm. of solution yielded 1.7163 gm. of WO_3 .

Composition of the solution = $\frac{(1.7163)(100)}{8.2569} = 20.79\%$ by weight WO_3 .

7.7568 gm. of solution yielded 1.6144 gm. of WO_3 .

Composition of the solution = $\frac{(1.6144)(100)}{7.7568} = 20.81\%$ by weight WO_3 .

Average composition = 20.80% by weight WO_3 .

Composition of catalyst

Weight of impregnated balls	2517.9 gm.
Weight of oven-dried balls	2319.7 gm.
Weight of WO_3	198.2 gm.

Composition of catalyst on oven-dried basis

$$= \frac{(198.2)(100)}{2517.9} = 7.87\% \text{ by weight } WO_3.$$

Particle diameter

The particle diameter is an average of measurements made on 300 balls and is 0.523 cm.

Bulk density of the catalyst

The bulk density, ρ_b , of the catalyst was found to be 1.002 g./cc.

Particle density of catalyst

The volume of a single ball = $\frac{4}{3} \pi R^3 = 0.5236 D_p^3$.

The volume of n balls = $0.5236 \sum_{i=1}^{i=n} D_{p_i}^3$

For n = 63 $\sum_{i=1}^{63} D_{p_i}^3 = 8.9539 \text{ cc.}$

and the volume is $(0.5236)(8.9539) = 4.6883 \text{ cc.}$

Weight of 63 oven-dried catalyst balls = 7.9164 gm.

Particle density, ρ_p , = $(7.9164)/(4.6883) = 1.6886 \text{ gm./cc.}$

Absolute density of catalyst

Temperature = 21.9°C.

Weight of dry sample of catalyst = 1.9001 gm.

Density of water at 21.9°C. = 0.9978219 gm./cc.

Weight of water to fill pycnometer - without catalyst = 10.3176 gm.

Volume of water = $(10.3176)/(0.9978219) = 10.3401$ cc.

Weight of water to fill pycnometer - with catalyst = 9.8272 gm.

Volume of water = $(9.8272)/(0.9978219) = 9.8486$ cc.

Volume of solid = $10.3401 - 9.8486 = 0.4915$ cc.

Absolute density of catalyst, ρ_c , = $\frac{1.9001}{0.4915} = 3.8659$ gm./cc.

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

3.8525 g./cc.

3.8625

3.8594

The absolute density, ρ_c = average of the four determinations
= 3.860 gm./cc.

Void-fraction within the particles

Internal void fraction, $\gamma = 1 - \rho_p/\rho_c$

$$= 1 - \frac{1.6886}{3.860} = 0.5625.$$

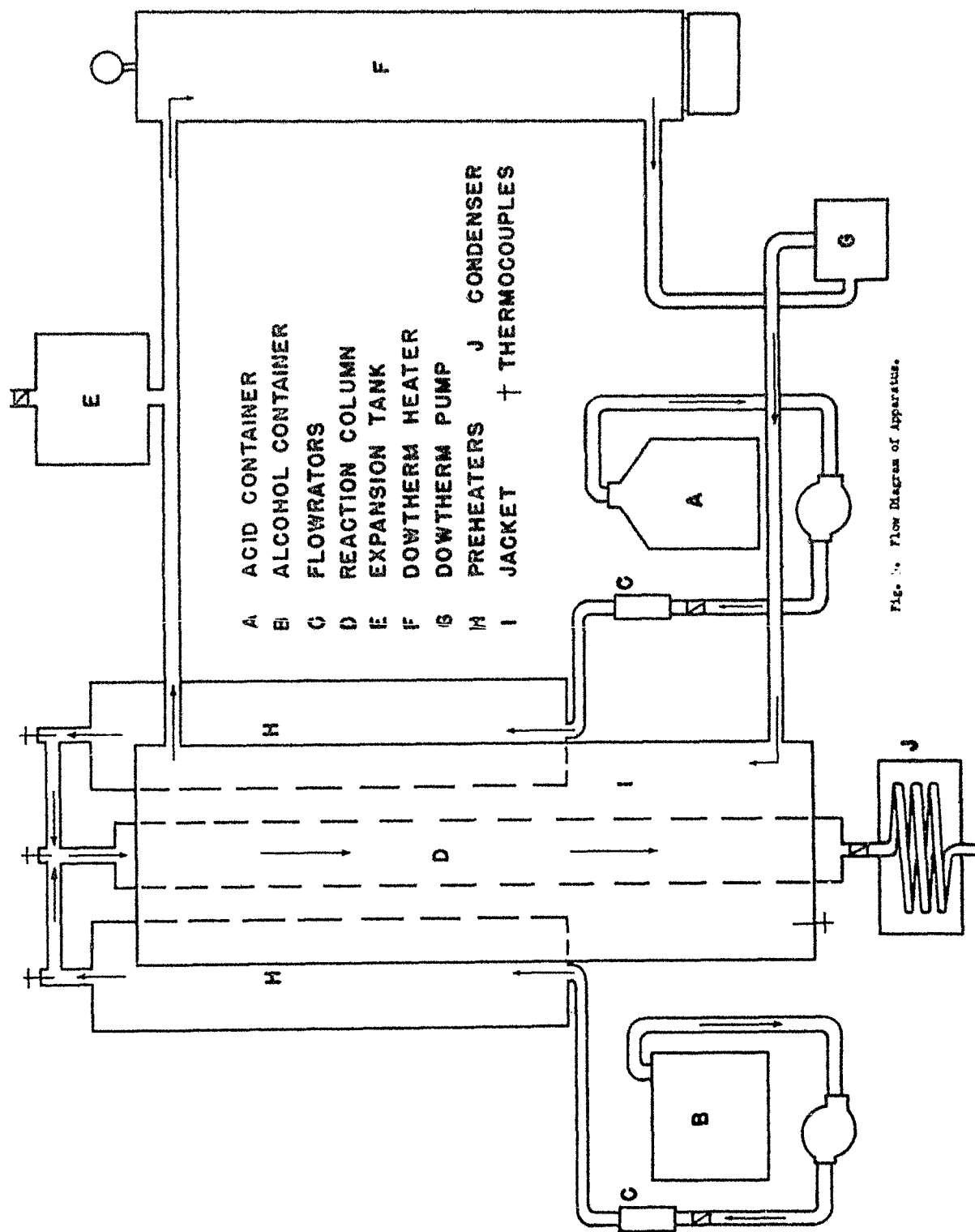


Fig. 1. Flow Diagram of Apparatus.

The Apparatus

The apparatus embraced a reactants pumping section, vaporizer-preheaters for the alcohol and acid, an isothermal reactor, a product condenser, and a Dowtherm circulating heater. A flow diagram is given in Figure 5 and photographs are shown in Figures 1, 2, 3 and 4.

The pumping section comprised containers (A, B, Figure 5) for the alcohol and acid, pumps and flowrators (C, Figure 5). The container for alcohol was constructed from type 316 stainless steel and had a capacity of five gallons. A drying tube at the top of the tank kept out moisture. To eliminate handling, the acid was left in the bottle in which it was bought. Moisture was kept out of the bottle by placing a specially designed cup filled with desiccant around the neck and cap. Two Model PPI-M Low Volume (Precision) multi-purpose gearless pumps manufactured by Eco Engineering Company delivered the reactants to the pre-heaters. The pumps were made from type 316 stainless steel and were close coupled to Model 2OEM Graham variable speed transmissions. The reactant containers stood on a small platform directly above the pumps. The liquid reactants were metered with Fischer & Porter precision flowrators calibrated at room temperatures between 24°C. and 28°C. The calibration is described in Appendix D. Semi-needle valves of type 316 stainless steel were installed in the liquid lines between the flowrators and

the pumps for better adjustment of rates of flow. Provision was made in the pumping section for passing nitrogen through the system before and after a run.

The vaporizer-preheaters (H, Figure 5) were electrically heated and built identically. Each was constructed from a $44\frac{1}{2}$ " length of $\frac{3}{4}$ N.P.S. type 316 stainless steel pipe. Sheet asbestos was wrapped twice around the pipe. Twenty-nine feet of No. 18 Nichrome IV wire wound over the asbestos delivered 1060 watts at 115 volts. The heaters were mounted vertically inside 6" sheet metal cylinders capped with $\frac{3}{8}$ " transite plate and filled with vermiculite.

The tubular reactor (D, Figure 5) 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 5) 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 $2\frac{1}{2}$ ". 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 $\frac{3}{4}$ " connection for the preheaters, whereas the bottom one had a $\frac{1}{8}$ " connection for the product condenser.

The catalyst was supported on a stainless steel perforated plate about 4.25 in. from the bottom cap. A bed 100 cm.

deep was used for all the runs. The volume, V , and weight, W , of the catalyst that corresponded to this depth were 2165 cc. and 2170 g., respectively. The inside diameter, D , of the reactor was measured carefully at both ends with calipers. A value of 5.25 cm. was obtained. The external void fraction of the bed was 0.4065 and was determined from the relation $\alpha = 1 - \rho_b/\rho_p$. Table 6 summarizes the properties of the bed and the catalyst.

An effective product condenser (J, Figure 5, was made out of a coil of 1/8" N.P.S. stainless steel pipe and a cylindrical container about eight inches in diameter and ten inches deep. Ice was used as the cooling medium. A stainless steel valve was installed between the reactor and the condenser. This valve was throttled during runs at pressures above atmospheric and was closed when the reactor was not in operation.

Although Figure 3 shows the circulation heater quite clearly, a brief description is given 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 one at the top. An auxiliary heater supplied 1060 watts at 115 volts. This heater was made from 29 ft. of No. 18 Nichrome IV wire wound round the 3" pipe which had been previously coated with No. 1 Sauereisen cement.

Dowtherm A was circulated with a heavy duty, single

suction centrifugal pump (G, Figure 5) manufactured by Dean Brothers Pumps, Inc. The hot liquid entered the jacket of the reactor at the bottom and left at the top. The suction nozzle of the pump was directly below the immersion heater. The capacity of the circulating system was about four gallons. An expansion tank (E, Figure 5) fabricated from 20" of 5" pipe was installed between the outlet of the jacket and the inlet of the heater.

Temperature Measurement and Control

Temperatures were measured with iron-constantan thermocouples in type 316 stainless steel pressure-tight wells located as shown in Figure 5. The couples were Type 3D35S "Midgets" produced by Brown Instrument Company. The temperatures at the outlets to the two vaporizer-preheaters and at the inlet to the jacket were recorded separately with Leeds and 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 thermocouples 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 and Northrup No. 8657-C double range potentiometer-indicator. Before any runs were made, the recorders were checked

against this same instrument.

The recorder-controllers were connected to Leeds and Northrup No. 10764 M.E.C. control units (Figure 1), and the M.E.C. units were connected to Leeds and Northrup No. 10224-25 driving mechanisms which operated Variacs (Figure 4) that supplied power to the heaters. The preheaters 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 vaporizer-preheater was controlled manually with the "manual setter" on its respective M.E.C. unit. Power to the immersion heater was controlled differently. The "manual setter" on the M.E.C. unit was adjusted until the recorder-controller indicated that the Dowtherm 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.

Temperatures at other points were checked. A thermocouple well made out of 1/4" copper tubing was located near the outlet of the 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 measurements are tabulated in Appendix A. 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.

When the apparatus was tested with nitrogen, the temperature at the inlet to the reactor was $10-15^{\circ}\text{C}$, 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.

Pressure Measurement and Control

Pressures were measured with $4\frac{1}{2}$ " 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. The pressure was controlled with the valve between the reactor and the product condenser.

Operating Procedure

Trial runs were made to develop an operating procedure. After the fourth run the following procedure was adopted. Nitrogen was passed through the catalyst bed while the reactor and vaporizer-preheaters were being heated. When the operating temperature was reached, the nitrogen was shut off and the M.E.C. unit controlling the power to the immersion heater was switched to automatic operation. The feed pumps were started and the feed rates adjusted. Steadier flows were achieved when the reactant containers were pressured with nitrogen to about 5 psi. If this pressure was used at low flow rates the pumps could be stopped. Temperatures and feed rates were checked frequently during a run. Samples of the product were analyzed immediately after being taken. When steady-state conditions were attained as many as ten samples were analyzed. The number depend on the rate at which the reactants were being fed to the system. When a run was completed the pumps were stopped and the preheaters were drained. The power was left on while nitrogen was passed through the bed for about three-quarters of an hour or until material no longer formed in the condenser. Finally, the power was turned off and the valve between the reactor and product condenser was closed.

Analysis of the Product

The product was analyzed for acetic acid in the following way. A 1.5 or 2.0 g. sample was collected at ice temperature 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 resultant solution titrated with carbonate-free standard sodium hydroxide solution. Persistent end-points were obtained for all titrations.

EXPERIMENTAL RESULTS

The weight of catalyst, W , was the same for all runs. Consequently, the quantity W/F was varied by changing F . For this research, F is the feed rate of the acid which in the data is represented by F_{A_0} . Values of F were such that W/F varied between 307 and 1152.

From the time the feed pumps were started, four to six hours were needed to complete a run. Only runs for which steady state conditions were attained have been considered. In Tables 1 through 4 the runs are grouped into a number of series. Each series includes runs made under a chosen set of conditions. The fraction of the acid converted, X , was calculated from the composition of the feed, the gravimetric feed rate and the analysis of the product. A sample calculation based on one hour of operation follows:

Sample Calculation:

Temperature of reactor ($t^{\circ}\text{C.}$)	140
Pressure of reactor (atm.)	0.963
Rate of flow of acid (g./hr.)	232.5
Rate of flow of alcohol (g./hr.)	178.2
Mass rate of flow (g./hr.)	410.7
Normality of sodium hydroxide solution	0.3837
Composition of acid (wt. %)	99.62
Composition of alcohol (wt. %)	100.
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.)	2170.
For one hour of operation	

$$\text{G. moles of acid fed, } F_{A_0} = \frac{0.9962 \times 232.5}{60.052} = 3.8569$$

$$\text{G. moles of alcohol fed, } F_{B_0} = \frac{178.2}{46.068} = 3.8682$$

$$\text{G. of solid/g. mole acid fed, } W/F_{A_0} = 2170/3.8569 = 563.$$

$$\text{Moles of alcohol/mol. of acid, } R = 3.8682/3.8569 = 1.003$$

$$\text{Mass velocity, } G, \text{ lb./hr.)(sq.ft.)} = 410.7/(453.6)(0.0233) = 38.9$$

$$\text{G. moles of unreacted acid/g. of product} = \frac{(212.15)(0.3837)}{(1000)(10.5985)} = 0.007680$$

$$\text{G. moles of unreacted acid} = 410.7 (0.007680) = 3.1542$$

$$\text{Fractional conversion of acid, } X = \frac{3.8569 - 3.1542}{3.8569} = 0.182$$

Table 1.

Run	W/F _A	G	X
Series 1: Temperature 140°C., Pressure 0.974 atm., R = 1.003			
5	563	38.9	0.182
7	820	26.6	0.243
8	562	38.9	0.183
12	697	31.4	0.213
13	1152	19.0	0.307
15	1152	19.0	0.304
16	1025	21.3	0.275
17	405	54.0	0.140
18	405	54.0	0.137
19	307	71.2	0.108
Series 2: Temperature 160°C., Pressure 0.972 atm., R = 1.003			
21	1025	21.3	0.366
23	819	26.6	0.338
24	698	31.4	0.282
26	405	54.0	0.164
27	1151	19.0	0.397
27a	1151	19.0	0.390
28	307	71.2	0.136
29	562	38.9	0.236
30	405	54.0	0.175

Table 1 (continued)

Run	W/F_A	G	X
Series 4: Temperature 180°C., Pressure 0.971 atm., R = 1.003			
41	820	26.6	0.516
42	698	31.4	0.458
43	1026	21.3	0.586
44	563	38.9	0.381
44a	563	38.9	0.397
45	307	71.2	0.258
46	1151	19.0	0.646
47	405	54.0	0.315
59	1150	19.0	0.647

Table 2.

Run	W/F _A	G	X
Series 2: Temperature 160°C., Pressure 0.972 atm., R = 1.003			
21	1025	21.3	0.366
23	819	26.6	0.338
24	698	31.4	0.282
26	405	54.0	0.164
27	1151	19.0	0.397
27a	1151	19.0	0.390
28	307	71.2	0.136
29	562	38.9	0.236
30	405	54.0	0.175
Series 3: Temperature 160°C., Pressure 0.970 atm., R = 1.502			
31	563	47.2	0.264
31a	563	47.2	0.269
32	1026	26.0	0.418
33	698	38.1	0.342
38	820	32.4	0.362
39	1152	23.1	0.437
40	405	65.6	0.205

Table 2 (continued)

Run	W/F _A	G	X
Series 5: Temperature 160°C., Pressure 0.970 atm., R = 2.000			
49	1026	30.5	0.457
50	1154	27.2	0.497
51	821	38.2	0.406
52	698	44.8	0.350
55	405	77.3	0.207
Series 8: Temperature 160°C., Pressure 0.974 atm., R = 0.751			
65	819	23.8	0.275
67	404	48.1	0.139
70	698	27.9	0.238

Table 3.

Run	N_{A_0}	P_{A_0}	G	X
Series 6: Temperature 160°C., Pressure 0.973 atm., $W/F_{A_0} = 820$				
23	0.3736	0.3631	26.6	0.3175
38	0.3080	0.2993	32.4	0.362
51	0.2630	0.2557	38.2	0.406
56	0.2309	0.2244	44.0	0.399
57	0.2057	0.2000	49.7	0.402
63	0.2309	0.2244	44.0	0.398
64	0.2056	0.1999	49.7	0.396
65	0.4191	0.4074	23.8	0.275
66	0.1695	0.1648	61.2	0.401

Table 4.

Run	P	P ²	G	X
Series 7: Temperature 160°C., $W/F_{A_0} = 819$, $R = 1.001$				
23	0.972	0.945	26.6	0.3175
60	1.112	1.236	26.6	0.338
61	1.247	1.555	26.6	0.380
62	1.383	1.913	26.6	0.432

Table 5.

Purging Experiment on Run No. 61

Time of Sampling O, min.	Moles of Unreacted Acid per gram of Product
0.5	0.00922
5.5	0.00987
16.5	0.01170
23.5	0.01212
29.5	0.01238
35.5	0.01258
41.5	0.01271

Table 6.

Properties of the Catalyst

Composition = 7.87% by weight WO_3

Particle diameter, $D_p = 0.523$ cm.

Bulk density, $\rho_b = 1.002$ g./cc.

Particle density, $\rho_p = 1.6826$ g./cc.

Absolute density, $\rho_c = 3.860$ g./cc.

Internal void fraction, $\tau = 0.5625$

Properties of the Bed

Depth, $h = 100$ cm.

Diameter, $D = 5.25$ cm.

Volume, $V = 2165$ cc.

Weight, $W = 2170$ g.

External void fraction, $\alpha = 0.4065$

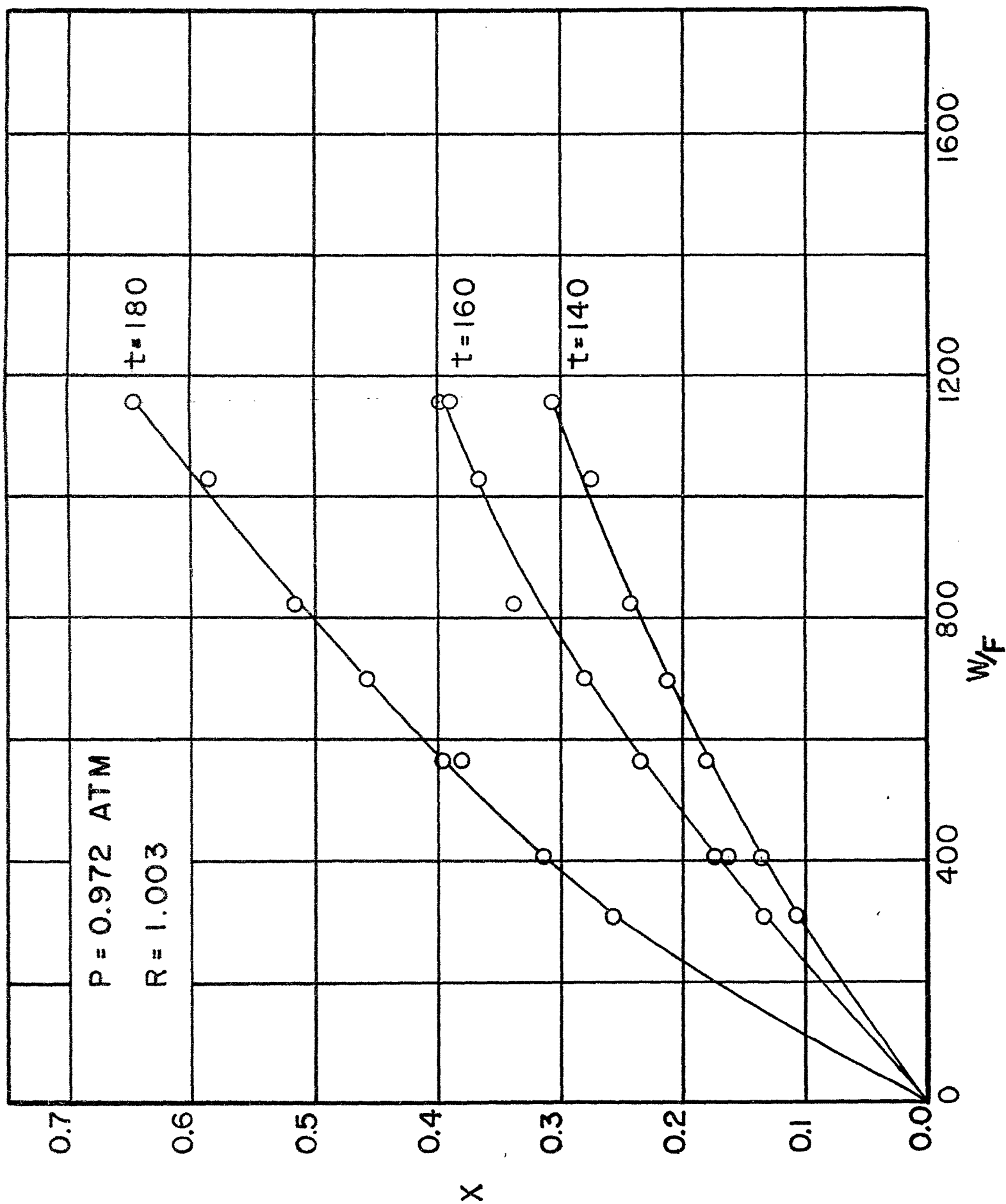


Fig. 6. Conversion Curves at 140°C., 160°C. and 180°C. for an Equimolar Feed.

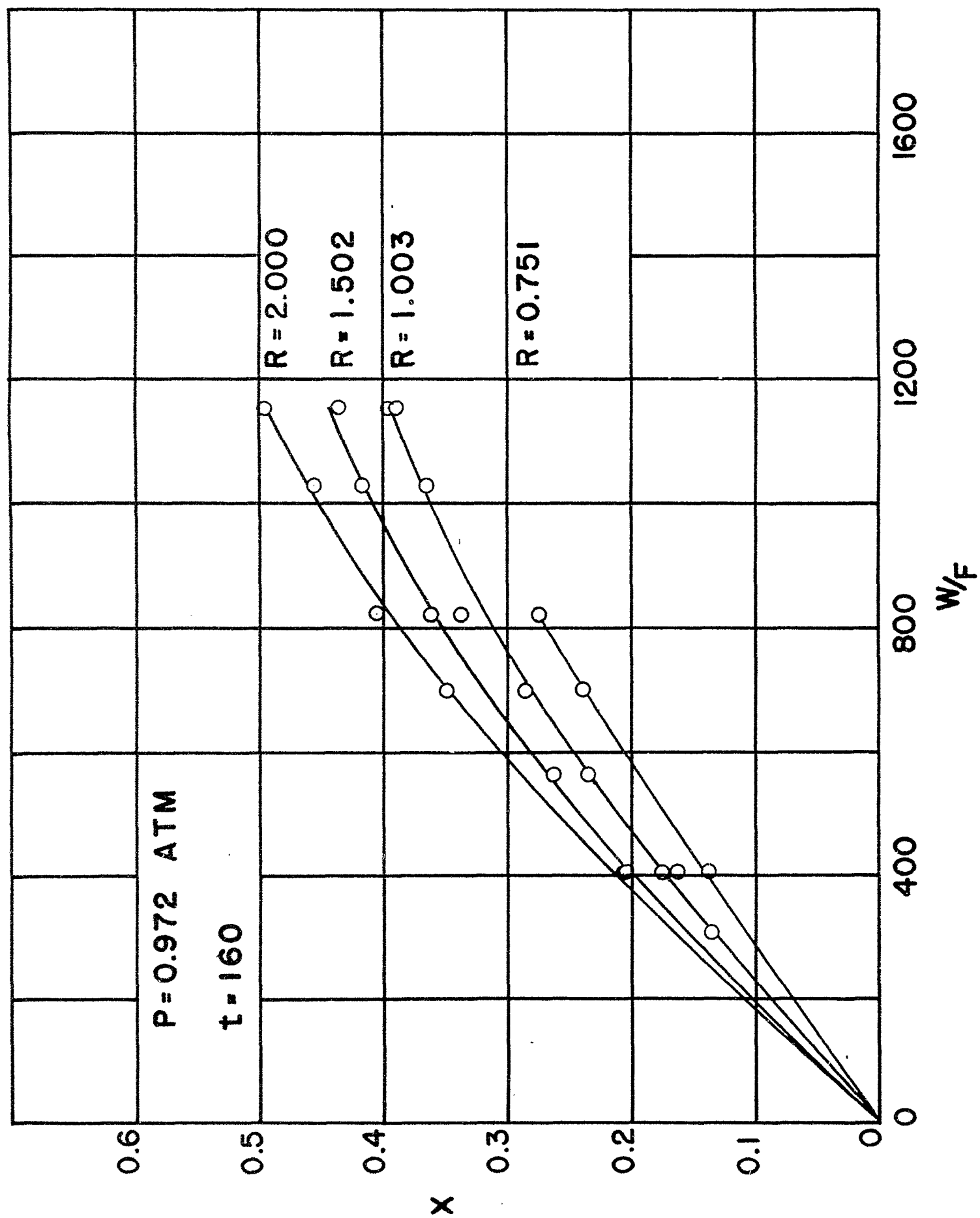


Fig. 7. Comparison Curves at 1.50%.

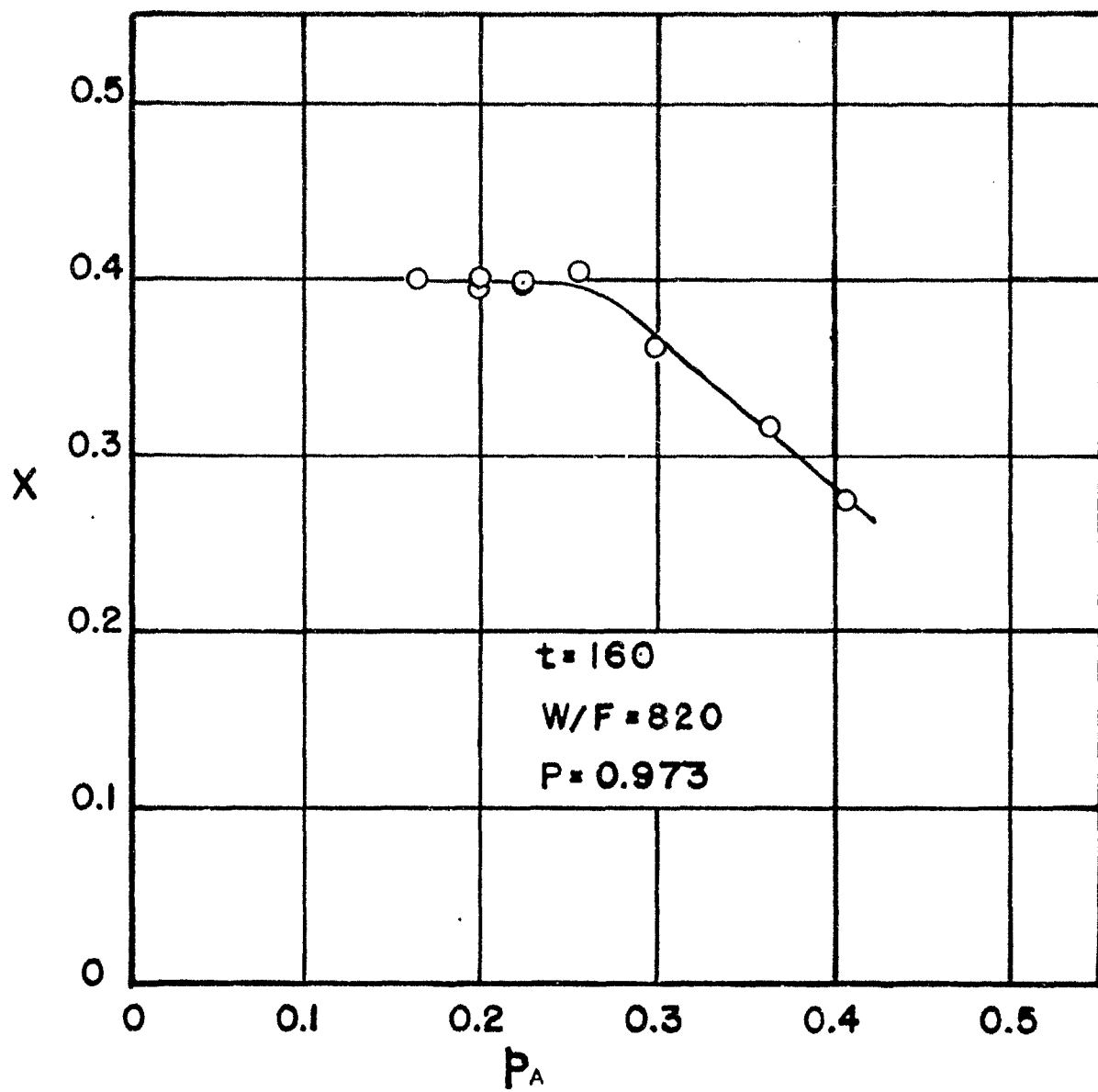


Fig. 8. Conversion vs. p_{A_0} for 160° and $W/F = 820$.

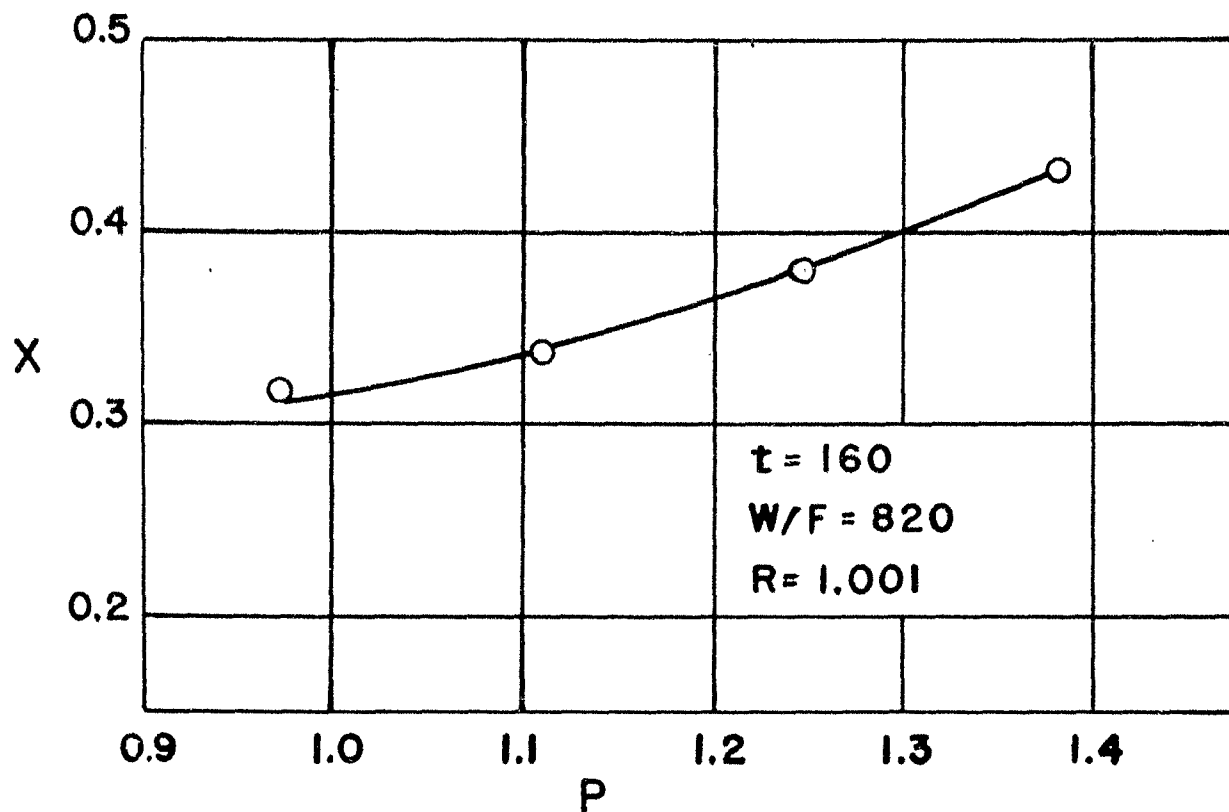


Fig. 9. Effect of Total Pressure on Conversion at 160°C. for an Equimolal Feed and $W/F = 820$.

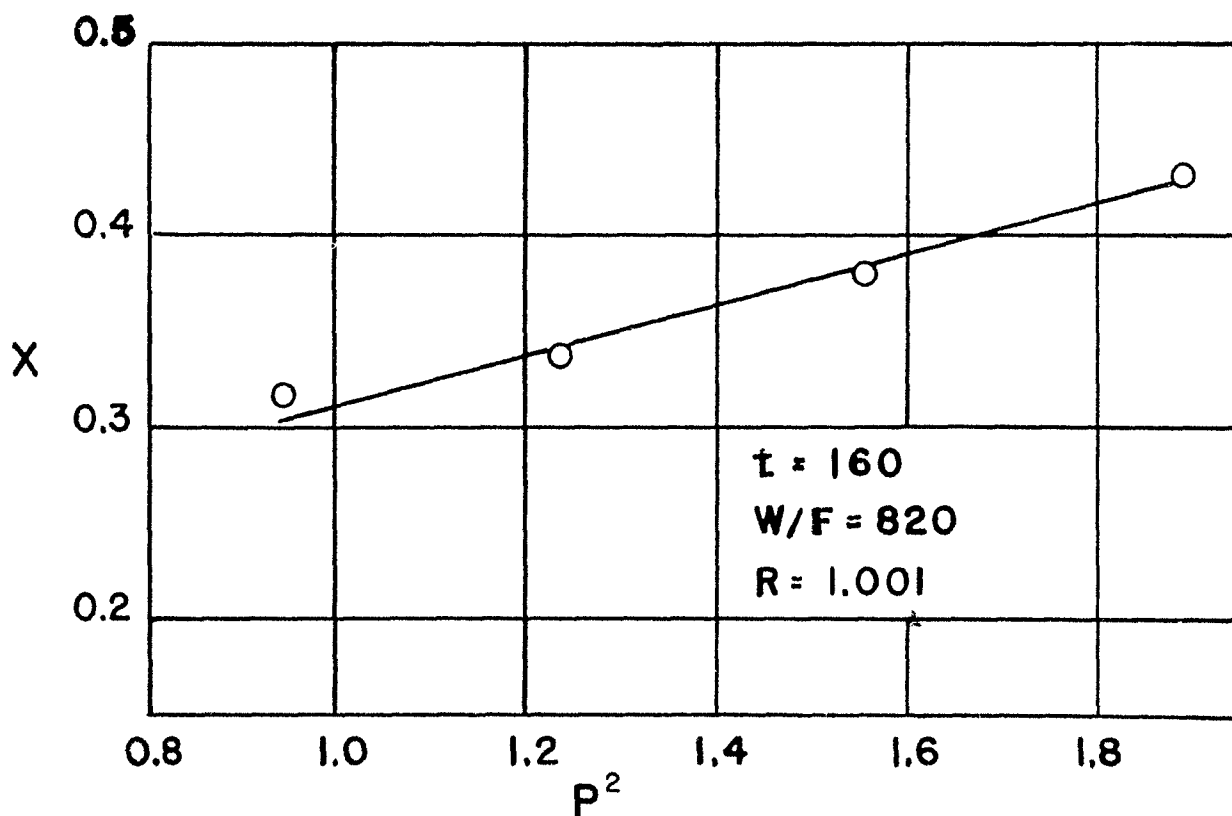


Fig. 10. Conversion vs. P^2 at 160°C. for an Equimolal Feed and $W/F = 820$.

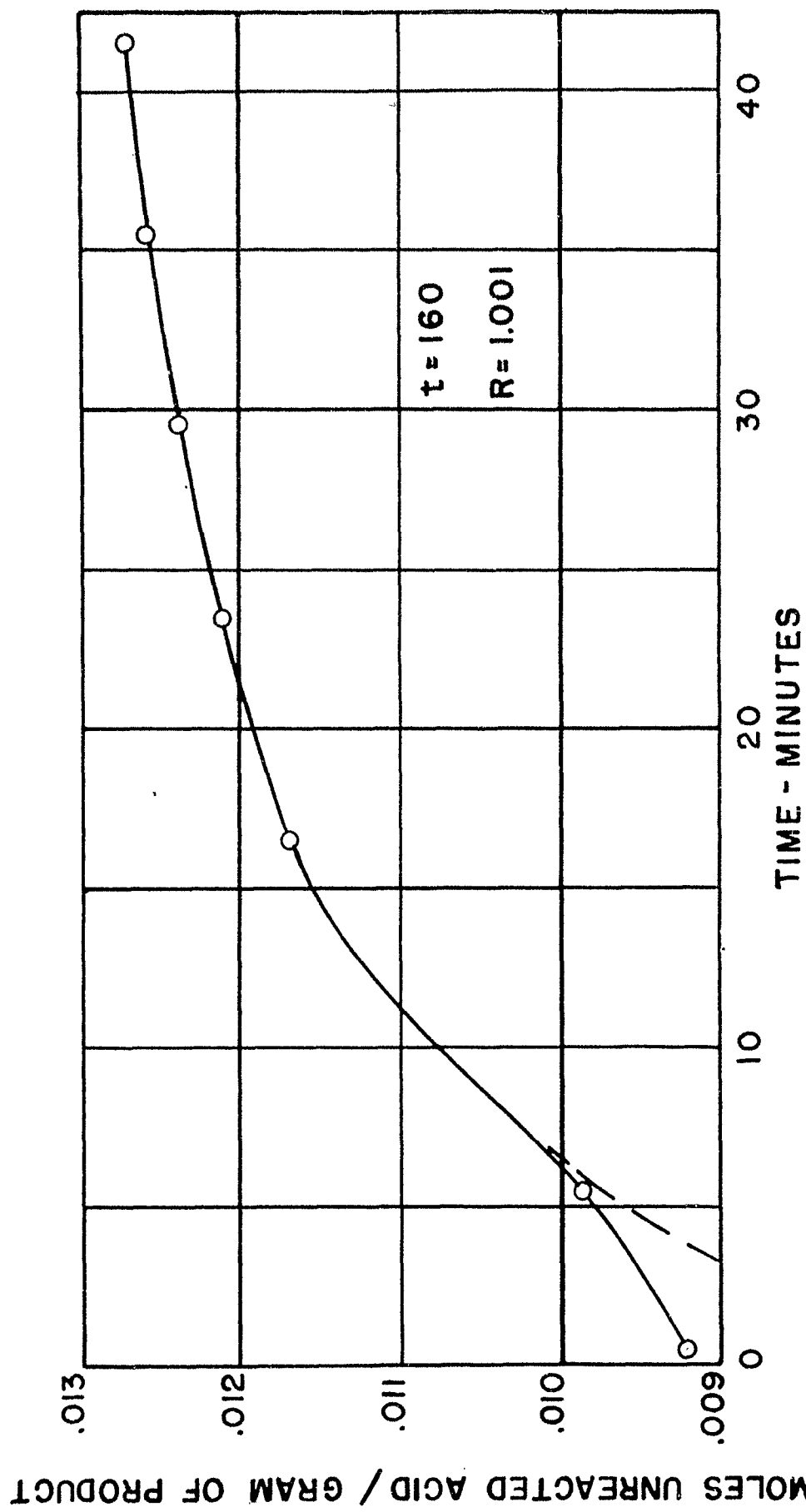


Fig. 11. Composition of Material Removed from Bed after a Run at 160°C. vs. Time.

Figures 6 through 11 were derived from Tables 1 through 5. In Figure 6 and 7, X is plotted against W/F . Figure 6 shows the effect of W/F on the conversion at 140° , 160° and 180°C . when the molar ratio of alcohol to acid is 1.003 and the average total pressure is 0.972 atmospheres. Figure 7, on the other hand, shows the effect of W/F on the conversion for molar ratios of alcohol to acid of 0.751, 1.003, 1.502 and 2.00 when the temperature is 160°C . and the average total pressure is 0.972 atmospheres. In Figure 8, X is plotted against p_{A_0} , the initial partial pressure of acetic acid monomer to show the effect of feed composition on conversion at a given value of W/F . The data for the figure were obtained at 160°C ., an average total pressure of 0.973 atmospheres, and for W/F equal to 820. Figure 9, arising from Table 4, shows the relationship between conversion and total pressure over a narrow range of pressure at 160°C ., for a molar ratio of alcohol to acid of 1.001 and for W/F equal to 819. In Figure 10 values of conversion are plotted against the square of the total pressure.

Figure 11 requires some explanation. When the last sample from Run No. 61 was analyzed the feed pumps were stopped and the vaporizer-preheaters were drained. While the power was still on, the system was purged with nitrogen flowing at about $0.4 \text{ ft}^3/\text{min}$. Samples of condensate from the product condenser were collected and weighed and the time of sampling was noted.

The samples were analyzed for acetic acid and the results of the analyses were expressed as moles of unreacted acid per gram of product. Figure 11 is a plot of the results of this purging experiment. For Run No. 61 W/F was 820 and molar ratio of alcohol to acid was 1.001.

The properties of the catalyst and the bed are summarized in Table 6.

DISCUSSION OF RESULTS

It will be recalled that the reactor was packed with catalyst that had been oven-dried at 450-460°C. In the early stages of the initial run, which was made at 140°C., only alcohol was delivered to the system. Ether, recognized by its odor, was undeniably present in the first sample of product, 4-5 ml., that was collected. Apparently the dehydrating action of the catalyst, at least in its early history, was strong and could not be overlooked. The odor of ether diminished noticeably after the acid was admitted to the system. In addition to the first sample, twenty others ranging in volume from 10 to 20 ml. were collected. The odor of ether had seemingly disappeared by about the fourth sample and the odor of ethyl acetate was unmistakable. The amount of acid increased in progressive samples. Undoubtedly the formation of ether was a possible side reaction. Consequently, the extent or importance of this reaction had to be determined. Two experiments were performed which showed that the formation of ether was unimportant in subsequent runs.

In the first experiment three batches of product from a number of runs were separately distilled in a 1" glass distillation column packed with glass spirals and lagged with magnesia. The column was operated at nearly total reflux. The results of the separation follow:

Table 7.

Batch 1.

<u>Volume of Product Collected, ml.</u>	<u>Temperature Range, °C.</u>
25 ml.	69-70°C.
25	69-70
250	70-70.5
250	70.5-71
25	71-72
25	72-72.5
25	72.5-73
25	73-74
25	74-76
25	76-79
25	79-92
25	92-99

Batch 2.

<u>Volume of Product Collected, ml.</u>	<u>Temperature Range, °C.</u>
25	69-70
250	70-71
25	71-73
25	73-75
25	75-77
25	77-80
25	80-82
25	82-85
25	85-89

Batch 3.

<u>Volume of Product Collected, ml.</u>	<u>Temperature Range, °C.</u>
5	60-64
25	69-70
250	70
250	70
250	70-71
25	71-72
25	72-73
25	73-76
25	76-80
25	80-91
25	91-99

The distillation should indicate whether products were formed by side reactions. A possible side reaction is the formation of ether. If no ether was formed an azeotrope of water, ethyl alcohol and ethyl acetate boiling at 70.3°C . would distill off first. An examination of the results of the distillation shows that this was probably the case and that ether was not formed after the initial run or was formed only in very small amounts.

In the second experiment two samples of product were saponified with an excess of carbonate-free standard sodium hydroxide solution after being analyzed for acetic acid. When the saponification was complete, standard hydrochloric acid was

added in excess and the excess acid titrated with standard base. The total base should equal the total acid if no side products are formed and if all errors are eliminated. The results follow:

Normality of base	0.3716 and 0.3720
Normality of acid	0.2024
Composition of acid, % by wt.	99.81
Molar ratio of alcohol to acid, R	1

Sample 1:

Weight of sample of product	1.6646 g.
-----------------------------	-----------

Moles of acid entering = moles of alcohol entering

$$= \frac{1.6646}{\left(\frac{60.052}{0.9981} + 46.068\right)} = 0.01567$$

Moles of base for analysis of sample

$$= \frac{(27.14)(0.3716)}{1000} = 0.01009$$

Moles of base added for saponification

$$= \frac{(25.02)(0.3716)}{1000} = 0.00930$$

Moles of base for excess acid

$$= \frac{(9.35)(0.3720)}{1000} = 0.00348$$

Total moles of base

0.02287

Moles of HCl added

$$= \frac{(40.65)(0.2024)}{1000} = 0.00823$$

Difference

0.01464

The difference should be

0.01567

$$\frac{0.01464}{0.01567} = 0.934$$

Sample 2:

Weight of sample of product

1.5657

$$\text{Moles of acid entering} = \frac{1.5657}{\left(\frac{60.052}{0.9981} + 46.068\right)} = 0.01474$$

Moles of base for analysis of sample

$$= \frac{(25.50)(0.3716)}{1000} = 0.00948$$

Moles of base added for saponification

$$= \frac{(25.00)(0.3716)}{1000} = 0.00929$$

Moles of base for excess acid

$$= \frac{(8.49)(0.3720)}{1000} = 0.00316$$

Total moles of base

0.02193

$$\text{Moles of HCl added} = \frac{(40.05)(0.2024)}{1000} = 0.00811$$

Difference

0.01382

The difference should be

0.01474

$$\frac{0.01382}{0.01474} = 0.938$$

For each sample of product the agreement is nearly 94%. In order that this figure have more meaning, four mixtures having essentially the same composition as the product were prepared and treated in the same way. For each of the four mixtures the agreement was 94.5, 95.5, 97.1 and 97.2%. Although the results for the product do not agree with those for the mixtures as well as could be expected, it was felt that they were good enough to refute the formation of ether as an important side reaction.

Dehydration of ethyl alcohol to ethylene and water occurs at temperatures considerably higher than those used in this research. With coarse granules of alumina a temperature of 350-400°C. is required. A complete material balance could be made for each run in order to eliminate the possibility of this side-reaction. A simpler method was used. The flow rate of the liquid product was determined and compared with the feed rate. The results for ten runs are given in Table 8. For each of them the agreement is entirely satisfactory, being within 2%.

Other side reactions are also unlikely. Support is given to this statement by the work of Pearce and Rice (29) who studied the adsorption of water, ethyl alcohol, acetic acid, and ethyl acetate vapors on WO_3 and ZrO_2 at 99.4°C. The authors compared their results with those obtained by Pearce and Alvarado (28) for the adsorption of the same

Table 8.

Run No.	Temp. °C.	Feed Rate g./hr.	Wt. of Sample g.	Time of Sampling sec.	Product Rate g./hr.	Difference, %
16	140	225.3	14.1916	225	227.0	+ 0.75
24	160	331.5	20.5626	220	336.5	+ 1.51
25	160	410.7	22.1958	195	409.8	- 0.22
26	160	570.6	12.6977	80	571.4	+ 0.14
30	160	570.6	11.2369	70	577.8	+ 1.26
32	160	274.5	10.6542	140	274.0	- 0.18
33	160	402.6	6.7122	60	402.7	+ 0.02
47	180	570.6	17.5198	110	573.4	+ 0.49
55	160	817.0	11.0447	49	811.4	- 0.068
56	160	464.5	26.9657	210	462.3	- 0.50

substances at the same temperature on ThO_2 and Al_2O_3 and concluded that for unit volume of adsorbent the adsorption capacities for water vapor decrease in the order ThO_2 , Al_2O_3 , WO_3 and ZrO_2 . This is also the order of the dehydrating power of these oxides towards alcohol. Pearce and Rice support the view that both the alcohol and acid must be adsorbed when the vapor phase esterification reaction is catalyzed by metallic oxides. They mention no side reactions other than those which have been discussed.

The question of catalyst activity arises. It was necessary to prove that the activity of the catalyst did not change. This was accomplished by making check runs during the course of the research. The assumption was made that the activity had not changed if conversions were the same for check runs made under like conditions. Table 9 shows that runs could be checked and therefore the activity of the catalyst did not change.

Table 9.

<u>Run No.</u>	<u>Temperature, °C.</u>	<u>W/F</u>	<u>X</u>
5	140	563	0.182
8	140	562	0.183
13	140	1152	0.307
15	140	1152	0.304
26	160	405	0.164
30	160	405	0.175
46	180	1151	0.646
59	180	1150	0.647
56	160	820	0.399
63	160	820	0.398
57	160	820	0.402
64	160	820	0.396

Something should be said about the appearance of the product. The first material to be collected during a run was usually a pale brown. This color faded from the product stream very quickly. The product became clear in the time required to collect 10-15 ml.

As previously stated, one of the objectives of this research was to determine a mechanism for which a rate equation

could be developed that would correlate the kinetic data. In general, the effect of temperature is of little importance in selecting a mechanism. Because of this, most of the data were obtained at one temperature, i.e., at 160°C. Figure 7 shows that conversions at 160°C. for a given value of W/F decrease as the molar ratio of alcohol to acid decreases. This result is represented more clearly by Figure 8 where conversion is plotted against the partial pressure of the acid monomer in the feed when W/F is 820. The curve becomes flat for values of p_{A_0} less than about 0.25 atmospheres. It could not be extended in the direction of smaller values of p_{A_0} because of the limitations of the apparatus. However, one would expect that the curve would bend fairly sharply and pass through the origin. The points on the flat portion of the curve were checked and are not questionable. For an equimolar feed and W/F equal to 820 the relationship between conversion and total pressure over the small range of total pressures studied is not linear. When the conversion was plotted against the total pressure (Figure 9) a curve was obtained that was concave upwards. A more linear relationship was obtained when the conversion was plotted against the square of the total pressure (Figure 10).

Figure 11 demonstrates how the amount of acid in the material removed from the bed varied with time when nitrogen

was passed through the bed immediately after a run. The material analyzed 0.0127 g. moles of acid/g. in less than forty-five minutes. Pure acid is 0.01667 g.moles/g. The first point on the curve corresponds to 0.00922 g.moles of acid/g. of material at 0.5 min. If time could have been measured from the amount that Run No. 61 was completed, then at zero time the material should have analyzed 0.00583 g.moles of acid/g., the steady-state value of the product. Inasmuch as the vaporizer-preheaters had to be drained before nitrogen could be used, time was measured from the moment the nitrogen was turned on. However, the time required for the composition of the material to change from 0.00583 g.moles acid/g. to 0.00922 g.moles acid/g. is doubtless quite short. The broken curve was drawn to show how the correct curve might have appeared. Figure 11 does not prove that any one of the four components was not adsorbed, but rather it suggests that the acid was more strongly adsorbed than the alcohol and that there are more adsorbed acid molecules than alcohol or ester and water molecules.

The marked effect of temperature on conversion for equimolar mixtures of reactants is clearly shown in Figure 6. When W/F is 1100 the conversion is about 0.298 at 140°C., 0.384 at 160°C. and 0.626 at 180°C. These values imply that the rate of the reaction increases appreciably with temperature. Data were obtained for only three curves because it was felt

that data at other temperatures would not contribute much to the determination of a mechanism.

No runs were made without catalyst in the reactor because it has been established that the rate of the homogeneous reaction is negligible (4, 9, 17). Moreover, no effort was made to determine the extent of conversion during sampling and analysis. Buckley and Altpeter (4) have shown that it is very small and can be disregarded.

DETERMINATION OF A MECHANISM

When a gaseous reaction is catalyzed by porous particles the following physical and chemical rate steps are always present (18):

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 chemisorption of reactants on the surface of the catalyst.
4. The activated desorption of products.
5. The surface reaction of adsorbed reactants.

A mechanism that defines the rate of a 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

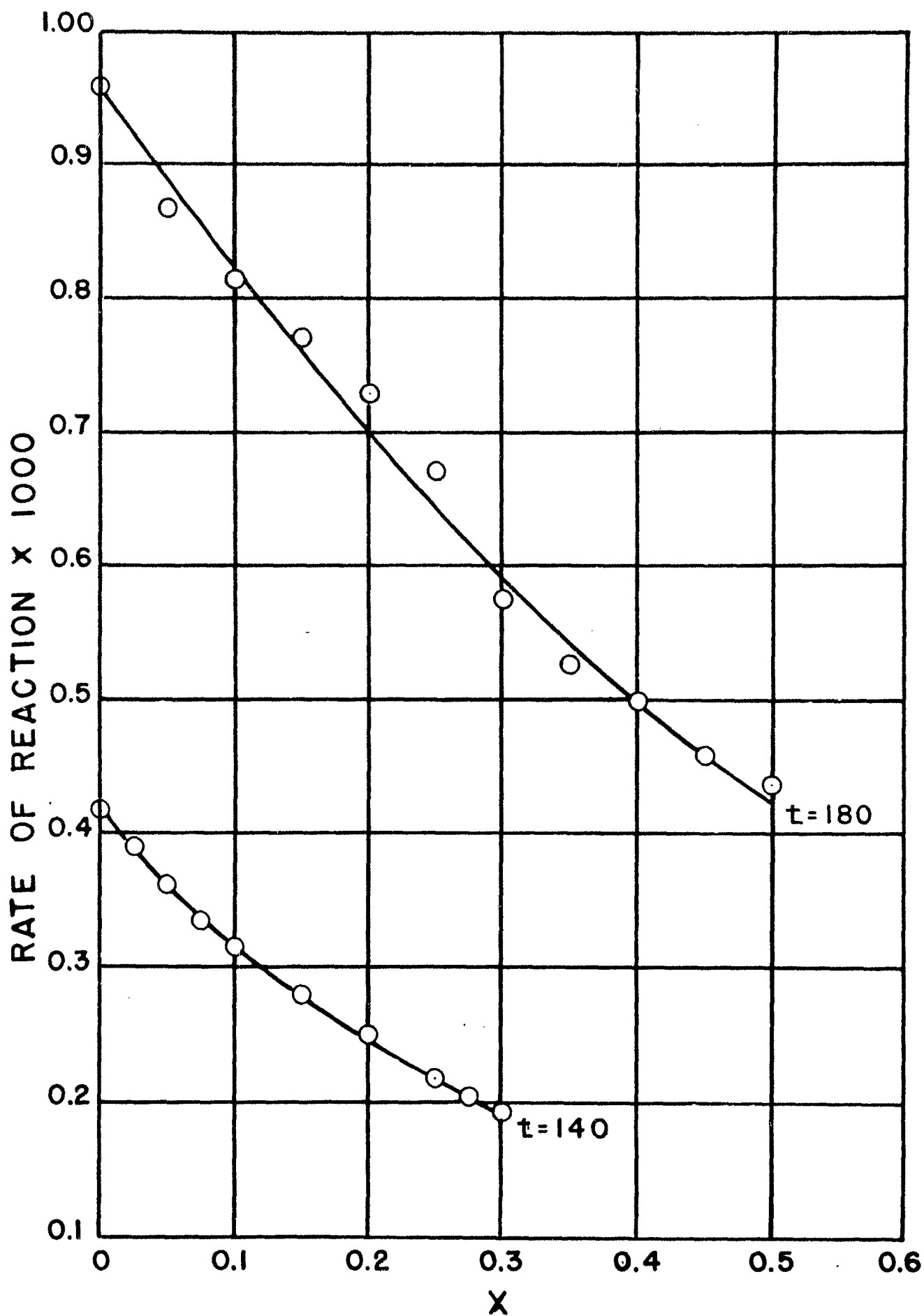


Fig. 12. Rate of Reaction x 1000 vs. Conversion at 140° and 180°C. for an Equimolar Feed.

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 (39). Figure 12 will also be used. In this figure the (rate of reaction $\times 1000$) is plotted against conversion for 140°C and 180° and 0.972 atmospheres. The rates are the measured slopes of curves in Figure 6.

Step 1:

It is evident from Figure 6 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 Figure 6, 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 0.000192 g.moles/(g.catalyst)(hr.) at 140°C for a mass velocity of 19 lbs./(hr)(sq.ft.), and 0.000672 g.moles/(g.catalyst)(hr.) at 180°C for a mass velocity of 71.2 lbs./(hr)(sq.ft.). 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 (39) were used instead. In their paper the authors plotted the reaction rate number,

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

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 two rates and mass velocities mentioned previously. Calculations for the two cases follow:

Case 1:

$$t = 140^\circ\text{C}, r = 0.000192 \text{ g, moles}/(\text{g.catalyst})(\text{hr.}),$$

$$G = 19 \text{ lbs.}/(\text{hr.})(\text{sq.ft.})$$

$$M_m = 53 \quad p_f = 0.972 \text{ atms.} \quad p_A = 0.2309 \text{ atms.}$$

$$a_p = \pi D_p^2 = 0.8594 \text{ sq. cm.} \quad \sqrt{a_p} = 0.927 \text{ cm.}$$

$$a_m = \frac{\pi D_p^2}{(\pi D_p^3 \rho_p)/6} = \frac{6}{D_p \rho_p} = 6.79 \text{ sq. cm./g. of catalyst}$$

Viscosities in centipoises at 140°C and 1 atmosphere (30):

	H O A_c	H_2O	E t O H	E t O A_c
$\mu =$	0.0112	0.0138	0.0120	0.0105

The values are similar and for the purpose of this calculation any one of the four listed could be taken. The value for acetic acid was used.

Diffusivities of the vapors in air at 25°C and 1 atmosphere (30):

	<u>D, sq.cm./sec.</u>	<u>$\mu/\rho D$</u>
H O A _c	0.133	1.16
H ₂ O	0.256	0.60
E t O H	0.119	1.30
E t O A _c	0.086	1.79

Although the diffusivity varies markedly with temperature theory and experiment indicate that the Schmidt number, $\mu/\rho D$ is independent of pressure and varies only slightly with temperature. Consequently, the diffusivities can be used only at a given temperature, whereas the Schmidt number can be used with some assurance at various temperatures. Since the vapor under consideration is a mixture of the four components, a correct value of $\mu/\rho D$ cannot be obtained. The value for ethyl acetate, being the largest, was used.

Therefore, the reaction rate number is

$$\frac{(0.927)(0.000192)(53)(0.972)}{(0.2309)(3600)(0.000112)(6.79)} \cdot (1.79)^{2/3} = 0.0214$$

and the modified Reynolds number is

$$\frac{(0.927)(19)(453.6)}{(929)(3600)(0.000112)} = 21.3$$

Under these conditions $\frac{\Delta p_A}{p_A} < 0.005$

Case 2:

$$t = 180^{\circ}\text{C}, r = 0.000672 \text{ g.moles}/(\text{g. of catalyst})(\text{hr.}),$$

$$G = 71.2 \text{ lbs.}/(\text{hr.})(\text{sq.ft.})$$

$$M_m = 53$$

$$p_f = 0.972 \text{ atms.}$$

$$p_A = 0.309 \text{ atms.}$$

$$\sqrt{a_p} = 0.927 \text{ cm.}, a_m = 6.79 \text{ sq.cm.}/\text{g.of catalyst}, u/\rho D = 1.79$$

Viscosities in centipoises at 180°C and 1 atmosphere (30):

H O A_c	H_2O	E t O H	E t O A_c
$\mu = 0.0124$	0.0153	0.0130	0.0115

The value for acetic was used. Therefore, the reaction rate number is,

$$\frac{(0.927)(0.000672)(53)(0.972)}{(0.309)(3600)(0.000124)(6.79)} (1.79)^{2/3} = 0.0342$$

and the modified Reynolds number is

$$\frac{(0.927)(71.2)(453.6)}{(929)(3600)(0.000124)} = 72.3$$

$$\text{Again } \Delta p_A/p_A < 0.005.$$

These calculations show not only that mass transfer is not the rate-controlling step, but also that the film resistance can be neglected without incurring an error of more than 0.5%.

Step 2.

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 0.523 cm. and an internal void fraction of 0.5625. 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. Therefore, for particles with an internal void fraction of 0.5625, the effective pore radius should be quite large. The diffusion coefficients of the reactants and products can not be calculated because of the complexity of the system, but are probably rather high. The comparatively high temperatures that have been used favor high diffusion coefficients. The molecular volumes and molecular weights of all the components, except possibly ethyl acetate, are relatively small and also suggest high

diffusion coefficients. The coefficient for alcohol in acetic acid at 160°C and 0.972 atmospheres was estimated as 0.123 sq.cm/sec. Under Step 1 it was mentioned that the rates of reaction were low. 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. The results obtained support this statement. For a given value of W/F, the increase of conversion with temperature in Figure 6 cannot be explained by diffusion in pores alone. Furthermore, a curve of the type shown in Figure 8 cannot be explained by a diffusion mechanism. Therefore, the assumption is made that diffusion in the pores of the catalyst is not the rate-controlling step.

Step 3:

The data show that neither the rate of adsorption of acetic acid nor the rate of adsorption of ethyl alcohol is the controlling step. If adsorption of the acid were rate-controlling the order of the curves in Figure 7 would necessarily be reversed; i.e., the curve for R equal to 0.751 would be at the top. If the adsorption of the alcohol were rate-controlling, even though the curves of Figure 7 are in the proper order, the curves in Figures 9 and 12 would have to be concave downward (39) and Figure 8 could not have been obtained.

Step 4:

Figures 7, 8, 9 and 12 eliminate desorption of water of ethyl acetate as the rate-controlling steps. 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 and of the total pressure. The results show that this was certainly not the case.

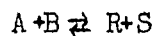
Step 5:

The first four steps have been eliminated as rate-controlling and the reasons for eliminating them have been given. Therefore, a surface reaction appears to be the rate-controlling step. Indeed, Figures 7, 8, 9, 10 and 12 support surface reaction as the rate-controlling step. Figure 11 suggested that acetic acid was more strongly adsorbed than alcohol and that there were more adsorbed acid molecules than alcohol molecules, or water and ester molecules. This would explain the order of the curves in Figure 7. If alcohol were more strongly adsorbed than the acid and if there were more adsorbed alcohol molecules than acid molecules the order of the curves would be reversed. The curve in Figure 8 could not be extended experimentally but it is apparent that this curve must bend and pass through the origin. The maximum in the complete curve can be explained by a surface reaction of the type $A+B \rightleftharpoons R+S$. When the initial rate of this type of reaction is plotted against

the total pressure at low pressures a curve is obtained which is concave upwards if the surface reaction is rate-controlling. The curve in Figure 9 is also concave upwards although conversion rather than the initial rate has been plotted against the total pressure. This is to be expected if the surface reaction is rate-controlling. A curve of conversion versus the square of the total pressure should have less curvature than the curve of Figure 9. This is borne out of Figure 10. In general, where adsorption is controlling, the curve obtained by plotting the rate of the reaction against conversion at constant temperature and pressure is concave downward and where surface reaction is controlling is concave upwards (39). The curves in Figure 12 for 140° and 180°C. and 0.972 atmospheres are concave upwards. The results of this research indicate that a surface reaction is the rate-controlling step.

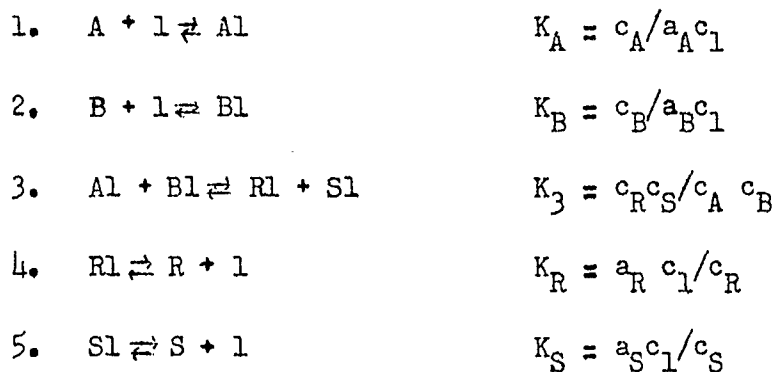
There is no reason to assume at this time that any one of the reactants or products is not adsorbed. As a matter of fact, the results of Pearce and Alvarado (28) and Pearce and Rice (29) on the adsorption of acetic acid, ethyl alcohol, water and ethyl acetate vapors on Al_2O_3 , ThO_2 , WO_3 and ZrO_2 at 99.4°C. indicate that all of the components are probably adsorbed. Therefore, the assumption is made for the time being that the reactants and products are adsorbed and that equilibrium is maintained in all adsorption and desorption steps.

Two mechanisms will now be written and a rate equation for each will be developed. The reaction will be represented by the expression



where A, B, R and S refer to the acetic acid, ethyl alcohol, water and ethyl acetate, respectively.

Mechanism I:



Step 3 is the rate-controlling step.

Adsorbed molecule A reacts with adsorbed molecule B. The rate of the forward reaction is proportional to the number of pairs of adjacently adsorbed A and B molecules per gram of catalyst. Therefore, the rate of the forward reaction is

$$\frac{k_s}{L} \cdot c_A c_B \quad (1)$$

Adsorbed molecule R reacts with adsorbed molecule S. Therefore, the rate of the reverse reaction is

$$\frac{k'_s}{L} c_R c_S \quad (2)$$

Therefore, the net rate of the forward reaction is,

$$r = \frac{S}{L} (k_3 c_A c_B - k'_3 c_R c_S) \quad (3)$$

$$= \frac{k_3 s}{L} (c_A c_B - \frac{c_R c_S}{K_3}) \quad (4)$$

where $K_3 = k_3/k'_3$, the equilibrium constant for step 3.

The surface concentrations may be expressed in terms of the activities of the components in the gas phase as follows:

$$c_A = K_A a_A c_1 \quad (5) ; \quad c_B = K_B a_B c_1 \quad (6)$$

$$c_R = a_R c_1 / K_R \quad (7) ; \quad c_S = a_S c_1 / K_S \quad (8)$$

Substitution of Equations (5), (6), (7) and (8) in (4) gives

$$r = \frac{k_3 s K_A K_B c_1^2}{L} (a_A a_B - \frac{a_R a_S}{K_A K_B K_3 K_R K_S}) \quad (9)$$

Since $K_A K_B K_3 K_R K_S = K$, the overall equilibrium constant

$$r = \frac{k_3 s K_A K_B c_1^2}{L} (a_A a_B - \frac{a_R a_S}{K}) \quad (10)$$

The term c_1 represents the concentration of unoccupied active sites per gram of catalyst and is related to total concentration of active sites by the expression

$$L = c_1 + c_A + c_B + c_R + c_S \quad (11)$$

Substitution of Equations (5), (6), (7) and (8) in (11) gives

$$L = c_1 + K_A a_A c_1 + K_B a_B c_1 + \frac{a_R c_R}{K_R} + \frac{a_S c_R}{K_S} \quad (12)$$

and

$$c_1 = L / (1 + K_A a_A + K_B a_B + a_R/K_R + a_S/K_S) \quad (13)$$

Therefore,

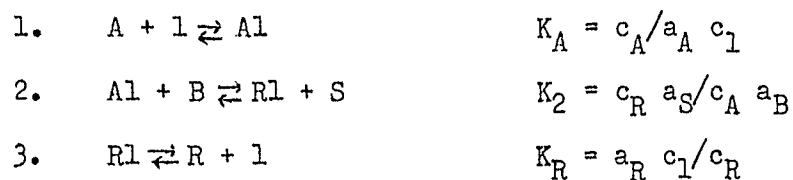
$$r = \frac{k_3 s K_A K_B L (a_A a_B - a_R a_S/K)}{(1 + K_A a_A + K_B a_B + a_R/K_R + a_S/K_S)^2} \quad (14)$$

If the interior of the catalyst is not 100% effective the right side of Equation (14) can be multiplied by the effectiveness factor, E, to give

$$r = \frac{E k_3 s K_A K_B L (a_A a_B - a_R a_S/K)}{(1 + K_A a_A + K_B a_B + a_R/K_R + a_S/K_S)^2} \quad (15)$$

$$= \frac{k (a_A a_B - a_R a_S/K)}{(1 + K_A a_A + K_B a_B + a_R/K_R + a_S/K_S)^2} \quad (16)$$

$$\text{where } K = E k_3 s K_A K_B L \quad (17)$$

Mechanism II:

Step 2 is the rate-controlling step.

Adsorbed molecule A reacts with molecule B in the gaseous phase. The rate of the forward reaction is proportional to the concentration of adsorbed A molecules and to the activity of B molecules in the gaseous phase. Therefore, the rate of the forward reaction is

$$k_2 c_A a_B \quad (18)$$

The rate of the reverse reaction is given by

$$k_2' c_R a_S \quad (19)$$

Therefore, the net rate of the forward reaction is

$$r = k_2 c_A a_B - k_2' c_R a_S \quad (20)$$

$$= k_2 (c_A a_B - c_R a_S / K_2) \quad (21)$$

where $K_2 = k_2/k_2'$, the equilibrium constant for Step 2. Again the surface concentrations may be expressed in terms of activities.

$$c_A = K_A a_A c_l \quad (22) \quad ; \quad c_R = a_R c_l / K_R \quad (23)$$

Substitution of Equations (22) and (23) in (21) gives

$$r = k_2 K_A c_l (a_A a_B - \frac{a_R a_S}{K_A K_2 K_R}) \quad (24)$$

$$= k_2 K_A c_l (a_A a_B - a_R a_S / K) \quad (25)$$

where $K_A K_2 K_R = K$, the overall equilibrium constant. The total concentration of active sites is,

$$L = c_l + c_A + c_R \quad (26)$$

$$= c_l + K_A a_A c_l + K_R a_R c_l \quad (27)$$

Therefore, $c_l = L / (1 + K_A a_A + K_R a_R)$ (28)

and
$$r = \frac{k_2 K_A L (a_A a_B + \frac{a_R a_S}{K})}{(1 + K_A a_A + K_R a_R)} \quad (29)$$

or more correctly if the effectiveness factor is not 1

$$r = \frac{E k_2 K_A L (a_A a_B - \frac{a_R a_S}{K})}{(1 + K_A a_A + K_R a_R)} \quad (30)$$

$$= \frac{k (a_A a_B - \frac{a_R a_S}{K})}{(1 + K_A a_A + K_R a_R)} \quad (31)$$

where $k = E k_2 K_A L$ (32)

The adsorption term for alcohol and the desorption term for ester do not appear in the rate equation developed from Mechanism II. This does not mean that they are not adsorbed but rather that adsorbed alcohol and ester molecules do not contribute directly to the reaction.

The rate equations 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 (17) that ethyl alcohol, water and ethyl acetate vapors behave like ideal gases at pressures less than one atmosphere in the range of temperature used in this research. Therefore, the partial pressures 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 dimer is significant and must be taken into account.

Equilibrium constants for the association of acetic acid were determined at three temperatures by Essex and Clarke (8).

From their results they obtained the following relationship between the association constant, K_x , and the absolute temperature:

$$K_x = \frac{8082}{T} + 29.12 \log_{10} T - 95.653 \quad (33)$$

The number of moles of associated and unassociated acid and other components that were present in mixtures resulting from various feeds and corresponding to definite conversions were calculated from the stoichiometry of the reaction and values of K_x obtained from Equation (33). The total number of moles in each mixture was obtained and the partial pressure of each component was calculated. An expression developed by Essex and Clarke (8) was used to determine the fugacities of acetic acid vapor for the different mixtures. Comparison showed that the fugacity of the vapor and the partial pressure of the monomer were equal at 140°C, 160°C and 180°C. Therefore, the assumption was made that acetic acid monomer also behaved like an ideal gas. The results of the above calculations are presented in the form of tables in Appendix A.

The rate equations for the two mechanisms can be written completely in terms of the partial pressures of the reactants and products:

Mechanism I.

$$r = \frac{k \left(p_A p_B - \frac{p_R p_S}{K} \right)}{(1 + K_A p_A + K_B p_B + p_R/K_R + p_S/K_S)^2} \quad (34)$$

$$= \frac{\left(p_A p_B - \frac{p_R p_S}{K} \right)}{(a + b p_A + c p_B + d p_R + e p_S)^2} \quad (35)$$

where $a = 1/k^{1/2}$, $b = K_A/k^{1/2}$, $c = K_B/k^{1/2}$, $d = 1/K_R k^{1/2}$, $e = 1/K_S k^{1/2}$.

Mechanism II.

$$r = \frac{k \left(p_A p_B - \frac{p_R p_S}{K} \right)}{(1 + K_A p_A + K_R p_R)} \quad (36)$$

$$= \frac{\left(p_A p_B - \frac{p_R p_S}{K} \right)}{(a + b p_A + c p_R)} \quad (37)$$

where $a = 1/k$, $b = K_A/k$, $c = K_R/k$. Equations (35) and (37) can be transformed to give

$$\sqrt{\frac{\left(p_A p_B - \frac{p_R p_S}{K} \right)}{r}} = a + b p_A + c p_B + d p_R + e p_S \quad (38)$$

and

$$\frac{p_A p_B - \frac{p_R p_S}{K}}{r} = a + b p_A + c p_R \quad (39)$$

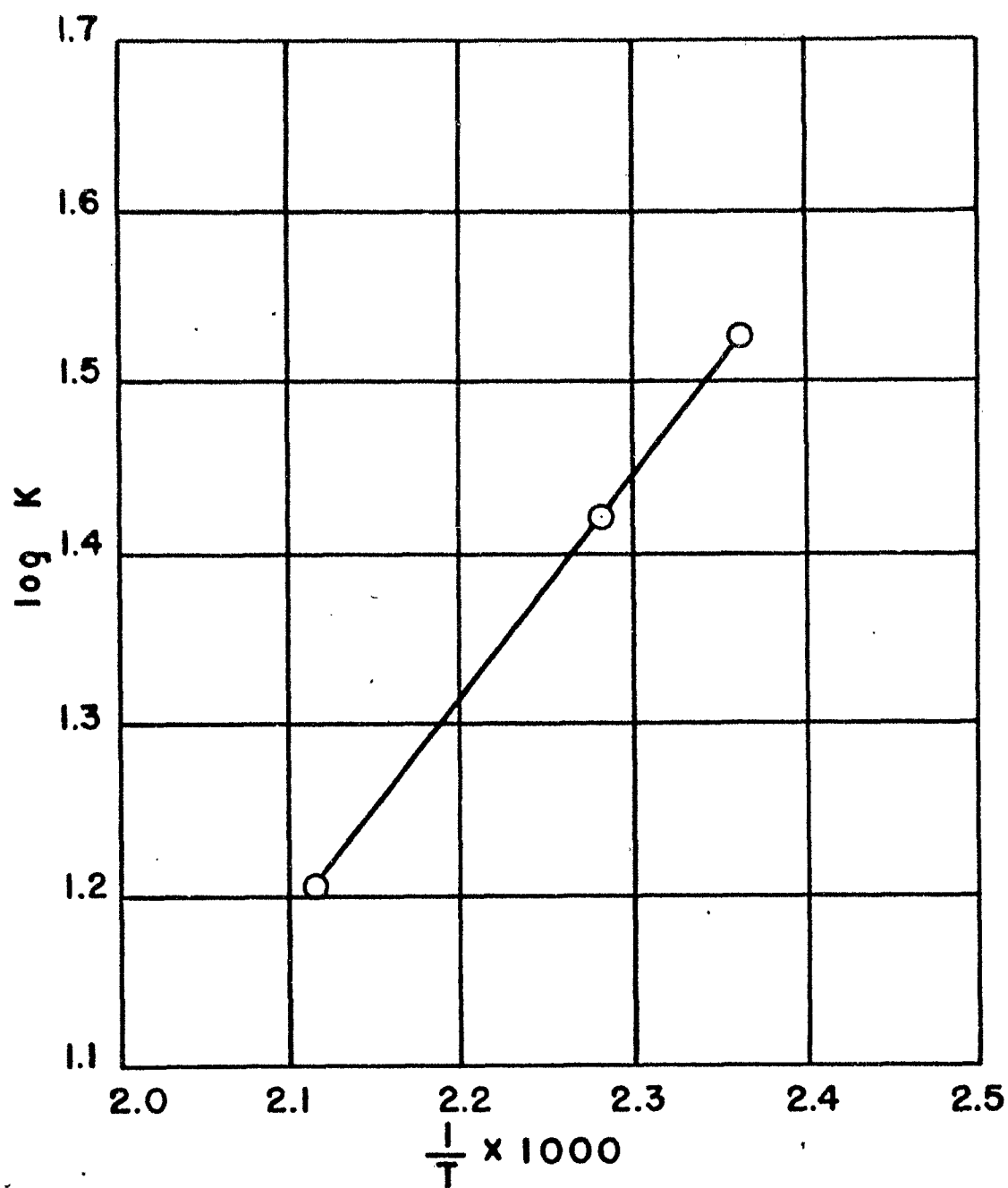


Fig. 13. Effect of Temperature on the Equilibrium Constant for Gaseous Esterification Reaction.

The unknown constants appear on the right side of the equations whereas the quantities obtained from experiment appear on the left side. Partial pressures were calculated as previously described and values of r were obtained by graphically differentiating curves of X versus W/F . The equilibrium constant was derived from Figure 13 where $\log K$ is plotted against the reciprocal of the absolute temperature. The values of K for this figure were taken from the paper by Essex and Clark (8).

In this work p_R and p_S were not varied independently. Therefore, Equation (38) is written

$$\sqrt{\frac{p_A p_B - \frac{p_R p_S}{K}}{r}} = a + b p_A + c p_B + (d+e) p_S$$

$$= a + b p_A + c p_B + d' p_S \quad (40)$$

If $K_A \gg K_B$, as suggested by Figure 11, it is permissible to write

$$\sqrt{\frac{p_A p_B - \frac{p_R p_S}{K}}{r}} = a + b p_A + c p_S \quad (41)$$

If the rate of adsorption of alcohol had been controlling the following expression would have been developed

$$\frac{p_B - \frac{p_R p_S}{K p_A}}{r} = a + b p_A + c \frac{p_R p_S}{p_A} + (d + e) p_S \quad (42)$$

$$= a + b p_A + c \frac{p_R p_S}{p_A} + d' p_S \quad (43)$$

If $K_A \gg K_B$

then

$$\frac{p_B - \frac{p_R p_S}{K p_A}}{r} = a + b p_A + c p_S \quad (44)$$

Constants were evaluated for 160°C by the method of least squares for Equations (39), (40) and (41) and as a check for Equations (43) and (44). The data which were used apply to Figure 7 and are tabulated in Table 10. The values of the constants for the five equations are listed in Table 11.

Table 10.

r	P _A	P _B	P _R	P _S
Temperature = 160°C, Pressure = 0.972 atms., K = 28.51				
0.000412	0.317	0.438	0.080	0.074
0.000327	0.276	0.368	0.144	0.139
0.000219	0.243	0.316	0.192	0.187
0.000443	0.346	0.490	0.034	0.028
0.000341	0.3515	0.3525	0.099	0.093
0.000298	0.315	0.3525	0.156	0.150
0.000328	0.3357	0.325	0.125	0.118
0.000409	0.235	0.502	0.1015	0.0975
0.000274	0.197	0.442	0.156	0.152
0.000466	0.255	0.536	0.072	0.068
0.000502	0.211	0.597	0.071	0.066
0.000359	0.164	0.525	0.1355	0.131

Table 11.

Equation	Rate-controlling Step	a	b	c	d'
39	Surface Reaction	103.04	669.91	298.92	
40	Surface Reaction	7.956	23.89	3.805	15.80
41	Surface Reaction	11.54	19.37	9.380	
43	Adsorption of Alcohol	-668.33	4103.8	2716.2	1574.5
44	Adsorption of Alcohol	-601.72	3525.8	3855.7	

The constant a is negative for Equations (43) and (44). This is further proof that the adsorption of alcohol is not the rate-controlling step. The constants for Equations (39), (40) and (41) are all positive indicating that mechanisms represented by these equations are probable.

Equations (39), (40) and (41) were examined further. At zero conversion or for an infinite value of W/F they become, respectively

$$\frac{p_{A_0} p_{B_0}}{r_0} = a + b p_{A_0} \quad (39a)$$

$$\sqrt{\frac{p_{A_0} p_{B_0}}{r_0}} = a + b p_{A_0} + c p_{B_0} \quad (40a)$$

and

$$\sqrt{\frac{p_{A_0} p_{B_0}}{r_0}} = a + b p_{A_0} \quad (41a)$$

if pure reactants are used. It will be recalled that the alcohol was assumed to be pure and the acid contained less than 0.5% water. Initial rates, r_0 , were first evaluated graphically from Figures 6 and 7 and then checked by extrapolating curves of $X/(W/F)$ versus W/F to $W/F = 0$. Initial partial pressures for several molar ratios of alcohol to acid can be found in the tables in Appendix A. The data in Table 12 are for 160°C and a total pressure of 0.972 atmospheres.

Table 12.

R	r_o	p_{A_o}	p_{B_o}
Temperature = 160°C, Pressure = 0.972 atms.			
0.75	0.0003524	0.4075	0.4570
1.00	0.0004844	0.3632	0.5232
1.50	0.0005672	0.2997	0.6133
2.00	0.0006246	0.2561	0.6716

The method of least squares was used again. In Equation (39a) constants a and b were found to be, respectively, negative and positive. Such being the case, Mechanism I was considered improbable and was rejected. The constants in Equation (40a) could not be obtained by the method of least squares because p_{A_o} and p_{B_o} are not completely independent at a fixed pressure. If the assumption is made that $K_A \gg K_B$, Equation (41a) can be considered instead. This assumption is reasonable because for Equation (40) b is much larger than c while for Equation (41) b is large and all the constants are positive. For Equation (41a), a and b were found to be +8.981 and +29.88, respectively. Therefore, Equation (41) becomes

$$\sqrt{\frac{p_A p_B - \frac{p_R p_S}{K}}{r}} = 8.981 + 29.88 p_A + c p_S \quad (45)$$

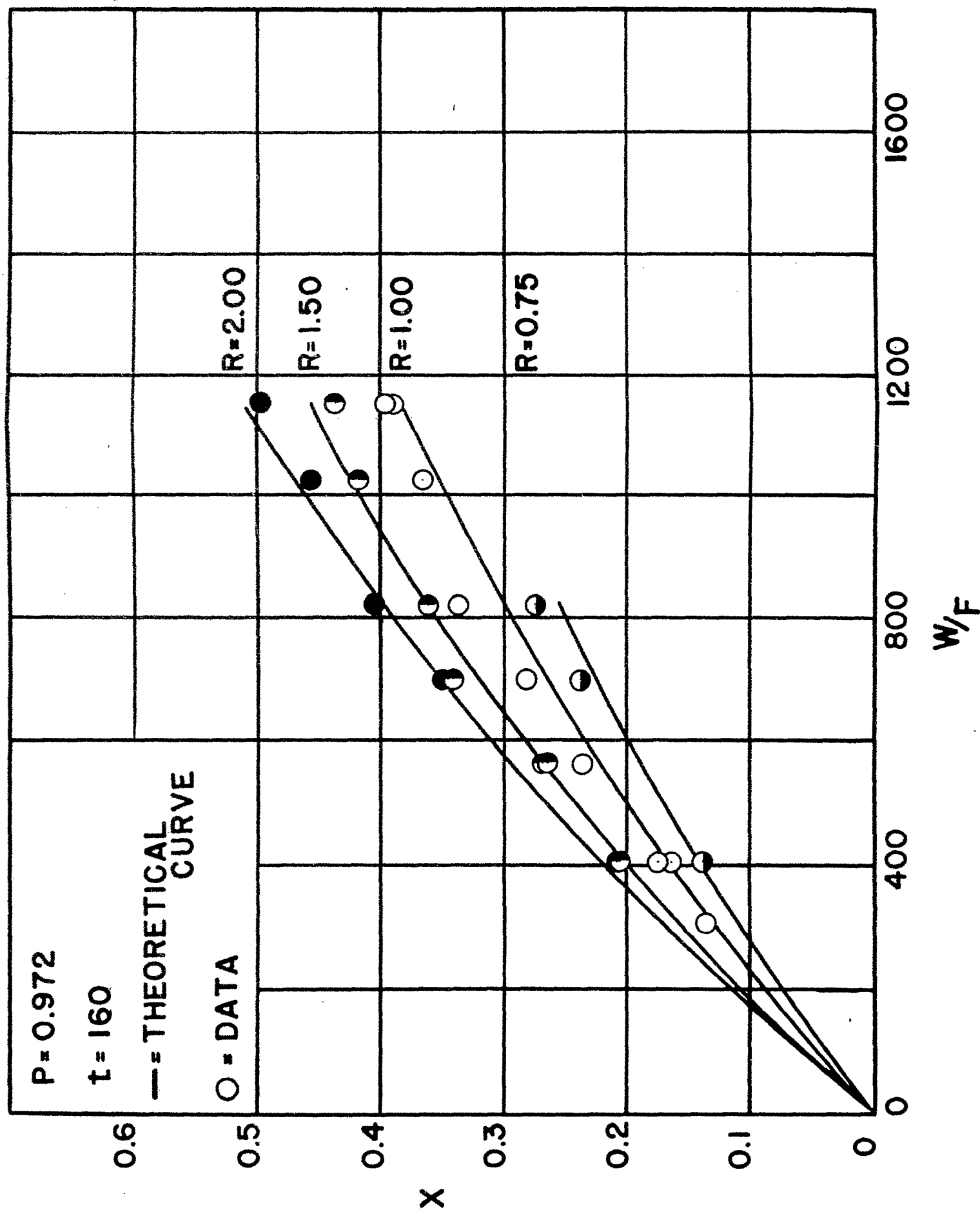


Fig. 14. Conversion vs. W/F at 160°C . — Experimental Data and Theoretical Lines.

An average value of C equal to 9.66 was evaluated from Equation (45) by use of the data in Table 10. Therefore,

$$\sqrt{\frac{p_A p_B - \frac{p_R p_S}{K}}{r}} = 8.891 + 29.88 p_A + 9.66 p_S \quad (46)$$

or

$$r = \frac{p_A p_B - \frac{p_R p_S}{K}}{(8.891 + 29.88 p_A + 9.66 p_S)^2} \quad (47)$$

$$= \frac{0.0123 (p_A p_B - \frac{p_R p_S}{28.51})}{(1 + 3.327 p_A + 1.075 p_S)^2} \quad (48)$$

It can be seen from Equation (48) that $k = 0.0123$, $K_A = 3.327$ and $(1/K_R + 1/K_S) = 1.075$. The average value of C was checked by plotting values of $1/r$ calculated from Equation (47) against X, graphically integrating to get values of W/F and plotting these values of W/F against X in an attempt to reproduce the curves of Fig. 7. Other values of C were tried but the average value correlated the data for Figure 7 most satisfactorily. The theoretical curves and experimental points for R equal to 0.75, 1.00, 1.50 and 2.00 are shown in Figure 14.

An attempt was made to reproduce the curve in Figure 8. Conversions were obtained for W/F equal to 820 from the curves of W/F versus X resulting from graphical integration and

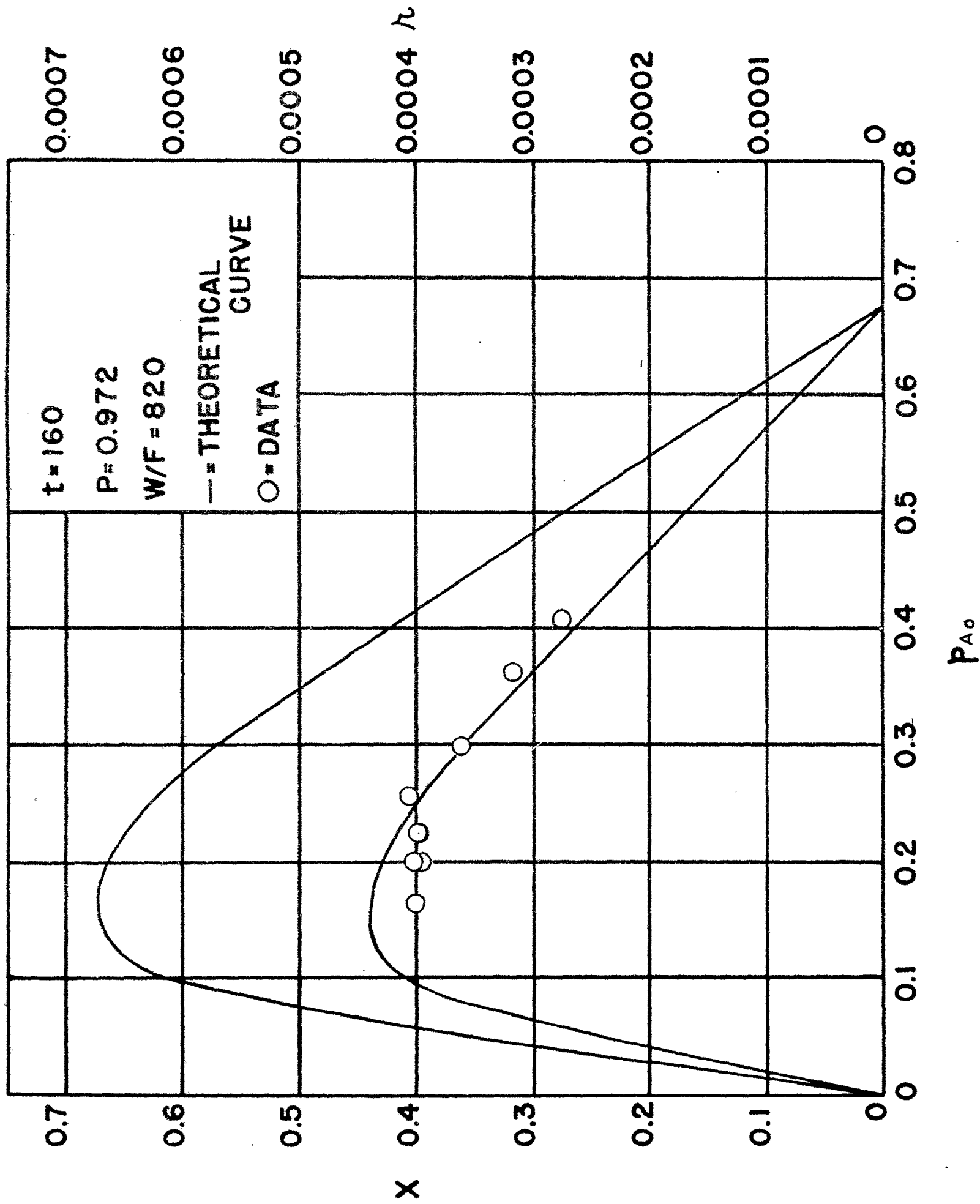


FIG. 15. Conversion vs. P_{A0} for $t = 160$, $W/F = 820$.
 - Experimental data; --- Theoretical curve.

were plotted in Figure 15 against p_{A_0} , the partial pressure of acetic acid monomer in the feed. In the same figure the initial rates, calculated from the rate equation, have also been plotted against p_{A_0} . The data which were used are given in Tables 13 and 14 for several values of R .

Table 13.

R	X	p_{A_0}
Temperature = 160°C., Pressure = 0.972 atms., W/F = 820		
0.20	0.095	0.5705
0.40	0.165	0.4959
0.75	0.255	0.4075
1.00	0.301	0.3632
1.50	0.362	0.2997
2.00	0.398	0.2561
2.50	0.421	0.2244
4.00	0.440	0.1644
8.00	0.402	0.0970

Table 14.

R	r_o	p_{A_o}
Temperature = 160°C., Pressure = 0.972 atms.		
0.20	0.000163	0.5705
0.40	0.000278	0.4959
0.75	0.000404	0.4075
1.00	0.000483	0.3632
1.50	0.000571	0.2947
2.00	0.000622	0.2561
2.50	0.000651	0.2244
4.00	0.000672	0.1644
8.00	0.000597	0.0970

The calculated curves at higher values of p_{A_o} should approach each other and should meet on the p_{A_o} -axis at the value of p_{A_o} equal to the partial pressure of acetic acid monomer when no alcohol is present. The calculated value of p_{A_o} for pure acid at 160°C. and 0.972 atmospheres is 0.686 atmospheres. The two curves meet at p_{A_o} equal to about 0.677 atmospheres. The theoretical X versus p_{A_o} curve checks the experimental points quite well and predicts a maximum conversion in the same range of p_{A_o} as that in which experimental conversions were highest. The curve and the experimental points start to drop off sharply

at about the same value of p_{A_0} ; namely, $p_{A_0} = 0.255$ atmospheres.

It can be said in summary that a surface reaction appears to be the rate-controlling step. A rate equation based on Mechanism I correlates the data taken at 160°C. The equation is

$$r = \frac{(p_A p_B - \frac{p_R p_S}{K})}{(a + b p_A + c p_S)^2}$$

where at 160°C., $K = 28.51$, $a = 8.981$, $b = 29.88$ and $c = 9.66$.

More data are needed at 140°C. and 160°C. before a , b , and c can be determined at these temperatures.

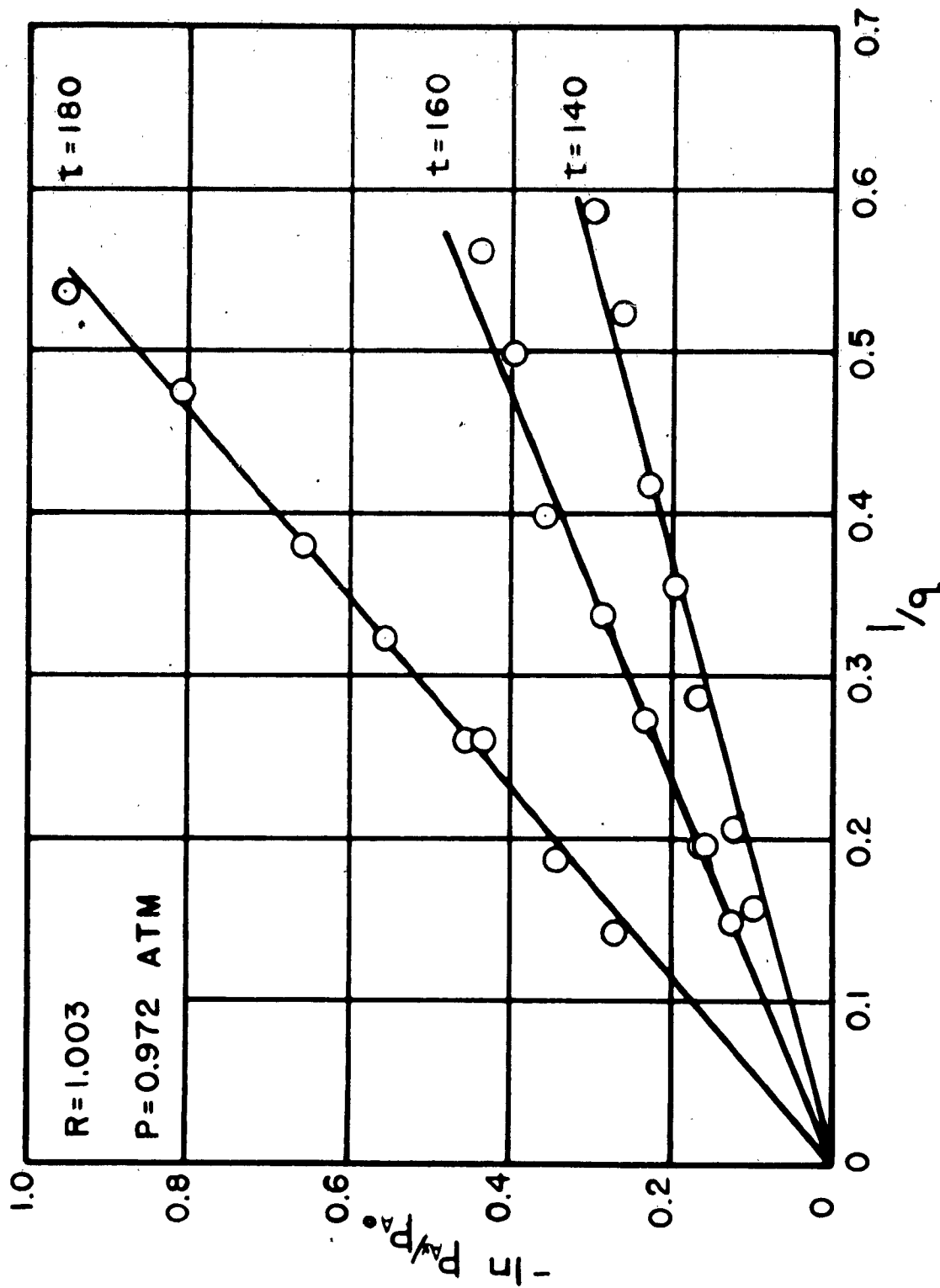


Fig. 14. A plot of $-\ln P_A/P_{A_0}$ against L/q for an Equimolar Feed and for 140°C , 160°C , and 180°C .

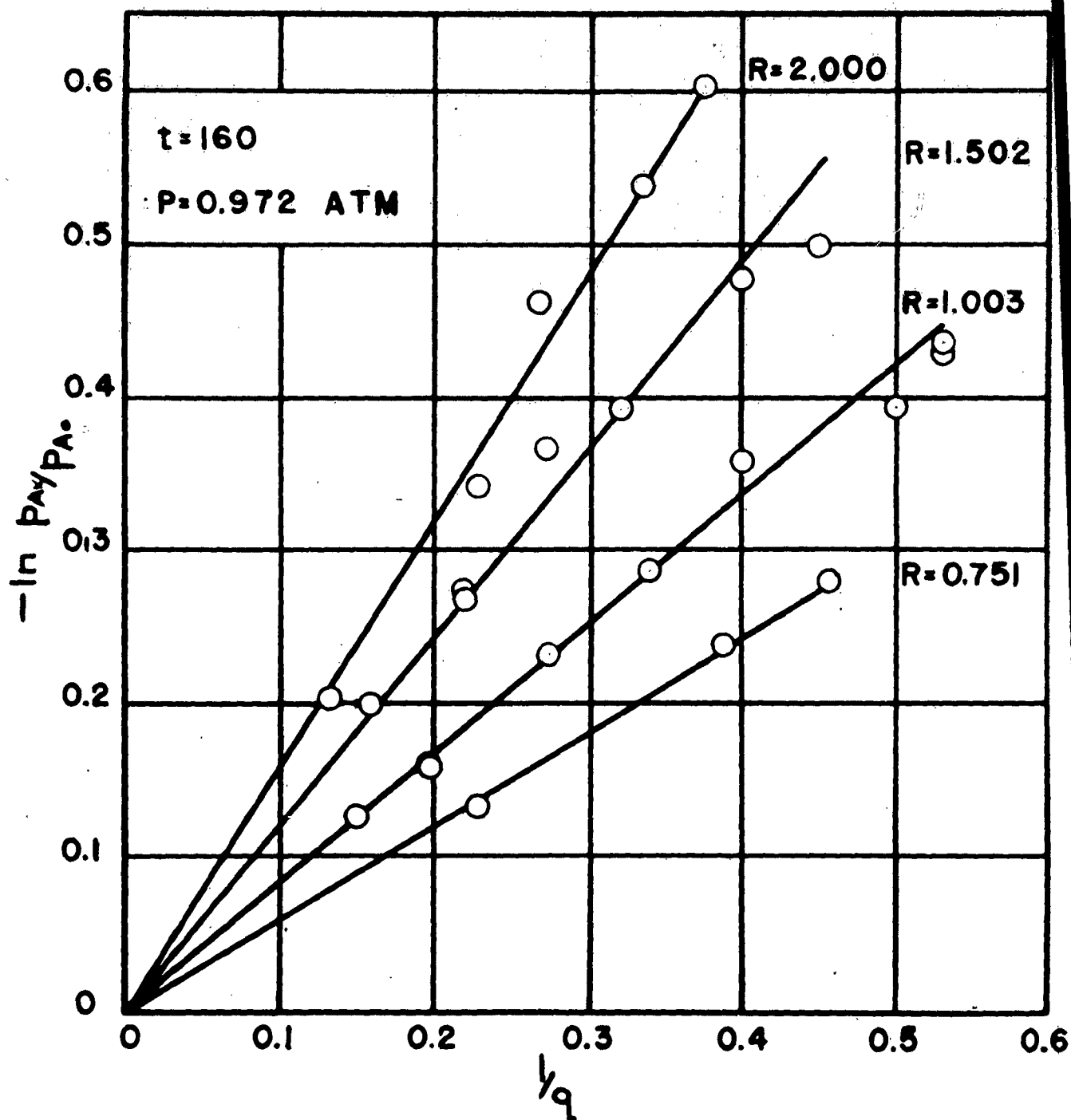


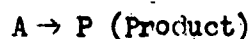
Fig. 17. A Plot of $-\ln p_{Ax}/p_{A_0}$ against $1/q$
 at 160°C . for Four Different Feeds.

size and that the activity of the catalyst did not change. The same assumptions were made in the present work. It will be recalled that the catalyst retained its activity and was carried on alumina balls averaging 0.00523 cm. in diameter. The methods of the above authors were used to derive the necessary equations.

The rate of disappearance of A by chemical reaction within the catalyst can be written

$$-\frac{d C_A}{d \theta} = k_A C_A \quad (49)$$

if the reaction is



If a single catalyst particle is considered and a material balance is made over a spherical shell of thickness Δr , the following expression is obtained:

$$(4\pi r^2 D_A \gamma \frac{d C_A}{dr})_{r+\Delta r} - (4\pi r^2 D_A \gamma \frac{d C_A}{dr})_r - 4\pi \gamma \Delta r (r^2 R_X)_{\bar{r}} = 0$$

where $r < \bar{r} < r + \Delta r$, D_A is the effective diffusivity of A in the catalyst and R_X is the rate of disappearance of A as given by Equation (49). The limit as $\Delta r \rightarrow 0$ after division by $4\pi \gamma \Delta r$ is

$$D_A \left[\frac{d^2 C_A}{dr^2} + \frac{2}{r} \left(\frac{d C_A}{dr} \right) \right] - k_A C_A = 0 \quad (50)$$

For the product a similar development gives

$$D_P = \left[\frac{d^2 C_P}{dr^2} + \frac{2}{r} \left(\frac{d C_P}{dr} \right) \right] + k_A C_A = 0 \quad (51)$$

Equations (50) and (51) give the relationship between diffusion and chemical reaction within the particle if the reaction is first-order in one direction only.

The concentration inside the particle and that in the main body of the vapor can be related. The rate at which A enters a single sphere is

$$4\pi R^2 \gamma D_A \left(\frac{d C_A}{dr} \right)_{r=R} \quad (52)$$

and the rate at which it enters W' gm./cc. of spheres is

$$\frac{3 \gamma W' D_A}{R \rho_p} \left(\frac{d C_A}{dr} \right)_{r=R} \quad (53)$$

This is the rate at which the vapor passing through the bed loses A by diffusion into the catalyst.

From a rate balance on A over a length dx of bed the equation

$$-q \frac{d \bar{C}_A}{dx} = \frac{3 W' \gamma D_A}{R \rho_p} \left(\frac{d C_A}{dr} \right)_{r=R} \quad (54)$$

is obtained. A similar balance on the product gives

$$-q \frac{d \bar{C}_P}{dx} = \frac{3 W' \tau D_P}{P \rho_p} \left(\frac{d \bar{C}_P}{dr} \right) \quad (55)$$

Since the resistance of the film at the external surface of the catalyst was negligible the boundary conditions holding at the interface of the catalyst and vapor stream can be written

$$C_A = \bar{C}_A \quad \text{when } r = R \quad (56)$$

$$\text{and} \quad C_P = \bar{C}_P \quad \text{when } r = R \quad (57)$$

In Equations (54) and (55) x is an independent variable. Hence, the following additional conditions can be written;

$$\bar{C}_A = \bar{C}_{A_0} \quad \text{when } x = 0 \quad (58)$$

$$\bar{C}_P = 0 \quad \text{when } x = 0 \quad (59)$$

For the steady state operation of the reactor, Equations (50), (51), (54), (55), (56), (57), (58) and (59) give a complete mathematical description of the system. The condition is added that concentrations inside the particle remain finite. In order to obtain a solution for the simple case being considered, only Equation (50) need be used. A change of dependent variable

$$u_A = r C_A$$

reduces this equation to

$$D_A \left(\frac{d^2 u_A}{dr^2} \right) = k_A u_A \quad (60)$$

or
$$\frac{d^2 u_A}{dr^2} - P u_A = 0 \quad (61)$$

where
$$P = k_A/D_A$$

The general solution of Equation (61) is

$$u_A = c e^{r\sqrt{P}} + d e^{-r\sqrt{P}} \quad (62)$$

where c and d are arbitrary constants. It is apparent that $d = -c$.

Consequently,

$$u_A = 2c \sinh r \sqrt{P} \quad (63)$$

and
$$C_A = 2c \frac{\sinh r \sqrt{P}}{r} \quad (64)$$

It is evident from Equation (56) that

$$2c = \frac{R \bar{C}_A}{\sinh R \sqrt{P}}$$

Therefore,
$$C_A = \frac{R \bar{C}_A}{\sinh R \sqrt{P}} \cdot \frac{\sinh r \sqrt{P}}{r} \quad (65)$$

Differentiation of Equation (65) gives

$$\left(\frac{\partial C_A}{\partial r} \right)_{r=R} = \frac{\bar{C}_A}{R} \left(\frac{R \sqrt{P} - \tanh R \sqrt{P}}{\tanh R \sqrt{P}} \right) \quad (66)$$

Substitutions in Equation (54) yields

$$\frac{d \bar{C}_A}{\bar{C}_A} = \frac{3 W' \gamma D_A}{R^2 \rho_p q} \cdot \left(\frac{\tanh R \sqrt{P} - R \sqrt{P}}{\tanh R \sqrt{P}} \right) dx \quad (67)$$

After using Equation (58) the solution to Equation (67) is

$$\ln \frac{\bar{C}_A}{\bar{C}_{A_0}} = \frac{3 W' \gamma D_A x}{R^2 \rho_p q} \cdot \left(\frac{\tanh R \sqrt{P} - R \sqrt{P}}{\tanh R \sqrt{P}} \right), \quad (68)$$

an expression obtained by Smith and Amundson (32), or

$$\bar{C}_A = \bar{C}_{A_0} \cdot \exp. \left[\frac{3 W' \gamma D_A x}{R^2 \rho_p q} \left(\frac{\tanh R \sqrt{P} - R \sqrt{P}}{\tanh R \sqrt{P}} \right) \right] \quad (69)$$

An expression for $\bar{C}_P$ can readily be obtained. Since $\bar{C}_P = 0$ when $x = 0$, at steady state conditions

$$\bar{C}_P = \bar{C}_{A_0} - \bar{C}_A.$$

Therefore,

$$\bar{C}_P = \bar{C}_{A_0} \left[1 - \exp. \left[\frac{3 W' \gamma D_A x}{R^2 \rho_p q} \left(\frac{\tanh R \sqrt{P} - R \sqrt{P}}{\tanh R \sqrt{P}} \right) \right] \right] \quad (70)$$

In Equation (68) partial pressures can be used instead of concentrations. Therefore,

$$\ln p_{A_x} / p_{A_0} = \frac{3 W' \gamma D_A x}{R^2 \rho_p q} \left(\frac{\tanh R \sqrt{P} - R \sqrt{P}}{\tanh R \sqrt{P}} \right) \quad (71)$$

This expression shows that straight lines of positive slope

$$m = - \frac{3 W^2 \gamma D_A x}{R^2 \rho_p} \left(\frac{\tanh R \sqrt{P} - R \sqrt{P}}{\tanh R \sqrt{P}} \right)$$

and passing through the origin can be expected for a uni-directional first-order reaction if $-\ln p_{Ax}/p_{Ao}$ is plotted against $1/q$. As previously mentioned, Figures 16 and 17 indicate that straight lines passing through the origin were obtained. Data pertaining to these figures are listed in Appendix A. Slopes of the lines were determined by taking the arithmetic average of values of $(-\ln p_{Ax}/p_{Ao})/(1/q)$ for each set of conditions. The values of the slopes are given in Table 15.

Table 15.

<u>t°C.</u>	<u>R</u>	<u>Slope m</u>
Average Pressure = 0.972 atm.		
140	1.003	0.5741
160	0.751	0.6042
160	1.003	0.8452
160	1.502	1.2451
160	2.000	1.5958
180	1.003	1.7493

For the time being, only Figure 16 will be considered. It was hoped that values of D_A and k_A could be found such that calculated values of m would be equal to the measured slopes of the three lines. As a start, diffusivities for acetic acid in alcohol were calculated for 140°C., 160°C., and 180°C. using the equation

$$D_A = 0.0043 \frac{T^{3/2}}{P (V_A^{1/3} - V_B^{1/3})^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}$$

Then, for each temperature probable values of $\sqrt{P}$ were selected and corresponding values of m were calculated. The velocity constant was obtained from the value of $\sqrt{P}$ that gave an m equal to the measured slope. Other values of D_A were selected and the procedure was repeated. The results of the calculations are given in Table 16. The diffusivities in Set 1 are for acetic acid in alcohol and were obtained as described above. The diffusivities in Set 2 are weighted means based on an average conversion of 0.7 for an equimolar mixture of acid and alcohol. A mean diffusivity is not necessarily accurate but it was felt that for the purpose of the present calculations a satisfactory order of magnitude would be obtained. The diffusivities for 160°C. in Sets 3 and 4 were chosen arbitrarily. The values for 140°C. and 180°C. were found by assuming that the diffusivity depended on the temperature to the three-halves power,

Table 16.

$t^{\circ}\text{C.}$	D_A	k_A/D_A	k_A
Set 1			
140	0.1139	0.152	0.0173
160	0.1223	0.206	0.0252
180	0.1308	0.400	0.0523
Set 2			
140	0.1258	0.136	0.0172
160	0.135	0.188	0.0253
180	0.1444	0.363	0.0524
Set 3			
140	0.0886	0.194	0.0172
160	0.095	0.267	0.0254
180	0.102	0.442	0.0524
Set 4			
140	0.0233	0.747	0.0174
160	0.025	1.013	0.0253
180	0.0268	2.005	0.0525

Table 16 shows that four different values of k_A/D_A resulting from the four choices of D_A , give the same value for k_A . It appears, then, that the rate of diffusion within the catalyst is not an important factor in determining the rate of the over-all reaction. This can also be demonstrated by transforming Equation (71). If the hyperbolic tangent terms are expanded in a power series the equation

$$\begin{aligned}
 -\ln p_{A_x}/p_{A_0} &= -\frac{3 W' \gamma D_A x}{R^2 \rho_p q} \left(-\frac{R^2 k_A}{3 D_A} + \frac{R^4 k_A^2}{45 D_A^2} - \frac{2 R^6 k_A^3}{945 D_A^3} + \dots \right) \\
 &= \frac{W' \gamma x k_A}{\rho_p q} \left(1 - \frac{R^2 k_A}{15 D_A} + \frac{2 R^4 k^2}{315 D_A^2} - \dots \right) \quad (72)
 \end{aligned}$$

is obtained instead. It can be seen that the diffusivity appears in the denominator of the second and succeeding terms. All terms after the second are negligibly small and can be omitted without further consideration. For 160°C. and the four values of k_A/D_A listed downwards in Table 16 the second term is equal to 0.00094, 0.00086, 0.00122 and 0.00462, respectively. These values are all very small and indicate the unimportance of intraparticle diffusion on the overall rate process. Even if the diffusivity were as small as 0.025 sq. cm./sec. at 160°C. the second term could be neglected without introducing an error of more than 0.5%. As a matter of fact, if the diffusivity were equal to the improbable

value of 0.00115 sq. cm./sec. and if $k_A = 0.0253 \text{ sec.}^{-1}$ were accepted as correct, an error of only about 10% would be incurred by neglecting the second term. Therefore, for reasonable values of the diffusion coefficient it is permissible to write

$$-\ln p_{A_x}/p_{A_0} = k_A \frac{W' \gamma x}{\rho_p q} \quad (73)$$

This is the expression that would be derived if the assumption were made that the concentration of reactant A inside the catalyst is equal to the concentration of reactant A in the main body of the vapor; i.e., if

$$C_A = \bar{C}_A \quad \text{for any } r \text{ including } r = 0$$

The rate of disappearance of A can now be written

$$-\frac{dC_A}{d\theta} = k_A \bar{C}_A \quad (74)$$

A rate balance over a length dx of the bed gives

$$\begin{aligned} -q \frac{d\bar{C}_A}{dx} &= \frac{W' \gamma}{\rho_p} R_x \\ &= k_A \bar{C}_A \frac{W' \gamma}{\rho_p} \end{aligned} \quad (75)$$

instead of Equation (54). The solution to Equation (75) is

$$-\ln \bar{C}_A/\bar{C}_{A_0} = \frac{k_A W' \gamma x}{\rho_p q} \quad (76)$$

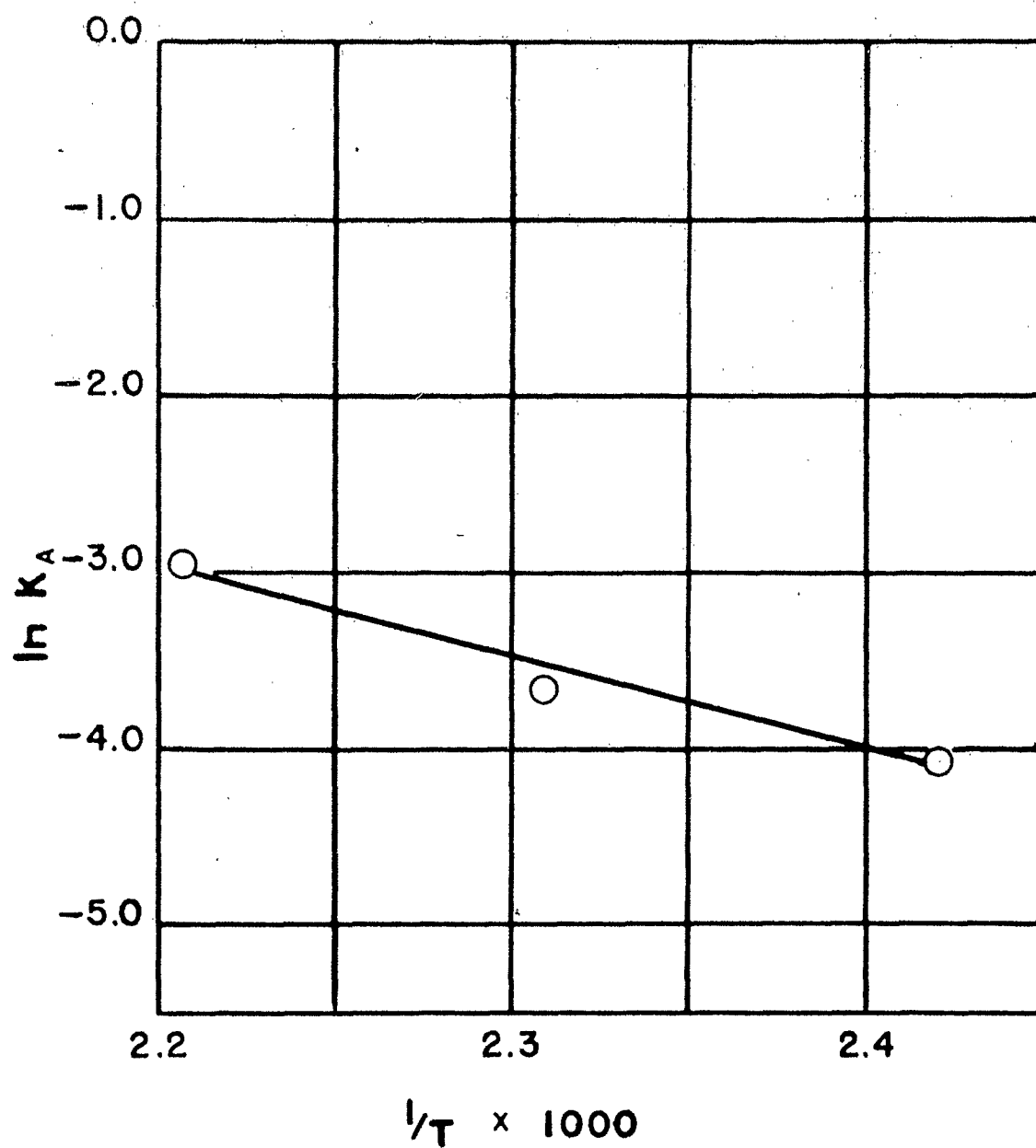


Fig. 18. Effect of Temperature on the Velocity Constant Assuming a First-order Relationship.

and

$$-\ln p_{A_x}/p_{A_0} = \frac{k_A W' \gamma x}{\rho_p q}$$

The measured slope can now be equated to

$$\frac{k_A W' \gamma x}{\rho_p}$$

and k_A calculated. At 140°C., 160°C., and 180°C. k_A was found to be 0.01719 sec.⁻¹, 0.02531 sec.⁻¹ and 0.05239 sec.⁻¹, respectively. These values were used for Figure 18 where $\ln k_A$ is plotted against $1/T \times 1000$. The three points do not lie on a straight line, and this is not too surprising because the rate equation derived from Mechanism I contains adsorption terms which are temperature dependent. The heat effects associated with these terms would be included in the measured activation energy. Even so, the slope of the best straight line which can be drawn yields an activation energy of 10,320 cal./g.mol.

Equation (73) gives a ready means of determining velocity constants if intraparticle diffusion is unimportant and if the reaction is uni-directional first order or pseudo-first order. The conversion can be calculated at various bed depths if the velocity constant is known and if the flowrate q is maintained constant.

Figure 17 shows that for 160°C. and 0.972 atm. four lines, one for each ratio of alcohol to acid, were obtained.

Velocity constants of $0.01810 \text{ sec.}^{-1}$, $0.02531 \text{ sec.}^{-1}$, $0.03729 \text{ sec.}^{-1}$ and $0.04779 \text{ sec.}^{-1}$ were calculated from the slopes in Table 15 for R equal to 0.751, 1.003, 1.502 and 2.000, respectively. Graphing revealed an exponential relationship between k_A and p_{A_0} for values of p_{A_0} that apply to Figure 17. The relationship is

$$k_A = 0.2482 e^{-6.37 p_{A_0}}$$

and shows that k_A decreases as p_{A_0} increases. This is in agreement with Equation (48) for the same range of p_{A_0} .

It should be repeated in conclusion that equation

$$-\ln \frac{\bar{C}_A}{\bar{C}_{A_0}} = -\frac{3 W \tau D_A x}{R^2 \rho_p q} \left(\frac{\tanh R\sqrt{P} - R\sqrt{P}}{\tanh R\sqrt{P}} \right) \quad (68)$$

holds for a continuous-flow, packed tubular reactor when the reaction is first-order in one direction or is pseudo-first-order, when $\bar{C}_P = 0$ and when $C_A = \bar{C}_A$ for $r = R$. For a continuous-flow, well agitated reactor, the equation

$$\frac{\bar{C}_{A_0} - \bar{C}_A}{\bar{C}_A} = -\frac{3 W \tau D_A}{R^2 \rho_p q} \left(\frac{\tanh R\sqrt{P} - R\sqrt{P}}{\tanh R\sqrt{P}} \right) \quad (77)$$

has been derived in the literature (32). In this expression W is the weight of catalyst in grams and q is the flow-rate in cc./sec. With the exception of the terms on the left-hand side

the similarity between the two equations is striking. Equation (68) can be written

$$-\ln \frac{\bar{C}_A}{\bar{C}_{A_0}} = -3 B_A' \frac{\tanh R \sqrt{P} - R\sqrt{P}}{\tanh R\sqrt{P}}$$

where

$$B_A' = \frac{W \gamma D_A x}{R^2 \rho_p q}$$

is a dimensionless parameter, and Equation (77) can be written

$$\frac{\bar{C}_{A_0} - \bar{C}_A}{\bar{C}_A} = -3 B_A \frac{\tanh R\sqrt{P} - R\sqrt{P}}{\tanh R\sqrt{P}}$$

where

$$B_A = \frac{W \gamma D_A}{R^2 \rho_p q}$$

is also a dimensionless parameter. A comparison of the equations shows that for a given system and catalyst the behavior of one of the types of reactors can be predicted if the behavior of the other type is known.

SUMMARY

1. Tungstic acid carried on porous alumina balls was used to esterify acetic acid and ethyl alcohol in the vapor-phase.

2. A bench-scale apparatus was constructed for carrying out the reaction. A continuous-flow, packed tubular reactor was employed.

3. Kinetic data were obtained at 140°C., 160°C. and 180°C. with most of the data being for 160°C. and 0.972 atm. A surface reaction was found to be the rate-controlling step.

4. A rate equation was determined that reproduced the data. At 160°C. the equation was

$$r = \frac{0.0123 \left(p_A p_B - \frac{p_R p_S}{28.51} \right)}{(1 + 3.327 p_A + 1.075 p_S)^2}$$

5. The data showed and the assumption was made that the reaction approximated a pseudo-first-order relationship when only the feed rate was varied. Diffusion and chemical reaction within a particle of catalyst were related using this simplification. Intraparticle diffusion was not an important factor in determining the rate of the over-all reaction.

NOMENCLATURE

- a = activity.
 $a, b, c, \text{etc.}$ = empirical constants.
 c = surface concentration.
 C = concentration inside of particle.
 $\bar{C}$ = concentration in main body of vapor.
 D = diameter, cm.; diffusivity, sq. cm./sec.
 E = effectiveness factor.
 F = rate of feed of HOAc, g. moles/hr.
 G = mass velocity, lbs./(hr.)(sq.ft.).
 h = depth of the bed, cm.
 K = overall equilibrium constant.
 K_A, K_B, K_R, K_S = adsorption equilibrium constants for acetic acid, ethyl alcohol, water and ethyl acetate, respectively.
 K_X = equilibrium constant for association of HOAc into $(\text{HOAc})_2$.
 k = reaction velocity constant.
 L = total number of active sites, g.moles/gram of catalyst.
 l = symbol for an active site.
 n = number of g.moles.
 N = normality, mole fraction.
 P = total pressure, atm.
 p = partial pressure, atm.
 q = flow rate.

- r = rate of reaction, g.moles/(g.solid catalyst)(hr.); radius variable inside particle.
 R = molar ratio of alcohol to acid in feed; radius of particle.
 s = number of neighbouring sites when surface is bare.
 t = temperature, °C.
 T = temperature, °A.
 V = volume of packed bed, cc.
 w = mass flow rate, g./hr.
 W = mass of catalyst, g.
 W' = mass of catalyst, g./cc.
 x = distance measured along bed.
 X = fraction of acid in feed converted, g.moles acid converted/(g.mole acid in feed).
 α = external void fraction.
 γ = internal void fraction.
 ρ = density, g./cc.
 θ = time, sec.

Subscripts:

- A = acetic acid
 A_2 = acetic acid dimer.
 B = alcohol
 P = product
 R = water

S = ethyl acetate.

b = bulk.

c = solid.

l = active center.

o = initial conditions.

p = particle.

t = total moles.

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APPENDIX

APPENDIX A.

DataRun No. 5

$t = 140^{\circ}\text{C.}$	$N = 0.3837$	$R = 1.003$
$P = 0.963 \text{ atm.}$	$A = 99.62\% \text{ by wt.}$	$W = 2170 \text{ g.}$
$w_{A_o} = 232.5 \text{ g./hr.}$	$B = 100\% \text{ by wt.}$	$W/F_{A_o} = 562.6$
$w_{B_o} = 178.2 \text{ g./hr.}$	$F_{A_o} = 3.8569 \text{ g.moles/hr.}$	$G = 38.9$
$w = 410.7 \text{ g./hr.}$	$F_{B_o} = 3.8682 \text{ g.moles/hr.}$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.7985 g.	36.01 ml.
1.7483	35.04
1.8004	36.12
1.7510	35.02
1.7452	34.81
<u>1.7551</u>	<u>35.15</u>
10.5985	212.15

$$\text{Moles of unreacted acid/gm. of product} = \frac{212.15}{1000} \times \frac{0.3837}{10.5985} = 0.007680$$

$$\text{Moles of unreacted acid/hr.} = 410.7 \times 0.007680 = 3.1542$$

$$\text{Conversion} = X = \frac{3.8569 - 3.1542}{3.8569} = 0.182$$

Run No. 7

$$t = 140^{\circ}\text{C.}$$

$$N = 0.5487$$

$$R = 1.002$$

$$P = 0.972$$

$$A = 99.70\%$$

$$W = 2170$$

$$w_{A_o} = 159.5$$

$$B = 100\%$$

$$W/F_{A_o} = 819.5$$

$$w_{B_o} = 122.3$$

$$F_{A_o} = 2.6481$$

$$G = 26.6$$

$$w = 281.8$$

$$F_{B_o} = 2.6547$$

Weight of SampleVolume of Base

2.1934

28.31

2.3147

29.93

2.2021

28.71

2.1530

27.60

2.189228.75

11.0524

143.30

$$\text{Moles of unreacted acid/gm. of product} = \frac{143.30}{1000} \times \frac{0.5487}{11.0524} = 0.007114$$

$$\text{Moles of unreacted acid/hr.} = 281.8 \times 0.007114 = 2.0047$$

$$\text{Conversion} = \frac{2.6481 - 2.0047}{2.6481} = 0.243$$

Run No. 8

$t = 140^{\circ}\text{C.}$	$N = 0.4117$	$R = 1.003$
$P = 0.973$	$A = 99.66\%$	$W = 2170$
$w_{A_o} = 232.5$	$B = 100\%$	$W/F_{A_o} = 562.4$
$w_{B_o} = 178.2$	$F_{A_o} = 3.8585$	$G = 38.9$
$w = 410.7$	$F_{B_o} = 3.8682$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.6998	31.51
1.7589	32.80
1.7349	32.60
<u>1.6916</u>	<u>31.50</u>
6.8852	128.41

$$\text{Moles of unreacted acid/gm. of product} = \frac{128.41}{1000} \times \frac{0.4117}{6.8852} = 0.007678$$

$$\text{Moles of unreacted acid/hr.} = 410.7 \times 0.007678 = 3.1534$$

$$\text{Conversion} = \frac{3.8585 - 3.1534}{3.8585} = 0.183$$

Run No. 12

$t = 140^{\circ}\text{C.}$

$N = 0.4694$

$R = 1.004$

$P = 0.978$

$A = 99.70\%$

$W = 2170$

$w_{A_o} = 187.5$

$B = 100\%$

$W/F_{A_o} = 697.1$

$w_{B_o} = 144.0$

$F_{A_o} = 3.1129$

$G = 31.4$

$w = 331.5$

$F_{B_o} = 3.1258$

Weight of SampleVolume of Base

1.9619

30.65

1.8412

28.99

1.8993

29.78

1.8472

29.15

1.7959

28.47

1.8583

29.48

1.784327.92

12.9881

204.44

$$\text{Moles of unreacted acid/gm. of product} = \frac{204.44}{1000} \times \frac{0.4694}{12.9881} = 0.007389$$

$$\text{Moles of unreacted acid/hr.} = 33.5 \times 0.007389 = 2.4494$$

$$\text{Conversion} = \frac{3.1129 - 2.4494}{3.1129} = 0.213$$

Run No. 13

$t = 140^{\circ}\text{C.}$

$N = 0.4846$

$R = 1.002$

$P = 0.978$

$A = 99.70\%$

$W = 2170$

$w_{A_o} = 113.5$

$B = 100\%$

$W/F_{A_o} = 1152$

$w_{B_o} = 87.0$

$F_{A_o} = 1.8843$

$G = 19.0$

$w = 200.5$

$F_{B_o} = 1.8885$

Weight of SampleVolume of Base

1.6824

22.70

1.7217

23.14

1.679322.48

5.0834

68.32

$$\text{Moles of unreacted acid/gm. of product} = \frac{68.32}{1000} \times \frac{0.4846}{5.0834} = 0.006513$$

$$\text{Moles of unreacted acid/hr.} = 200.5 \times 0.006513 = 1.3058$$

$$\text{Conversion} = \frac{1.8843 - 1.3058}{1.8843} = 0.307$$

Run No. 15

$t = 140^{\circ}\text{C.}$

$N = 0.5200$

$R = 1.003$

$P = 0.971$

$A = 99.66\%$

$W = 2170$

$w_{A_o} = 113.5$

$B = 100\%$

$W/F_{A_o} = 1152$

$w_{B_o} = 87.0$

$F_{A_o} = 1.8836$

$G = 19.0$

$w = 200.5$

$F_{B_o} = 1.8885$

Weight of SampleVolume of Base

1.7054

21.40

1.7602

22.20

1.7111

21.54

1.713221.52

6.8899

86.66

$$\text{Moles of unreacted acid/gm. of product} = \frac{86.66}{1000} \times \frac{0.5200}{6.8899} = 0.006540$$

$$\text{Moles of unreacted acid/hr.} = 200.5 \times 0.006540 = 1.3113$$

$$\text{Conversion} = \frac{1.8836 - 1.3113}{1.8836} = 0.304$$

Run No. 16

$t = 140^{\circ}\text{C.}$	$N = 0.5203$	$R = 1.003$
$P = 0.977$	$A = 99.71\%$	$W = 2170$
$w_{A_o} = 127.5$	$B = 100\%$	$W/F_{A_o} = 1025$
$w_{B_o} = 97.8$	$F_{A_o} = 2.1170$	$G = 21.3$
$w = 225.3$	$F_{B_o} = 2.1229$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.5261	19.99
1.6881	22.10
1.5380	20.15
1.5306	20.02
<u>1.6932</u>	<u>22.21</u>
7.9760	104.47

$$\text{Moles of unreacted acid/gm. of product} = \frac{104.47}{1000} \times \frac{0.5203}{7.9760} = 0.006815$$

$$\text{Moles of unreacted acid/hr.} = 225.3 \times 0.006815 = 1.5354$$

$$\text{Conversion} = \frac{2.1170 - 1.5354}{2.1170} = 0.275$$

Run No. 17

$t = 140^{\circ}\text{C.}$

$N = 0.5203$

$R = 1.002$

$P = 0.977$

$A = 99.71\%$

$W = 2170$

$w_{A_o} = 323.0$

$B = 100\%$

$W/F_{A_o} = 404.6$

$w_{B_o} = 247.6$

$F_{A_o} = 5.3631$

$G = 54.0$

$w = 570.6$

$F_{B_o} = 5.3747$

Weight of SampleVolume of Base

1.6582

25.83

1.6805

26.14

1.570324.33

4.9090

76.30

$$\text{Moles of unreacted acid/gm. of product} = \frac{76.30}{1000} \times \frac{0.5203}{4.9090} = 0.008087$$

$$\text{Moles of unreacted acid/hr.} = 570.6 \times 0.008087 = 4.6144$$

$$\text{Conversion} = \frac{5.3631 - 4.6144}{5.3631} = 0.140$$

Run No. 18

$t = 140^{\circ}\text{C.}$

$N = 0.4842$

$R = 1.003$

$P = 0.975$

$A = 99.60\%$

$W = 2170$

$w_{A_o} = 323.0$

$B = 100\%$

$W/F_{A_o} = 405.1$

$w_{B_o} = 247.6$

$F_{A_o} = 5.3572$

$G = 54.0$

$w = 570.6$

$F_{B_o} = 5.3747$

Weight of SampleVolume of Base

1.7625

29.30

1.7572

29.30

1.7337

29.19

1.651327.71

6.9047

115.50

$$\text{Moles of unreacted acid/gm. of product} = \frac{115.50}{1000} \times \frac{0.4842}{6.9047} = 0.008100$$

$$\text{Moles of unreacted acid/hr.} = 570.6 \times 0.008100 = 4.6219$$

$$\text{Conversion} = \frac{5.3572 - 4.6219}{5.3572} = 0.137$$

Run No. 19

$t = 140^{\circ}\text{C.}$	$N = 0.4842$	$R = 1.003$
$P = 0.975$	$A = 99.60\%$	$W = 2170$
$w_{A_o} = 426.0$	$B = 100\%$	$W/F_{A_o} = 307.1$
$w_{B_o} = 326.6$	$F_{A_o} = 7.0655$	$G = 71.2$
$w = 752.6$	$F_{B_o} = 7.0895$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.5701	27.17
1.5787	27.29
1.5829	27.40
<u>1.5959</u>	<u>27.59</u>
6.3276	109.45

$$\text{Moles of unreacted acid/gm. of product} = \frac{109.45}{1000} \times \frac{0.4842}{6.3276} = 0.008375$$

$$\text{Moles of unreacted acid/hr.} = 752.6 \times 0.008375 = 6.3030$$

$$\text{Conversion} = \frac{7.0655 - 6.3030}{7.0655} = 0.108$$

Run No. 21

$t = 160^{\circ}\text{C.}$

$N = 0.4926$

$R = 1.003$

$P = 0.975$

$A = 99.70\%$

$W = 2170$

$w_{A_o} = 127.5$

$B = 100\%$

$W/F_{A_o} = 1025$

$w_{B_o} = 97.8$

$F_{A_o} = 2.1168$

$G = 21.3$

$w = 225.3$

$F_{B_o} = 2.1229$

Weight of SampleVolume of Base

2.0043

24.33

1.9166

23.15

1.9650

23.60

1.998324.25

7.8842

95.33

$$\text{Moles of unreacted acid/gm. of product} = \frac{95.33}{1000} \times \frac{0.4926}{7.8842} = 0.005956$$

$$\text{Moles of unreacted acid/hr.} = 225.3 \times 0.005956 = 1.3419$$

$$\text{Conversion} = \frac{2.1168 - 1.3419}{2.1168} = 0.366$$

Run No. 23

t = 160°C.	N = 0.4811	R = 1.002
P = 0.972	A = 99.75%	W = 2170
w _{A_o} = 159.5	B = 100%	W/F _{A_o} = 819.0
w _{B_o} = 122.3	F _{A_o} = 2.6494	G = 26.6
w = 281.8	F _{B_o} = 2.6547	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.7326	22.35
1.5633	20.27
<u>1.6884</u>	<u>21.83</u>
4.9843	64.45

$$\text{Moles of unreacted acid/gm. of product} = \frac{64.45}{1000} \times \frac{0.4811}{4.9843} = 0.006221$$

$$\text{Moles of unreacted acid/hr.} = 281.8 \times 0.006221 = 1.7531$$

$$\text{Conversion} = \frac{2.6494 - 1.7531}{2.6494} = 0.338$$

Run No. 24

$t = 160^{\circ}\text{C.}$	$N = 0.4803$	$R = 1.005$
$P = 0.962$	$A = 99.58\%$	$W = 2170$
$w_{A_o} = 187.5$	$B = 100\%$	$W/F_{A_o} = 697.9$
$w_{B_o} = 144.0$	$F_{A_o} = 3.1092$	$G = 31.4$
$w = 331.5$	$F_{B_o} = 3.1258$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.8112	25.45
1.8655	26.32
1.8654	26.19
1.9065	26.57
1.9073	26.80
2.0252	28.40
1.9147	26.66
<u>1.8431</u>	<u>25.78</u>
15.1389	212.17

$$\text{Moles of unreacted acid/gm. of product} = \frac{212.17}{1000} \times \frac{0.4803}{15.1389} = 0.006731$$

$$\text{Moles of unreacted acid/hr.} = 331.5 \times 0.006731 = 2.2313$$

$$\text{Conversion} = \frac{3.1092 - 2.2313}{3.1092} = 0.282$$

Run No. 26

$$t = 160^{\circ}\text{C.}$$

$$N = 0.4806$$

$$R = 1.003$$

$$P = 0.973$$

$$A = 99.60\%$$

$$W = 2170$$

$$w_{A_o} = 323.0$$

$$B = 100\%$$

$$W/F_{A_o} = 405.1$$

$$w_{B_o} = 247.6$$

$$F_{A_o} = 5.3572$$

$$G = 54.0$$

$$w = 570.6$$

$$F_{B_o} = 5.3747$$

Weight of SampleVolume of Base

1.6473

26.90

1.5401

25.23

1.6905

27.69

1.5427

25.05

1.538925.10

7.9595

129.97

$$\text{Moles of unreacted acid/gm. of product} = \frac{129.97}{1000} \times \frac{0.4806}{7.9595} = 0.007848$$

$$\text{Moles of unreacted acid/hr.} = 570.6 \times 0.007848 = 4.4781$$

$$\text{Conversion} = \frac{5.3572 - 4.4781}{5.3572} = 0.164$$

Run No. 27

$t = 160^{\circ}\text{C.}$	$N = 0.4712$	$R = 1.001$
$P = 0.976$	$A = 99.79\%$	$W = 2170$
$w_{A_o} = 113.5$	$B = 100\%$	$W/F_{A_o} = 1151$
$w_{B_o} = 87.0$	$F_{A_o} = 1.8860$	$G = 19.0$
$w = 200.5$	$F_{B_o} = 1.8885$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.6477	19.60
1.6423	19.30
1.6938	20.63
1.7448	21.23
1.7547	21.38
1.4994	18.24
1.6852	20.15
1.6221	19.40
<u>1.7289</u>	<u>20.80</u>
15.0189	180.73

$$\text{Moles of unreacted acid/gm. of product} = \frac{180.73}{1000} \times \frac{0.4712}{15.0189} = 0.005670$$

$$\text{Moles of unreacted acid/hr.} = 200.5 \times 0.005670 = 1.1368$$

$$\text{Conversion} = \frac{1.8860 - 1.1368}{1.8860} = 0.397$$

Run No. 27a

$t = 160^{\circ}\text{C.}$	$N = 0.4712$	$R = 1.001$
$P = 0.976$	$A = 99.79\%$	$W = 2170$
$w_{A_o} = 113.5$	$B = 100\%$	$W/F_{A_o} = 1151$
$w_{B_o} = 87.0$	$F_{A_o} = 1.8860$	$G = 19.0$
$w = 200.5$	$F_{B_o} = 1.8885$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.6938	20.63
1.7448	21.23
1.7547	21.38
<u>1.4994</u>	<u>18.24</u>
6.6927	81.48

$$\text{Moles of unreacted acid/gm. of product} = \frac{81.48}{1000} \times \frac{0.4712}{6.6927} = 0.005737$$

$$\text{Moles of unreacted acid/hr.} = 200.5 \times 0.005737 = 1.1503$$

$$\text{Conversion} = \frac{1.8860 - 1.1503}{1.8860} = 0.390$$

This run was a repeat on the same day of Run No. 27.

Run No. 28

$t = 160^{\circ}\text{C.}$

$N = 0.4712$

$R = 1.002$

$P = 0.976$

$A = 99.79\%$

$W = 2170$

$w_{A_o} = 426.0$

$B = 100\%$

$W/F_{A_o} = 306.5$

$w_{B_o} = 326.6$

$F_{A_o} = 7.0790$

$G = 71.2$

$w = 752.6$

$F_{B_o} = 7.0895$

Weight of SampleVolume of Base

1.4659

24.63

1.5263

25.83

1.5758

26.95

1.4831

26.02

1.4794

25.85

1.4849

25.80

1.7032

29.60

1.5230

26.40

1.5298

26.55

1.4646

25.26

1.438924.87

16.6794

287.76

$$\text{Moles of unreacted acid/gm. of product} = \frac{287.76}{1000} \times \frac{0.4712}{16.6794} = 0.008129$$

$$\text{Moles of unreacted acid/hr.} = 752.6 \times 0.008129 = 6.1179$$

$$\text{Conversion} = \frac{7.0790 - 6.1179}{7.0790} = 0.136$$

Run No. 29

$t = 160^{\circ}\text{C.}$

$N = 0.4706$

$R = 1.003$

$P = 0.972$

$A = 99.64\%$

$W = 2170$

$w_{A_o} = 232.5$

$B = 100\%$

$W/F_{A_o} = 562.5$

$w_{B_o} = 178.2$

$F_{A_o} = 3.8577$

$G = 38.9$

$w = 410.7$

$F_{B_o} = 3.8582$

Weight of SampleVolume of Base

1.6820

25.56

1.7895

27.41

1.8038

27.48

1.8006

27.57

1.7631

26.85

1.730026.40

10.5690

161.27

$$\text{Moles of unreacted acid/gm. of product} = \frac{161.27}{1000} \times \frac{0.4706}{10.5690} = 0.007181$$

$$\text{Moles of unreacted acid/hr.} = 410.7 \times 0.007181 = 2.9492$$

$$\text{Conversion} = \frac{2.8577 - 2.9492}{3.8577} = 0.236$$

Run No. 30

$t = 160^{\circ}\text{C.}$

$N = 0.4706$

$R = 1.003$

$P = 0.973$

$A = 99.64\%$

$W = 2170$

$w_{A_o} = 323.0$

$B = 100\%$

$W/F_{A_o} = 404.9$

$w_{B_o} = 247.6$

$F_{A_o} = 5.3593$

$G = 54.0$

$w = 570.6$

$F_{B_o} = 5.3747$

Weight of SampleVolume of Base

1.5415

25.35

1.5918

26.25

1.7057

28.08

1.5609

25.84

1.6226

26.53

1.560325.72

9.5828

157.77

$$\text{Moles of unreacted acid/gm. of product} = \frac{157.77}{1000} \times \frac{0.4706}{9.5828} = 0.007748$$

$$\text{Moles of unreacted acid/hr.} = 570.6 \times 0.007748 = 4.4210$$

$$\text{Conversion} = \frac{5.3593 - 4.4210}{5.3593} = 0.175$$

Run No. 31

$t = 160^{\circ}\text{C.}$

$N = 0.4709$

$R = 1.501$

$P = 0.972$

$A = 99.64\%$

$W = 2170$

$w_{A_o} = 232.5$

$B = 100\%$

$W/F_{A_o} = 562.5$

$w_{B_o} = 266.7$

$F_{A_o} = 3.8577$

$G = 47.2$

$w = 499.2$

$F_{B_o} = 5.7893$

Weight of SampleVolume of Base

1.7189

20.65

1.7714

21.25

1.7730

21.47

1.7212

20.92

1.7311

21.01

1.749021.18

10.4646

126.48

$$\text{Moles of unreacted acid/gm. of product} = \frac{126.48}{1000} \times \frac{0.4709}{10.4646} = 0.005692$$

$$\text{Moles of unreacted acid/hr.} = 499.2 \times 0.005692 = 2.8414$$

$$\text{Conversion} = \frac{3.8577 - 2.8414}{3.8577} = 0.264$$

Run No. 31a

$t = 160^{\circ}\text{C.}$

$N = 0.4709$

$R = 1.501$

$P = 0.972$

$A = 99.64\%$

$W = 2170$

$w_{A_o} = 232.5$

$B = 100\%$

$W/F_{A_o} = 562.5$

$w_{B_o} = 266.7$

$F_{A_o} = 3.8577$

$G = 47.2$

$w = 499.2$

$F_{B_o} = 5.7893$

Weight of SampleVolume of Base

1.7189

20.65

1.7714

21.25

3.4903

41.90

$$\text{Moles of unreacted acid/gm. of product} = \frac{41.90}{1000} \times \frac{0.4709}{3.4903} = 0.005653$$

$$\text{Moles of unreacted acid/hr.} = 499.2 \times 0.005653 = 2.8220$$

$$\text{Conversion} = \frac{3.8577 - 2.8220}{3.8577} = 0.269$$

This run was a repeat on the same day of Run No. 31.

Run No. 32

$t = 160^{\circ}\text{C.}$ $N = 0.4750$ $R = 1.508$
 $P = 0.972$ $A = 99.62\%$ $W = 2170$
 $w_{A_o} = 127.5$ $B = 100\%$ $W/F_{A_o} = 1026$
 $w_{B_o} = 147.0$ $F_{A_o} = 2.1151$ $G = 26.0$
 $w = 274.5$ $F_{B_o} = 3.1909$

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.5090	14.20
1.5622	14.77
<u>1.5076</u>	<u>14.22</u>
4.5788	43.19

$$\text{Moles of unreacted acid/gm. of product} = \frac{43.19}{1000} \times \frac{0.4750}{4.5788} = 0.004480$$

$$\text{Moles of unreacted acid/hr.} = 274.5 \times 0.004480 = 1.2298$$

$$\text{Conversion} = \frac{2.1151 - 1.2298}{2.1151} = 0.418$$

Run No. 33

$$t = 160^{\circ}\text{C.}$$

$$N = 0.4750$$

$$R = 1.501$$

$$P = 0.972$$

$$A = 99.62\%$$

$$W = 2170$$

$$w_{A_o} = 187.5$$

$$B = 100\%$$

$$W/F_{A_o} = 697.7$$

$$w_{B_o} = 215.1$$

$$F_{A_o} = 3.1104$$

$$G = 38.1$$

$$w = 402.6$$

$$F_{B_o} = 4.6692$$

Weight of SampleVolume of Base

1.7000

18.19

1.6285

17.53

1.6780

17.98

1.571116.75

6.5776

70.45

$$\text{Moles of unreacted acid/gm. of product} = \frac{70.45}{1000} \times \frac{0.4750}{6.5776} = 0.005088$$

$$\text{Moles of unreacted acid/hr.} = 402.6 \times 0.005088 = 2.0484$$

$$\text{Conversion} = \frac{3.1104 - 2.0484}{3.1104} = 0.342$$

Run No. 38

$t = 160^{\circ}\text{C.}$	$N = 0.4747$	$R = 1.501$
$P = 0.964$	$A = 99.62\%$	$W = 2170$
$w_{A_o} = 159.5$	$B = 100\%$	$W/F_{A_o} = 820.1$
$w_{B_o} = 183.0$	$F_{A_o} = 2.6459$	$G = 32.4$
$w = 342.5$	$F_{B_o} = 3.9724$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
2.1978	22.88
2.2691	23.23
2.1496	22.11
1.9723	20.43
2.0971	21.74
2.0322	21.19
2.1898	22.74
2.1404	22.45
<u>2.2051</u>	<u>23.06</u>
19.2534	199.83

$$\text{Moles of unreacted acid/gm. of product} = \frac{199.83}{1000} \times \frac{0.4747}{19.2534} = 0.004927$$

$$\text{Moles of unreacted acid/hr.} = 342.5 \times 0.004927 = 1.6875$$

$$\text{Conversion} = \frac{2.6459 - 1.6875}{2.6459} = 0.362$$

Run No. 39

$t = 160^{\circ}\text{C.}$	$N = 0.4747$	$R = 1.501$
$P = 0.966$	$A = 99.62\%$	$W = 21.70$
$w_{A_o} = 113.5$	$B = 100\%$	$W/F_{A_o} = 1152$
$w_{B_o} = 130.2$	$F_{A_o} = 1.8828$	$G = 23.1$
$w = 243.7$	$F_{B_o} = 2.8263$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.7991	16.46
1.7911	16.43
<u>1.7952</u>	<u>16.47</u>
5.3854	49.36

$$\text{Moles of unreacted acid/gm. of product} = \frac{49.36}{1000} \times \frac{0.4747}{5.3854} = 0.004351$$

$$\text{Moles of unreacted acid/hr.} = 243.7 \times 0.004351 = 1.0603$$

$$\text{Conversion} = \frac{1.8828 - 1.0603}{1.8828} = 0.437$$

Run No. 40

$t = 160^{\circ}\text{C.}$	$N = 0.4744$	$R = 1.501$
$P = 0.975$	$A = 99.60\%$	$W = 2170$
$w_{A_o} = 323.0$	$B = 100\%$	$W/F_{A_o} = 405.1$
$w_{B_o} = 370.5$	$F_{A_o} = 5.3572$	$G = 65.6$
$w = 693.5$	$F_{B_o} = 8.0425$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.5608	20.30
1.5667	20.29
1.6577	21.40
1.6166	20.90
1.5689	20.28
1.6350	21.17
<u>1.6053</u>	<u>20.81</u>
11.2110	115.15

$$\text{Moles of unreacted acid/gm. of product} = \frac{115.15}{1000} \times \frac{0.4744}{11.2110} = 0.006142$$

$$\text{Moles of unreacted acid/hr.} = 693.5 \times 0.006142 = 4.2595$$

$$\text{Conversion} = \frac{5.3572 - 4.2595}{5.3572} = 0.205$$

Run No. 41

$$t = 180^{\circ}\text{C.}$$

$$N = 0.4843$$

$$R = 1.004$$

$$P = 0.972$$

$$A = 99.60\%$$

$$W = 2170$$

$$w_{A_o} = 159.5$$

$$B = 100\%$$

$$W/F_{A_o} = 820.3$$

$$w_{B_o} = 122.3$$

$$F_{A_o} = 2.6454$$

$$G = 26.6$$

$$w = 281.8$$

$$F_{B_o} = 2.6547$$

Weight of SampleVolume of Base

1.7178

16.09

1.7435

16.28

1.6881

15.90

1.7360

16.39

1.733516.27

8.6189

80.93

$$\text{Moles of unreacted acid/gm. of product} = \frac{80.93}{1000} \times \frac{0.4843}{8.6189} = 0.004547$$

$$\text{Moles of unreacted acid/hr.} = 281.8 \times 0.004547 = 1.2813$$

$$\text{Conversion} = \frac{2.6454 - 1.2813}{2.6454} = 0.516$$

Run No. 42

$$t = 180^{\circ}\text{C.}$$

$$N = 0.4843$$

$$R = 1.005$$

$$P = 0.972$$

$$A = 99.60\%$$

$$W = 2170$$

$$w_{A_o} = 187.5$$

$$B = 100\%$$

$$W/F_{A_o} = 697.8$$

$$w_{B_o} = 144.0$$

$$F_{A_o} = 3.1098$$

$$G = 31.4$$

$$w = 331.5$$

$$F_{B_o} = 3.1258$$

Weight of SampleVolume of Base

2.0217

21.20

1.9166

20.25

1.8841

19.74

1.974820.70

7.7972

81.89

$$\text{Moles of unreacted acid/gm. of product} = \frac{81.89}{1000} \times \frac{0.4843}{7.7972} = 0.005086$$

$$\text{Moles of unreacted acid/hr.} = 331.5 \times 0.005086 = 1.6860$$

$$\text{Conversion} = \frac{3.1098 - 1.6860}{3.1098} = 0.458$$

Run No. 43

$t = 180^{\circ}\text{C.}$	$N = 0.4849$	$R = 1.004$
$P = 0.970$	$A = 99.60\%$	$W = 2170$
$w_{A_o} = 127.5$	$B = 100\%$	$W/F_{A_o} = 1026$
$w_{B_o} = 97.8$	$F_{A_o} = 2.1147$	$G = 21.3$
$w = 225.3$	$F_{B_o} = 2.1229$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
2.0075	16.19
2.1057	16.77
1.9834	16.06
2.0937	16.90
1.9870	15.84
2.0477	16.29
2.0284	16.38
2.1075	16.84
<u>2.0585</u>	<u>16.50</u>
18.4194	147.77

$$\text{Moles of unreacted acid/gm. of product} = \frac{147.77}{1000} \times \frac{0.4849}{18.4194} = 0.003890$$

$$\text{Moles of unreacted acid/hr.} = 225.3 \times 0.003890 = 0.8764$$

$$\text{Conversion} = \frac{2.1147 - 0.8764}{2.1147} = 0.586$$

Run No. 44

$t = 180^{\circ}\text{C.}$	$N = 0.4849$	$R = 1.003$
$P = 0.971$	$A = 99.60\%$	$W = 2170$
$w_{A_o} = 232.5$	$B = 100\%$	$W/F_{A_o} = 562.7$
$w_{B_o} = 178.2$	$F_{A_o} = 3.8562$	$G = 38.9$
$w = 410.7$	$F_{B_o} = 3.8682$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.9122	22.38
1.7872	20.83
1.7736	21.27
1.8610	22.23
1.7590	21.09
1.8305	22.18
1.7594	21.20
1.9067	23.20
1.7748	21.42
<u>1.7680</u>	<u>21.45</u>
18.1324	217.25

$$\text{Moles of unreacted acid/gm. of product} = \frac{217.25}{1000} \times \frac{0.4849}{18.1324} = 0.005810$$

$$\text{Moles of unreacted acid/hr.} = 410.7 \times 0.005810 = 2.3862$$

$$\text{Conversion} = \frac{3.8562 - 2.3862}{3.8562} = 0.381$$

Run No. 44a

$t = 130^{\circ}\text{C.}$	$N = 0.4849$	$R = 1.003$
$P = 0.971$	$A = 99.60\%$	$W = 2170$
$w_{A_o} = 232.5$	$B = 100\%$	$W/F_{A_o} = 562.7$
$w_{B_o} = 178.2$	$F_{A_o} = 3.8562$	$G = 38.9$
$w = 410.7$	$F_{B_o} = 3.8682$	

Weight of SampleVolume of Base

1.9122

23.38

1.787220.83

3.6994

43.21

$$\text{Moles of unreacted acid/gm. of product} = \frac{43.21}{1000} \times \frac{0.4849}{3.6994} = 0.005664$$

$$\text{Moles of unreacted acid/hr.} = 410.7 \times 0.005664 = 2.3262$$

$$\text{Conversion} = \frac{3.8562 - 2.3262}{3.8562} = 0.397$$

This run was a repeat on the same day of Run.No. 44.

Run No. 45

$t = 180^{\circ}\text{C.}$

$N = 0.4852$

$R = 1.003$

$P = 0.974$

$A = 99.68\%$

$W = 2170$

$W_{A_o} = 426.0$

$B = 100\%$

$W/F_{A_o} = 306.9$

$W_{B_o} = 326.6$

$F_{A_o} = 7.0711$

$G = 71.2$

$w = 752.6$

$F_{B_o} = 7.0895$

Weight of SampleVolume of Base

1.7736

25.50

1.7833

25.59

1.7699

25.55

1.8524

26.64

1.9231

27.60

1.863526.74

10.9658

157.62

$$\text{Moles of unreacted acid/gm. of product} = \frac{157.62}{1000} \times \frac{0.4852}{10.9658} = 0.006974$$

$$\text{Moles of unreacted acid/hr.} = 752.6 \times 0.006974 = 5.2486$$

$$\text{Conversion} = \frac{7.0711 - 5.2486}{7.0711} = 0.258$$

Run No. 46

$t = 180^{\circ}\text{C.}$	$N = 0.4946$	$R = 1.002$
$P = 0.968$	$A = 99.75\%$	$W = 2170$
$w_{A_o} = 113.5$	$B = 100\%$	$W/F_{A_o} = 1151$
$w_{B_o} = 87.0$	$F_{A_o} = 1.8853$	$G = 19.0$
$w = 200.5$	$F_{B_o} = 1.8885$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.7465	11.77
1.8110	12.22
<u>1.8037</u>	<u>12.14</u>
5.3612	36.13

$$\text{Moles of unreacted acid/gm. of product} = \frac{36.13}{1000} \times \frac{0.4946}{5.3612} = 0.003333$$

$$\text{Moles of unreacted acid/hr.} = 200.5 \times 0.003333 = 0.6683$$

$$\text{Conversion} = \frac{1.8853 - 0.6683}{1.8853} = 0.646$$

Run No. 47

$t = 180^{\circ}\text{C.}$

$N = 0.4946$

$R = 1.002$

$P = 0.969$

$A = 99.75\%$

$W = 2170$

$w_{A_0} = 323.0$

$B = 100\%$

$W/F_{A_0} = 404.5$

$w_{B_0} = 247.6$

$F_{A_0} = 5.3652$

$G = 54.0$

$w = 570.6$

$F_{B_0} = 5.3747$

Weight of SampleVolume of Base

1.6388

21.37

1.7234

22.32

1.6057

20.99

1.5993

20.89

1.6121

21.01

1.543120.10

9.7224

126.68

$$\text{Moles of unreacted acid/gm. of product} = \frac{126.68}{1000} \times \frac{0.4946}{9.7224} = 0.006444$$

$$\text{Moles of unreacted acid/hr.} = 570.6 \times 0.006444 = 3.6769$$

$$\text{Conversion} = \frac{5.3652 - 3.6769}{5.3652} = 0.315$$

Run No. 49

$t = 160^{\circ}\text{C.}$	$N = 0.4946$	$R = 1.996$
$P = 0.968$	$A = 99.62\%$	$W = 2170$
$w_{A_o} = 127.5$	$B = 100\%$	$W/F_{A_o} = 1026$
$w_{B_o} = 194.5$	$F_{A_o} = 2.1151$	$G = 30.5$
$w = 322.0$	$F_{B_o} = 4.2220$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.8126	12.91
1.8726	13.47
<u>1.8700</u>	<u>13.66</u>
5.5552	40.04

$$\text{Moles of unreacted acid/gm. of product} = \frac{40.04}{1000} \times \frac{0.4946}{5.5552} = 0.003565$$

$$\text{Moles of unreacted acid/hr.} = 322.0 \times 0.003565 = 1.1479$$

$$\text{Conversion} = \frac{2.1151 - 1.1479}{2.1151} = 0.457$$

Run No. 50

t = 160°C.	N = 0.4076	R = 2.003
P = 0.968	A = 99.54%	W = 2170
w _{A_o} = 113.5	B = 100%	W/F _{A_o} = 1153
w _{B_o} = 173.6	F _{A_o} = 1.8813	G = 27.2
w = 287.1	F _{B_o} = 3.7683	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.7007	13.72
1.7086	13.84
1.7093	13.82
1.7022	13.72
<u>1.5337</u>	<u>12.49</u>
8.3545	67.59

$$\text{Moles of unreacted acid/gm. of product} = \frac{67.59}{1000} \times \frac{0.4076}{8.3545} = 0.003298$$

$$\text{Moles of unreacted acid/hr.} = 287.1 \times 0.003298 = 0.9469$$

$$\text{Conversion} = \frac{1.8813 - 0.9469}{1.8813} = 0.497$$

Run No. 51

$t = 160^{\circ}\text{C.}$	$N = 0.4076$	$R = 2.003$
$P = 0.969$	$A = 99.54\%$	$W = 2170$
$w_{A_o} = 159.5$	$B = 100\%$	$W/F_{A_o} = 820.8$
$w_{B_o} = 244.0$	$F_{A_o} = 2.6438$	$G = 38.2$
$w = 403.5$	$F_{B_o} = 5.2965$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.8389	17.61
1.6820	16.03
1.8002	17.09
1.7437	16.75
1.7922	17.10
1.6811	16.03
<u>1.6698</u>	<u>15.97</u>
12.2079	116.58

$$\text{Moles of unreacted acid/gm. of product} = \frac{116.58}{1000} \times \frac{0.4076}{12.2079} = 0.003892$$

$$\text{Moles of unreacted acid/hr.} = 403.5 \times 0.003892 = 1.5704$$

$$\text{Conversion} = \frac{2.6438 - 1.5704}{2.6438} = 0.406$$

Run No. 52

$t = 160^{\circ}\text{C.}$

$N = 0.4074$

$R = 1.996$

$P = 0.971$

$A = 99.66\%$

$W = 2170$

$w_{A_0} = 187.5$

$B = 100\%$

$W/F_{A_0} = 697.6$

$w_{B_0} = 286.0$

$F_{A_0} = 3.117$

$G = 44.8$

$w = 473.5$

$F_{B_0} = 6.2082$

Weight of SampleVolume of Base

1.7263

18.10

1.7103

17.93

1.6211

17.00

1.6954

17.80

1.6919

17.74

1.6560

17.38

1.5695

16.50

1.632317.11

13.3028

139.56

$$\text{Moles of unreacted acid/gm. of product} = \frac{139.56}{1000} \times \frac{0.4074}{13.3028} = 0.004274$$

$$\text{Moles of unreacted acid/hr.} = 473.5 \times 0.004274 = 2.0237$$

$$\text{Conversion} = \frac{3.1117 - 2.0237}{3.1117} = 0.350$$

Run No. 55

$t = 160^{\circ}\text{C.}$

$N = 0.4078$

$R = 2.000$

$P = 0.975$

$A = 99.68\%$

$W = 2170$

$W_{A_0} = 323.0$

$B = 100\%$

$W/F_{A_0} = 404.7$

$W_{B_0} = 494.0$

$F_{A_0} = 5.3615$

$G = 77.3$

$w = 817.0$

$F_{B_0} = 10.7233$

Weight of SampleVolume of Base

1.5146

19.30

1.5606

19.95

1.527419.50

4.6026

58.75

$$\text{Moles of unreacted acid/gm. of product} = \frac{58.75}{1000} \times \frac{0.4078}{4.6026} = 0.005205$$

$$\text{Moles of unreacted acid/hr.} = 817.0 \times 0.005205 = 4.2525$$

$$\text{Conversion} = \frac{5.3615 - 4.2525}{5.3615} = 0.207$$

Run No. 56

$$t = 160^{\circ}\text{C.}$$

$$N = 0.4430$$

$$R = 2.499$$

$$P = 0.977$$

$$A = 99.73\%$$

$$W = 2170$$

$$w_{A_o} = 159.5$$

$$B = 100\%$$

$$W/F_{A_o} = 819.2$$

$$w_{B_o} = 305.0$$

$$F_{A_o} = 2.6489$$

$$G = 44.0$$

$$w = 464.5$$

$$F_{B_o} = 6.6206$$

Weight of SampleVolume of Base

1.9115

14.80

2.0092

15.55

1.8622

14.43

1.9423

15.02

2.052415.89

9.7776

75.69

$$\text{Moles of unreacted acid/gm. of product} = \frac{75.69}{1000} \times \frac{0.4430}{9.7776} = 0.003429$$

$$\text{Moles of unreacted acid/hr.} = 464.5 \times 0.003429 = 1.5928$$

$$\text{Conversion} = \frac{2.6489 - 1.5928}{2.6489} = 0.399$$

Run No.57

$t = 160^{\circ}\text{C.}$	$N = 0.4430$	$R = 2.999$
$P = 0.976$	$A = 99.73\%$	$W = 2170$
$w_{A_o} = 1595$	$B = 100\%$	$W/F_{A_o} = 819.2$
$w_{B_o} = 366.0$	$F_{A_o} = 2.6489$	$G = 49.7$
$w = 525.5$	$F_{B_o} = 7.9448$	

<u>Weight of Sample</u>	<u>Volume of Sample</u>
1.9884	13.53
1.8980	12.90
1.9803	13.49
1.9692	13.38
1.8793	12.82
1.8974	12.84
2.0283	13.78
<u>2.0145</u>	<u>13.69</u>
15.6554	106.43

$$\text{Moles of unreacted acid/gm. of product} = \frac{106.43}{1000} \times \frac{0.4430}{15.6554} = 0.003012$$

$$\text{Moles of unreacted acid/hr.} = 525.5 \times 0.003012 = 1.5828$$

$$\text{Conversion} = \frac{2.6489 - 1.5828}{2.6489} = 0.402$$

Run No. 59

$t = 180^{\circ}\text{C.}$	$N = 0.4436$	$R = 1.001$
$P = 0.974$	$A = 99.87\%$	$W = 2170$
$w_{A_o} = 113.5$	$B = 100\%$	$W/F_{A_o} = 1150$
$w_{B_o} = 87.0$	$F_{A_o} = 1.8876$	$G = 19.0$
$w = 200.5$	$F_{B_o} = 1.8885$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.7393	12.93
1.7111	12.82
1.6787	12.57
<u>1.7122</u>	<u>12.87</u>
6.8413	51.19

$$\text{Moles of unreacted acid/gm. of product} = \frac{51.19}{1000} \times \frac{0.4436}{6.8413} = 0.003319$$

$$\text{Moles of unreacted acid/hr.} = 200.5 \times 0.003319 = 0.6655$$

$$\text{Conversion} = \frac{1.8876 - 0.6655}{1.8876} = 0.647$$

Run No. 60

t = 160°C.	N = 0.4436	R = 1.001
P = 1.112	A = 99.83 %	W = 2170
w _{A_o} = 159.5	B = 100%	W/F _{A_o} = 818.44
w _{B_o} = 122.3	F _{A_o} = 2.6515	G = 26.6
w = 281.8	F _{B_o} = 2.6547	

<u>Weight of Sample</u>	<u>Volume of Base</u>	<u>Pressure</u>
1.3173	18.45	1.1089
1.3687	19.05	1.1102
1.3704	19.06	1.1136
1.4238	20.01	1.1130
1.4716	20.71	1.1130
1.4326	20.35	1.1123
1.4308	20.17	1.1123
1.4845	20.79	1.1130
1.4840	20.79	1.1130
<u>1.4881</u>	<u>20.95</u>	1.1096
14.2718	200.33	

$$\text{Moles of unreacted acid/gm. of product} = \frac{200.33}{1000} \times \frac{0.4436}{14.2718} = 0.006227$$

$$\text{Moles of unreacted acid/hr.} = 281.8 \times 0.006227 = 1.7547$$

$$\text{Conversion} = \frac{2.6515 - 1.7547}{2.6515} = 0.338$$

Run No. 61

$t = 160^{\circ}\text{C.}$	$N = 0.4436$	$R = 1.001$
$P = 1.247$	$A = 99.83\%$	$W = 2170$
$w_{A_o} = 159.5$	$B = 100\%$	$W/F_{A_o} = 818.4$
$w_{B_o} = 122.3$	$F_{A_o} = 2.6515$	$G = 26.6$
$w = 281.8$	$F_{B_o} = 2.6547$	

<u>Weight of Sample</u>	<u>Volume of Base</u>	<u>Pressure</u>
1.4746	19.30	1.2463
1.5314	20.11	1.2484
1.4814	19.45	1.2477
1.4831	19.40	1.2477
1.5406	20.29	1.2477
1.8932	24.90	1.2477
1.5363	20.17	1.2477
1.5348	20.23	1.2477
1.5286	20.13	1.2463
<u>1.4815</u>	<u>19.60</u>	<u>1.2463</u>
15.4855	203.58	

$$\text{Moles of unreacted acid/gm. of product} = \frac{203.58}{1000} \times \frac{0.4436}{15.4855} = 0.005832$$

$$\text{Moles of unreacted acid/hr.} = 281.8 \times 0.005832 = 1.6434$$

$$\text{Conversion} = \frac{2.6515 - 1.6434}{2.6515} = 0.380$$

Run No. 62

t = 160°C	N = 0.3716	R = 1.001
P = 1.383	A = 99.81%	W = 2170
w _{A₀} = 159.5	B = 100%	W/F _{A₀} = 818.6
w _{B₀} = 122.3	F _{A₀} = 2.6510	G = 26.6
w = 281.8	F _{B₀} = 2.6547	

<u>Weight of Sample</u>	<u>Volume of Base</u>	<u>Pressure</u>
0.9736	13.89	1.3824
<u>1.0868</u>	<u>15.75</u>	1.3831
2.0604	29.64	

$$\text{Moles of unreacted acid/gm. of product} = \frac{29.64}{1000} \times \frac{0.3716}{2.0604} = 0.005346$$

$$\text{Moles of unreacted acid/hr.} = 281.8 \times 0.005346 = 1.5065$$

$$\text{Conversion} = \frac{2.6510 - 1.5065}{2.6510} = 0.432$$

Run No. 63

$t = 160^{\circ}\text{C}$	$N = 0.3721$	$R = 2,500$
$P = 0.977$	$A = 99.71\%$	$W = 2170$
$w_{A_0} = 159.5$	$B = 100\%$	$W/F_{A_0} = 819.4$
$w_{B_0} = 305.0$	$F_{A_0} = 2.6483$	$G = 44.0$
$w = 464.5$	$F_{B_0} = 6.6206$	

Weight of SampleVolume of Base

1.9553	18.35
1.9259	17.93
1.9610	18.51
1.9464	17.66
1.9671	18.30
1.9702	18.50
1.9688	18.59
1.9599	18.40
1.9539	17.45
1.9357	17.60
1.9407	17.30
1.9298	17.59
<u>1.9840</u>	<u>18.25</u>
25.3987	234.43

$$\text{Moles of unreacted acid/gm of product} = \frac{234.43}{1000} \times \frac{0.3721}{25.3987} = 0.003434$$

$$\text{Moles of unreacted acid/hr.} = 464.5 \times 0.003434 = 1.5951$$

$$\text{Conversion} = \frac{2.6483 - 1.5951}{2.6483} = 0.398$$

Run No. 64

$t = 160^{\circ}\text{C}$

$N = 0.3721$

$R = 3.000$

$P = 0.977$

$A = 99.71\%$

$W = 2170$

$w_{A_0} = 159.5$

$B = 100\%$

$W/F_{A_0} = 819.4$

$w_{B_0} = 366.0$

$F_{A_0} = 2.6483$

$G = 49.7$

$w = 525.5$

$F_{B_0} = 7.9448$

Weight of SampleVolume of Base

1.9584	16.16
1.9412	15.75
1.9539	15.85
1.8992	15.60
1.9445	15.90
1.9442	16.10
1.9797	16.02
<u>1.9401</u>	<u>15.94</u>
15.5612	127.32

$$\text{Moles of unreacted acid/gm. of product} = \frac{127.32}{1000} \times \frac{0.3721}{15.5612} = 0.003044$$

$$\text{Moles of unreacted acid/hr.} = 525.5 \times 0.003044 = 1.5996$$

$$\text{Conversion} = \frac{2.6483 - 1.5996}{2.6483} = 0.396$$

Run No. 65

$t = 160^{\circ}\text{C}$	$N = 0.4875$	$R = 0.754$
$P = 0.970$	$A = 99.79\%$	$W = 2170$
$w_{A_0} = 159.5$	$B = 100\%$	$W/F_{A_0} = 819.0$
$w_{B_0} = 92.0$	$F_{A_0} = 2.6495$	$G = 23.80$
$w = 251.5$	$F_{B_0} = 1.9970$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
2.2199	34.79
2.1412	33.58
<u>2.1468</u>	<u>33.63</u>
6.5079	102.00

$$\text{Moles of unreacted acid/gm. of product} = \frac{102.00}{1000} \times \frac{0.4875}{6.5079} = 0.007641$$

$$\text{Moles of unreacted acid/hr.} = 251.5 \times 0.007641 = 1.9217$$

$$\text{Conversion} = \frac{2.6495 - 1.9217}{2.6495} = 0.275$$

Run No. 66

$t = 160^{\circ}\text{C}$	$N = 0.4867$	$R = 3.990$
$P = 0.971$	$A = 99.75\%$	$W = 2170$
$w_{A_0} = 159.5$	$B = 100\%$	$W/F_{A_0} = 819.0$
$w_{B_0} = 487.0$	$F_{A_0} = 2.6494$	$G = 61.2$
$w = 646.5$	$F_{B_0} = 10.5713$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
4.3934	22.10
3.3995	17.03
3.6938	18.78
4.0679	20.50
3.9304	19.80
3.8511	19.49
<u>3.9035</u>	<u>19.61</u>
27.2396	137.31

$$\text{Moles of unreacted acid/gm. of product} = \frac{137.31}{1000} \times \frac{0.4867}{27.2396} = 0.002453$$

$$\text{Moles of unreacted acid/hr.} = 646.5 \times 0.002453 = 1.5859$$

$$\text{Conversion} = \frac{2.6494 - 1.5859}{2.6494} = 0.401$$

Run No. 67

$t = 160^{\circ}\text{C}$	$N = 0.4689$	$R = 0.749$
$P = 0.976$	$A = 99.79\%$	$W = 2170$
$w_{A_0} = 323.0$	$B = 100\%$	$w/F_{A_0} = 404.3$
$w_{B_0} = 185.3$	$F_{A_0} = 5.3674$	$G = 48.1$
$w = 508.3$	$F_{B_0} = 4.0223$	

<u>Weight of Sample</u>	<u>Volume of Base</u>
1.5617	30.30
1.5142	29.40
1.5771	30.55
1.5691	30.45
<u>1.5259</u>	<u>29.59</u>
7.7480	150.29

$$\text{Moles of unreacted acid/gm. of product} = \frac{150.29}{1000} \times \frac{0.4689}{7.7480} = 0.009095$$

$$\text{Moles of unreacted acid/hr.} = 508.3 \times 0.009095 = 4.6230$$

$$\text{Conversion} = \frac{5.3674 - 4.6230}{5.3674} = 0.139$$

Run No. 70

$t = 160^{\circ}\text{C}$

$N = 0.4649$

$R = 0.751$

$P = 0.978$

$A = 99.59\%$

$W = 2170$

$w_{A_0} = 187.5$

$B = 100\%$

$W/F_{A_0} = 697.9$

$w_{B_0} = 107.6$

$F_{A_0} = 3.1095$

$G = 27.9$

$w = 295.1$

$F_{B_0} = 2.3357$

Weight of SampleVolume of Base

1.5527

26.82

1.6159

27.91

1.5572

26.84

1.8534

32.00

1.723729.77

8.3029

143.34

$$\text{Moles of unreacted acid/gm. of product} = \frac{143.34}{1000} \times \frac{0.4649}{8.3029} = 0.008026$$

$$\text{Moles of unreacted acid/hr.} = 295.1 \times 0.008026 = 2.3685$$

$$\text{Conversion} = \frac{3.1095 - 2.3685}{3.1095} = 0.238$$

Purging Experiment after Run No. 61

Normality of base = 0.4436

Rate of flow of nitrogen = 0.4 cu. ft./min.

<u>Time</u>	<u>Weight of Sample</u>	<u>Volume of Base</u>
0.5 min.	1.1886 g.	24.70 ml.
5.5	0.4268	9.50
16.5	0.3705	9.77
23.5	0.7874	21.51
29.5	0.3853	10.75
35.5	0.3902	11.07
41.5	0.4087	11.71

Determination of the Average Diameter of a Catalyst Sphere

The average diameter of a catalyst particle was determined by measuring the diameters of three hundred spheres with a micrometer and averaging. The diameters are given in millimeters.

5.305	5.020	5.320	5.495
5.400	5.180	5.155	5.215
5.130	5.280	5.285	5.390
5.245	5.010	5.170	5.250
5.435	5.110	4.990	5.375
5.085	5.210	5.275	5.400
5.500	5.125	5.190	5.195
5.435	5.415	5.220	5.005
5.395	5.475	5.060	5.035
5.055	5.300	5.030	5.385
5.050	5.125	5.060	5.215
5.130	5.475	5.315	4.970
5.210	5.035	5.370	5.250
5.335	5.155	5.150	4.955
5.205	5.075	5.105	5.455

4.990	5.150	5.415	5.130	5.330	5.095
5.105	5.310	5.105	5.345	5.160	5.135
5.145	5.310	5.255	5.045	5.195	5.455
5.240	5.160	4.990	5.185	5.145	5.260
5.355	5.355	5.355	5.070	5.220	5.345
5.355	5.400	5.175	5.200	5.520	5.070
5.165	5.410	5.280	5.060	5.385	5.095
5.070	5.315	5.195	5.350	5.370	5.105
5.215	5.235	5.090	5.455	5.425	5.405
5.225	5.300	5.095	5.170	5.450	5.150
5.420	5.185	5.015	5.070	5.290	5.265
5.320	5.430	5.440	5.395	5.325	5.020
4.975	5.075	5.420	5.125	5.065	5.165
4.975	5.125	5.055	5.185	5.460	5.065
5.245	5.090	5.030	5.275	5.090	5.380
5.405	5.100	5.155	5.535	5.425	5.270
5.485	5.120	5.125	5.130	5.170	5.335
5.405	5.220	5.130	5.165	5.265	5.175
5.420	5.235	5.150	5.180	5.120	5.460
5.315	5.350	5.180	5.165	4.965	5.160
5.175	5.420	5.210	5.360	5.410	5.305
5.165	5.165	5.210	5.065	5.125	5.200
5.310	5.070	5.270	5.475	5.000	5.080
4.995	5.410	5.125	5.040	5.180	5.395

5.340	5.070	5.130	5.060	5.065	5.405
5.165	5.230	5.125	5.355	5.160	5.200
5.260	5.100	5.330	5.205	5.510	5.260
5.325	5.225	5.100	5.520	5.075	5.080
5.375	5.455	5.135	5.235	5.510	5.095
5.455	5.385	5.205	5.330	5.175	5.075
5.540	5.305	5.105	5.150	5.375	5.080
5.475	5.315	5.135	5.450	5.355	5.360
5.210	5.335	5.230	5.130	5.345	5.330
5.175	5.150	5.075	5.235	5.065	5.340
5.275	5.170	5.145	5.265	5.115	5.380
4.955	5.170	5.020	5.215	5.400	5.350
5.240	5.115	5.105	5.065	5.450	5.435
5.115	5.350	5.305	5.305	5.390	5.280
5.360	5.175	5.080	5.465	5.280	5.115
5.365	5.000	5.205	5.450	5.075	5.070

$$\sum_{1}^{300} D_{pi} = 1568.850$$

$$\begin{aligned} \text{Average diameter of particle} = D_p &= \frac{1568.850}{300} = 5.230 \text{ mm.} \\ &= 0.523 \text{ cm.} \end{aligned}$$

Determination of the Particle Density of the Catalyst

Weight of a random sample of 63 dry catalyst balls = 7.9164 gm.

$$\text{Volume of one ball} = \frac{4}{3} \pi R^3 = 0.5236 D_p^3.$$

$$\text{Volume of } n \text{ balls} = 0.5236 \sum_{i=1}^n D_{p_i}^3.$$

<u>Ball No.</u>	<u>D_p, cm.</u>	<u>D_p³, cc.</u>
1	0.5165	0.137787867
2	0.548	0.164566592
3	0.5345	0.152701439
4	0.5425	0.159661141
5	0.520	0.140608000
6	0.5385	0.156155442
7	0.5265	0.145946985
8	0.5035	0.127643418
9	0.504	0.128024064
10	0.525	0.144703125
11	0.524	0.143877824
12	0.511	0.133432831
13	0.515	0.136590875
14	0.528	0.147197952
15	0.5285	0.147616524

Ball No.	D_p	D_p^3
16	0.5455	0.162325582
17	0.534	0.152273304
18	0.5265	0.145946985
19	0.5245	0.144290081
20	0.5435	0.160545688
21	0.537	0.154854153
22	0.510	0.132651000
23	0.5075	0.130709797
24	0.5185	0.139394707
25	0.524	0.143877824
26	0.498	0.123505992
27	0.519	0.139798359
28	0.4975	0.123134359
29	0.520	0.140608000
30	0.5065	0.129938650
31	0.535	0.153130375
32	0.5155	0.136989099
33	0.516	0.137388096
34	0.5495	0.165921662
35	0.5125	0.134611328
36	0.5435	0.160545688
37	0.5115	0.133824896
38	0.5225	0.142645766
39	0.525	0.144703125

<u>Ball No.</u>	<u>D_p</u>	<u>D_p²</u>
40	0.5195	0.140202790
41	0.497	0.122763473
42	0.525	0.144703125
43	0.5055	0.129170541
44	0.5065	0.129938650
45	0.507	0.130323843
46	0.511	0.133432831
47	0.506	0.129554216
48	0.5385	0.156155442
49	0.5095	0.132261232
50	0.5225	0.142645766
51	0.532	0.150568768
52	0.512	0.134217728
53	0.517	0.138188413
54	0.5055	0.129170541
55	0.5465	0.163218920
56	0.511	0.133432831
57	0.525	0.144703125
58	0.538	0.155720872
59	0.5465	0.163218920
60	0.5115	0.133824896
61	0.533	0.151419437
62	0.506	0.129554216
63	0.5135	0.135400835

$$\sum_{i=1}^{65} D_{p_i}^3 = 8.953920006 \text{ cc.}$$

$$\text{Volume} = (0.5236)(8.953920006) = 4.6883 \text{ cc.}$$

$$\text{Particle density, } \rho_p = (7.9164)/(4.6883) = 1.6886 \text{ gm/cc.}$$

Comparison of Top and Bottom Jacket Temperatures

Temperature, °C.

<u>Top</u>	<u>Bottom</u>
24.4	24+
49.0	49
50.0	50
51.5	51.5
54.2	55.0
56.2	57
61.0	61
68.5	68.5
76.4	76
83.8	84
93.4	93+
104.5	104+
114	113+
127	126
135.5	135
140	140
143	143
144.2	144.5

Data for Figure 12:

Temperature = 140° C.

<u>X</u>	<u>Rate of Reaction, r</u>
0	0.000416
0.025	0.000390
0.05	0.000361
0.075	0.000334
0.10	0.000315
0.15	0.000279
0.20	0.000250
0.25	0.000217
0.275	0.000204
0.30	0.000192

Temperature = 180° C.

0	0.000956
0.05	0.000867
0.10	0.000814
0.15	0.000772
0.20	0.000730
0.25	0.000672
0.30	0.000574
0.35	0.000526
0.40	0.000498
0.45	0.000459
0.50	0.000438

Partial Pressures at 140°C. and 0.972 Atmospheres for R equal to 1.000

X	n_{A_2}	n_A	n_B	n_R	n_S	n	P_{A_2}	P_A	P_B	P_R	P_S
0.0	0.2156	0.5687	1.0000	0.0108	0.0000	1.7951	0.1170	0.3086	0.5426	0.0058	0.0000
0.1	0.1845	0.5309	0.9000	0.1108	0.1000	1.8262	0.0984	0.2832	0.4800	0.0591	0.0533
0.2	0.1548	0.4903	0.8000	0.2108	0.2000	1.8559	0.0812	0.2573	0.4198	0.1106	0.1050
0.3	0.1266	0.4467	0.7000	0.3108	0.3000	1.8841	0.0654	0.2309	0.3619	0.1607	0.1551
0.4	0.1001	0.3999	0.6000	0.4108	0.4000	1.9108	0.0510	0.2038	0.3058	0.2094	0.2039
0.5	0.0754	0.3493	0.5000	0.5108	0.5000	1.9355	0.0379	0.1758	0.2516	0.2570	0.2516
0.6	0.0528	0.2943	0.4000	0.6108	0.6000	1.9579	0.0263	0.1464	0.1990	0.3038	0.2985
0.7	0.0331	0.2339	0.3000	0.7108	0.7000	1.9778	0.0163	0.1152	0.1477	0.3500	0.3447

Partial Pressures at 160°C. and 0.972 Atmospheres for R equal to 0.750

X	n_{A2}	n_A	n_B	n_R	n_S	n	P_{A2}	P_A	P_B	P_R	P_S
0.0	0.1657	0.6687	0.7500	0.0108	0.0000	1.5952	0.1010	0.4075	0.4570	0.0066	0.0000
0.1	0.1101	0.6198	0.6500	0.1108	0.1000	1.6207	0.0840	0.3717	0.3898	0.0664	0.0600
0.2	0.1160	0.5681	0.5500	0.2108	0.2000	1.6449	0.0685	0.3357	0.3250	0.1246	0.1182
0.3	0.0934	0.5133	0.4500	0.3108	0.3000	1.6675	0.0544	0.2992	0.2623	0.1812	0.1749
0.4	0.0725	0.4550	0.3500	0.4108	0.4000	1.6883	0.0417	0.2620	0.2015	0.2365	0.2303
0.5	0.0535	0.3930	0.2500	0.5108	0.5000	1.7073	0.0305	0.2237	0.1423	0.2908	0.2847
0.6	0.0366	0.3268	0.1500	0.6108	0.6000	1.7242	0.0206	0.1842	0.0846	0.3443	0.3382
0.7	0.0222	0.2556	0.0500	0.7108	0.7000	1.7386	0.0124	0.1429	0.0280	0.3974	0.3913

Partial Pressures at 160°C. and 0.972 Atmospheres for R equal to 1.000

X	n_{A_2}	n_A	n_B	n_R	n_S	n	p_{A_2}	p_A	p_i	p_R	p_S
0.0	0.1529	0.6942	1.0000	0.0108	0.0000	1.8579	0.0800	0.3632	0.5132	0.0056	0.0000
0.05	0.1408	0.6684	0.9500	0.0608	0.0500	1.8700	0.0732	0.3474	0.1138	0.0316	0.0260
0.1	0.1291	0.6419	0.9000	0.1108	0.1000	1.8818	0.0667	0.3316	0.1649	0.0572	0.0516
0.15	0.1176	0.6147	0.8500	0.1608	0.1500	1.8931	0.0604	0.3156	0.4364	0.0826	0.0770
0.20	0.1066	0.5868	0.8000	0.2108	0.2000	1.9042	0.0544	0.2995	0.4084	0.1076	0.1021
0.3	0.0856	0.5288	0.700	0.3108	0.3000	1.9252	0.0432	0.2670	0.3534	0.1569	0.1515
0.4	0.0667	0.4675	0.6000	0.4108	0.4000	1.9450	0.0333	0.2336	0.2998	0.2053	0.1999
0.5	0.0486	0.4027	0.5000	0.5108	0.5000	1.9621	0.0241	0.1995	0.2477	0.2530	0.2477
0.6	0.0331	0.3337	0.4000	0.6108	0.6000	1.9774	0.0163	0.1640	0.1966	0.3001	0.2949
0.7	0.0200	0.2600	0.3000	0.7108	0.7000	1.9906	0.0098	0.1270	0.1465	0.3470	0.3418

Partial Pressures at 160°C. and 0.972 Atmospheres for R equal to 1.500

X	n_{A_2}	n_A	n_B	n_R	n_S	n	P_{A_2}	P_A	P_B	P_R	P_S
0.0	0.1336	0.7329	1.5000	0.0108	0.0000	2.3773	0.0546	0.2997	0.6133	0.0044	0.0000
0.1	0.1124	0.6753	1.4000	0.1108	0.1000	2.3985	0.0456	0.2737	0.5674	0.0449	0.0405
0.2	0.0924	0.6151	1.3000	0.2108	0.2000	2.4183	0.0371	0.2472	0.5225	0.0847	0.0804
0.3	0.0739	0.5522	1.2000	0.3108	0.3000	2.4369	0.0295	0.2203	0.4786	0.1240	0.1197
0.4	0.0569	0.4862	1.1000	0.4108	0.4000	2.4539	0.0225	0.1926	0.4357	0.1627	0.1584
0.5	0.0416	0.4168	1.0000	0.5108	0.5000	2.4692	0.0164	0.1641	0.3936	0.2011	0.1968
0.6	0.0281	0.3438	0.9000	0.6108	0.6000	2.4827	0.0110	0.1346	0.3524	0.2391	0.2349
0.7	0.0168	0.2664	0.8000	0.7108	0.7000	2.4940	0.0066	0.1038	0.3118	0.2770	0.2728

Partial Pressures at 160°C. and 0.972 Atmospheres for R equal to 2.000

X	n_{A_2}	n_A	n_B	n_R	n_S	n	P_{A_2}	P_A	P_B	P_R	P_S
0.0	0.1187	0.7625	2.000	0.0132	0.0000	2.8944	0.0399	0.2561	0.6716	0.0044	0.0000
0.1	0.0996	0.7008	1.9000	0.1132	0.1000	2.9136	0.0332	0.2338	0.6339	0.0378	0.0334
0.2	0.0817	0.6366	1.8000	0.2132	0.2000	2.9315	0.0271	0.2111	0.5968	0.0707	0.663
0.3	0.0651	0.5699	1.7000	0.3132	0.3000	2.9482	0.0215	0.1879	0.5605	0.1033	0.0989
0.4	0.0499	0.5002	1.6000	0.4132	0.4000	2.9633	0.0164	0.1641	0.5248	0.1355	0.1312

Partial Pressures at 180°C. and 0.972 Atmospheres for R equal to 1.000

X	n_A	n_A	n_B	n_R	n_S	n	P_{A_2}	P_A	P_B	P_R	P_S
	n_{A_2}										
0.0	0.1071	0.7858	1.0000	0.0108	0.0000	1.9037	0.0546	0.4008	0.5101	0.0055	0.0000
0.1	0.0894	0.7212	0.9000	0.1108	0.1000	1.9214	0.0452	0.3645	0.4548	0.0560	0.0505
0.2	0.0729	0.6542	0.8000	0.2108	0.2000	1.9379	0.0365	0.3278	0.4008	0.1056	0.1002
0.3	0.0578	0.5844	0.7000	0.3108	0.3000	1.9530	0.0287	0.2906	0.3480	0.1545	0.1492
0.4	0.0440	0.5120	0.6000	0.4108	0.4000	1.9668	0.0217	0.2528	0.2962	0.2028	0.1975
0.5	0.0318	0.4364	0.5000	0.5108	0.5000	1.9790	0.0156	0.2141	0.2453	0.2506	0.2453
0.6	0.0212	0.3576	0.4000	0.6108	0.6000	1.9896	0.0104	0.1745	0.1952	0.2981	0.2928
0.7	0.0125	0.2750	0.3000	0.7108	0.7000	1.9983	0.0061	0.1336	0.1458	0.3454	0.3401

Partial Pressures at 160°C. and 0.972 Atmospheres for R equal to 2.500

X	n_A 2	n_A	n_B	n_R	n_S	n	P_{A_2}	P _A	P _B	P _R	P _S
0.0	0.1072	0.7856	2.5000	0.0108	0.0000	3.4036	0.0306	0.2244	0.7140	0.0031	0.0000
0.1	0.0896	0.7207	2.4000	0.1108	0.1000	3.4211	0.0255	0.2048	0.6819	0.0315	0.0284
0.2	0.0733	0.6533	2.3000	0.2108	0.2000	3.4374	0.0207	0.1847	0.6504	0.0596	0.0566
0.3	0.0583	0.5835	2.2000	0.3108	0.3000	3.4526	0.0164	0.1643	0.6194	0.0875	0.0845
0.4	0.0445	0.5110	2.1000	0.4108	0.4000	3.4663	0.0125	0.1433	0.5889	0.1152	0.1122
0.5	0.0323	0.4355	2.0000	0.5108	0.5000	3.4786	0.0090	0.1217	0.5588	0.1427	0.1397

Partial Pressures at 160°C. and 0.972 Atmospheres. for R equal to 4.000

0.0	0.0833	0.8334	4.000	0.0108	0.0000	4.9275	0.0164	0.1644	0.7890	0.0021	0.0000
0.1	0.0693	0.7614	3.9000	0.1108	0.1000	4.9415	0.0136	0.1498	0.7671	0.0218	0.0197
0.2	0.0564	0.6873	3.8000	0.2108	0.2000	4.9545	0.0111	0.1348	0.7455	0.0414	0.0392
0.3	0.0445	0.6111	3.7000	0.3108	0.3000	4.9664	0.0087	0.1196	0.7241	0.0608	0.0587
0.4	0.0336	0.5327	3.6000	0.4108	0.4000	4.9771	0.0066	0.1040	0.7031	0.0802	0.0781
0.5	0.0242	0.4517	3.5000	0.5108	0.5000	4.9867	0.0047	0.0880	0.6822	0.0996	0.0975

Partial Pressures at 160°C. and 0.972 Atmospheres for R equal to 8.000

X	n_{A_2}	n_A	n_B	n_R	n_S	n	PA_2	PA	P_B	P_R	P_S
0.0	0.0528	0.8944	8.0000	0.0108	0.0000	8.9580	0.0057	0.0970	0.8681	0.0012	0.0000
0.1	0.0435	0.8129	7.9000	0.1108	0.1000	8.9672	0.0047	0.0881	0.8563	0.0120	0.0108
0.2	0.0351	0.7299	7.8000	0.2108	0.2000	8.9758	0.0038	0.0790	0.8447	0.0228	0.0217
0.3	0.0274	0.6453	7.7000	0.3108	0.3000	8.9835	0.0030	0.0698	0.8331	0.0336	0.0325
0.4	0.0205	0.5589	7.6000	0.4108	0.4000	8.9902	0.0022	0.0604	0.8217	0.0444	0.0432
0.5	0.0145	0.4709	7.5000	0.5108	0.5000	8.9962	0.0016	0.0509	0.8103	0.0552	0.0540

Partial Pressures at 160°C. and 0.972 Atmospheres for R equal to 0.4000

X	n_{A_2}	n_A	n_B	n_R	n_S	n	PA_2	PA	P_B	P_R	P_S
0.0	0.1882	0.6239	0.4000	0.0108	0.0000	1.2229	0.1496	0.4959	0.3179	0.0086	0.0000
0.05	0.1735	0.6029	0.3500	0.0608	0.0500	1.2372	0.1363	0.4737	0.2750	0.0478	0.0393
0.1	0.1595	0.5811	0.3000	0.1108	0.1000	1.2514	0.1239	0.4514	0.2330	0.0861	0.0777
0.15	0.1457	0.5585	0.2500	0.1608	0.1500	1.2650	0.1119	0.4291	0.1921	0.1236	0.1153
0.2	0.1324	0.5352	0.2000	0.2108	0.2000	1.2784	0.1007	0.4069	0.1521	0.1603	0.1521
0.3	0.1070	0.4860	0.1000	0.3108	0.3000	1.3038	0.0798	0.3623	0.0746	0.2317	0.2237

Partial Pressures at 160°C. and 0.972 Atmospheres for R equal to 0.2000

X	n_{A2}	n_A	n_B	n_R	n_S	n	p_{A2}	p_A	p_B	p_R	p_S
0.0	0.2047	0.5905	0.2000	0.0108	0.0000	1.0060	0.1978	0.5705	0.1932	0.0104	0.0000
0.05	0.1891	0.5718	0.1500	0.0608	0.0500	1.0217	0.1799	0.5440	0.1427	0.0578	0.0476
0.1	0.1738	0.5523	0.1000	0.1108	0.100	1.0369	0.1629	0.5177	0.0937	0.1039	0.0937
0.15	0.1590	0.5320	0.0500	0.1608	0.1500	1.0518	0.1469	0.4916	0.0462	0.1486	0.1386
0.2	0.1446	0.5108	0.0000	0.2108	0.2000	1.0662	0.1318	0.4657	0.0000	0.1922	0.1823

Partial Pressures and Fugacities of Acetic Acid Monomer

<u>X</u>	<u>p_A</u>	<u>f</u>
Temperature = 140°C., Pressure = 0.972 atms., R = 1.000		
0.0	0.3086	0.3086
0.1	0.2832	0.2831
0.2	0.2573	0.2573
0.3	0.2309	0.2309
0.4	0.2038	0.2038
0.5	0.1758	0.1759
0.6	0.1464	0.1464
0.7	0.1152	0.1152

Temperature = 160°C., Pressure = 0.972 atms., R = 1.000		
0.0	0.3632	0.3630
0.05	0.3474	0.3473
0.1	0.3316	0.3315
0.15	0.3156	0.3155
0.2	0.2995	0.2994
0.3	0.2670	0.2669
0.4	0.2336	0.2337
0.5	0.1995	0.1994
0.6	0.1640	0.1639
0.7	0.1270	0.1270

Partial Pressures and Fugacities of Acetic Acid Monamer

<u>X</u>	<u>P_A</u>	<u>f</u>
Temperature = 180°C., Pressure = 0.972 atms., R = 1.000		
0.0	0.4008	0.4007
0.1	0.3645	0.3644
0.2	0.3278	0.3278
0.3	0.2906	0.2905
0.4	0.2528	0.2528
0.5	0.2141	0.2141
0.6	0.1745	0.1745
0.7	0.1336	0.1336

Values for Graphical Integration -
Calculated Using Rate Equation

<u>X</u>	<u>r</u>	<u>1/r</u>	<u>W/F</u>
R = 0.20			
0.0	0.0001627	6146	
0.05	0.0001174	8518	
0.1	0.0000749	13351	893
R = 0.40			
0.0	0.0002784	3592	
0.05	0.0002355	4246	
0.10	0.0001947	5136	428
0.15	0.0001560	6410	
0.20	0.0001194	8375	1081
0.30	0.0000522	19157	
R = 0.75			
0.0	0.0004035	2478	
0.05	0.0003768	2654	
0.10	0.0003389	2951	267
0.15	0.0003025	3306	
0.20	0.0002674	3740	599
0.30	0.0002012	4970	1031
0.40	0.0001405	7117	1625

<u>X</u>	<u>r</u>	<u>1/r</u>	<u>W/F</u>
R = 1.00			
0.0	0.0004831	2070	
0.05	0.0004459	2243	
0.10	0.0004098	2440	225
0.15	0.0003748	2668	
0.20	0.0003408	2934	492
0.30	0.0002756	3268	818
0.40	0.0002143	4666	1229
0.50	0.0001572	6361	1773

R = 1.50			
0.0	0.0005714	1750	
0.10	0.0005040	1984	183
0.20	0.0004387	2280	396
0.30	0.0003753	2664	642
0.40	0.0003136	3189	933
0.50	0.0002537	3942	1286

<u>X</u>	<u>r</u>	<u>1/r</u>	<u>W/F</u>
R = 2.00			
0.0	0.0006217	1608	
0.05	0.0005899	1695	
0.10	0.0005584	1791	170
0.15	0.0005271	1897	
0.20	0.0004959	2016	360
0.30	0.0004341	2304	574
0.40	0.0003724	2685	824
0.50	0.0003108	3218	1119

R = 2.50			
0.00	0.0006512	1536	
0.05	0.0006208	1611	
0.10	0.0005907	1693	161
0.15	0.0005604	1784	
0.20	0.0005301	1886	340
0.30	0.0004694	2130	540
0.40	0.0004078	2452	768
0.50	0.0003531	2832	1032

<u>X</u>	<u>r</u>	<u>1/r</u>	<u>W/F</u>
R = 4.00			
0.00	0.0006720	1488	
0.05	0.0006447	1551	
0.10	0.0006169	1621	155
0.15	0.0005888	1698	
0.20	0.0005604	1784	325
0.30	0.0005023	1991	513
0.40	0.0004420	2262	725
0.50	0.0003789	2639	969
R = 8.00			
0.00	0.0005967	1676	
0.05	0.0005734	1744	
0.10	0.0005494	1820	175
0.15	0.0005250	1905	
0.20	0.0005000	2000	365
0.30	0.0004487	2229	576
0.40	0.0003949	2532	812
0.50	0.0003385	2954	1086

Data for Figures 16 and 17

Run No.	X	p_{A_x}	$-\ln p_{A_x}/p_{A_o}$	$1/q$
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Series I: $t = 140^\circ\text{C.}$, $P = 0.974$ atms., $R = 1.003$, $p_{A_o} = 0.3086$ atms.

5	0.182	0.262	+0.1637	0.2875
7	0.243	0.246	+0.2267	0.4194
8	0.183	0.2615	+0.1656	0.2876
12	0.213	0.254	+0.1947	0.3564
13	0.307	0.229	+0.2983	0.5894
15	0.304	0.230	+0.2940	0.5891
16	0.275	0.238	+0.2598	0.5246
17	0.140	0.273	+0.1226	0.2071
18	0.137	0.274	+0.1189	0.2069
19	0.108	0.280	+0.0972	0.1568

Series 2: $t = 160^\circ\text{C.}$, $P = 0.972$ atm., $R = 1.003$, $p_{A_o} = 0.3632$ atm.

21	0.366	0.245	+0.3937	0.5003
23	0.338	0.254	+0.3576	0.4002
24	0.282	0.273	+0.2855	0.3395
26	0.164	0.310	+0.1584	0.1973
27	0.397	0.235	+0.4354	0.5628
27a	0.390	0.237	+0.4269	0.5628
28	0.136	0.320	+0.1266	0.1499
29	0.236	0.288	+0.2320	0.2743
30	0.175	0.3075	+0.1665	0.1974

Run No.	X	p_{A_x}	$-\ln p_{A_x}/p_{A_0}$	$1/q$
Series 8: $t = 160^\circ\text{C.}$, $P = 0.974 \text{ atm.}$, $R = 0.751$, $p_{A_0} = 0.4075 \text{ atm.}$				
65	0.275	0.308	0.2799	0.4569
67	0.139	0.357	0.1323	0.2260
70	0.238	0.321	0.2386	0.3883

Run No.	X	p_{A_x}	$-\ln p_{A_x}/p_{A_0}$	$1/q$
Series 4: $t = 180^\circ\text{C.}$, $P = 0.971 \text{ atm.}$, $R = 1.003$, $p_{A_0} = 0.4008 \text{ atm.}$				
41	0.516	0.208	+0.6559	0.3819
42	0.458	0.230	+0.5554	0.3246
43	0.586	0.179	+0.8061	0.4776
44	0.381	0.260	+0.4328	0.2620
44a	0.397	0.254	+0.4561	0.2620
45	0.258	0.306	+0.2699	0.1431
46	0.646	0.155	+0.9500	0.5377
47	0.315	0.285	+0.3410	0.1889
59	0.647	0.154	+0.9565	0.5384

Series 3: $t = 160^\circ\text{C.}$, $P = 0.970 \text{ atm.}$, $R = 1.502$, $p_{A_0} = 0.2997 \text{ atm.}$				
31	0.264	0.2295	+0.2669	0.2199
31a	0.269	0.2282	+0.2726	0.2199
32	0.418	0.186	+0.4770	0.3997
33	0.342	0.208	+0.3652	0.2726
38	0.362	0.2025	+0.3920	0.3205
39	0.437	0.182	+0.4988	0.4504
40	0.205	0.2455	+0.1995	0.1582

Series 5: $t = 160^\circ\text{C.}$, $P = 0.970 \text{ atm.}$, $R = 2.000$, $p_{A_0} = 0.2561 \text{ atm.}$				
49	0.457	0.1495	+0.5383	0.3350
50	0.497	0.1400	+0.6039	0.3754
51	0.406	0.1615	+0.4611	0.2671
52	0.350	0.1820	+0.3416	0.2279
55	0.207	0.209	+0.2032	0.1321

APPENDIX B.

Additional Information about the Catalyst

Several pellets of the catalyst were leached overnight with concentrated ammonium hydroxide solution. The resultant solution was evaporated slowly to dryness. The white crystalline residue which remained was transferred to a crucible and heated at 500°C for four hours in a muffle furnace. Decomposition occurred yielding a substance which appeared orange while hot but which turned lemon yellow on cooling. This indicated the formation of WO_3 which changes color the same way.

About two liters of impregnating solution were evaporated very slowly but not to dryness. The excellent crop of white needle-like crystals that was grown was filtered, washed with alcohol and dried in an oven. Three accurately weighed samples of this salt were ignited at 500°C in a muffle furnace to constant weight. The residue because of the characteristic yellow color was taken as WO_3 .

The results of the analyses follow;

Sample 1.

Weight of sample before ignition	3.1431 g.
Weight of sample after ignition	2.7260
Loss in weight	0.4171
Percent loss in weight	13.26

Sample 2.

Weight of sample before ignition	3.5230
Weight of sample after ignition	3.0566
Loss in weight	0.4664
Percent loss in weight	13.24

Sample 3.

Weight of sample before ignition	3.0122
Weight of sample after ignition	2.6131
Loss in weight	0.3991
Percent loss in weight	13.25

Average percent loss in weight 13.25

Formula weight of WO_3 231.92

Weight of NH_3 and H_2O associated with one

$$\text{formula weight of } WO_3 = \frac{(231.92)(0.1325)}{(0.8675)} = 35.42$$

Therefore the formula of the salt could be written

$[(NH_3)_2O]_n (WO_3)_m$ where n and m are equal for this particular salt.

APPENDIX C.

Analytical Procedures1. Preparation of Standard Sodium Hydroxide.

Concentrated carbonate-free sodium hydroxide was prepared according to the procedure outlined by Kolthoff and Sandell (23) using Mallinckrodt Analytical Reagent assaying 97.0% NaOH and 2.5% Na_2CO_3 . A given weight of the pellets was dissolved in an equal weight of water in a Pyrex flask. The suspended sodium carbonate was removed by filtering the solution through a Gooch crucible. The strong carbonate-free sodium hydroxide solution was stored in a paraffin-lined bottle and used as required.

An automatic buret with a two liter reservoir was available for titrating samples of the product. Standard carbonate-free base, around 0.4N was prepared by transferring a required amount of concentrated sodium hydroxide solution to the reservoir, diluting with carbonate-free distilled water, and standardizing against Mallinckrodt potassium acid phthalate primary standard (assaying 99.95-100.05% $\text{KHC}_8\text{H}_4\text{O}_4$), using phenolphthalein as indicator.

The normality of the standard solution was checked two or three times during each run. 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. Analysis of the Acetic Acid

Du Pont C.P. reagent grade glacial acetic acid was used for all the runs. Before every run two portions of acid, analyzed separately and each about 0.75 g., were weighed in small glass-stoppered weighing bottles. A bottle and its contents was quickly transferred to a beaker containing sufficient water to immerse the bottle and titrated with standard sodium hydroxide using phenolphthalein as indicator.

Sample Analysis:

Normality of standard sodium hydroxide =	0.3721
Weight of acetic acid sample, by difference =	0.8017 g.
Volume of base required =	35.78 ml.
Weight of HOAc in sample =	
$(60.052) \frac{(35.78)}{1000} (0.3721) =$	0.7995 g.
Composition of acid (wt. %) = $\frac{(0.7995)(100)}{0.8017}$	99.73

A good balance was attained for all samples of acid weighed.

3. Analysis of Ethyl Alcohol

U.S.P. synthetic absolute alcohol obtained from United States Industrial Corporation was used for every run. This grade of alcohol was assumed to contain no impurities other than water and possibly aldehydes.

Alkaline silver nitrate reagent (10) gave a satisfactory

qualitative test for aldehydes. It was prepared by dissolving 3 g. of silver nitrate in a small amount of water in a 100 ml. volumetric flask, adding 3 g. of pure NaOH, 20 ml. of concentrated ammonium hydroxide, and distilled water until the volume was 100 ml.

For the test, 10 ml. of the sample were diluted with an equal volume of distilled water in a glass-stoppered bottle. When 1 ml. of the alkaline silver nitrate reagent had been added, the bottle was placed in a dark chamber. After one hour the liquid was filtered and the filtrate made acid with nitric acid and a few drops of hydrochloric acid added. A precipitate of silver chloride would indicate no reduction of the silver salt and consequently a negligible amount of aldehyde in the sample.

Tests were carried out on two samples of alcohol obtained from two different batches. In both cases a relatively large amount of silver chloride was formed, showing that aldehydes were present in negligible amounts, if at all. The assumption was made that all samples of alcohol were completely free of aldehydes. Water remained as the only impurity.

The alcohol was analyzed for water by measuring its density with a Westphal balance. The composition was then obtained by referring to a table of densities (30). For every sample the purity appeared to be 100% and was taken to be such.

APPENDIX D.

Calibration of Flowrators

Ethyl alcohol and acetic acid were metered with Fischer & Porter flowrators calibrated at room temperatures between 24°C. and 28°C. Samples of the alcohol and acid based on different rates of flow were collected in glass-stoppered weighing bottles over definite intervals of time and weighed. Evaporation losses through the ground-glass stoppers were negligible. Three calibrations were made for each component but only one, an average, was presented because the small differences in temperature were insufficient to cause a noticeable change in mass rate of flow.

1. Alcohol Flowrator

Temperature 26° - 28°0.

Tube 03 B 15

Float FG-031, aluminum

Tube Scale
Reading, mm.Flow Rate
g./hr.

10	82.48
15	103.1
20	127.8
25	152.5
30	188.3
35	221.6
40	258.2
45	297.9
50	342.2
55	383.2
60	426.8
70	520.1
80	630.0
90	748.1
100	872.3
110	1001.
120	1134.

2. Acid Flowrator

Temperature 26° - 28°C.

Tube 04 B 15

Float FL-042, stainless steel

Tube Scale Reading , mm.	Flow Rate g./hr.
0	36.05
5	52.21
10	74.76
15	100.1
20	127.5
25	159.7
30	191.8
35	231.8
40	280.4
45	322.2
50	375.0
55	417.0
60	481.6
65	520.8
70	587.7
80	706.9
90	825.8