HYDRATION OF PROPYLENE WITH A CATION EXCHANGE RESIN CATALYST

John Harold Hiestand

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in The
University of Michigan
Department of Chemical Engineering
1961

May, 1961

IP-515

Doctoral Committee:

      Associate Professor Kenneth F. Gordon, Chairman
      Associate Professor Wilbur C. Bigelow
      Professor Giuseppe Parravano
      Assistant Professor Dale F. Rudd
      Associate Professor Milton Tamres

ACKNOWLEDGMENTS

The author wishes to express his appreciation to the members of his committee for their discussion and comments on the various aspects of this work, and particularly to Professor K. F. Gordon for his guidance during the completion of the experimental work and to Professor R. R. White for his guidance and encouragement throughout the beginning of this investigation; to the shop and office staff who gave freely of their time and aid; and to the many graduate students who contributed much through their stimulating discussions of the study.

Materials supplied by the Phillips Petroleum Company and Dow Chemical Company are gratefully acknowledged.

Financial assistance in the form of fellowships and grants from the Socony-Mobil Oil Company, Gulf Research and Development Company, E. I. du Pont Company, and Dow Chemical Company is much appreciated.

Finally, the author wishes to thank his family: his wife, Carol, and his parents for their inspiration and assistance.

TABLE OF CONTENTS

ABSTRACT

The hydration of propylene to isopropyl alcohol in the presence of an acid cation exchange resin catalyst was studied in a flow reactor under steady-state conditions. The experimental variables investigated were:

Temperature: 100° to 160°C

Pressure: 450 psig and 1440 psig

Resin size: 32-42 mesh and 100-150 mesh

Hydrogen ion concentration: 0.462-1.678 meq./ml

Feed composition: 0-60% (wt. % isopropyl alcohol)

Incremental reaction rates were measured as a function of temperature, pressure, resin size, hydrogen-ion concentration, and feed composition. The reaction rate, correlated as a function of temperature and concentration in the liquid on the propylene-free basis, is:

$$r = \exp(-21,600/RT)\{(-37.94 + 0.668t - 0.0026t^2) \cdot 10^9$$
$$+ (2.059 - 0.06517t) \cdot 10^{10}x + (1.952 + 0.00937t) \cdot 10^{11}x^2\}$$
$$\text{gm.-moles/eq.-min.} \quad @ \ 450 \text{ psig}$$

and

$$r = \exp(-21,600/RT)\{(1.68 - 0.005t) \cdot 10^{10} - (4.32 - 0.023t) \cdot 10^{11}x$$
$$+ (20.98 - 0.122t) \cdot 10^{11}x^2\} \text{ gm.-moles/eq.-min.} \quad @ \ 1440 \text{ psig}$$

where R = 1.987 cal/gm.-mole-°K, T = °K, t = °C, and the mole fraction of isopropyl alcohol in the liquid (propylene-free), x = 0 to 0.12. This yields an apparent activation energy of 21,600 cal/gm.-mole for the 8% crosslinked, sulfonated polystyrene resin catalyst used, Dowex 50WX8. Resin size had no apparent effect on the reaction rate, indicating that diffusion is not important in this system under the conditions investigated.

The rate per unit of catalyst volume is not a linear function of hydrogen-ion concentration. Initial rates are correlated by:

$$r_i = \left\{ 12.952[H^+] + 4.002[H^+]^2 \right\} \times 10^{-3} \text{ gm-moles/liter-min.}$$

where $[H^+]$ = meq./ml. of saturated resin.

Because the formation of di-isopropyl ether becomes increasingly noticeable above 140°C, only a few exploratory runs were made in this area, and no attempt was made to correlate the data.

The resin half-life is 155 days at 130°C, found by extrapolating data at 200°C and 170°C on a log half-life versus 1/T plot.

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Since the first commercial production of isopropyl alcohol, about 1920, it has been widely used as a solvent, a dehydrating agent, a disinfectant, and a raw material for the manufacture of acetone and other compounds. Production in 1960 was 1,250,000,000 pounds with a value of $88,360,000.[15] Petroleum refining companies are currently interested in a relatively simple and inexpensive method of converting by-product propylene to isopropyl alcohol for use as an anti-icing additive for gasoline.

The most obvious route for making isopropyl alcohol is the catalytic hydration of an olefin in the vapor phase or the use of a mineral acid or the acid form of a cation exchange resin as the catalyst in the liquid phase.

General Background of Hydrolysis and Hydration

The hydrolysis of olefins to alcohols has been carried out with a number of catalysts. The original commercial process[1] is a two-step operation. The olefin is first contacted with concentrated sulfuric acid in a counter-current absorber to form the alkyl sulfuric acid. This intermediate product is passed through a hydrolyzer and reacted with water forming the alcohol and sulfuric acid which are separated by distillation.

Recently many alternate processes have been investigated. Some make use of direct hydration on a solid catalyst while others involve direct hydration with strong mineral acids or their salts.

Most reactions in the solid catalyst group take place at high temper-
ature and high pressure in the vapor phase. The mineral acid or salt
reactions occur in the liquid phase. The use of the acid form of
cation exchangers as hydration catalysts has also become of interest.

Table I lists some of the hydrolysis and hydration catalysts
investigated with their references. McDonald and Hamner[27,28,29] dis-
cuss the latest developments in the field.

General Background of Ion Exchanger Catalysis

Like mineral acids, the acid form of cation exchanger catalysts
are highly active at relatively low temperatures and pressures because of
the high hydrogen ion concentrations. However, the advantage of direct
reaction on a solid catalyst, namely the easy separation of catalyst
from product, is enjoyed. Ion exchangers have been used as catalysts
for many types of organic reactions. Table II lists reactions which are
catalyzed by either cation or anion exchangers or in some cases both,
presumably through different mechanisms.

The reaction under investigation is catalyzed by the acid
form of a cation exchanger, Dowex 50, a sulfonated polystyrene cross-
linked with divinylbenzene. This resin, described by Bauman and
Eichhorn[5], has been used as a catalyst in numerous investigations
of organic reactions[35,4,18,11,25] The newer form of the resin,
Dowex 50W, sulfonated under controlled conditions, was used in this
study.

TABLE I

HYDRATION CATALYSTS

Catalyst   Author

Mineral Acids   Ipatieff & Monroe[14], Majewski & Marek[26],
                                  Runge, et al[34], Stanley, et al[40],
                                  Sherwood[36].

Ion-exchangers   Chambers[8], Douglas[11], Keith[16], Kreps
                                  & Nachod[19], Langer[21], Young[44]

Inorganic Oxides   Levy & Greenhalgh[23], Lukasiewicz, et al[24],
(alumina, silica, zir-   Muller & Waterman[30], Reynolds & Pittwell[32],
conia, thoria, titania,   Robinson[33], Runge, et al[34]
tungstic, and ferric)

Activated Copper   Cottle & Young[9]

Permanganates, Alumi-   Teter, Gring, and Hettinger[42]
nates and Silicates

Silicaphosphoric Acid   Wegner[43]

Chrysocolla   Smith[39]

Halogenated Poly-   Friedman & Morritz[12]
carboxylic Acid

Organic Nitrogen Bases   Bent & Wik[6]

TABLE II

ION-EXCHANGER CATALYZED REACTIONS

Reaction Type	Author
Hydration-dehydration	Hamilton & Metzner[13], Kressman[20] Reed, et al[31], Sussman[41]
Alcoholysis	Sussman[41]
Esterification	Kressman[20], Sussman[41]
Sucrose Inversion	Kressman[20], Sussman[41]
Acetal Synthesis	Kressman[20], Sussman[41]
Alkylation	Kelly[17]
Condensation	Astle & Pinns[2], Kressman[20]

THEORY

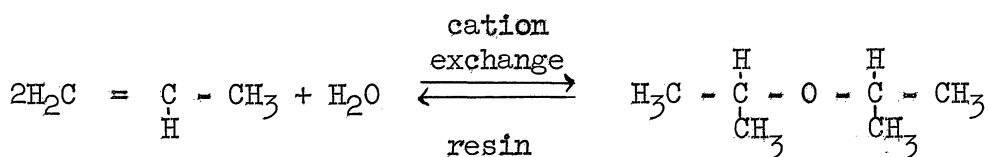### Hydration Reaction

The hydration of propylene to form isopropyl alcohol was

investigated using a cation exchange resin as catalyst.

$$H_2C = \underset{\underset{H}{|}}{C} - CH_3 + H_2O \underset{\text{resin}}{\overset{\substack{\text{cation} \\ \text{exchange}}}{\rightleftarrows}} H_3C - \underset{\underset{H}{|}}{\overset{OH}{\underset{|}{C}}} - CH_3$$
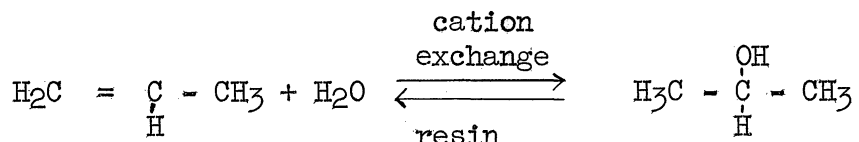
The reactants form a vapor-liquid mixture since the temperature required

to obtain useful rates is above the critical of propylene.

Vapor-phase chromatography was used to determine the products

by comparison of chromatograms with those of standard samples of ex-

pected products, isopropyl alcohol, di-isopropyl ether, n-propyl alcohol,

and acetone. The only compounds found in the product were isopropyl

alcohol and di-isopropyl ether. The rate of formation of di-isopropyl

ether is much slower than that of isopropyl alcohol; therefore, this

reaction does not consume an appreciable amount of reactants below 160° C.

$$2H_2C = \underset{\underset{H}{|}}{C} - CH_3 + H_2O \underset{\text{resin}}{\overset{\substack{\text{cation} \\ \text{exchange}}}{\rightleftarrows}} H_3C - \underset{\underset{CH_3}{|}}{\overset{H}{\underset{|}{C}}} - O - \underset{\underset{CH_3}{|}}{\overset{H}{\underset{|}{C}}} - CH_3$$

In runs at atmospheric pressure and 130° C, where the reaction

mixture is entirely vapor phase, no reaction was apparent with the cation

exchange resin catalyst, so the vapor-phase rate must be negligible in

comparison with the catalyzed liquid-phase rate. Marberry[25] found that

the rate of cumene hydroperoxide decomposition catalyzed by Dowex 50

resin was dependent upon the water concentration in his reaction mixture.

Perhaps liquid water must be present for a reaction to take place in the resin phase. Liquid water causes an expansion of the resin allowing molecules to diffuse into the resin more freely, and it causes the functional groups to become more highly ionized favoring the carbonium ion reaction.

Since the vapor-phase rate is negligible, the reaction may be considered to take place between the propylene dissolved in the water and the water itself. Inside the resin phase, this reaction probably takes place much the same as the carbonium ion reaction in aqueous acid. The resin-liquid-vapor reaction system is much too complex to determine the mechanism from overall rate data alone. However, the carbonium ion mechanism[22] is chosen as a possible mechanism and a rate equation is developed which justifies the correlation of the rate data.

$$H_2C = \underset{\underset{H}{|}}{C} - CH_3 + H^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} (H_3C - \underset{\underset{H}{|}}{C} - CH_3)^+ \tag{1}$$

$$(H_3C - \underset{\underset{H}{|}}{C} - CH_3)^+ + H_2O \underset{k_4}{\overset{k_3}{\rightleftarrows}} H_3C - \underset{\underset{H}{|}}{\overset{OH}{C}} - CH_3 + H^+ \tag{2}$$
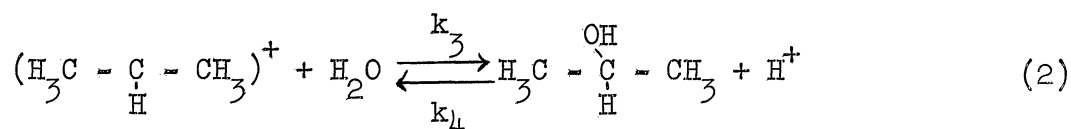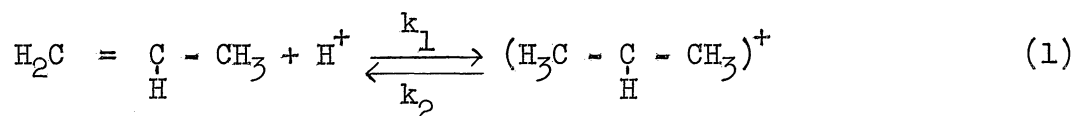
The equation for the rate of formation of isopropyl alcohol is derived in Appendix A.

$$\frac{d[i\text{-}C_3H_7OH]}{dt} = \frac{k_1 k_3 [H^+]}{k_2 + k_3 [H_2O]} \left\{ [C_3H_6][H_2O] - \frac{[i\text{-}C_3H_7OH]}{K} \right\} \tag{3}$$

The reaction is exothermic. The heat of reaction, calculated in Appendix G, is -10.74 kcal/gm.-mole corresponding to a heat generation of 2.69 - 107 cal/min. or 0.187 - 7.43 watts for rates measured in the

range 100° - 140°C. A typical power input to the reactor heaters is 130 watts. It is apparent that the heat of reaction is negligible compared to the heat required to maintain the reactor at operating temperature.

Nature of the Catalyst

Ion exchange materials have functional groups, capable of ionizing, attached to a non-ionizing skeleton which is insoluble in the exchange medium. Some occur naturally, such as silicates, micas, and feldspars, but the synthetic resins are more specific in their action since they contain only one functional group. Cation exchange resins may contain carboxylic, phenolic, sulphonic, or phosphonic groups. Resins containing sulphonic or phosphonic groups are the most useful for acid catalyzed reactions since both are strong acid groups.

Dowex 50 is a polystyrene, cross-linked with divinylbenzene and sulfonated with H_2SO_4. A newer type, Dowex 50W, is sulfonated under controlled conditions yielding a product which has a lighter color and a greater mechanical strength due to less charring of the organic material and smaller internal stresses. Dowex 50W was chosen as the catalyst for this reaction because other investigators had difficulty with Dowex 50 disintegrating at lower temperatures than those required for this reaction.

In the Dowex 50 resin, the sulphonic acid groups are attached to the benzene rings with the gel structure shown on the following page.

The amount of cross-linking determines the absorptive and swelling capacities of the resin. Highly cross-linked resins have low absorptive and swelling capacities. As a result, the rate of absorption

$$\left[\begin{array}{c} -CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2- \\ SO_3H \quad SO_3H \quad SO_3H \\ \\ -CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2- \\ SO_3H \quad SO_3H \quad SO_3H \end{array}\right]_n$$

of large molecules is limited by a highly cross-linked resin because the resin structure offers an obstruction to the migration of these molecules. Conversely, small molecules are little affected by cross-linking. An 8% cross-linked resin was chosen because it has the optimum cross-linking for most systems; it neither swells excessively nor offers too much diffusional resistance.

For the sake of simplicity, most authors assume that the gel phase has a continuous "liquid" structure. This phase is in equilibrium with the external liquid phase; the concentrations of the gel phase are determined by the external concentrations and the phase distribution coefficients of each of the components.

Ion exchange resins selectively absorb materials from a multicomponent mixture. This can be described by the phase distribution coefficients which are the ratios of internal to external concentration of each component.

In the treatment of ion exchange catalysis data phase dis-tribution coefficients receive various degrees of attention. Some authors ignore them; others use them but make simplifying assumptions such as their independence of temperature and concentration. It is

now recognized that distribution coefficients are important and are functions of concentration and temperature.

Correlating Equation

In Appendix B, the rate equation is developed from the theory, justifying the form of the equation used for correlating the rate data. Although the data are correlated by the equation, this does not prove that the assumed mechanism is correct.

Since the reaction system is complex and the phase diagram for the gel-liquid-vapor system of the three-component mixture is not available, it is necessary to simplify the derivation of the rate expression to arrive at an equation which may be written as a function of the liquid-phase mole fraction of isopropyl alcohol on the propylene-free basis.

$$\frac{d[i\text{-}C_3H_7OH]}{dt} = \frac{k_1k_3[H^+]}{G} \left\{ A+Bx+Cx^2+Dx^3+Ex^4+Fx^5 \right\} \qquad (4)$$

The constants, A through G, are defined in Appendix B. Although G is a function of x, it is assumed to be constant over the range of x investigated. A more exact rate equation would be a polynomial of higher degree, substituting a power series of x for G; however, rate data would scarcely warrant being fitted by an equation containing more than two or three constants while Equation (4) has eight constants after combining k_1 and k_3. The correlations are made with three-constant equations.

EQUIPMENT

Flow Description

Much of the equipment used was designed for the dehydration of n-butyl alcohol.[37] Details of the original equipment may be found in the dissertations of Sliepcevich[38], Dale[10], and Douglas[11]. Several modifications were made to adapt the equipment to the present investigation.

As shown in Figure 1, distilled water was pumped from its gaging cylinder (A), through a cation exchanger bed for metal ion removal (B), to the reactor (C). Oil was pumped from its gaging cylinder (D) to the first cylinder of the mercury displacement feed system (E), displacing mercury into the second cylinder (F) and in turn propylene to the reactor (C). To provide positive pressure to the pump intakes, assuring uniform pumping rates, a nitrogen pressure of 50 psi was applied to each gaging cylinder.

The two feed streams entered the reactor inlet tee from opposite sides, mixed in the center, and passed into the reactor through a feed preheater section where the reaction mixture was heated to reaction temperature. A stainless steel cone, with a 0.006" diameter hole at the apex, was placed in each of the feed lines at the entrance of the inlet tee. The feed streams were thus jetted into the tee producing good mixing of the two phases. After leaving the preheater, the two-phase mixture passed through the resin catalyst which surrounded a thermowell containing a traversing thermocouple (G). A gas loaded back-pressure regulator valve maintained the reactor pressure. The
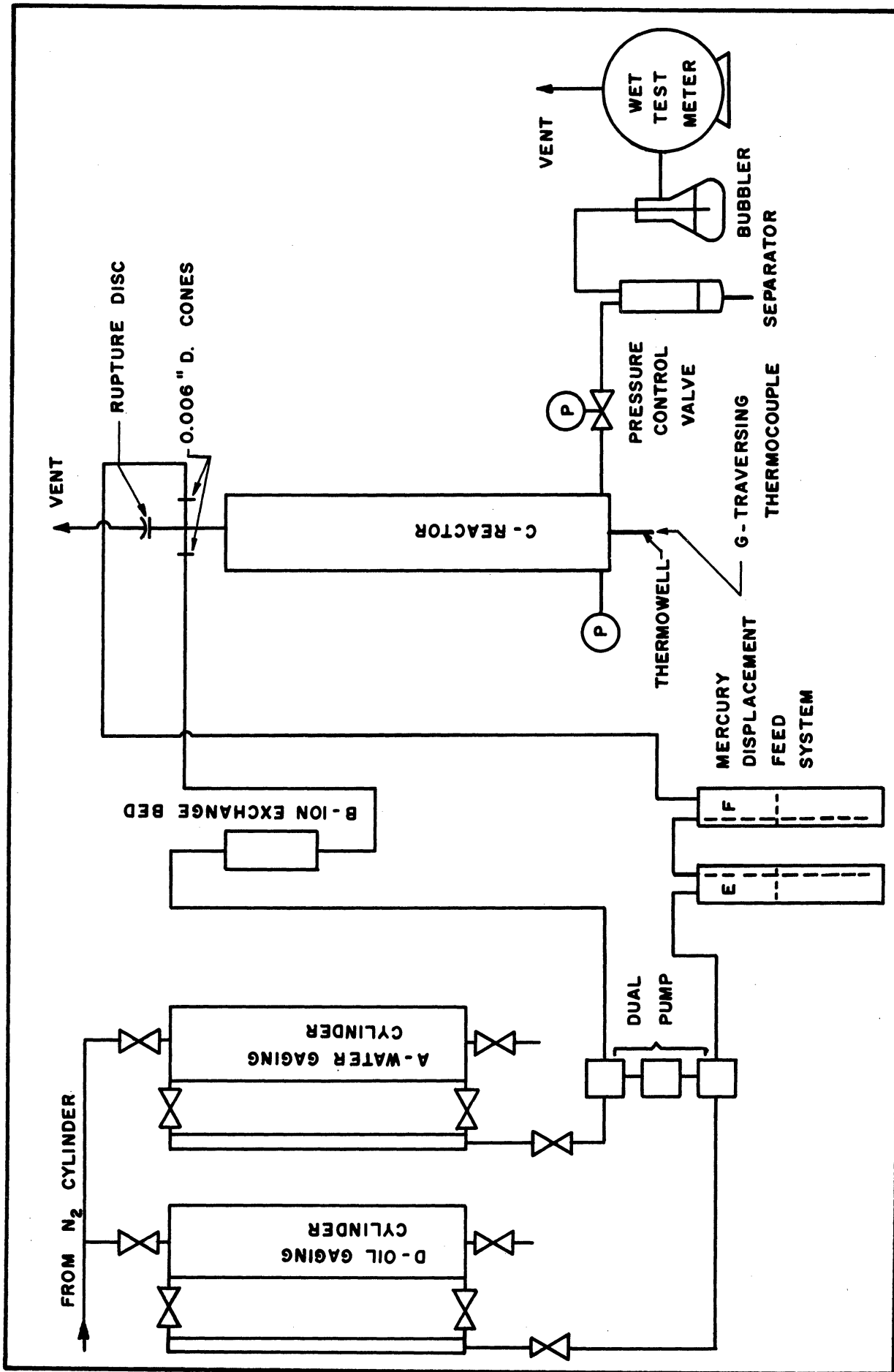
Figure 1. Apparatus

product passed to a separator from which the propylene flowed to a water bubbler and a wet test meter vented to the atmosphere.

Apparatus Description

The gaging cylinders (A) and (D) were constructed of 3" D. x 36" brass pipe with pipe caps threaded and soldered on each end. Each cylinder was equipped with a pair of Penberthy gage valves and a 3/4" O.D. heavy wall pyrex gage glass for the measurement of pump input rates. The pump was a Hills-McCanna type HAJD-3/8", dual unit rated at 10,000 psi maximum pressure with adjustable rates of 0.08 to 0.8 gph. The check valves of this pump operated erratically and were replaced by external twin seal check valves, Autoclave Engineers type 30K-4400. This valve has a spring loaded check which offers a metal to metal taper seal plus a neoprene "O" ring seal. The modified pump operated well at all pressures and flow rates used, i.e., 0.3 to 15cc/min.

The vessel used to contain the resin bed (B) was an Aminco type 406-38A reactor vessel, rated at 15,000 psi, with inside dimensions of 1" D. x 8" L.

The mercury displacement vessels were obtained from equipment storage. Vessel (E) was an Aminco type 21-4750 reaction vessel of manganese steel, rated at 15,000 psi, with an approximate volume of 1750 ml. Vessel (F) was an Aminco type 41-4675 reaction vessel of manganese steel, rated at 15,000 psi, with an approximate volume of 1150 ml. The tube which dipped into the mercury in each of these vessels was 1/4" stainless high pressure tubing threaded to the cap.

The reactor vessel was constructed of 19-9 W-Mo forged product of Universal Cyclops Company. It was approximately 30" long with a 2 1/2" O.D. and 3/4" I.D. The volume of the reactor with the 1/4" O.D. thermowell in place was approximately 150 ml. The reactor was lined with a 30" x 3/4" O.D. x 0.020" wall thickness tantalum liner, and the thermowell jacketed by a 34 1/16" x 1/4" I.D. x 0.010" wall thickness tantalum sleeve. To prevent bypassing of the reactants, the liner was rolled into place with a heat exchanger tube roller and the thermowell jacket was welded around the top. The resin was supported by 2" of pyrex wool in the bottom of the reactor, and approximately 2" of pyrex wool was placed on top of the bed to prevent the resin from being blown back into the inlet lines in the event of an accidental pressure release.

The reactor pressure was controlled with a Grove Model 90W back pressure regulator fitted with a teflon diaphragm, loaded with gas pressure from a nitrogen cylinder. This valve could be used to regulate the pressure from 100 to 2000 psi.

The temperature was controlled by a 300 watt heating wire wound over the reactor length. To obtain a uniform temperature distribution, the reactor was divided into 5 longitudinal heater sections: two end sections, 3 1/2" long, adjoining 7" sections with a 10" center section. On top of the 300 watt wire, each section was wound with a 100 watt heating wire controlled by a separate variable transformer. A thermocouple (between the reactor inlet flanges) actuated the temperature controller which regulated the feed preheater, a 275 watt heating tape wrapped around the reactor inlet tube.

As seen in Figure 2, the reactor was covered by a double layer of glass cloth held in place by Scotch No. 27 High Temperature Electrical Tape. Heater "O", 300 watts, was wound on this at 1/8" spacing along the entire reactor length. This was covered by a layer of No. 27 tape and two more layers of glass cloth over which were wound the five sectional heaters, "X", "T", "M", "B", and "E". These were also covered with tape and glass cloth for insulation. All of the heaters were wound on a lathe to obtain uniform wire spacing and tension. Table III shows the pertinent design data and measured ratings of the completed heaters. Figure 3 shows the heater wiring diagram.

TABLE III

HEATER DESIGN DATA

Heater	Wire Size	Length	Measured Resistance	Actual Rating
"O"	22 ga.	31"	105 ohms	349w @ 240v, 1.45A
"X"	30 ga.	3"	114 ohms	126w @ 120v, 1.05A
"T"	28 ga.	7"	150 ohms	96w @ 120v, 0.80A
"M"	26 ga.	10"	140 ohms	103w @ 120v, 0.86A
"B"	28 ga.	7"	148 ohms	97w @ 120v, 0.81A
"E"	30 ga.	3"	140 ohms	103w @ 120v, 0.81A

NOTE: All heaters were wound from Chromel A wire at 1/8" spacing.

HEATER WIRES

SCOTCH NO.27 TAPE

GLASS CLOTH
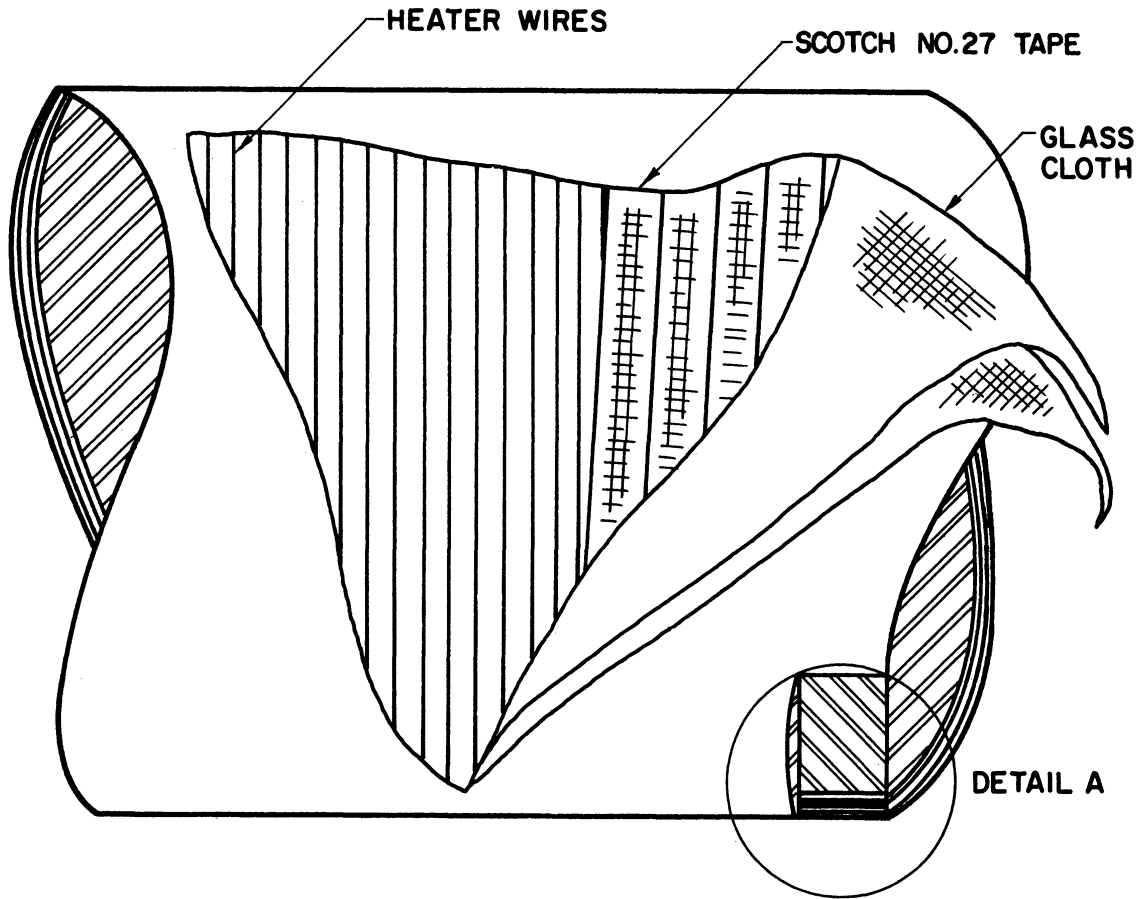
DETAIL A

REACTOR SECTION
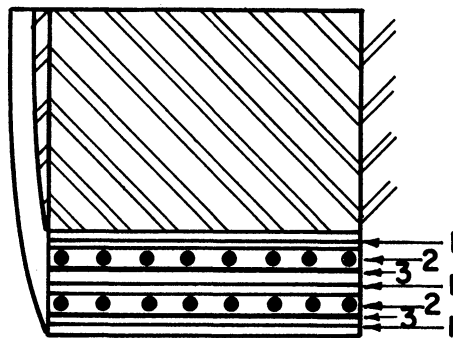
1-GLASS CLOTH (2 LAYERS)
2-HEATER WIRE
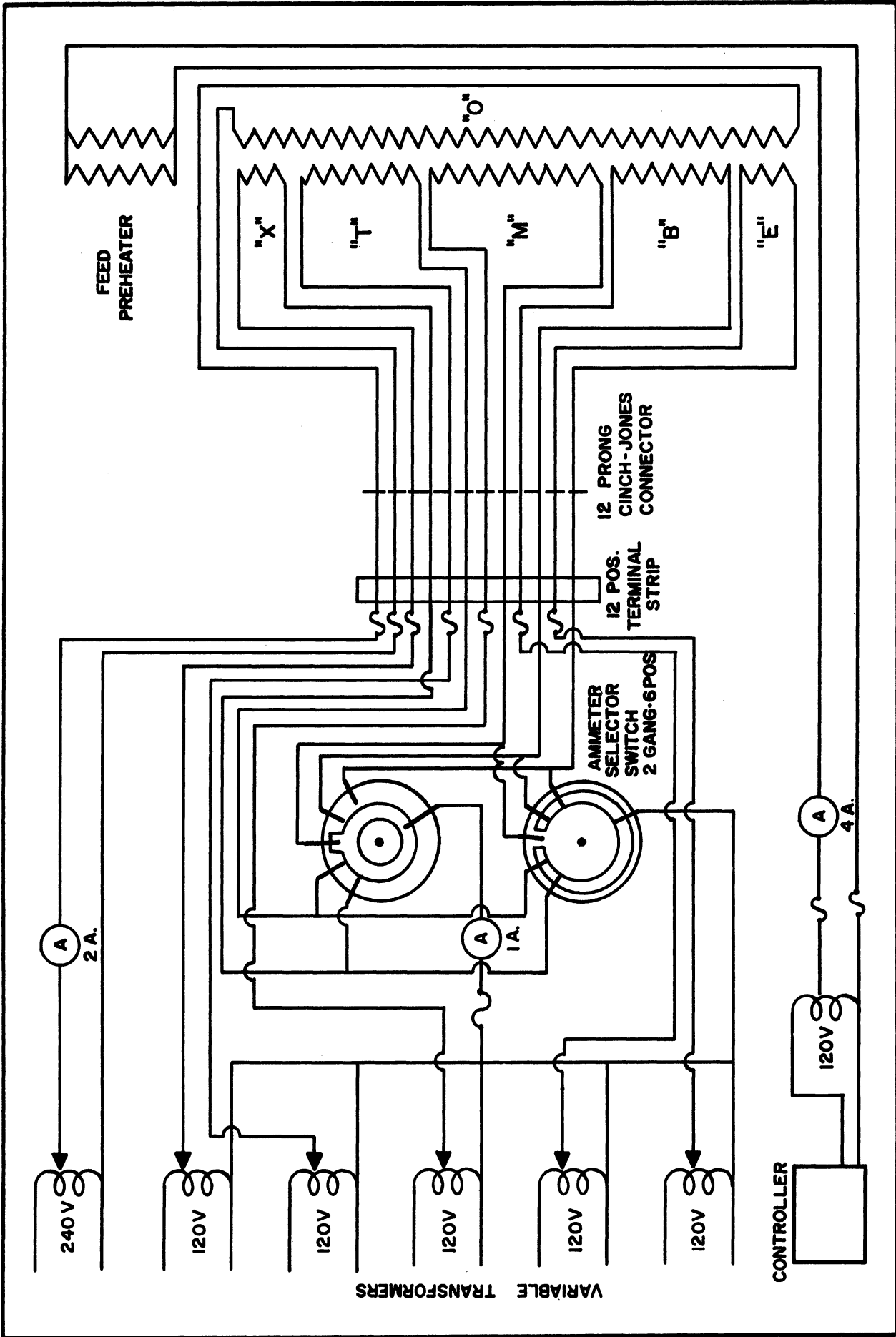3-TAPE

DETAIL A

Figure 2. Heater Details.

Figure 3. Wiring Diagram

MATERIALS

Chemicals

The propylene, supplied by the Phillips Petroleum Company, was Technical Grade Propylene, 95 mole % minimum. Our mass spectrometer yielded the following analysis:

	Mole %
Propylene	96.53
Propane	3.47

The isopropyl alcohol, supplied by the J. T. Baker Chemical Company, was reagent grade containing a maximum water impurity of 0.04%.

The water was taken from the East Engineering Building distilled water supply. This water is single distilled and contains some metal ions introduced in the storage and distribution system.

Cation Exchange Resin

The Dowex 50WX8 resin, supplied by the Dow Chemical Company, is a monosulfonated polystyrene with 8% divinylbenzene cross-linking. One sample was screened from a batch of 50-100 mesh resin and another sample from a batch of 100-200 mesh resin in the following manner:

1. The resin was allowed to stand submerged in distilled water for at least 10 minutes.

2. A small amount of resin was poured on a series of Taylor screens, 32, 42, and 100 mesh.

3. The resin on the 32 mesh screen was washed repeatedly until most of it had passed through.

4. The resin remaining on the 42 mesh screen was washed several more times.

5. The fractions were separated and the process repeated for another small amount of resin.

When approximately 600 ml. of the 32-42 mesh resin had been collected, it was put through the above sequence two more times. The 100-200 mesh resin was screened as above using 100, 150, and 200 mesh screens.

The resin obtained from screening was washed several times with 6N HCl and then with distilled water until the effluent was approximately neutral as determined by pH paper.

The resin was analyzed for capacity and water content by the following technique:

1. 5 ml. completely saturated samples were measured in a 5 ml. graduate.

2. The samples were transferred to Buchner funnels and centrifuged 4 minutes to remove excess water.

3. The samples were weighed and transferred to Erlenmeyer flasks.

4. Approximately 20 ml. of 1 M NaCl solution and 2 drops of phenolphthalein solution were added and the samples were titrated with 1 N NaOH solution.

5. Another small amount of the resin was dried in a vacuum oven for approximately 6 hours at 100°C.

6. Approximately 2 gram samples were weighed out into Erlenmyer flasks.

7. Approximately 20 ml. of 1 M NaCl solution and
2 drops of phenolphthalein solution were added
and the samples were titrated with 1 N NaOH
solution.

From the data obtained by the above, the following calculations were made: 1) meq./ml. (wet), 2) meq./gm. (wet), 3) meq./gm. (dry), and 4) % water.

DATA AND RESULTS

Rate data were obtained for the continuous hydration of propylene to isopropyl alcohol using an acid cation exchange resin, Dowex 50WX8, as catalyst. It is hoped that these results will be useful for extrapolating rates for this and similar reactions.

The range of variables was:

Temperature	$100° - 160°C$
Pressure	450 and 1440 psig
Resin Size	32-42 and 100-150 mesh
Hydrogen-Ion Concentration	0.462 - 1.678 meq./ml.
Feed Composition (liquid)	0 - 60% isopropyl alcohol

The reactor was operated as a) an incremental reactor and b) an integral reactor. In the incremental reactor propylene and mixtures of isopropyl alcohol and water were used as feed with relatively high flow rates and low conversions. In the integral reactor propylene and water were fed and the feed rate was varied. In both, sufficient propylene was fed to maintain a vapor phase as well as the liquid and resin phases over the reactor length.

Two runs were made to obtain resin life. A series of runs was also made at 130°C and 1440 psig to determine the effect of hydrogen-ion concentration in the resin on initial reaction rate.

Incremental Data and Results

Data at varying feed compositions, taken by the incremental method, were obtained for seven conditions. They were plotted as rate

versus composition on a propylene-free basis in Figures 4 - 10 and in

Tables IV - X. A detailed experimental procedure is outlined in

Appendix D and the product analysis procedure is found in Appendix E.

The feed rate was adjusted so that the change in concentration of

isopropyl alcohol was less than 5 wt. %. The incremental rate was

then calculated by the formula, Rate = $F\Delta x/N$. This was assumed to

be the rate at the average of inlet and outlet composition. This rate

was then corrected for isopropyl alcohol lost in the vapor product and

for the deviation from the correlating temperature. Sample calculations

are given in Appendix C.

The plotted data show that a parabolic curve fits the data.

Data were fitted by the least-squares method, and the mean deviation,

σ^*, was calculated. Points falling outside the range of 2.5σ (98%

confidence interval) were discarded and the data were recorrelated.

A summary of the correlations is given in Table XI and Figure 11. An

estimate of the experimental error is given in Appendix F.

The data, taken to determine the effect of temperature,

pressure and resin size on the reaction rates, were divided into

eleven groups in Tables IV - X and Tables XII - XV. A comparison of

Groups III and IV shows the effect of resin size. Both were run under

the same conditions, 130° C and 450 psig, but the resin for Group III

was 32 - 42 mesh and that for Group IV was 100 - 150 mesh. Although

the correlations are not identical, the deviation is less than 2.5σ;

therefore, the effect of resin size on the reaction rate is assumed to

be negligible.

---

* Statistically speaking, σ is the standard deviation of an infinite
sample. The σ used here is s, the mean deviation of a finite sample.

A comparison of Groups IV and V shows the effect of pressure on reaction rate. Both were run with temperature and resin size the same, but pressure was raised from 450 to 1440 psig. The rates increased, presumably due to an increased solubility of propylene in the liquid phase.

Equation (4), the theoretical equation, predicts that one equation could correlate all of the data. The constants, A through G, are made up of the fundamental system constants, i.e., solubility constants, distribution coefficients, equilibrium constant, and molal volume, as shown in the derivation in Appendix B. These system constants are functions of system properties, concentration, temperature, and pressure. The constants, A through C, obtained for the correlations of data were correlated as simple functions of temperature, with the knowledge that they are complex and unknown functions of temperature. Substituting these functions of temperature for the constants in the rate equation, a single rate correlation was obtained at each of the pressures which correlated all of the data with a fair degree of accuracy. The calculations are shown in Appendix H.

$$r = \exp(-21,600/RT)\{(-37.94 + 0.668t - 0.0026t^2) \cdot 10^9$$
$$+ (2.059 - 0.06517t) \cdot 10^{10}x + (1.952 + 0.00937t) \cdot 10^{11}x^2\} \tag{5}$$
$$\text{gm.-moles/eq.-min at 450 psig.}$$

and

$$r = \exp(-21,600/RT)\{(1.68 - 0.005t) \cdot 10^{10} - (4.32 - 0.023t)$$
$$\cdot 10^{11}x + (20.98 - 0.122t) \cdot 10^{11}x^2\} \text{ gm.-moles/eq.-min.} \tag{6}$$
$$\text{at 1440 psig}$$

TABLE IV

INCREMENTAL REACTOR DATA-GROUP I

Conditions: 100°C, 450 psig, 32-42 mesh resin

Run	Feed: Comp. x	Rates in cg.-moles/min. W	A	P	Product: Liq. Comp. x	Rates in cg.-moles/min. Liquid W	A	Gas W	A	P	Material Balance: % Output/Input W	P	Temp. °C t	Corrected Rate: gm-moles/eq-min r
1A	0	5.235	0	1.562	.0039	5.232	.020	.061	.0004	1.834	101.5	118.7	100.6	.7219 x 10^{-3}
1B	0	5.388	0	3.749	.00445	5.194	.023	.120	.0010	3.646	99.1	97.9	101.9	.7814
1C	0	5.198	0	.727	.00470	5.107	.024	.023	.0002	.682	99.2	97.1	103.4	.6870
2	.0166	4.110	.069	1.355	.0186	4.086	.077	.044	.0015	1.354	100.7	101.4	97.6	.4224
3	.0216	4.244	.093	1.454	.0226	4.310	.096	.045	.0019	1.391	100.4	96.0	100.9	.1697
6	.00837	2.170	.018	.566	.0164	2.176	.036	.020	.0006	.610	102.1	111.1	99.6	.6869
9	.0162	2.271	.037	.502	.0235	2.230	.054	.016	.0007	.504	99.7	103.9	100.4	.6261
12	.0333	2.708	.093	.610	.0368	2.700	.103	.022	.0015	.675	100.9	112.5	99.7	.4183
16	0	4.186	0	.370	.00281	4.105	.012	.012	.0001	.374	98.7	104.4	100.4	.4166
17	0	4.776	0	.566	.00317	4.755	.015	.017	.0001	.502	100.2	91.4	100.9	.5161
18	.0421	1.764	.077	.558	.0460	1.768	.085	.018	.0016	.558	101.8	101.7	100.0	.2972
24	.0745	2.325	.187	.571	.0761	2.237	.184	.016	.0024	.522	96.9	91.3	100.7	.2228
27	.0993	2.504	.276	.525	.1003	2.481	.277	.017	.0034	.559	99.9	107.3	100.3	.2273
30	.0985	.800	.087	.110	.1116	.883	.111	.004	.0009	.125	114.0	136.3	98.8	.4893
31	.1224	1.409	.196	.159	.1299	1.394	.208	.004	.0011	.144	100.1	98.8	103.2	.3652

No dectectable amount of ether in product

x   mole fraction of isopropyl alcohol in propylene-free liquid
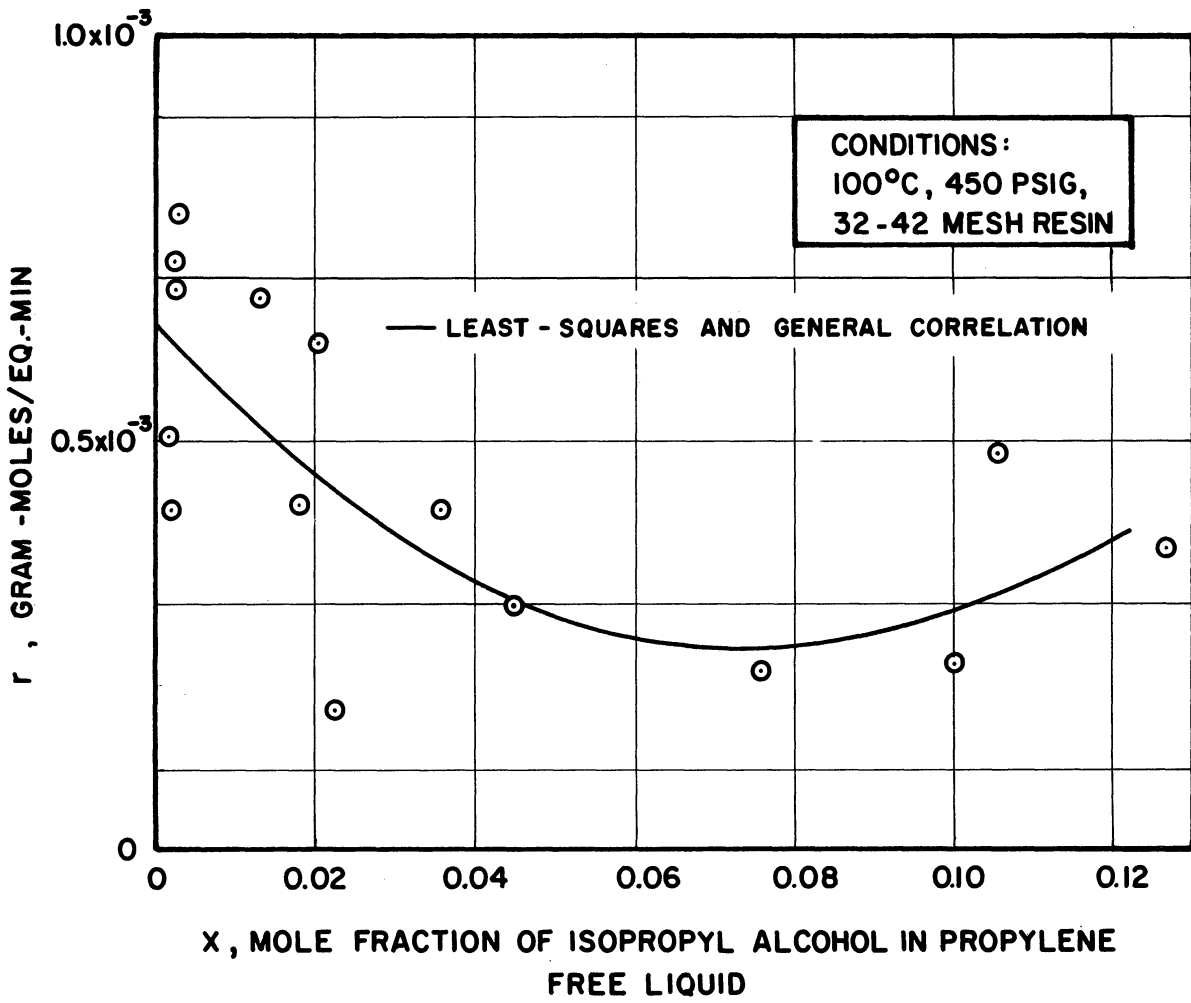
W   Water

A   Alcohol

P   Propylene

Figure 4. Group I Data.

TABLE V

INCREMENTAL REACTOR DATA-GROUP II

Conditions: 120°C, 450 psig, 32-42 mesh resin

Run	Feed: Comp. x	Rates in cg.-moles/min. W	A	P	Product: Liq. Comp. x	Rates in cg.-moles/min. Liquid W	A	W	Gas A	P	Material Balance: % Output/Input W	P	Temp. °C t	Corrected Rate: gm-moles/eq-min r
5	.0372	5.410	.209	.929	.0488	5.398	.277	.025	.0024	.799	101.5	93.6	117.1	3.026×10^{-3}
7	.00837	9.053	.076	.600	.0230	8.880	.290	.015	.0006	.471	100.6	114.3	121.3	4.456
10	.0162	8.717	.143	.541	.0285	8.545	.251	.014	.0008	.445	99.4	102.4	119.9	4.014
13	.0333	7.228	.249	.599	.0442	7.172	.332	.016	.0014	.507	100.6	98.7	121.4	2.732
19	.0421	6.206	.272	.596	.0520	6.146	.337	.017	.0017	.545	100.4	102.6	119.6	2.455
22	.0521	5.573	.306	.597	.0622	5.454	.362	.018	.0021	.562	99.2	103.9	118.2	2.540
25	.0745	4.807	.387	.559	.0872	4.705	.449	.013	.0023	.430	99.5	88.4	120.2	2.451
28	.0993	4.246	.468	.509	.1106	4.233	.526	.011	.0026	.385	101.4	87.5	119.7	2.049
32	.1224	2.095	.292	.149	.1539	---	---	.002	.0006	.067	---	---	118.8	3.011
34	0	16.091	0	.744	.00720	15.355	.111	.022	.0003	.670	96.1	105.0	118.8	4.589
36	0	8.031	0	.520	.0121	8.131	.100	.013	.0003	.383	102.7	92.9	118.4	3.924
39	.00747	7.672	.057	.444	.0199	7.434	.151	.010	.0004	.311	98.3	91.3	119.7	2.291
42	.0217	8.469	.188	.380	.0273	8.192	.230	.009	.0005	.284	97.3	85.9	119.9	1.792
43	.0217	7.135	.158	.620	.0250	6.953	.178	.018	.0008	.541	100.2	90.6	117.2	1.114
46	.0224	7.110	.163	.537	.0360	6.613	.247	.013	.0009	.408	94.4	91.8	120.4	3.480
49	.0326	5.573	.188	.522	.0438	5.433	.249	.014	.0011	.428	98.9	93.9	117.3	2.896
50	.0326	5.867	.198	.517	.0472	5.724	.284	.014	.0012	.430	99.3	102.7	119.4	3.382
53	.0415	3.763	.163	.533	.0633	3.605	.244	---	---	---	98.3	---	118.8	3.363
56	.0515	6.084	.330	.526	.0623	6.051	.402	.014	.0017	.451	100.9	99.8	120.3	2.577
59	.0617	4.973	.327	.508	.0757	4.817	.395	.015	.0022	.473	98.6	106.9	121.1	2.553
62	.0731	5.107	.403	.474	.0872	4.752	.454	.011	.0018	.345	94.3	83.9	120.3	2.708
65	.0840	5.080	.466	.779	.0967	3.730	.399	.018	.0035	.588	72.5	67.3	120.2	1.988
68	.0948	2.957	.310	.641	.1062	2.588	.307	.013	.0028	.438	88.0	68.3	119.4	1.349
71	.1075	2.811	.339	.674	.1135	2.570	.329	.013	.0030	.439	91.6	64.1	119.7	.755
74	.1195	3.261	.443	.709	.1207	3.092	.425	.005	.0014	.185	94.5	23.8	120.1	.193
77	0	7.099	0	.623	.0190	6.731	.130	.006	.0002	.171	96.7	48.3	121.4	4.298
80	.00701	9.461	.067	.882	.0196	8.948	.179	.026	.0009	.786	96.0	101.9	120.5	4.082
83	.0152	6.163	.095	.604	.0314	5.565	.180	.017	.0010	.518	92.0	100.0	119.0	3.683
86	.0231	7.249	.172	.459	.0384	6.695	.267	.009	.0007	.295	93.8	85.1	121.2	3.581
159	.1066	10.030	1.197	1.324	.1095	10.080	1.240	.036	.0080	1.197	101.4	94.3	120.2	1.450
161	.0861	7.142	.673	1.322	.0939	6.950	.720	.037	.0070	1.228	98.6	97.0	120.1	2.392

No detectable amount of ether in product

x mole fraction of isopropyl alcohol in propylene-free liquid
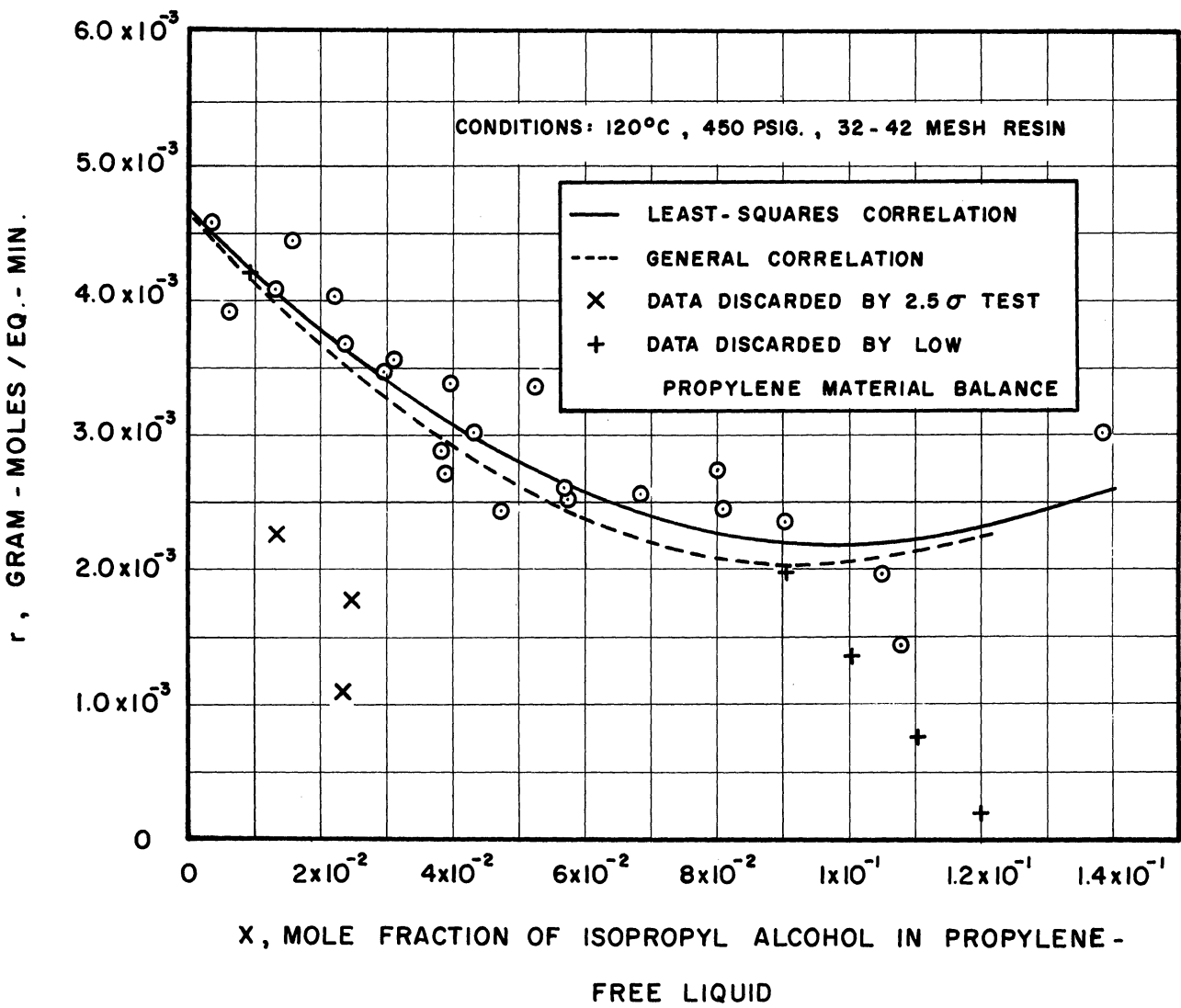
W   Water

A   Alcohol

P   Propylene

Figure 5. Group II Data.

TABLE VI

INCREMENTAL REACTOR DATA - GROUP III

Conditions: 130°C, 450 psig, 32-42 mesh resin

Run	Feed: Comp. x	Feed Rates in cg.-moles/min. W	A	P	Product: Liq. Comp. x	Product Rates in cg.-moles/min. Liquid W	Liquid A	Gas W	Gas A	P	% Output/Input W	P	Temp. °C t	Corrected Rate: gm-moles/eq-min r
35	0	18.202	0	.818	.0130	17.890	.235	.017	.0004	.511	99.7	91.2	128.2	9.734×10^{-3}
37	0	19.112	0	.507	.0125	18.924	.240	.009	.0002	.259	100.3	98.5	129.1	13.140
40	.00747	16.714	.125	.385	.0196	16.422	.328	.007	.0002	.200	99.5	104.7	128.9	8.380
44	.0217	13.862	.307	.552	.0292	14.218	.428	.011	.0006	.349	103.5	85.3	129.4	4.059
47	.0224	16.292	.374	.515	.0336	15.111	.525	.011	.0007	.347	93.7	96.8	129.0	6.888
51	.0326	13.725	.462	.509	.0465	13.269	.647	.009	.0008	.270	98.1	89.5	130.9	6.673
54	.0418	12.381	.540	.490	.0534	12.224	.690	.010	.0011	.331	100.0	98.4	128.7	5.993
57	.0515	---	---	.476	.0617	12.147	.799	.010	.0012	.317	---	---	129.6	5.001
60	.0617	11.001	.723	.597	.0713	10.864	.834	.006	.0019	.443	99.8	93.1	129.3	4.392
63	.0731	8.281	.653	.560	.0850	7.690	.714	.008	.0013	.251	93.7	55.9	130.4	3.615
66	.0840	8.208	.752	.756	.0917	7.664	.774	.017	.0031	.550	93.9	76.1	128.8	2.688
69	.0948	8.678	.909	.648	.1016	8.289	.937	.011	.0023	.376	96.0	62.7	128.6	2.600
72	.1075	8.299	.999	.641	.1107	8.083	1.006	.009	.0020	.296	97.6	47.6	128.8	1.229
75	.1195	7.475	1.015	.481	.1212	7.599	1.048	.002	.0006	.082	102.1	24.0	129.8	.557
78	0	15.581	0	.672	.0169	13.243	.228	.006	.0002	.178	86.5	60.4	129.4	8.621
81	.00701	16.462	.116	.889	.0204	16.072	.335	.023	.0009	.693	99.1	102.7	129.3	8.400
84	.0152	11.449	.176	.599	.0316	11.040	.360	.012	.0007	.365	98.1	91.8	128.6	7.545
87	.0231	12.861	.305	.500	.0372	12.690	.490	.009	.0006	.284	100.2	93.9	129.3	7.085
160	.1066	13.001	1.552	1.310	.1136	12.671	1.624	.032	.0754	1.086	98.8	94.2	129.6	3.986
162	.0856	11.026	1.033	1.312	.0950	10.490	1.101	.036	.0697	1.203	96.7	102.2	129.7	4.265

Scarcely detectable trace of ether in product

x   mole fraction of isopropyl alcohol in propylene-free liquid
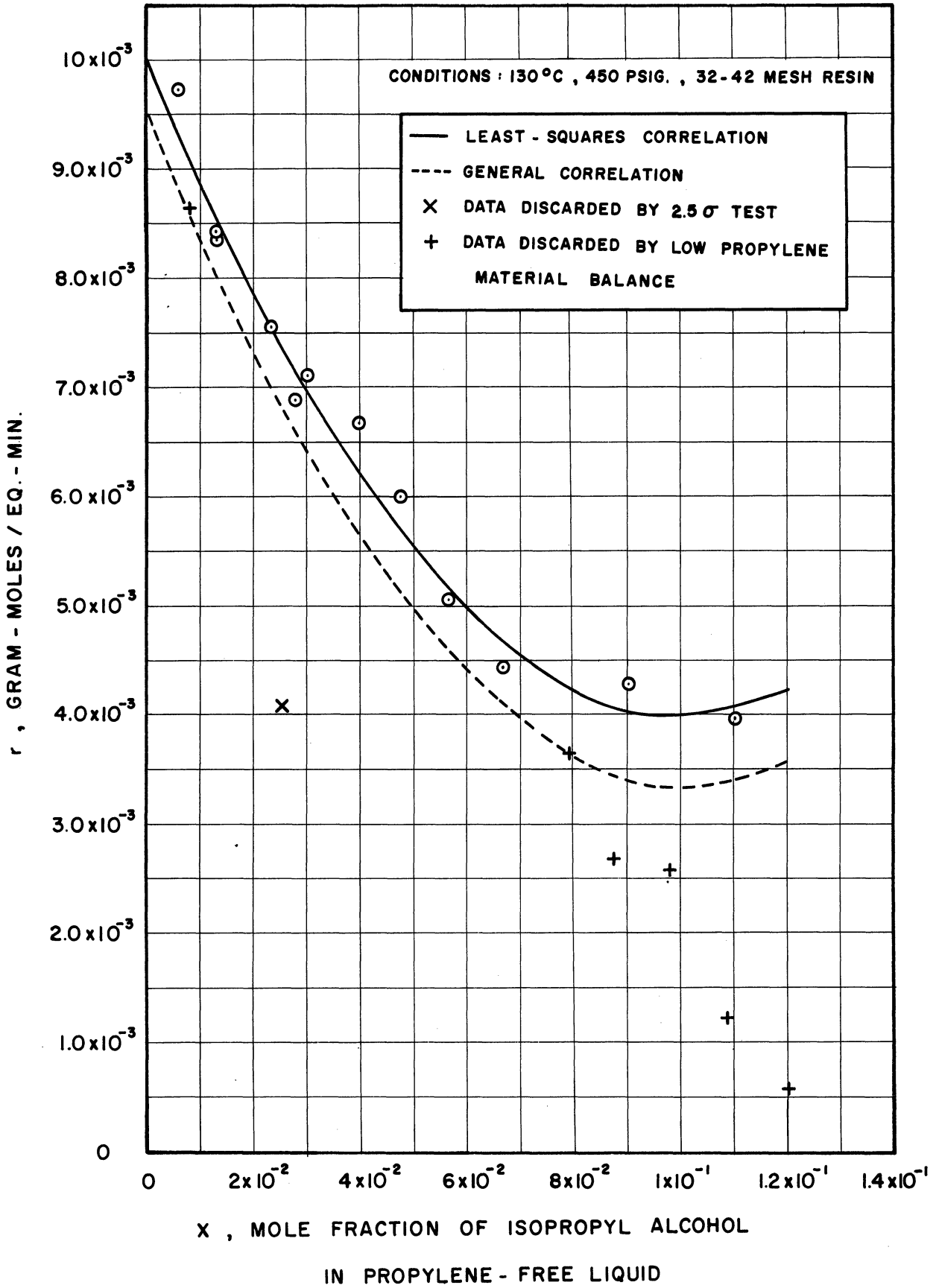W   Water
A   Alcohol
P   Propylene

Figure 6. Group III Data

TABLE VII

INCREMENTAL REACTOR DATA-GROUP IV

Conditions: 130°C, 450 psig, 100-150 mesh resin

Run	Feed: Comp. x	Rates in cg.-moles/min. W	A	P	Product: Liq. Comp. x	Rates in cg.-moles/min. Liquid W	A	Gas W	A	P	% Output/Input W	P	Temp. °C t	Corrected Rate: gm-moles/eq-min r
89	0	19.585	0	.822	.0130	18.990	.250	.019	.0005	.571	98.3	99.9	130.4	9.946 x 10⁻³
92	.00723	12.422	.090	.605	.0244	10.664	.267	.014	.0006	.420	87.4	128.5	130.2	7.591
93	.0145	17.025	.250	.966	.0246	16.986	.428	.030	.0014	.914	101.0	113.2	130.2	7.108
96	.0224	14.591	.335	1.299	.0341	14.399	.508	.036	.0024	1.132	100.1	100.6	130.5	6.960
97	.0319	13.902	.458	1.335	.0421	13.365	.587	.040	.0032	1.260	97.4	104.3	130.0	5.914
100	.0415	13.868	.600	1.407	.0493	13.384	.694	.041	.0039	1.311	97.5	100.1	129.9	4.699
101	.0510	13.284	.713	1.500	.0575	13.307	.812	.043	.0049	1.384	101.2	99.2	129.6	4.059
104	.0611	11.029	.718	.895	.0688	10.794	.797	.025	.0035	.832	98.8	102.2	130.5	3.654
109	.0730	13.857	1.092	.643	.0797	13.736	1.190	.019	.0030	.608	100.0	110.3	129.6	4.327
112	.0847	14.873	1.370	1.187	.0879	14.703	1.417	.035	.0061	1.145	99.4	100.9	130.0	2.446
113	.0971	14.137	1.465	1.027	.1021	13.512	1.536	.027	.0057	.910	96.3	96.1	129.9	3.331
116	.1107	4.977	.619	.988	.1218	4.849	.673	.025	.0064	.854	99.1	92.6	129.1	2.878

Scarcely detectable trace of ether in product

x   mole fraction of isopropyl alcohol in propylene-free liquid
W   Water
A   Alcohol
P   Propylene
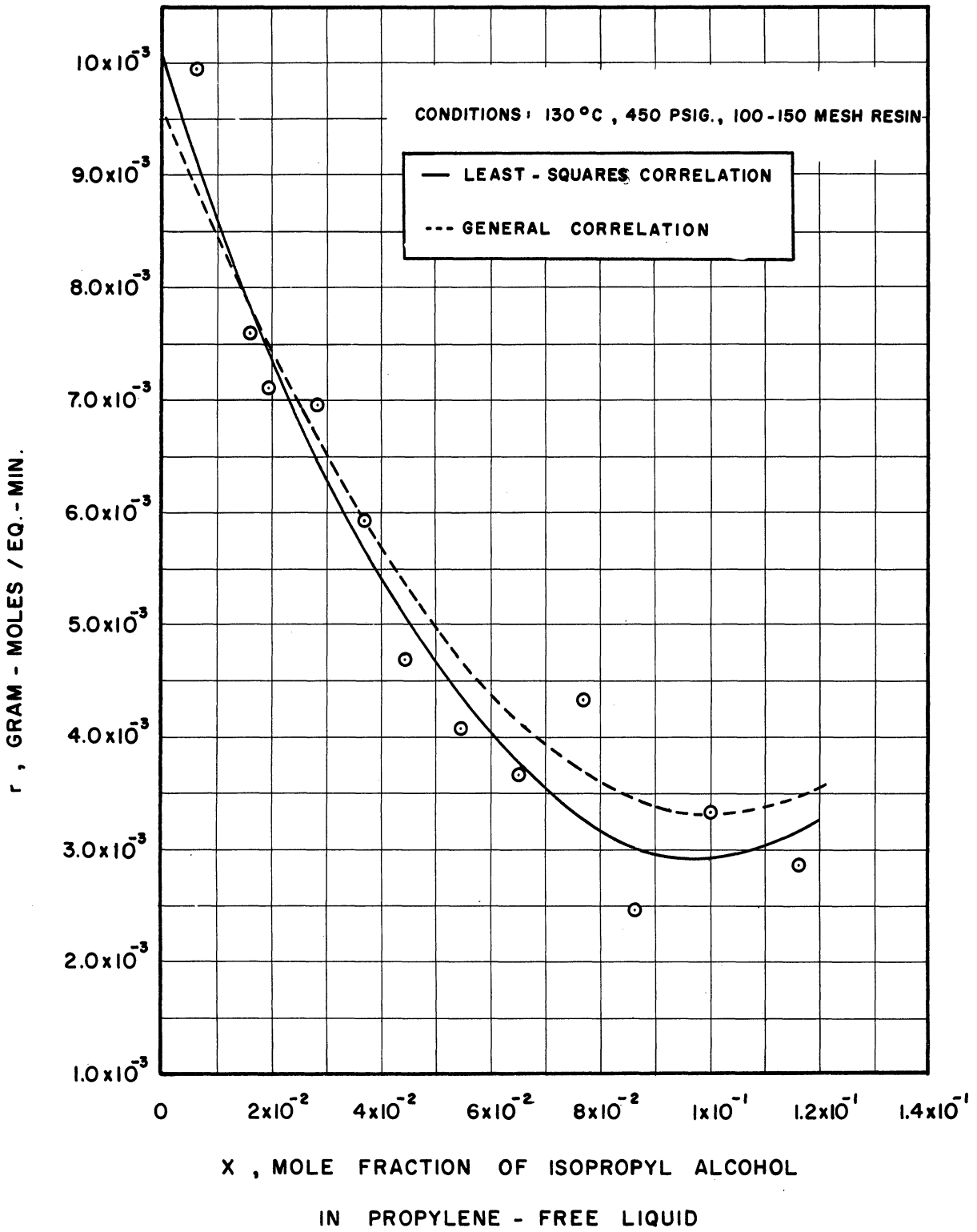
Figure 7. Group IV Data

TABLE VIII

INCREMENTAL REACTOR DATA - GROUP V

Conditions: 130°C, 1440 psig, 100-150 mesh resin

Run	Feed: Comp. x	Rates in cg.-moles/min.			Product: Liq. Comp. x	Rates in Liquid		Gas		P	Material Balance % Output/Input		Temp. °C t	Corrected Rate gm-moles/eq-min r
		W	A	P		W	A	W	A		W	P		
90	0	14.474	0	1.696	.0309	14.677	.468	.040	.0023	1.244	104.9	101.1	130.8	18.205 x 10^{-3}
91	.00723	27.954	.203	1.595	.0206	27.568	.580	.041	.0016	1.249	100.1	102.0	128.9	16.593
94	.0145	14.278	.210	.806	.0397	13.959	.577	.028	.0021	.878	100.5	154.7	129.7	15.346
95	.0224	12.864	.295	.890	.0466	12.378	.605	.020	.0018	.630	98.8	105.8	129.4	13.397
98	.0319	11.425	.376	1.050	.0591	11.021	.692	.022	.0025	.692	99.4	96.2	131.1	12.193
99	.0415	12.498	.541	.996	.0603	12.293	.789	.024	.0029	.779	100.6	103.4	128.0	11.615
102	.0510	9.746	.523	1.156	.0752	9.435	.767	.028	.0042	.921	99.6	101.1	129.8	10.357
103	.0611	8.685	.565	1.054	.0861	8.450	.796	.025	.0044	.831	100.3	101.2	129.6	9.859
110	.0730	16.975	1.338	.899	.0883	16.267	1.576	.020	.0035	.648	97.4	98.9	131.0	10.568
111	.0844	15.036	1.385	.991	.0967	14.846	1.589	.024	.0046	.784	100.3	100.2	129.8	8.600
114	.0976	10.831	1.167	.752	.1116	10.775	1.353	.016	.0037	.537	101.4	96.6	129.3	7.445
115	.1107	11.171	1.390	.844	.1277	11.001	1.610	.017	.0046	.585	100.6	95.9	129.9	8.954

Scarcely detectable trace of ether in product.

x mole fraction of isopropyl alcohol in propylene-free liquid
W Water
A Alcohol
P Propylene
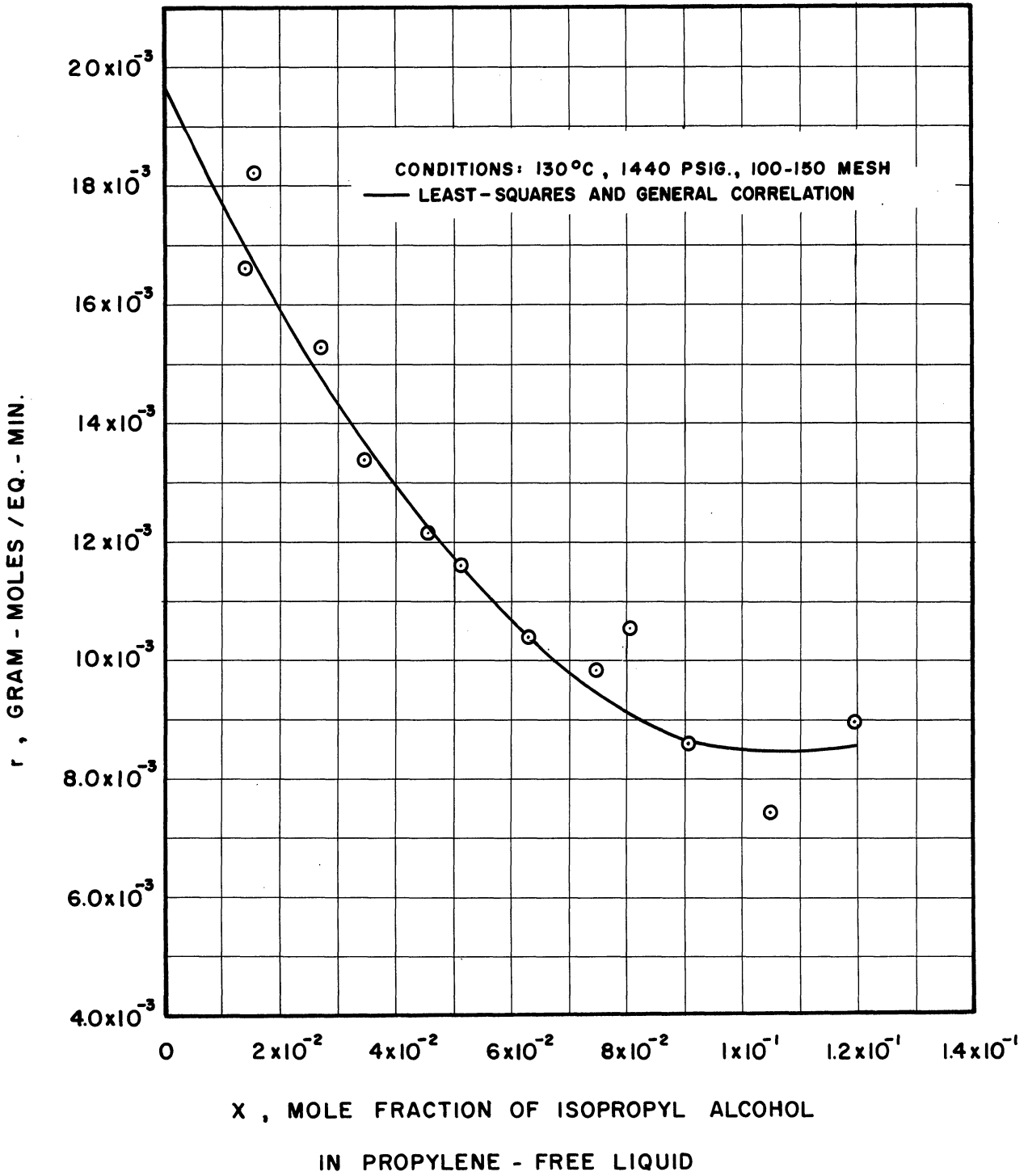
Figure 8. Group V Data.

TABLE IX

INCREMENTAL REACTOR DATA - GROUP VI

Conditions: 140°C, 450 psig, 32-42 mesh resin

Run	Feed: Comp. x	Rates in cg.-moles/min. W	A	P	Product: Liq. Comp. x	Rates in cg.-moles/min Liquid W	A	Gas W	A	P	Material Balance % Output/Input W	P	Temp °C t	Corrected Rate gm-moles/eq-min r	Approx. wt. % ether
8	.00837	33.105	.279	.641	.0206	33.185	.698	.004	.0002	.122	101.5	84.4	138.6	16.197 x10^{-3}	.12
11	.0162	31.165	.513	.606	.0265	31.523	.858	.008	.0004	.232	102.3	95.3	141.9	10.550	.24
14	.0333	27.275	.940	.606	.0406	26.769	1.133	.010	.0008	.327	98.9	85.9	138.8	8.111	.42
15	0	29.706	0	.595	.0143	28.583	.415	.007	.0002	.203	97.6	103.9	141.4	14.134	.24
20	.0421	23.709	1.039	.534	.0502	24.399	1.290	.009	.0009	.289	104.0	101.3	138.7	7.999	.42
23	.0521	22.819	1.253	.548	.0592	22.972	1.446	.011	.0012	.341	101.6	97.7	139.4	6.541	.63
26	.0745	---	---	.570	.0811	17.400	1.536	.010	.0016	.324	---	---	140.0	4.707	1.06
29	.0993	13.661	1.507	.523	.1056	13.714	1.619	.009	.0018	.285	101.3	76.2	138.1	3.974	2.12
33	.1218	---	---	.373	.1329	8.625	1.322	.006	.0018	.223	---	---	139.0	4.388	3.4
38	0	31.235	0	.642	.0114	31.768	.366	.005	.0001	.147	102.9	79.9	137.4	28.501	---
41	.00747	34.842	.260	.412	.0166	35.546	.600	.003	.0001	.104	103.0	107.8	138.5	12.889	.06
45	.0217	27.261	.604	.573	.0265	26.766	.729	.009	.0005	.291	98.7	72.7	137.9	5.606	.13
48	.0224	32.782	.752	.533	.0312	32.800	1.056	.007	.0004	.218	101.0	98.0	138.9	11.465	.14
52	.0326	28.277	.953	.503	.0425	27.958	1.241	.006	.0005	.183	99.9	88.4	139.6	10.864	.21
55	.0418	---	---	.490	.0486	28.621	1.462	.008	.0007	.240	---	---	139.3	7.894	.38
58	.0515	27.665	1.051	1.051	.0578	27.295	1.674	.025	.0029	.812	99.4	94.0	140.1	6.817	.41
61	.0617	25.475	1.675	.752	.0673	24.364	1.758	.019	.0025	.605	96.0	91.8	139.6	5.650	.47
64	.0731	22.207	1.750	.733	.0772	21.526	1.801	.008	.0013	.267	97.2	43.6	140.8	3.413	.89
67	.0840	17.892	1.640	.752	.0893	17.175	1.684	.014	.0024	.447	96.5	65.6	139.6	3.875	1.00
70	.0948	15.166	1.589	.765	.1003	14.733	1.643	.012	.0025	.414	97.6	61.5	140.4	3.261	0.98
73	.1075	14.467	1.742	.709	.1111	14.096	1.762	.010	.0023	.337	97.7	50.7	138.2	2.447	2.0
76	.1195	9.169	1.245	.579	.1259	8.712	1.255	.007	.0018	.234	95.2	42.5	140.6	2.300	3.5
79	0	---	0	.753	.0135	31.703	.434	.006	.0001	.180	---	---	140.9	14.947	.12
82	.00701	33.914	.239	.876	.0201	33.601	.689	.015	.0006	.458	100.4	103.7	139.8	16.558	.06
85	.0152	25.367	.390	.705	.0302	24.188	.753	.006	.0003	.186	96.8	77.9	139.8	13.827	.12
88	.0231	22.927	.543	.553	.0372	22.051	.852	.006	.0004	.186	97.6	89.6	140.1	11.639	.21

x   mole fraction of isopropyl alcohol in propylene-free liquid
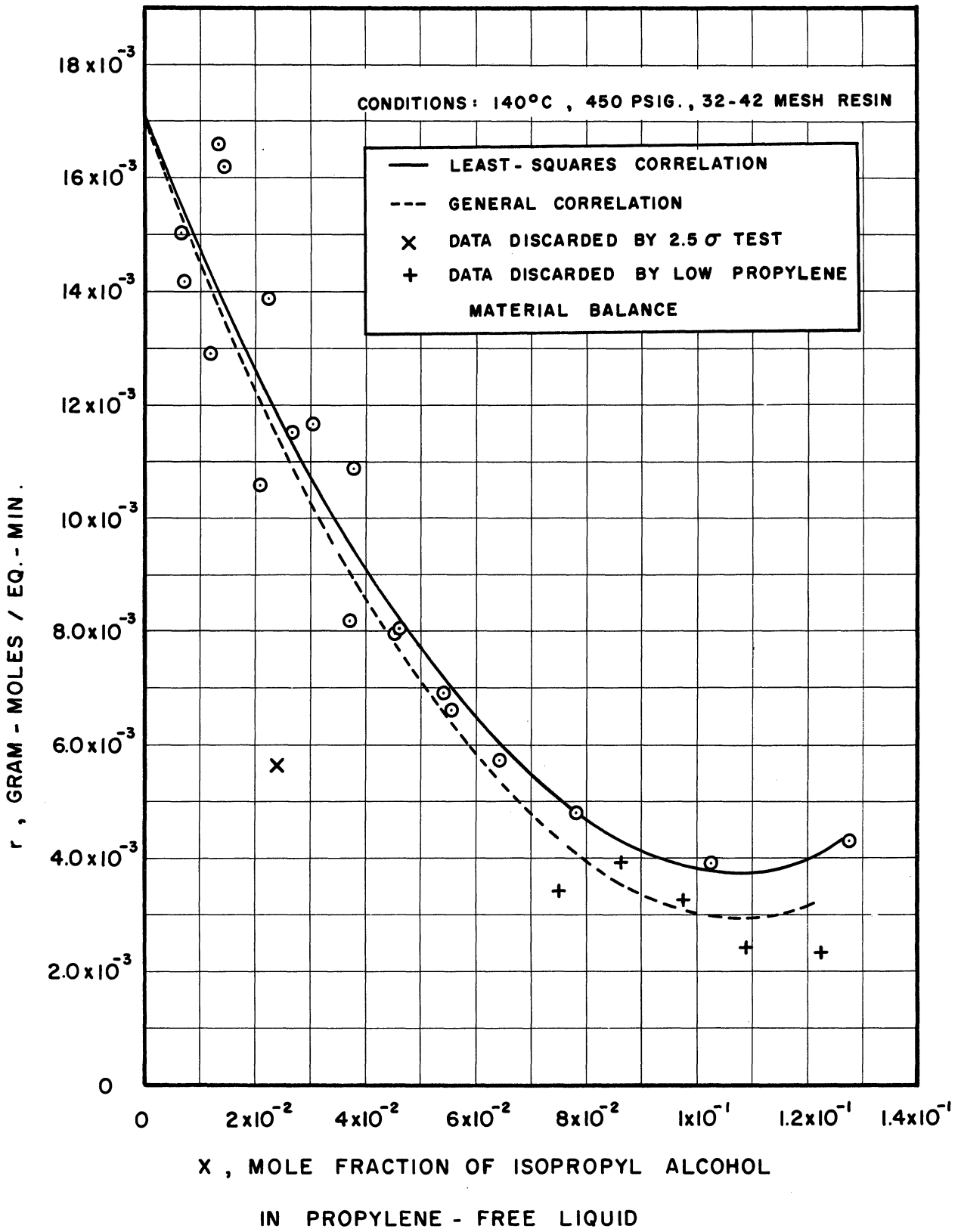W   Water
A   Alcohol
P   Propylene

Figure 9. Group VI Data.

TABLE X

INCREMENTAL REACTOR DATA - GROUP VII

Conditions: 140°C, 1440 psig, 32-42 mesh resin

Run	Feed Comp. x	Rates in cg.-moles/min W	A	P	Product Liq. Comp. x	Liquid W	A	Gas W	A	P	Material Balance % Output/Input W	P	Temp. °C t	Corrected Rate gm-moles eq-min r	Approx. Wt. % ether
140	0	66.983	0	1.836	.0133	66.214	.893	.031	.0008	.945	100.2	100.2	138.9	36.438 x 10⁻³	--
141	.0237	50.411	1.222	2.325	.0366	48.944	1.859	.051	.0036	1.603	98.5	96.5	139.3	25.160	.07
142	.0535	37.547	2.101	2.203	.0693	36.620	2.727	.046	.0063	1.484	99.3	96.1	140.6	23.102	.56
143	.0883	22.116	2.141	2.294	.1098	21.429	2.643	.049	.0111	1.655	99.4	94.5	139.9	20.289	1.48
144	.1252	14.311	2.049	2.478	.1587	13.415	2.531	.049	.0171	1.760	97.6	91.2	140.7	20.030	5.0
145	.1695	11.295	2.305	2.319	.2081	10.665	2.803	.043	.0209	1.642	99.4	93.2	140.6	19.776	6.0
146	.2272	8.835	2.597	2.345	.2771	8.088	3.100	.044	.0311	1.830	98.1	100.8	140.0	22.417	7.0
147	.3076	7.508	3.335	2.261	.3507	7.023	3.793	.037	.0368	1.707	100.6	97.4	141.4	17.513	12.0

x   mole fraction of isopropyl alcohol in propylene-free liquid
W   Water
A   Alcohol
P   Propylene
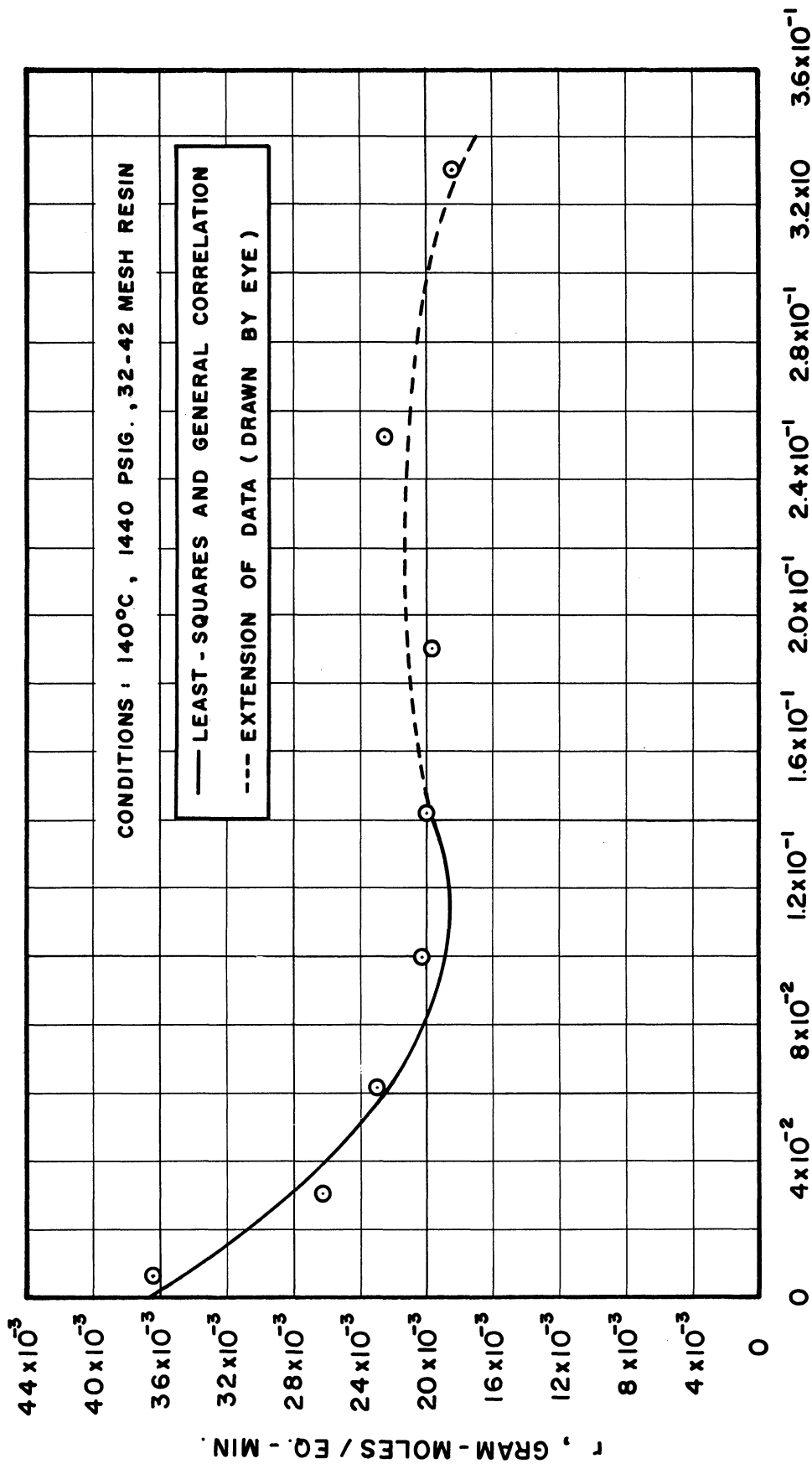
X , MOLE FRACTION OF ISOPROPYL ALCOHOL IN PROPYLENE -

FREE LIQUID

Figure 10. Group VII Data.

TABLE XI

SUMMARY OF CORRELATIONS

Group I $\quad r \cdot 10^3 = 0.6348 - 10.11x + 66.59x^2,$ $\quad 100°C,$ 450 psig

Group II $\quad r \cdot 10^3 = 4.668 - 49.65x + 249.2x^2,$ $\quad 120°C,$ 450 psig

Group III $\quad r \cdot 10^3 = 10.10 - 121.5x + 603.1x^2,$ $\quad 130°C,$ 450 psig

Group IV $\quad r \cdot 10^3 = 10.12 - 146.7x + 745.4x^2,$ $\quad 130°C,$ 450 psig

Group V $\quad r \cdot 10^3 = 19.89 - 213.6x + 992.3x^2,$ $\quad 130°C,$ 1440 psig

Group VI $\quad r \cdot 10^3 = 17.23 - 248.4x + 1147x^2,$ $\quad 140°C,$ 450 psig

Group VII $\quad r \cdot 10^3 = 36.72 - 324.9x + 1454x^2,$ $\quad 140°C,$ 1440 psig

General Correlations:

$t = 100° - 140°C,$ $P = 450$ psig

$r = \exp(-21,600/RT)\{(-37.94 + 0.668t - 0.0026t^2) \cdot 10^9$

$+ (2.059 - 0.06517t) \cdot 10^{10}x + (1.952 + 0.00937t)$

$\cdot 10^{11}x^2\}$ gm-moles/eq.-min.

$t = 130° - 140°C,$ $P = 1440$ psig

$r = \exp(-21,600/RT)\{(1.68 - 0.005t) \cdot 10^{10} - (4.32 - 0.023t)$

$\cdot 10^{11}x + (20.98 - 0.122t) \cdot 10^{11}x^2\}$ gm-moles/eq.min.

$R = 1.987$ cal/gm-mole°K, $T = °K,$ $t = °C.$
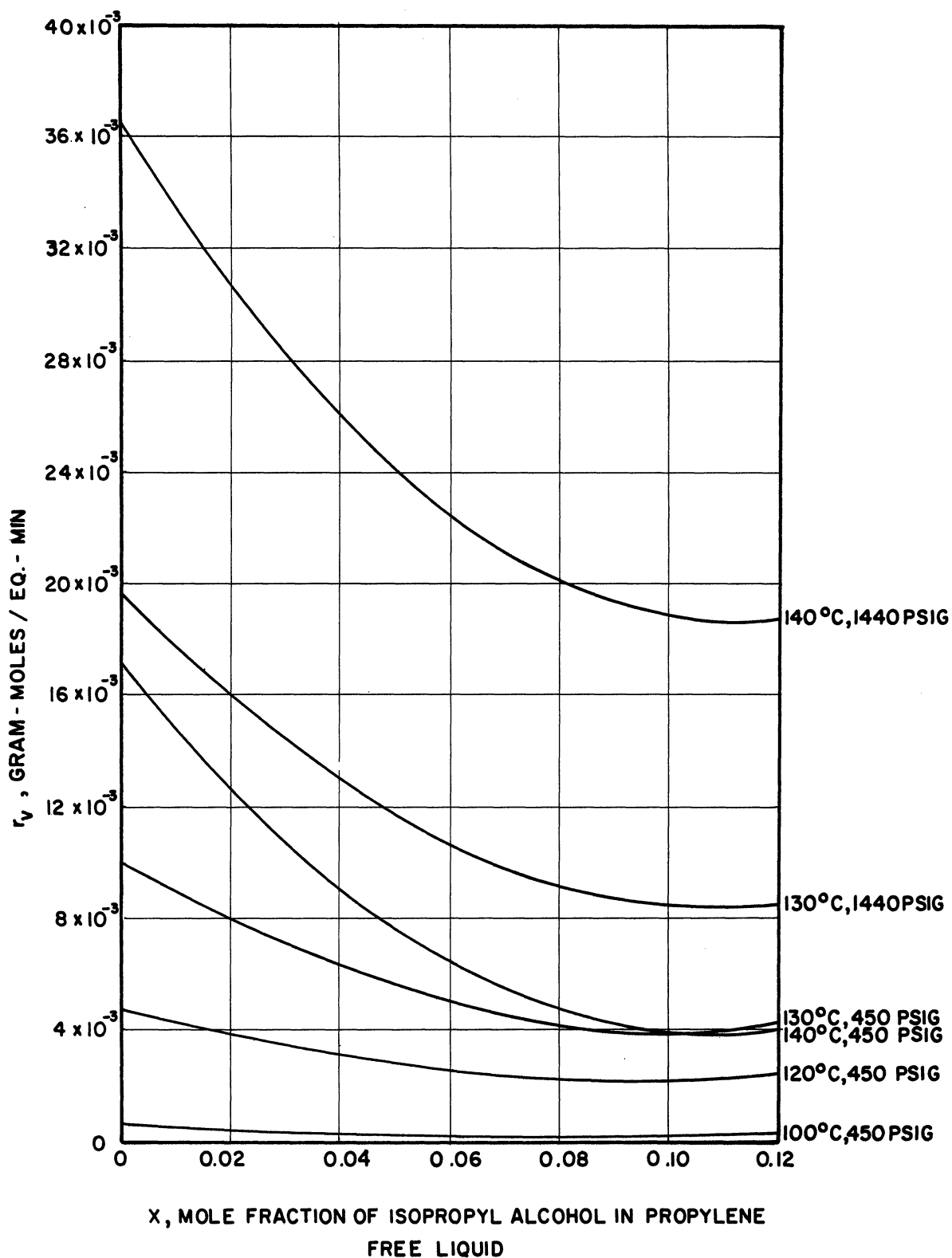
Figure 11. Summary of Correlations.

where R = 1.987 cal/gm.-mole-°K, T = °K, t = °C, and x = 0 to x = 0.12, the liquid-phase mole fraction of isopropyl alcohol on the propylene-free basis. These correlations are shown as dotted curves in Figures 4-10. On figures which show only one curve, the general correlation is identical with the individual correlation.

Integral Data and Results

Data from integral reactor operation are plotted in Figures 12-15. The differentiated data are given in Tables XII-XV and the calculations in Appendix C. These yield initial rates at higher temperatures as shown in Figure 16, log initial reaction rate versus 1/T. The initial rates at 150°C and 160°C deviate from the expected straight line. This could be due to the resin diffusion becoming a controlling factor or to a combination of a number of factors such as the changing of distribution coefficients in addition to the increased diffusional resistance. Further investigation in this region was not undertaken because of the increased rate of ether formation above 140°C.

The apparent reaction activation energy was found to be 21,600 cal/gm-mole from Figure 16. The initial rates are given by:

$$r_i = 4.87 \times 10^9 \exp(-21,600/RT) \text{ gm-moles/eq.-min. at } 450 \text{ psig, } 100\text{-}140°C$$

$$\cdots \cdots (7)$$

$$r_i = 10.05 \times 10^9 \exp(-21,600/RT) \text{ gm-moles/eq.-min. at } 1440 \text{ psig,}$$

$$130\text{-}140°C \qquad (8)$$

where T = °K, R = 1.987 cal/gm-mole-°K

Chemical analysis of the reaction products shows that increased temperature, pressure, and alcohol concentration favor the formation of di-isopropyl ether. Data were not taken above 160°C where the competing reaction of ether formation becomes important.

TABLE XII

INTEGRAL REACTOR DATA - GROUP VIII

Conditions: 140°C, 1440 psig, 100-150 mesh resin

Runs: 117-121

x	N/F	Δx	$\Delta N/F$	$\dfrac{\Delta x}{\Delta N/F}$ x10^3	r x 10^3 $\dfrac{\text{gm-mol.}}{\text{eq.-min.}}$
0	0				40.6
		.0241	.6654	36.17	
.0241	.6654				29.5
		.0156	.5902	26.45	
.0397	1.2556				24.9
		.0517	2.332	22.15	
.0913	3.5876				21.7
		.0554	2.593	21.37	
.1468	6.1806				21.6
		.1518	6.893	22.02	
.2986	13.074				

TABLE XIII

INTEGRAL REACTOR DATA - GROUP IX

Conditions: 150°C, 1440 psig, 100-150 mesh resin

Runs: 122-126

x	N/F	Δx	$\Delta N/F$	$\dfrac{\Delta x}{\Delta N/F}$ x10^3	r x 10^3 $\dfrac{\text{gm-mol.}}{\text{eq.-min.}}$
0	0				41.5
		.0129	.3127	41.09	
.0129	.3127				40.8
		.0045	.2797	16.09	
.0174	.5924				40.2
		.0355	.8904	39.92	
.0529	1.4828				39.2
		.0440	1.1215	39.24	
.0969	2.6043				40.3
		.0941	2.0727	45.42	
.1910	4.6313				

TABLE XIV

INTEGRAL REACTOR DATA - GROUP X

Conditions: 160°C, 1440 psig, 100-150 mesh resin

Runs: 127-130

x	N/F	Δx	$\Delta N/F$	$\dfrac{\Delta x}{\Delta N/F}$ x10^3	r x 10^3 $\dfrac{\text{gm-mol}}{\text{eq.-min.}}$
0	0				78.8
		.0282	.4621	60.92	
.0282	.4621				37.6
		.0057	.2913	19.46	
.0338	.7534				25.0
		.0159	.7844	20.28	
.0497	1.5378				20.6
		.0417	1.1878	35.07	
.0914	2.7256				

TABLE XV

INTEGRAL REACTOR DATA - GROUP XI

Conditions: 140°C, 1440 psig, 32-42 mesh resin

Runs: 131, 133-135

x	N/F	Δx	$\Delta N/F$	$\dfrac{\Delta x}{-\Delta N/F}$ x10^3	r x 10^3 $\dfrac{\text{gm-mol.}}{\text{eq.-min.}}$
0	0				35.9
		.0305	.9046	33.73	
.0305	.9046				30.7
		.0457	1.6618	27.41	
.0762	2.5664				22.4
		.0332	1.2187	27.21	
.1093	3.7851				18.0
		.0409	3.2889	12.42	
.1502	7.0740				

Figure 12. Group VIII Data
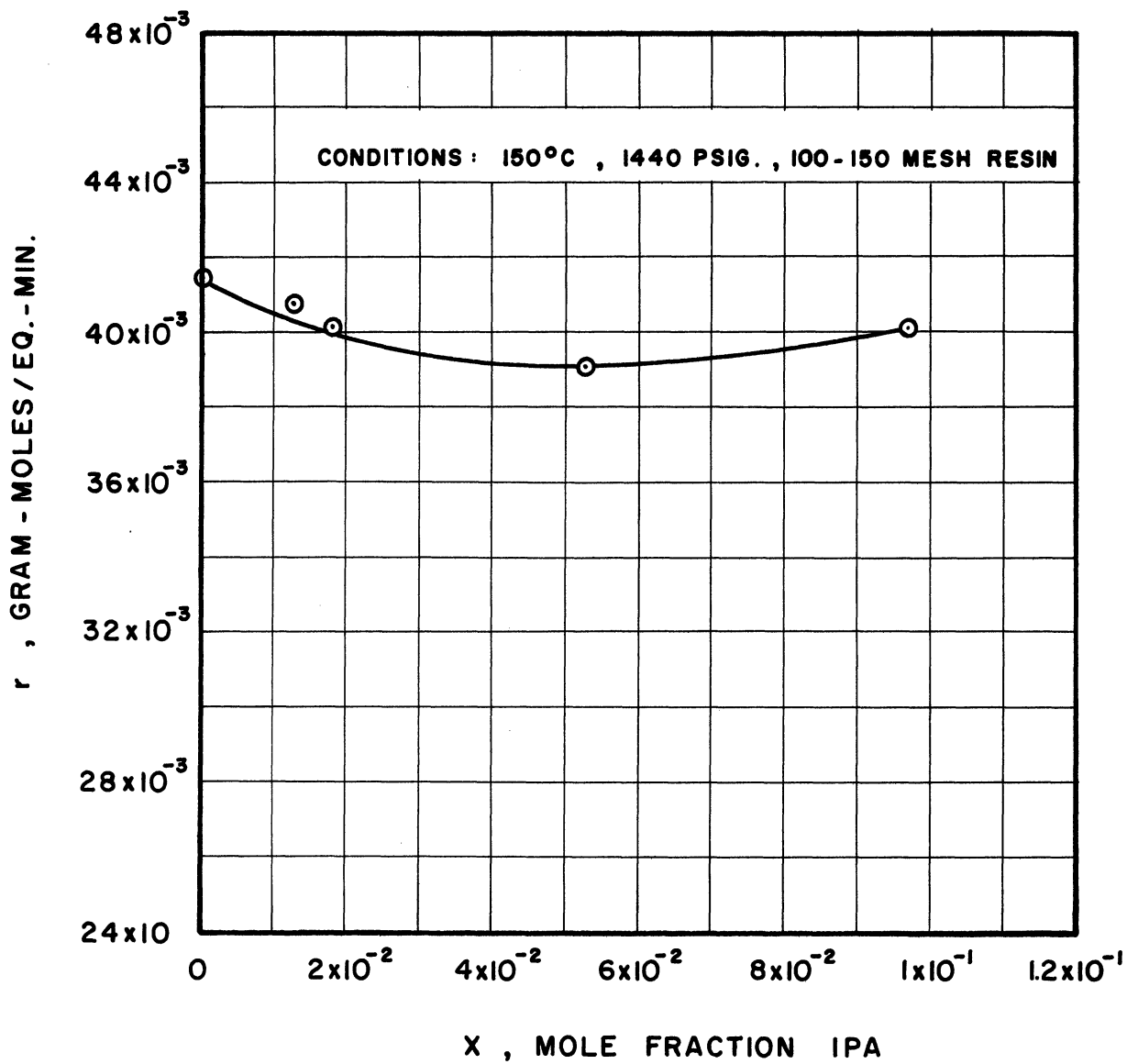
Figure 13. Group IX Data.
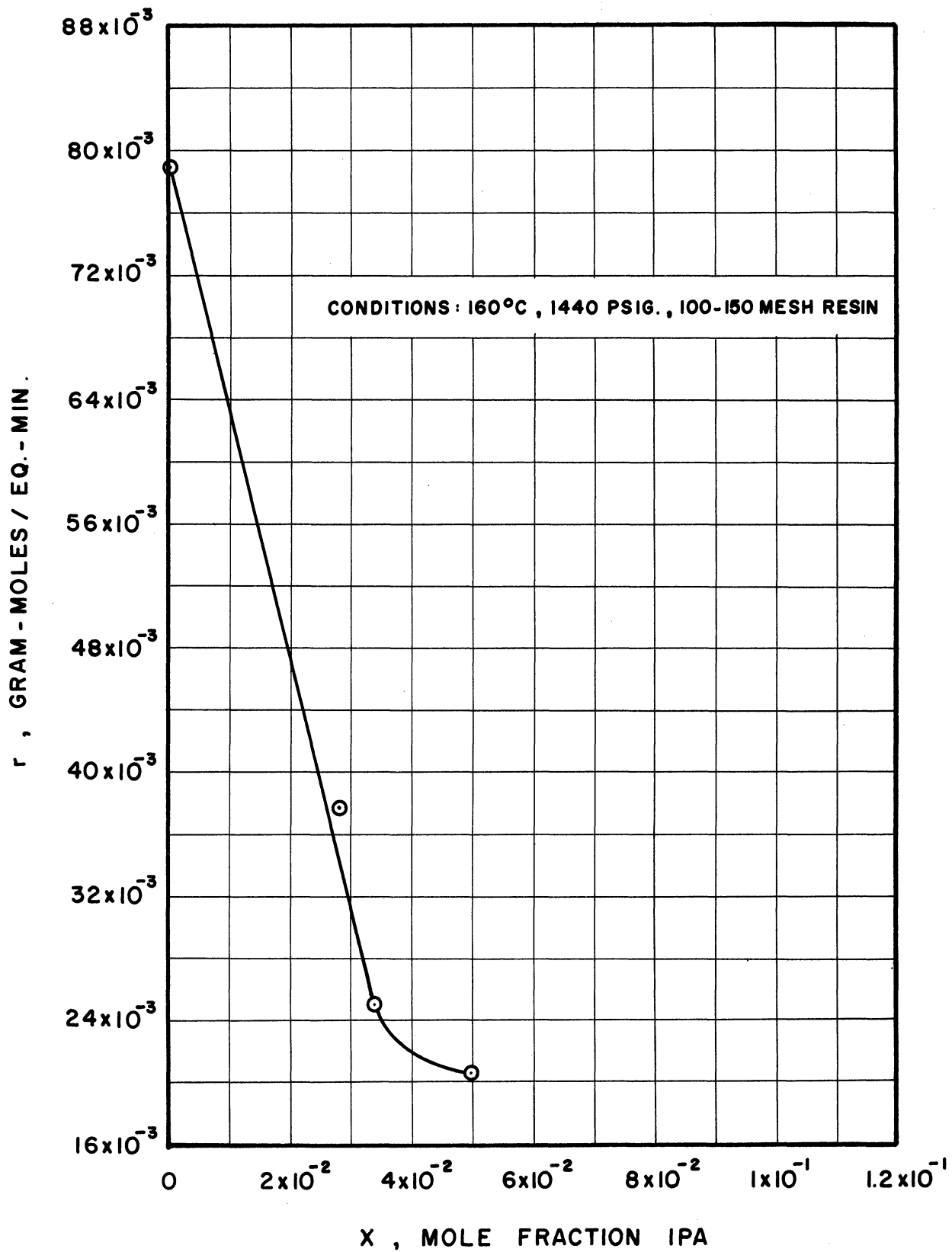
Figure 14. Group X Data.
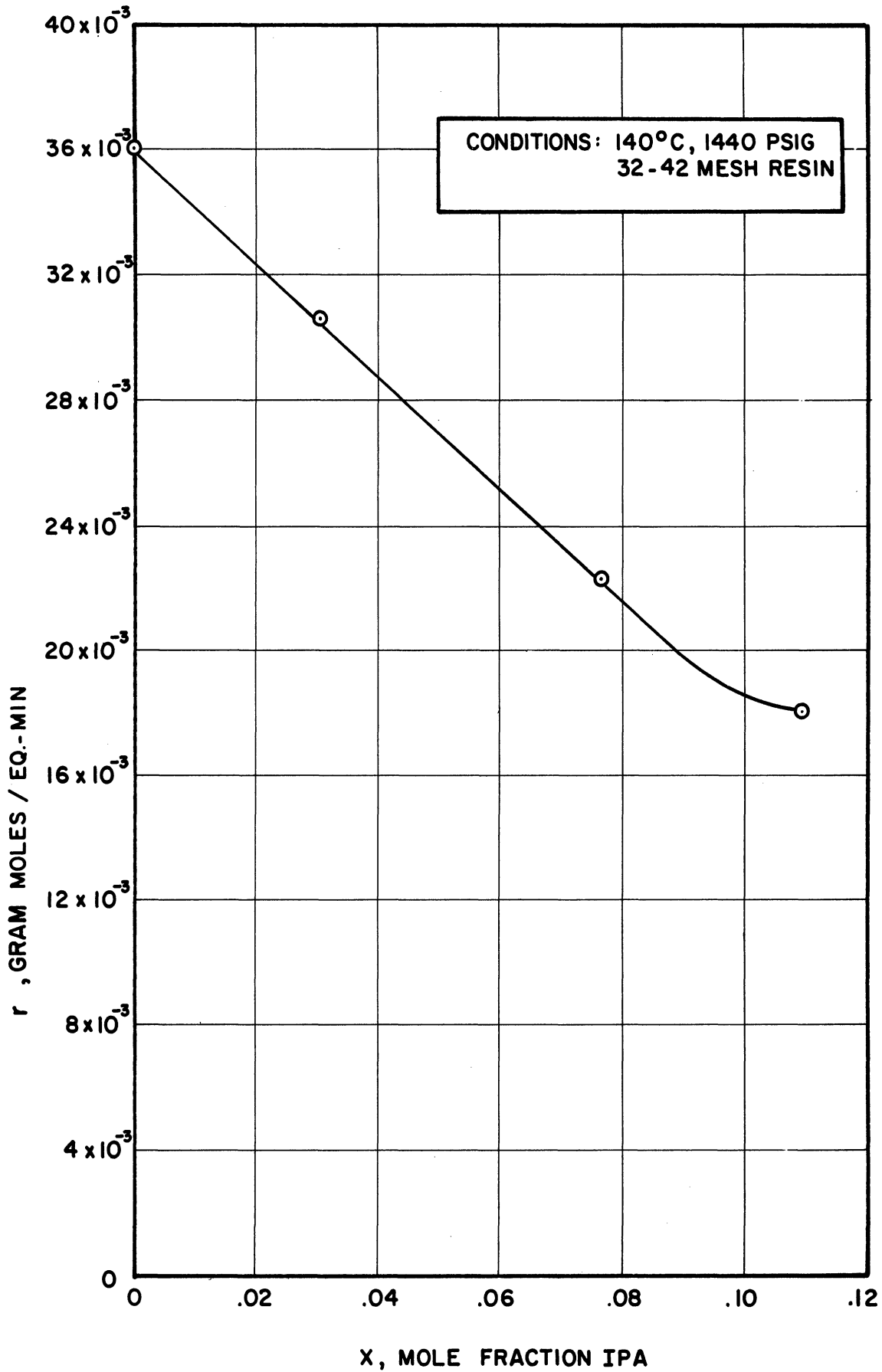
Figure 15.   Group XI Data
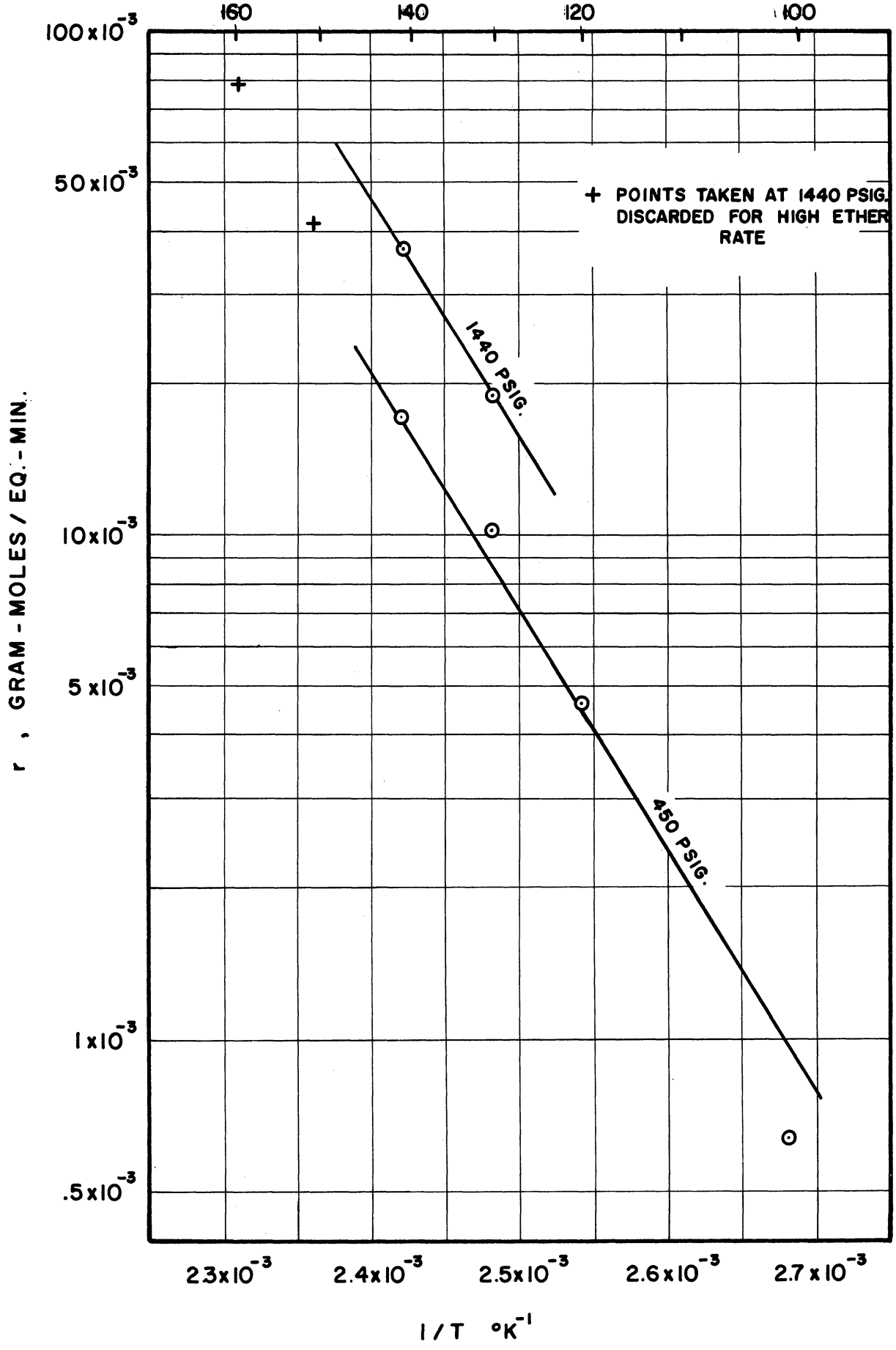
Figure 16. Log r_i vs. 1/T

Resin Life Data and Results

For the resin life runs, the reactor was operated at a high temperature for three days with analyzed new resin. The resin was analyzed for ion exchange capacity and water content. The first run was made at 200°C and the second at 170°C. The deactivation of the resin is considered to take place due to the desulfonation reaction. The half-life of the resin was calculated for each of these temperatures assuming the desulfonation reaction to be irreversible and first order in sulfonic group concentration (ion exchange capacity). Table XVI shows the results of the resin analyses. Figure 17 is a plot of half-life versus 1/T. The half-life at 130°C, found by extrapolating the high temperature data, is 155 days. After use at high temperature, the resin became lighter in color and the water content of the saturated resin decreased. This is presumably due to an increased cross-linking of the gel. The high temperature and pressure caused no apparent cracking or charring of the resin beads.

Hydrogen-Ion Data and Results

The initial rates were obtained for resin which had been neutralized with NaOH to approximately 3/4, 1/2, and 1/4 the original hydrogen-ion concentration. Incremental runs were made with pure water feed and the rates were corrected to zero alcohol concentration using the correlation of the Group V data. The data are shown in Table XVII and Figure 18. Rate in gm-moles/liter-min. versus hydrogen-ion concentration does not yield a linear relationship as might be expected; however, the presence of the sodium ion in the resin could change the

TABLE XVI

RESIN HALF-LIFE DATA

Run 148	Run 156

t = 200°C   t = 170°C

P = 1440 psig   P = 1440 psig

50WX8, 32-42 mesh   50WX8, 100-150 mesh

	New Resin	Used Resin	New Resin	Used Resin
Activity	4.930 meq/gm	0.517 meg/gm	4.861 meq/gm	3.854 meq/gm
% Water	52.83%	6.19%	55.22%	51.40%

Run duration = 76 hrs.   Run duration = 73 hrs.

$t_{1/2}$ = 23.3 hrs. = 0.971 days $t_{1/2}$ = 218.3 hrs. = 9.10 days

Ave. measured temp. = 201.6°C   Ave. measured temp. = 166.8°C

- - - - - - - - - - - - -

absorptive properties of the resin, changing the distribution coefficients,

and yield the above result.   The data are correlated by:

$$r_i = \left\{12.952 \ [H^+] + 4.002 \ [H^+]^2\right\} \times 10^{-3} \ \text{gm.-moles/liter-min.} \qquad (9)$$

where $[H^+]$ = meq./ml. of saturated resin.

TABLE XVII

HYDROGEN-ION DATA

$[H^+]$ meq/ml	$r_i[H^+]$ gm.-moles/liter	r_i, gm-moles/eq.-min
1.678	33.554×10^{-3}	19.890×10^{-3}
1.343	24.380	18.131
0.978	15.917	16.275
0.462	7.100	15.368
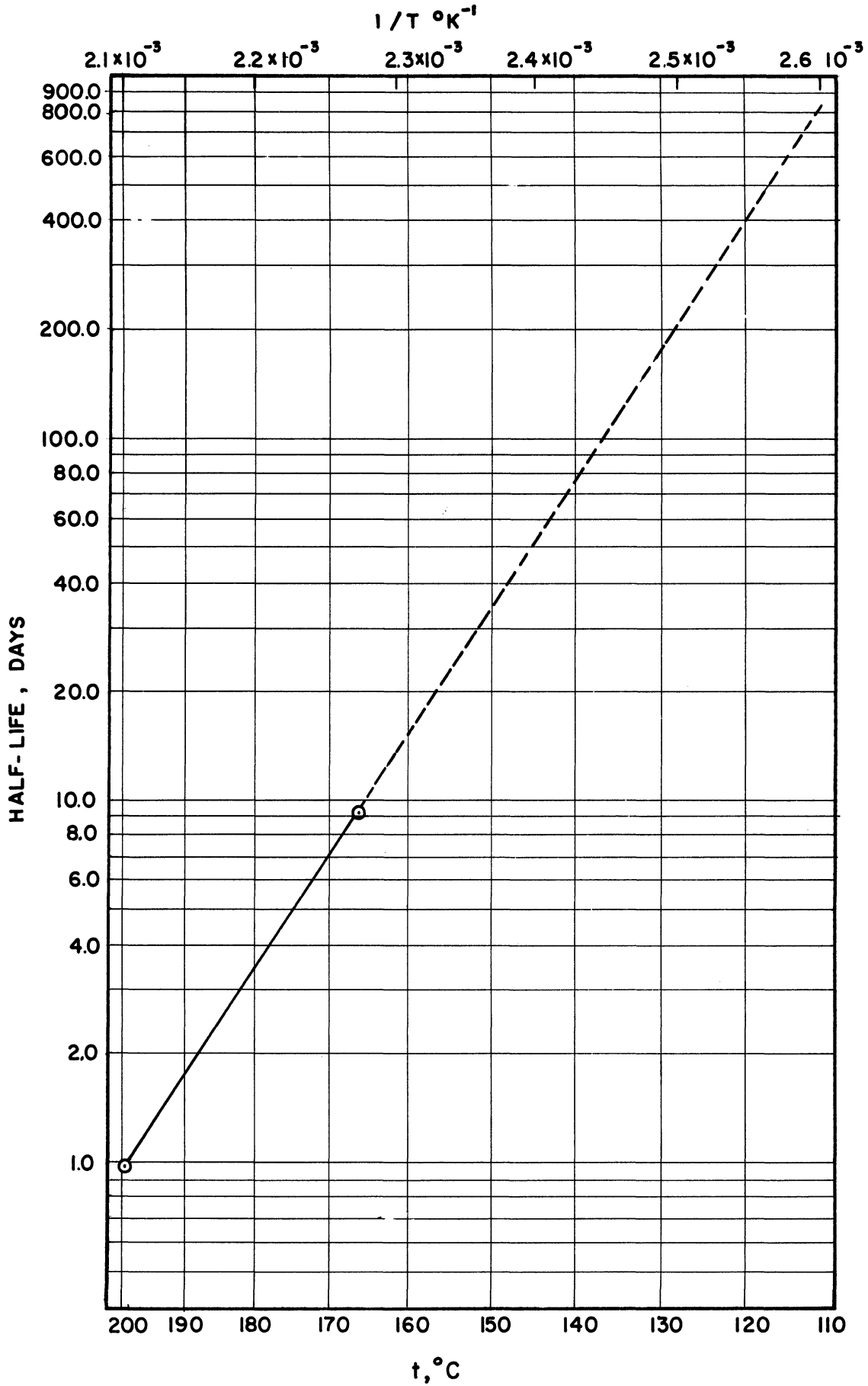
Figure 17. Resin Half-Life

X, MOLE FRACTION OF ISOPROPYL ALCOHOL IN
PROPYLENE-FREE LIQUID
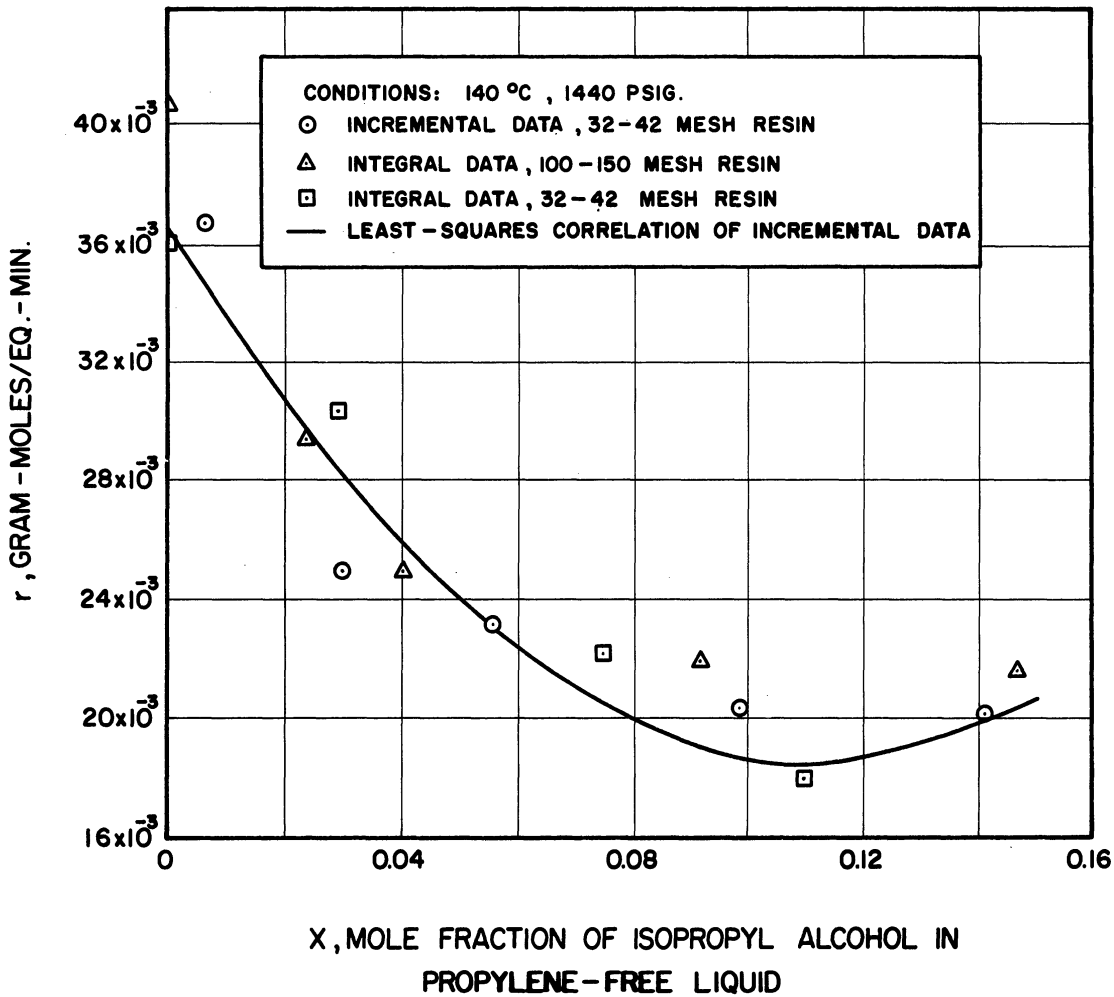
Comparison of Integral and Incremental Data

The above plot compares the data taken at 140°C and 1440 psig by both the integral and incremental methods (Groups VII, VIII, and XI). All points meet the 2.5σ test with the least-squares curve obtained from the incremental data correlation. This comparison is sufficient evidence that either method of reactor operation yields data of the same reliability and that integration of incremental data is valid for integral reactor design. Since resin size has an insignificant effect on rate, both resin sizes were used for this plot. Incremental runs were not made at 150° or 160°C; therefore no comparison of integral data at those temperatures was possible.
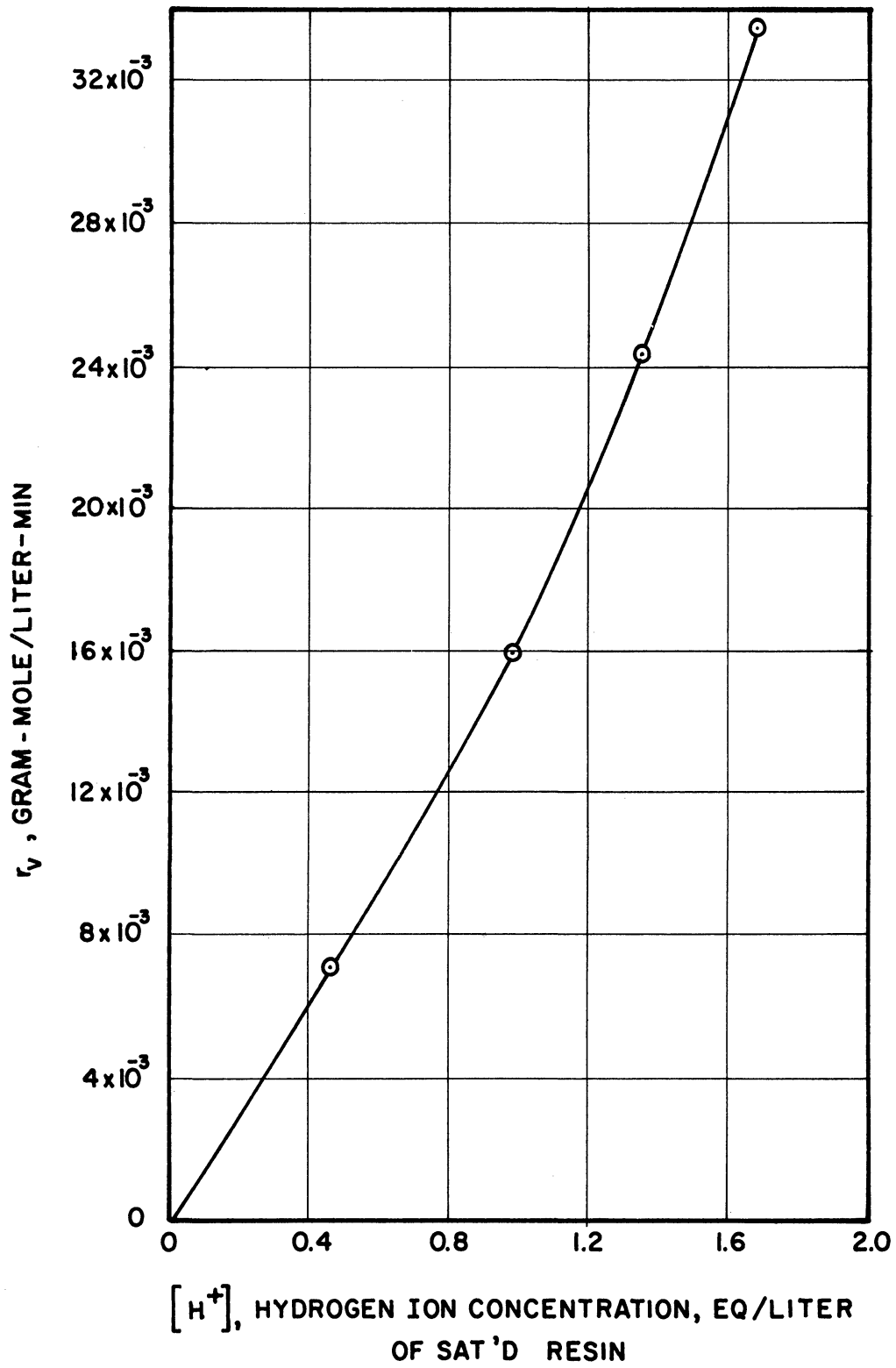
Figure 18. Volumetric Rate vs. [H^+]

CONCLUSIONS

1. The hydration of propylene with the cation exchange resin catalyst, Dowex 50WX8, is favorable in the range $100°-160°C$ and $450-1440$ psig. The initial reaction rates for these conditions are:

$$r_i = 4.87 \times 10^9 \exp(-21,600/RT) \text{ gm.-moles/eq.-min.}$$

   at 450 psig, $100-140°C$

$$r_i = 10.05 \times 10^9 \exp(-21,600/RT) \text{ gm.-moles/eq.-min.}$$

   at 1440 psig, $130-140°C$

   where $T = °K.$, $R = 1.987$ cal/mole $- °K.$

2. The rates become constant at a certain product composition presumably due to increasing solubility of the propylene in the liquid phase.

3. By assuming a mechanism, a rate equation may be derived which satisfactorily correlates the data for a mole fraction of isopropyl alcohol up to 0.12 and a temperature range $100°-140°C$. (It is given on page   as Equation (4)).

4. The competing reaction to form di-isopropyl ether is favored by increased temperature, pressure, and alcohol concentration becoming important above $160°C$ where it corresponds to approximately 10% of the propylene.

5. The half-life of the resin, found by extrapolating data at $200°C$ and $170°C$, is 62, 155, and 370 days for $140°$, $130°$, and $120°C$ respectively.

APPENDIX A

DERIVATION OF RATE EQUATION

The rate equation for the carbonium ion mechanism may be derived as follows:

$$H_2C = \underset{\underset{H}{|}}{C} - CH_3 + H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (H_3C - \underset{\underset{H}{|}}{C} - CH_3)^+ \qquad (1)$$

$$(H_3C - \underset{\underset{H}{|}}{C} - CH_3)^+ + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} H_3C - \underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}} - CH_3 + H^+ \qquad (2)$$
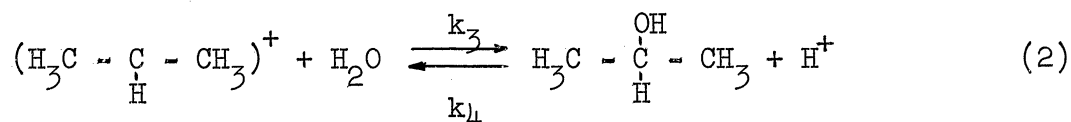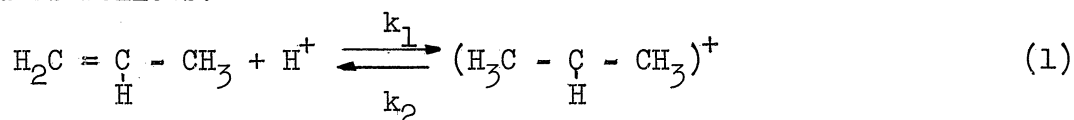
The rate of formation of isopropyl alcohol may be written:

$$\frac{d[i\text{-}C_3H_7OH]}{dt} = k_3[C_3H_7^+][H_2O] - k_4[i\text{-}C_3H_7OH][H^+] \qquad (10)$$

The concentration of the carbonium ion, $[C_3H_7^+]$, is indeterminant, but may be found by assuming it to be small and its net rate of formation to be zero.

$$\frac{d[C_3H_7^+]}{dt} = 0 = k_1[C_3H_6][H^+] - k_2[C_3H_7^+]_{s.s.} + k_4[i\text{-}C_3H_7OH][H^+]$$
$$-k_3[C_3H_7^+]_{s.s.}[H_2O] \qquad (11)$$

Solving Equation (11) for $[C_3H_7^+]_{s.s.}$, the steady-state concentration of carbonium ion, and substituting the result in Equation (10) yields the rate equation for isopropyl alcohol in terms of product and reactant concentrations.

$$[C_3H_7^+]_{s.s.} = \frac{k_1[C_3H_6][H^+] + k_4[i\text{-}C_3H_7OH][H^+]}{k_2 + k_3[H_2O]} \qquad (12)$$

$$\frac{d[i\text{-}C_3H_7OH]}{dt} = \frac{k_1k_3[H^+]}{k_2+k_3[H_2O]}\left\{[C_3H_6][H_2O] - \frac{[i\text{-}C_3H_7OH]}{K}\right\} \qquad (3)$$

where $K = k_1k_3/k_2k_4$, the equilibrium constant.

APPENDIX B

DERIVATION OF MODIFIED RATE EQUATION

Beginning with the rate equation derived in Appendix A,

$$\frac{d[i\text{-}C_3H_7OH]}{dt} = \frac{k_1k_3[H^+]}{k_2+k_3[H_2O]}\left\{[C_3H_6][H_2O] - \frac{[i\text{-}C_3H_7OH]}{K}\right\} \tag{3}$$

which is the rate equation for the carbonium ion reaction in a homogeneous liquid-phase reaction, the rate equation for the reaction in the resin phase may be written by adding the distribution coefficients.

$$\frac{d[i\text{-}C_3H_7OH]}{dt} = \frac{k_1k_3[H^+]}{k_2+k_3[H_2O]_s\alpha_W}\left\{[C_3H_6]_s\alpha_P[H_2O]_s\alpha_W - \frac{[i\text{-}C_3H_7OH]_s\alpha_A}{K}\right\} \tag{13}$$

where $[\quad]_s$ is the concentration of a component in the external liquid-phase at the surface of the resin and α is the resin phase distribution coefficient.

Simplifying assumptions may be made to reduce the number of unknown coefficients.

1. Concentration of each of the components is equal to the mole fraction of the component divided by the molal volume of the liquid.

2. The mole fraction of propylene is small and is a function of the mole fraction of isopropyl alcohol.

3. The distribution coefficients are not functions of composition.

One condition necessary to validate all of the above assumptions is that the range of composition must be very small. This condition is

fulfilled since the range of the mole fraction of isopropyl alcohol used in the correlations is 0 to 0.14.

A change of 0.14 in the mole fraction of isopropyl alcohol will yield a change of approximately 50% in the molal volume, if the solution is ideal. However, assumption 1 will stand since the purpose of this derivation is to show the general form of the correlating equation.

Solubility of propylene in water-siopropyl alcohol mixtures is not known. Azarnoosh and McKetta[3] have published the solubility of propylene in water in the range 200-500 psig and 100-220°F. This data may be extrapolated to reactor conditions with some degree of reliability with the least confidence being placed in the high temperature, high pressure values. The range of the mole fraction of propylene is 0.00091 - 0.00322.

An estimated ternary phase diagram may be prepared from estimated binary diagrams and a ternary low temperature liquid-phase diagram. Figure 19 is the ternary liquid-phase diagram, Figure 20 shows the estimated binary diagrams, and Figure 21 is the estimated ternary diagram at reactor conditions. From this diagram it can be assumed that a parabolic curve of the form $x_P = a + bx + cx^2$ will approximate the liquidus line.

It can be shown that x_A and x_W, the mole fractions of alcohol and water, may be written as functions of x, the mole fraction of alcohol on the propylene-free basos. amd x_P, the mole fraction of proplylene.

$$x_A = x(1-x_P) \tag{14}$$

$$x_W = (1-x)(1-x_P) \tag{15}$$

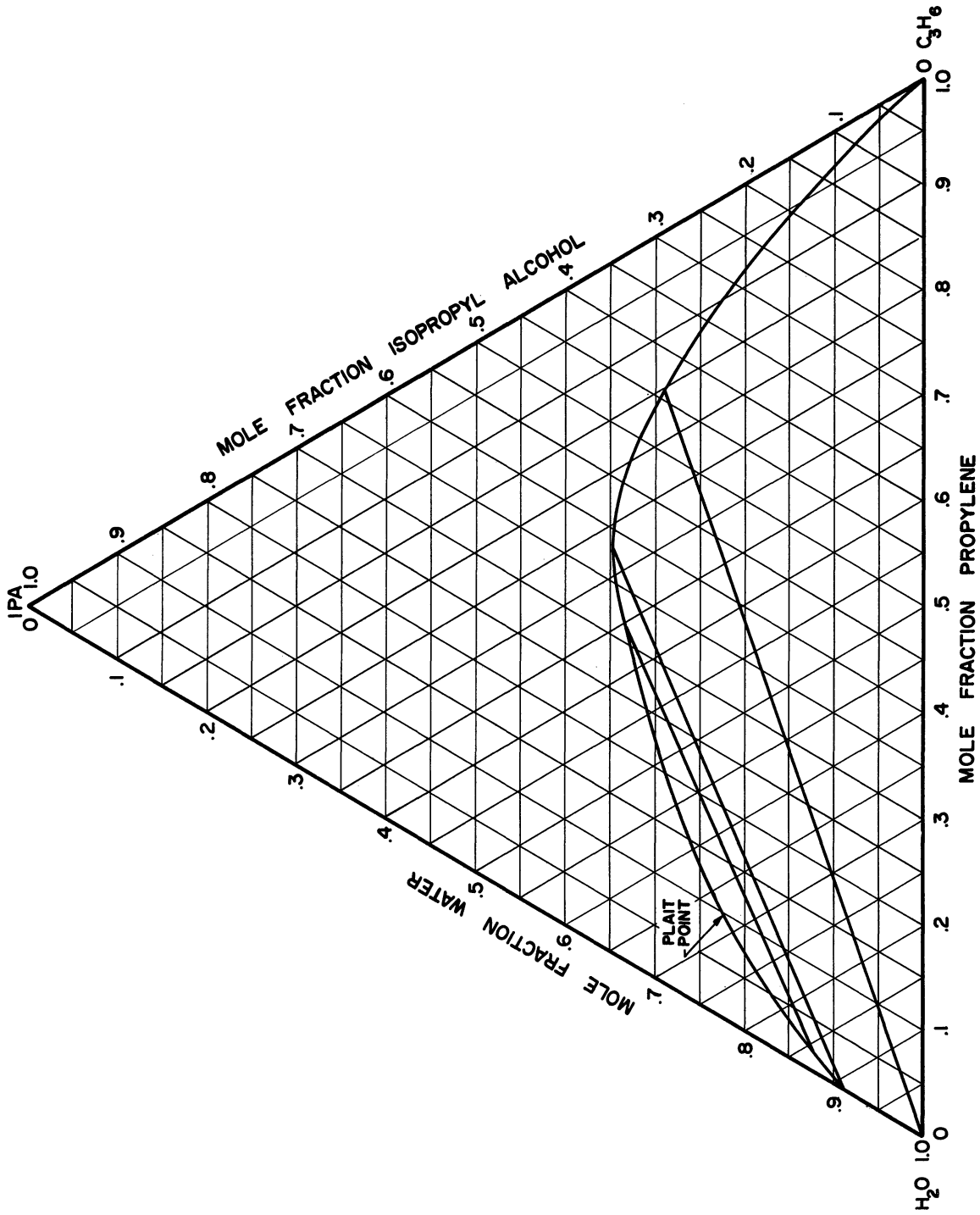Letting $\quad x_P = a + bx + cx^2 \tag{16}$

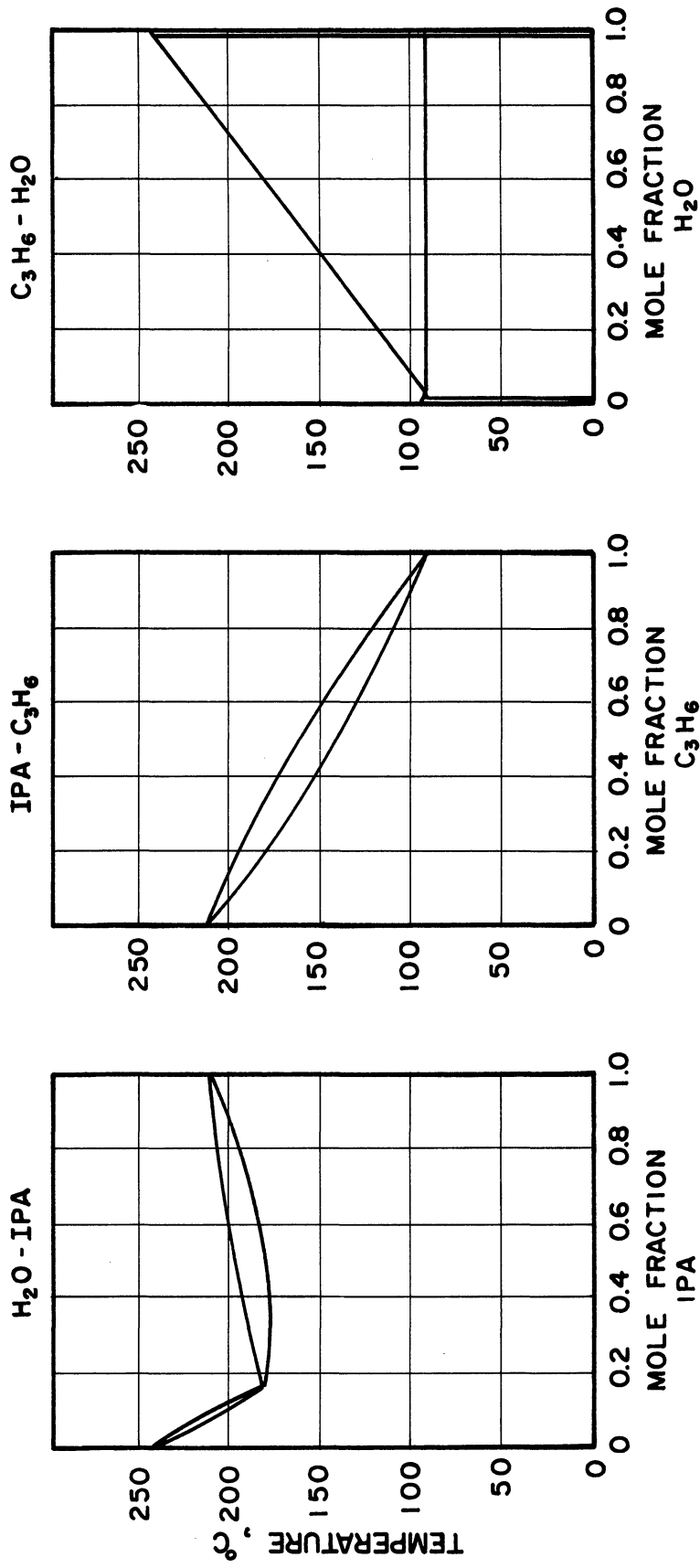Figure 19. Ternary Liquid Phase Diagram @ 25°C.
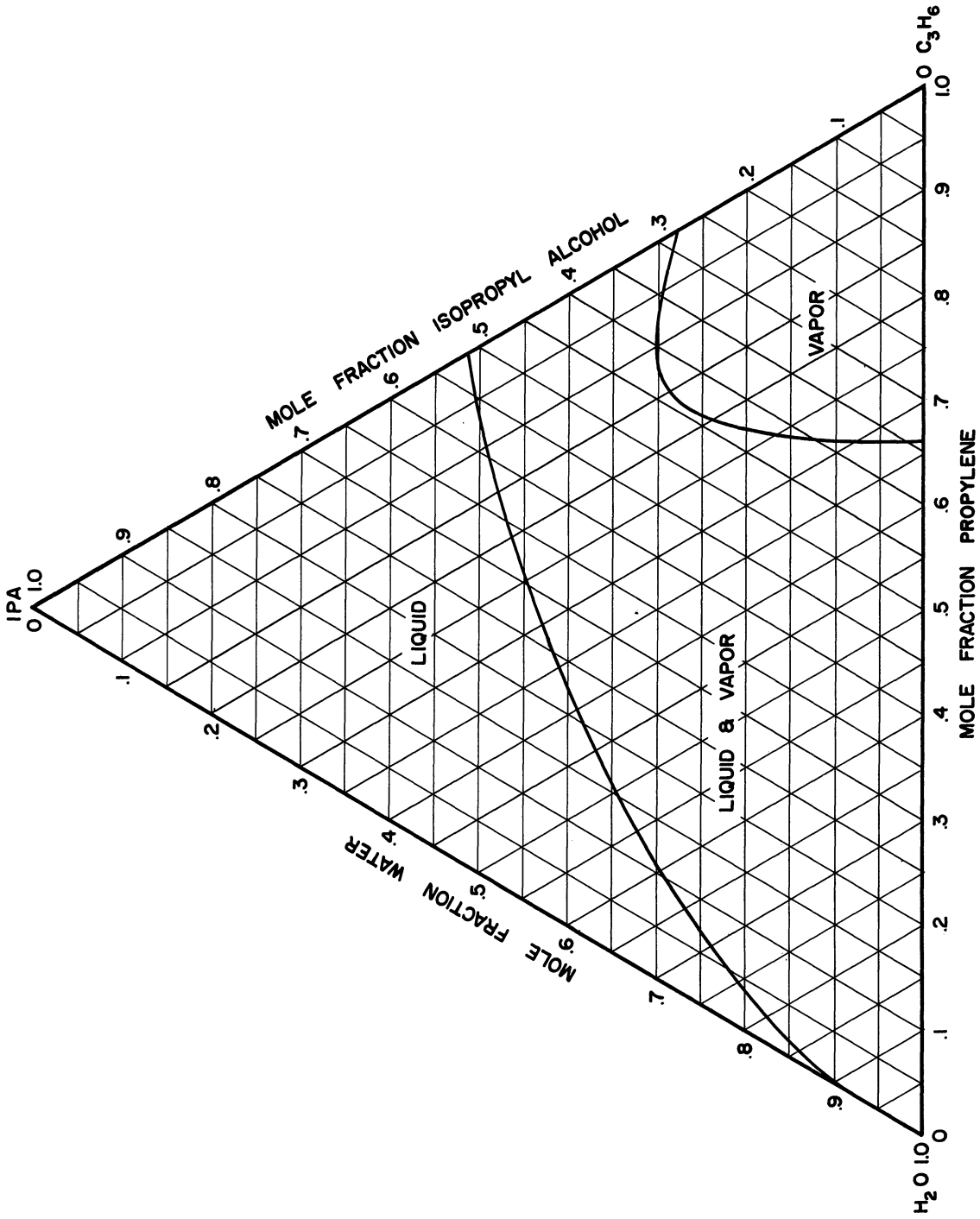
Figure 20. Estimated Binary Phase Diagram @500 psi

Figure 21. Estimated Ternary Liquid-Vapor Phase Diagram @ 140°C 500 psi.

$$x_A = x(1-a-bx-cx^2) = (1-a)x-bx^2-cx^3 \tag{17}$$

$$x_W = (1-x)(1-a-bx-cx^2) = (1-a)+ (a-b-1)x+ (b-c)x^2+cx^3 \tag{18}$$

Now the rate equation may be expressed as a function of x,

$$\frac{d[i-C_3H_7OH]}{dt} = \frac{k_1k_3[H^+]}{V} \left\{ \frac{1}{k_2V+k_3[(1-a) + (a-b-1)x+ (b-c)x^2 + cx^3]\alpha_W} \right\}$$

$$\left\{ (a-a^2)\alpha_P\alpha_W + (a^2-a+b-2ab)\alpha_P\alpha_W x + (2ab-b^2-b-2ac+c)\alpha_P\alpha_W x^2 \right.$$

$$+ (b^2+2ac-2bc-c)\alpha_P\alpha_W x^3 + (2bc-c^2)\alpha_P\alpha_W x^4+c^2\alpha_P\alpha_W x^5$$

$$\left. - \frac{V}{K} [(1-a)x-bx^2-cx^3]\alpha_A \right\} \tag{19}$$

where V = molal volume of liquid.

For an ideal solution,

$$V = x_A V_A + x_W V_W + x_P V_P \tag{20}$$

For small values of x, it is assumed that V and

$$\frac{1}{k_2V+k_3[(1-a) + (a-b-1)x+ (b-c)x^2+cx^3]\alpha_W} \quad \text{are constant.}$$

The rate equation may be written,

$$\frac{d[i-C_3H_7OH]}{dt} = \frac{k_1k_3[H^+]}{G} \left\{A + Bx + Cx^2 + Dx^3 + Ex^4 + Fx^5\right\} \tag{4}$$

where,

$$A = (a-a^2)\alpha_P\alpha_W$$

$$B = (b-a-2ab+a^2)\alpha_P\alpha_W - \frac{V\alpha_A}{K} (1-a)$$

$$C = (c-b-2ac+2ab-b^2)\alpha_P\alpha_W + \frac{bV\alpha_A}{K}$$

$$D = (2ac-c-2bc+b^2)\alpha_P\alpha_W + \frac{cV\alpha_A}{K}$$

$$E = (2bc-c^2)\alpha_P\alpha_W$$

$$F = c^2\alpha_P\alpha_W$$

$$G = \{k_2V+k_3[(1-a) + (a-b-1)x + (b-c)x^2 + cx^3]\alpha_W\} \, V$$

APPENDIX C

SAMPLE CALCULATIONS

Raw Data, Run 51

Product Samples	Analysis (wt. %)		Weight
Collected @ 10 minute intervals	H_2O	IPA	
G	86.26	13.74	26.35 gm.
H	86.06	13.94	30.09 gm.
I	85.98	14.02	26.47 gm.
J	85.98	14.02	28.29 gm.
K	85.90	14.10	
Average	86.01	13.99	27.80 gm.
Feed Sample Analysis	89.90	10.10	

Reactor Bed: 0.2745 eq. Dowex 50WX8, 32-42 mesh.

Average Temperature: 130.9° C

Gas Product Rate: 0.00248 ft.^{3}/min.

Gas Product Temperature: 76.2° F

Liquid Product Temperature: 24.3° C

Calculations

The average rate is calculated by the approximation,

$$r = \frac{F(x_f - x_i)}{N}$$

$$x_i = \frac{10.10/60.09}{10.10/60.09 + 89.9/18.02} = .03259, \text{ mole fr. IPA in feed.}$$

$$x_f = \frac{13.99/60.09}{13.99/60.09 + 86.01/18.02} = .04651, \text{ mole fr. IPA in product.}$$

$$F = \frac{27.80}{10} \frac{(13.99/60.09 + 86.01/18.02)}{100} = 0.13916 \text{ gm-moles/}$$

minute, molal feed rate.

$$r = \frac{(0.13916)(0.04651 - 0.03259)}{0.2745} = 7.057 \times 10^{-3} \text{ gm-moles/eq.-min.}$$

This rate is the uncorrected reaction rate based upon the liquid-phase

measurements. A small amount of the product is carried away by the

propylene flashed off in the liquid separator and a correction is made

in the rate for this lost product. The composition of the vapor is

assumed to be propylene with water and isopropyl alcohol in equilibrium

with the liquid product.

Vapor pressure of IPA @ 24.3° C = 41.4mm Hg.

Vapor pressure of H_2O @ 76.2°F = 23.1mm Hg.

$$\text{Volume rate of prod. gas @ STP} = 2.48 \times 10^{-3} \times \frac{492}{536.2} \times \frac{740}{760}$$

$$= 2.22 \times 10^{-3} \text{ ft.}^3/\text{min.}$$

$$\text{Volume rate of dry prod. gas @ STP} = 2.22 \times 10^{-3} \times (1 - \frac{23.1}{740})$$

$$= 2.15 \times 10^{-3} \text{ ft.}^3/\text{min.}$$

$$\text{Molal rate of dry prod. gas} = 2.15 \times 10^{-3} \times \frac{454}{359}$$

$$= 2.72 \times 10^{-3} \text{ gm-moles/min.}$$

$$\text{Alcohol rate in prod. gas} = 2.72 \times 10^{-3} \times \frac{41.4}{720} \times 0.04651$$

$$= 7.28 \times 10^{-6} \text{ gm-moles/min.}$$

$$\text{Alcohol rate/eq. in prod. gas} = 7.28 \times 10^{-6} \times \frac{1}{0.2745}$$

$$= 2.65 \times 10^{-5} \text{ gm-mole/eq.-min.}$$

$$\text{Rate} = (7.057 + 0.027) \times 10^{-3} = 7.084 \times 10^{-3} \text{ gm-mole/eq.-min.}$$

The rate is also corrected for temperature difference. This data point was used for a correlation at 130°C, but the average measured temperature was 130.9°C. The measured rate was multiplied by a correction factor $f = \exp[(-E/R)(1/T_0 - 1/T)]$ where E is the experimental apparent activation energy. For this run,

$$f = \exp[(-21,600/1.987)(1/403.1 - 1/404.0)] = 0.942,$$

Rate $= 7.084 \times 10^{-3} \times 0.942 = 6.673 \times 10^{-3}$ gm-moles/eq-min.

The usual technique of graphical differentiation was used to differentiate the integral data to obtain point rates. The data were differenced as shown in Tables XII - XV on pages 40 and 41, and the differences plotted as shown in Figure 22. The smoothed curves were drawn and point rates obtained.
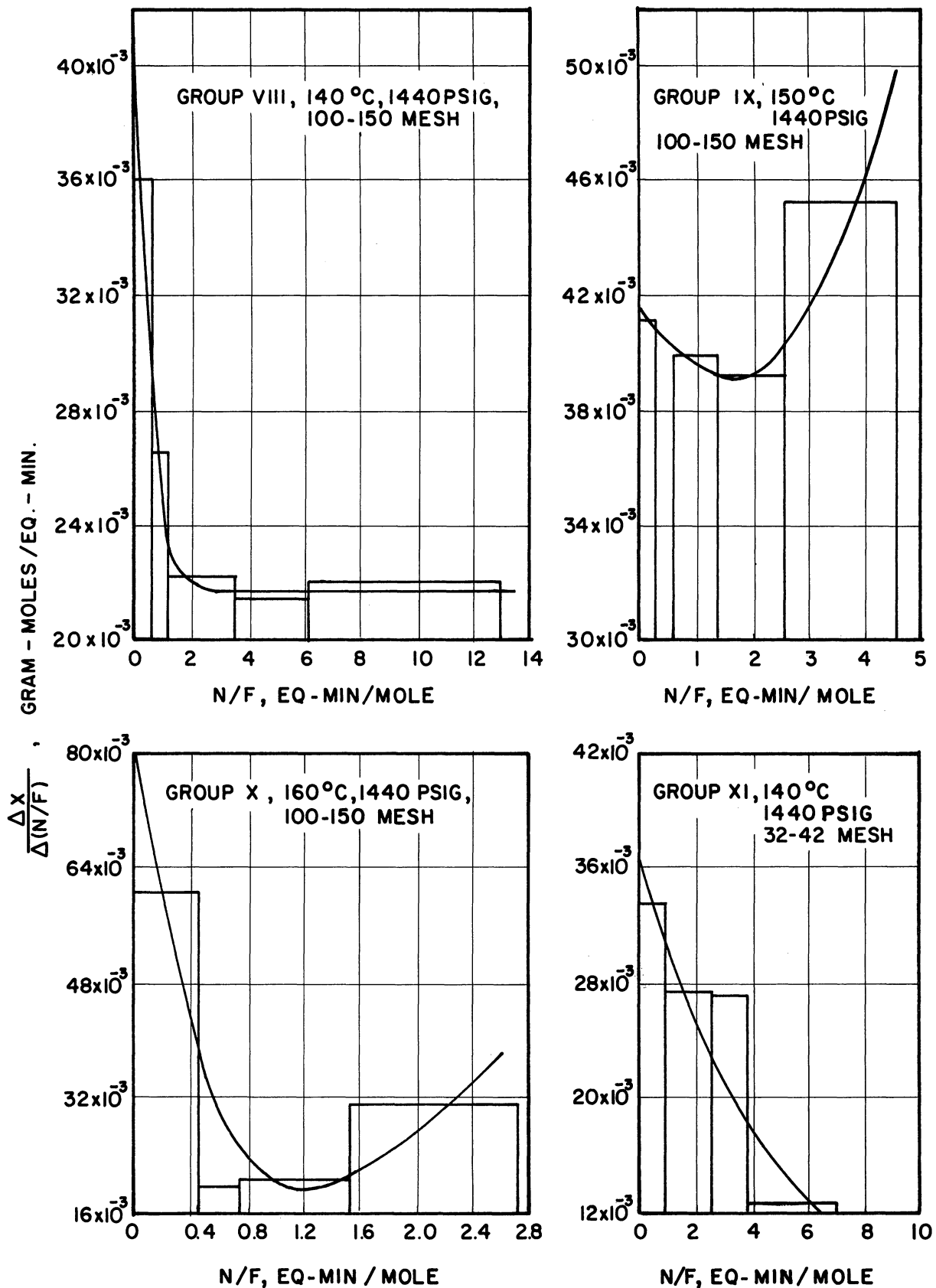
Figure 22. Graphical Differentiation

APPENDIX D

EXPERIMENTAL PROCEDURE

An alcohol-water mixture of approximate composition was prepared from Reagent Grade Isopropyl Alcohol and distilled water from the East Engineering Building distilled water supply. Before each run this mixture was charged into the water gaging cylinder (A), shown in Figure 1, page   , and flushed through the pump. This mixture was pumped through the reactor system for approximately an hour at a rate of approximately 4 cc/minute.

Propylene was charged into its storage cylinder (F) by allowing liquid propylene from an inverted cylinder to displace the mercury back into the oil cylinder (E) and oil to a collecting vessel at atmospheric pressure. Propylene pressure was increased from vapor pressure to reactor pressure by pumping oil into the displacement system with the valve in the propylene feed line closed.

The preheater controller was set to the desired temperature. All heaters were turned on and full voltage was applied to heater "O" for quick heat-up. Reactor temperature was measured periodically, and the voltage to heater "O" was reduced as the desired temperature was approached. Heater currents had been predetermined and only minor adjustments were necessary.

After the alcohol-water mixture had flowed for sufficient time, the pump was adjusted to a feed rate calculated to yield a 2-5% change in alcohol concentration. After the reactor reached operating temperature and the propylene reached operating pressure, the propylene feed

valve was opened and its feed rate was adjusted. The reactor was allowed to come to equilibrium for a period in which at least one free reactor volume of liquid passed through it. During this time, checks and adjustments were made to keep the temperature stable.

At the end of the equilibration period the run was begun. The temperatures of the feed systems, product streams, and the reactor were measured and recorded. The liquid product receiver was emptied, the wet test meter reading was recorded, and an electric timer was started. Independently, the levels in the oil and water gaging cylinders were recorded with the starting of a stopwatch.

Four liquid samples were collected at equal time intervals after the start of the run (e.g. at 5, 10, 15, and 20 minutes after time 0). The time interval was chosen to yield 20-40cc liquid samples. At the time of collection of the last sample, the wet test meter reading was again recorded.

Reactor temperature was read at 10 minute intervals during the run. This was done by means of a traversing copper-constantan thermocouple. The readings were taken at 2 1/2" intervals throughout the reactor length. The reactor temperature was then calculated as a time-length average for the run.

The liquid samples were weighed and analyzed by a refractive index technique described in Appendix E.

APPENDIX E

CHEMICAL ANALYSIS OF SAMPLES

Gas chromatograms of preliminary run samples showed the presence of only isopropyl alcohol, di-isopropyl ether, and water. An attempt to devise a quantitative analytical technique for this system using gas chromatography was not successful.

Analysis of this system was devised by Brey.[7] The technique used two of three physical properties (refractive index, density, and viscosity) of the mixture, depending upon the range of composition encountered. Brey measured all of these properties accurately for standard mixtures throughout the entire spectrum of composition.

Since the product mixtures obtained from this study were limited to 0 to 50% isopropyl alcohol and low concentrations of ether, a modified refractive index technique was used with Brey's data. This technique involves the measurement of the refractive index of the sample, titration with di-isopropyl ether to saturation, and measurement of the refractive index of the saturated sample. From the phase diagram on which the refractive index contours have been plotted, the composition of the sample may be determined. The isopropyl alcohol concentration was determined with high accuracy on three standard samples with this technique, and it was adopted for the chemical analysis of the samples.

In the range where the isopropyl alcohol concentration approaches 40-50% the accuracy of this technique is reduced because the rate of change of refractive index with ether addition is small;

i.e., the refractive index of the saturated sample is not much

different from that of the sample itself although a large amount of

ether has been added. Only a small number of samples fell into this

range.

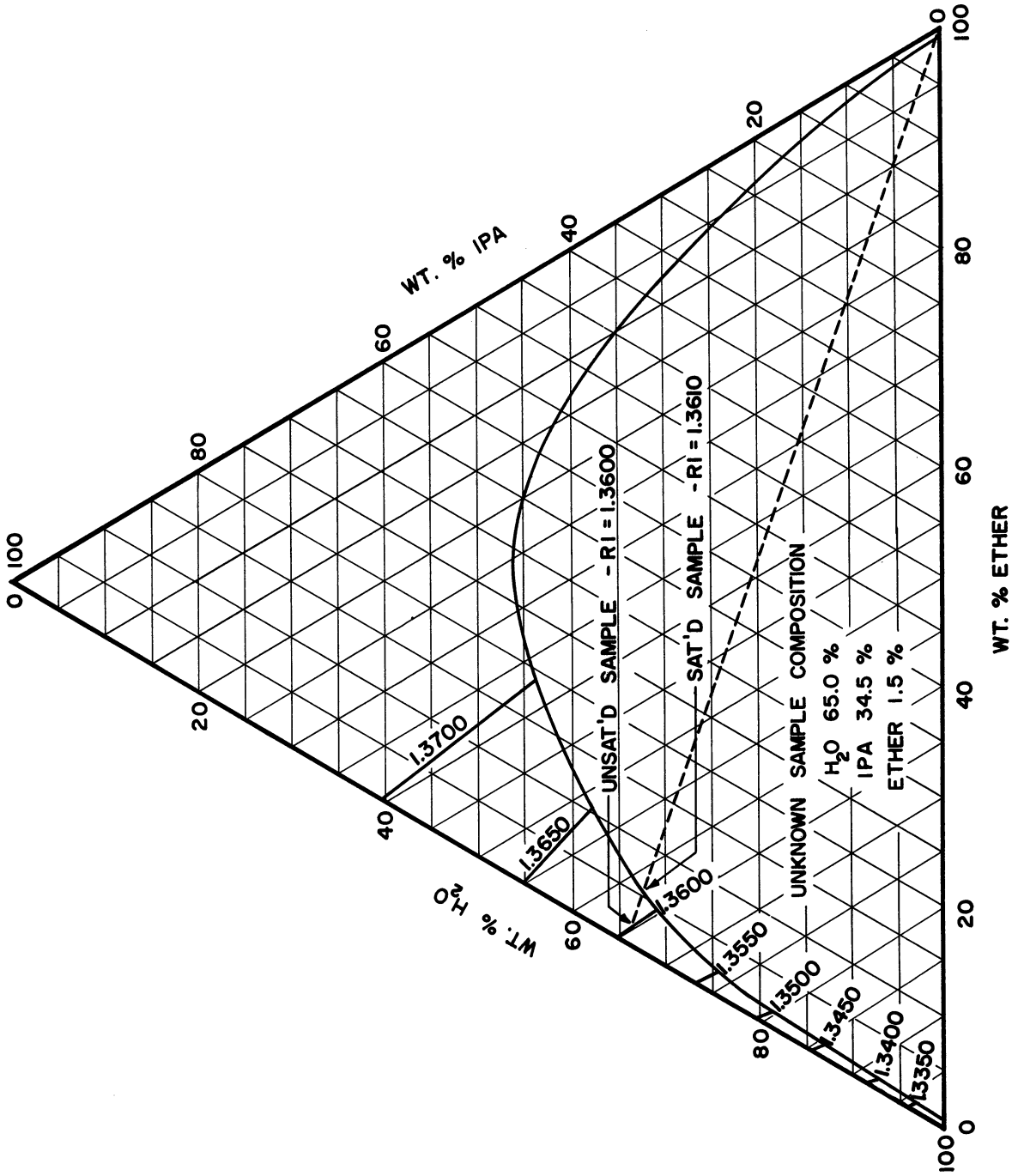Figure 23 gives an example of the use of this technique.

Figure 23. Example of Sample Analysis

APPENDIX F

ESTIMATE OF ERROR

Calibrations

The traversing thermocouple was calibrated against a standard thermometer in the range of temperatures used. Pressure gauges used in the system were calibrated with an Aminco Dead Weight Pressure Tester. All temperatures and pressures used herein are the corrected values.

Measurements

The sources of error in the experimental results are due to two groups of measurements: a.) the measurements used for the calculation of the rates, and b.) the measurements used for the correction of the rates to the desired conditions.

An estimate of the error of each of these measurements yields an estimate of error of the corrected rates.

Measurement	Maximum Error	%Error
a. Product rate	± 0.02 gm	± 0.10%
Composition	± 0.20 wt.%	± 10%
Resin capacity	± 0.01 meq/gm.(wet)	± 0.43%
b. Gas rate	± 0.01 ft.^{3}	± 0.03%
Product temperatures	± 0.5°F	± 0.03%
Barometric pressure	± 20mm Hg	± 0.09%
Reactor temperature	± 0.1°C	± 1.00%

The best method would be to obtain an error estimate for each run; however, one run was chosen which gives a maximum estimate. The items of group (a) were used to calculate the rate. Preliminary calculation showed that maximum values of F and Δx and a minimum value of N yielded a maximum error estimate.

Choosing Run 79, where

$$F = 0.322 \text{ gm-moles/min.} \pm 0.000322 \text{ gm-moles/min.}$$

$$\Delta x = 0.0135 \qquad \pm 0.00135$$

$N = 0.2745$ eq. ± 0.00118 eq.

Rate $= \dfrac{F\Delta x}{N} = 15.83 \times 10^{-3}$ gm.-moles/eq.-min.

$P =$ probable error $= \dfrac{\sqrt{\left(\dfrac{F\Delta x}{N}n\right)^2 + (F\delta)^2 + (\Delta x f)^2}}{N}$

Where, $\pm n =$ error of N

$\pm \delta =$ error of Δx

$\pm f =$ error of F

$P = \dfrac{\pm\sqrt{(15.83\times10^{-3}\times 1.18\times10^{-3})^2 + (.322\times1.35\times10^{-3})^2 + (1.35\times10^{-2}\times3.22\times10^{-4})^2}}{0.2745}$

$P = \dfrac{\pm\sqrt{18.93 \times 10^{-8}}}{0.2745} = \dfrac{\pm\,4.35 \times 10^{-4}}{0.2745} = \pm 1.58 \times 10^{-3}$ gm.-moles/eq.-min.

Group (b) measurements have an effect only on the correction of the rate to correlation conditions.

The correction for the alcohol lost in the vapor may be written as follows:

$C = G \cdot X \cdot A \cdot B \cdot D \cdot x$

where, $G =$ gas flow rate $= 1.65 \times 10^{-3}$ ft.^{3}/min. $\pm 1.65 \times 10^{-5}$

$X =$ conversion term $= 4.49$ gm-moles/ft.^{3} (includes pressure correction)

$A =$ water correction term $= 1 - \dfrac{P_W}{P} = 0.9635 \pm 0.001$

$B =$ temperature correction term $= 0.909$ (correction to STP)

$D =$ approximation of Henry's Law Constant $= \dfrac{P_A}{P} = 0.0624 \pm 0.0016$

$x =$ mole fraction of alcohol in liquid product $= 0.0135 \pm 0.00135$

$P =$ probable error $= XB\sqrt{(ADxg)^2 + (GDxa)^2 + (GAdx)^2 + (GAD\delta)^2}$

$$P = \pm\ 4.49 \text{x}.909\sqrt{(1.339\text{x}10^{-8})^2 + (1.39\text{x}10^{-9})^2 + (3.43\text{x}10^{-8})^2 + (1.339\text{x}10^{-7})^2}$$

$$P = \pm\ 4.49\text{x}.909\sqrt{1.926\text{x}10^{-14}} = \pm\ 4.49\text{x}.909\text{x}1.39\text{x}10^{-7} = \pm\ 5.67\text{x}10^{-7}\ \text{gm-mol/}$$

eq.-min.

An estimate of the maximum error due to temperature correction is made by substituting the expected temperature difference into the correction factor calculation. The difference in correction factors multiplied by the rate yields the probable error.

$$t = 140.9° C$$

$$f = \exp[(-21,600/1.987)(\frac{1}{413.1} - \frac{1}{414.0})] = 0.944$$

$$f' = \exp[(-21,600/1.987)(\frac{1}{413.1} - \frac{1}{414.1})] = 0.950$$

$$P = \pm\ 15.83 \times 10^{-3} \times (0.950 - 0.944) = 0.095 \times 10^{-3}$$

The probable error due to all of the experimental readings is due to the combination of the errors of the calculated rate plus the errors of the corrections.
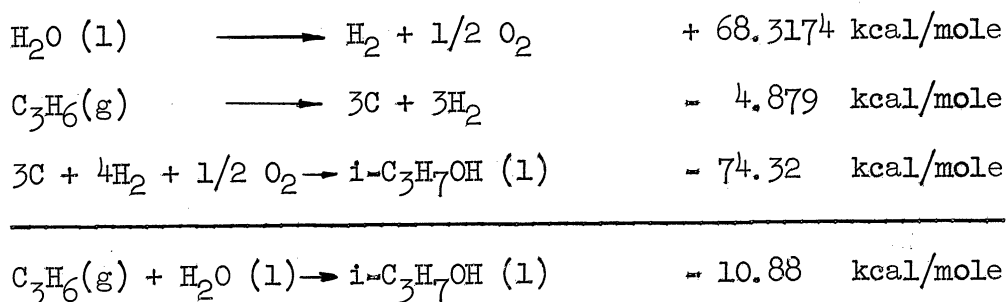
$$P = \text{total probable error} = \pm\ \sqrt{(1.585)^2 + (0.0006)^2 + (0.095)^2} \times 10^{-3}$$

$$P = \pm\ 1.586 \times 10^{-3}\ \text{gm-moles/eq.-min.}$$

APPENDIX G

HEAT OF REACTION

The heat of reaction is calculated from the heats of formation of the products and reactants at 25° C.

$$H_2O \ (l) \longrightarrow H_2 + 1/2 \ O_2 \qquad\qquad + 68.3174 \ \text{kcal/mole}$$

$$C_3H_6(g) \longrightarrow 3C + 3H_2 \qquad\qquad - 4.879 \ \text{kcal/mole}$$

$$3C + 4H_2 + 1/2 \ O_2 \longrightarrow i\text{-}C_3H_7OH \ (l) \qquad - 74.32 \ \text{kcal/mole}$$

$$C_3H_6(g) + H_2O \ (l) \longrightarrow i\text{-}C_3H_7OH \ (l) \qquad - 10.88 \ \text{kcal/mole}$$

The heat of reaction at 100° C is calculated by adding the heat required to raise the products and reactants from 25° C to 100° C.

$$\Delta H = \int \Delta C_p \, dT$$

The C_p data are not available for all of the compounds; therefore, ΔH for each compound will be evaluated by the best method available and the sum of the ΔH's calculated.

1. $C_3H_6(g)(25° C) \longrightarrow C_3H_6(g)(100° C)$

2. $H_2O \ (l)(25° C) \longrightarrow H_2O \ (l)(100° C)$

3. $i\text{-}C_3H_7OH \ (l)(25° C) \longrightarrow i\text{-}C_3H_7OH \ (l)(100° C)$

1. $\Delta H = (\dfrac{H^* - H}{T})_1 \ T_1 - (\dfrac{H^* - H}{T})_2 \ T_2$ (from generalized charts)

$\Delta H = (0.3)(537) - (2.4)(672) = 161 - 1612 = -1451 \ \text{Btu/lb-mole}$

$\Delta H = -1451/1.8 = -806 \ \text{cal/gm-mole}$

2. $\Delta H = H_1 - H_2$ (from steam tables)

$\Delta H = 45.02 - 180.07 = -135.05 \ \text{Btu/lb}$

$\Delta H = -135.05 \times 18.02/1.8 = -1352 \ \text{cal/gm-mole}$

3. $\Delta H = C_p(\text{ave})\ \Delta T = 0.654\text{x-}75 = -49\ \text{cal/gm} = -49\text{x}60.09$

$\Delta H = -2942\ \text{cal/gm-mole}$

$H = \Delta H_p - \Delta H_r = 2942 - (1352-1451) = 139\ \text{cal/gm-mole}$

H_p at $100°C = -10.88 + 0.14 = -10.74\ \text{kcal/gm-mole}$

At $100°C$, Rate $= 1 \times 10^{-3}\ \text{gm.-moles/eq.-min.}$

The reactor contains $\simeq 0.25$ eq. of catalyst

Heat evolved by reaction $\simeq 1 \times 10^{-3}\text{x}10.74 \times 10^{-3}\text{x}0.25$

$\simeq 2.69\ \text{cal/min.}$

$\simeq 2.69\text{x}60/860.57 = 0.187\ \text{watts}$

APPENDIX H

CORRELATION OF DATA

The corrected data were grouped according to the reactor conditions and a three-constant equation was fitted to each group of data by the least-squares technique. The mean deviation of the data from the correlations was calculated and the data which deviated by more than 2.5σ were discarded and the correlation process repeated.

From Figure 16, the apparent activation energy is 21,600 cal/gm-mole. Each of the correlating constants, A through C, was divided by exp (-21,600/RT) yielding a new set of constants, A' through C', which correspond to A through C of Equation (4). For the data at 450 psig, these constants were then correlated as functions of temperature in Figure 24, and the temperature functions substituted into the rate equation

$$r = \exp(-21,600/RT)\{A' + B'x + C'x^2\}. \tag{21}$$

Group	$A \times 10^3$	$B \times 10^3$	$C \times 10^3$	$\exp(-21,000/RT)$	A'	B'	C'
I	0.6348	-10.11	66.59	2.22×10^{-13}	2.86×10^9	-4.55×10^{10}	3.00×10^{11}
II	4.668	-49.65	249.2	9.77×10^{-13}	4.78×10^9	-5.08×10^{10}	2.55×10^{11}
III	10.10	-121.5	603.1	1.94×10^{-12}	5.21×10^9	-6.26×10^{10}	3.11×10^{11}
IV	10.12	-146.7	745.4	1.94×10^{-12}	5.21×10^9	-7.56×10^{10}	3.84×10^{11}
V	19.89	-213.6	992.3	1.94×10^{-12}	1.03×10^{10}	-1.10×10^{11}	5.12×10^{11}
VI	17.23	-248.4	1147	3.73×10^{-12}	4.62×10^9	-6.66×10^{10}	3.07×10^{11}
VII	36.72	-324.9	1454	3.73×10^{-12}	0.98×10^{10}	-0.87×10^{11}	3.90×10^{11}

$$A'_1 = (-37.94 + 0.6680t - 0.0026t^2) \times 10^9$$

$$\left.\begin{array}{l} B'_1 = (2.059 - 0.06517t) \times 10^{10} \\ C'_1 = (1.952 + 0.00937t) \times 10^{11} \end{array}\right\} \text{at 450 psig}$$

$$\left.\begin{array}{l} A'_2 = (1.68 - 0.005t) \times 10^{10} \\ B'_2 = (4.32 - 0.023t) \times 10^{11} \\ C'_2 = (20.98 - 0.122t) \times 10^{11} \end{array}\right\} \text{at 1440 psig}$$

A_1', B_1', and C_1' were obtained by fitting the best least squares curve with two or three constants through the points shown in Figure 24. A_2', B_2', and C_2' were obtained assuming a linear relationship to temperature and placing a straight line through the points as shown in Figure 25. The resultant rate equations are:

at 450 psig

$$r = \exp(-21,600/RT) \left\{ (-37.94 + 0.668t - 0.0026t^2) \cdot 10^9 \right.$$
$$\left. + (2.059 - 0.06517t) \cdot 10^{10}x + (1.952 + 0.00937t) \cdot 10^{11}x^2 \right\}$$
$$\text{gm-moles/eq.-min.}$$

at 1440 psig

$$r = \exp(-21,600/RT) \left\{ (1.68 - 0.005t) \cdot 10^{10} - (4.32 - 0.023t) \right.$$
$$\left. \cdot 10^{11}x + (20.98 - 0.122t) \cdot 10^{11}x^2 \right\} \text{gm-moles/eq.-min.}$$

Figure 26 shows the experimental rate vs. the rate calculated by both general correlations. All the 98 runs used for obtaining the correlations are plotted. There is no apparent trend away from the diagonal indicating the validity of the rate expression.
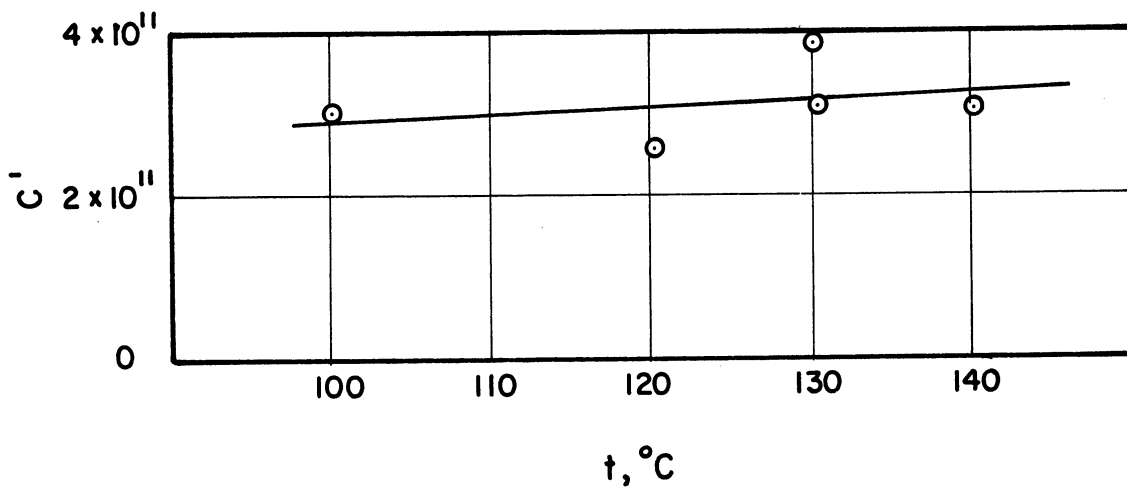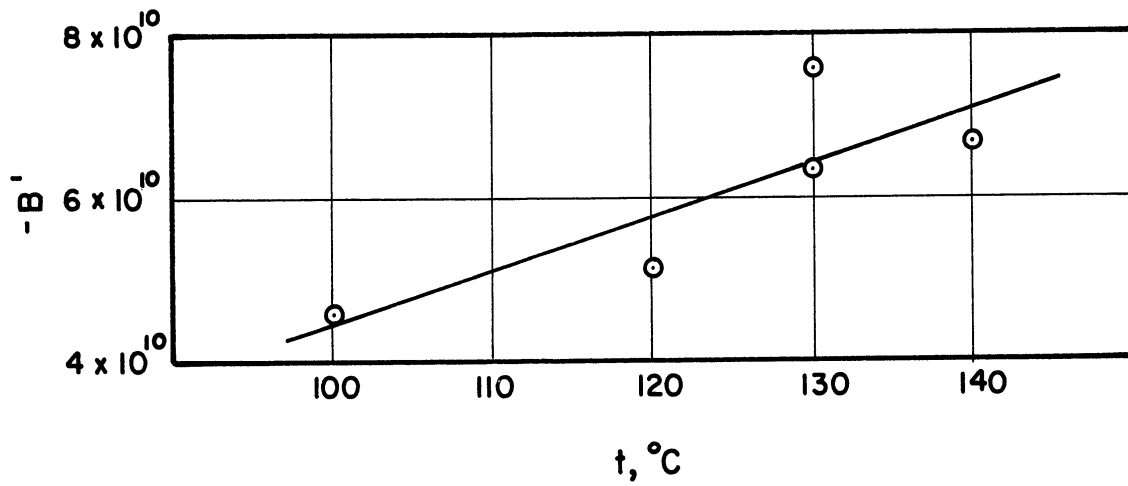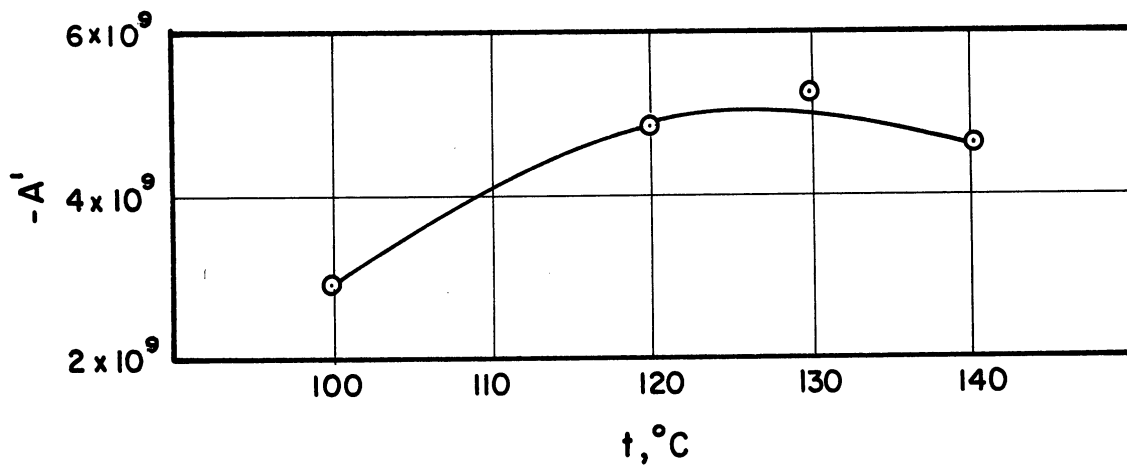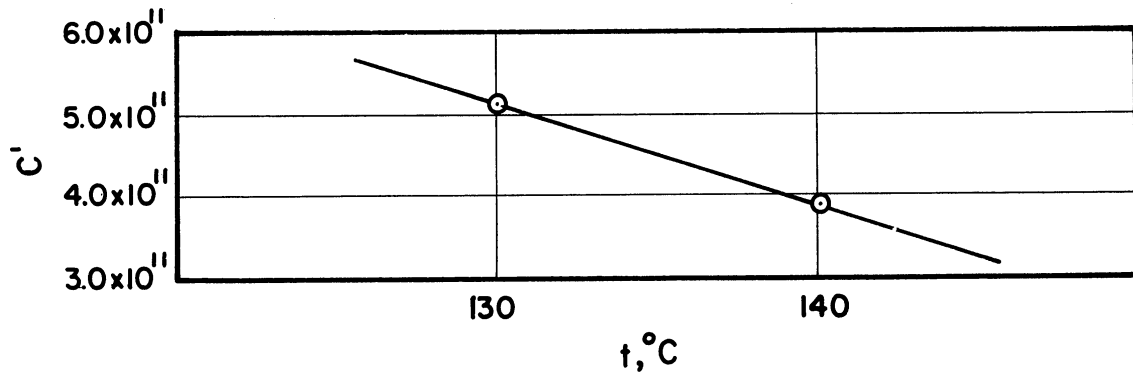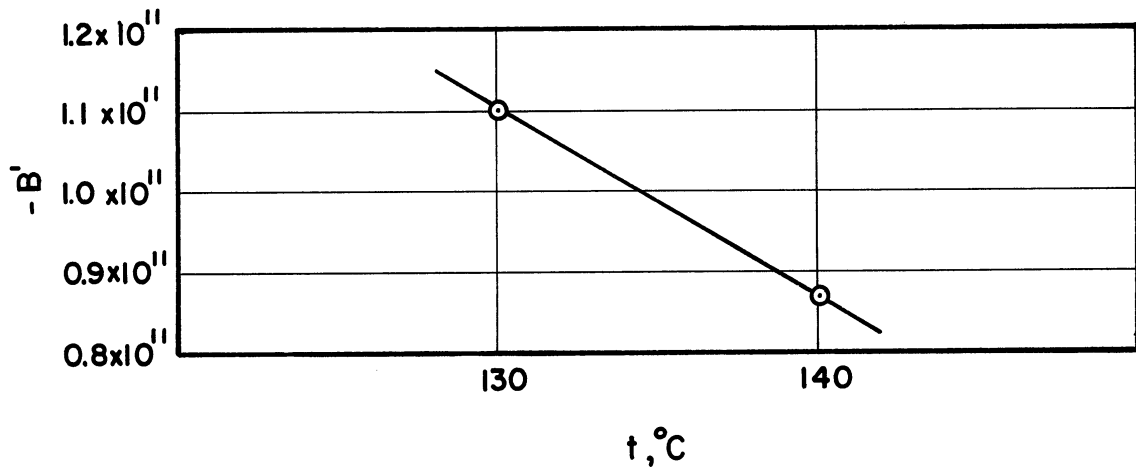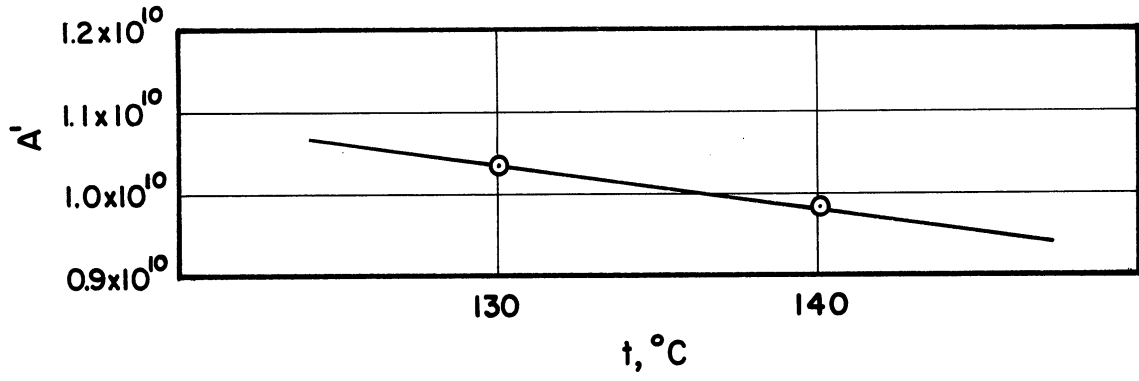
Figure 24. Correlating Constants, 450 psig.

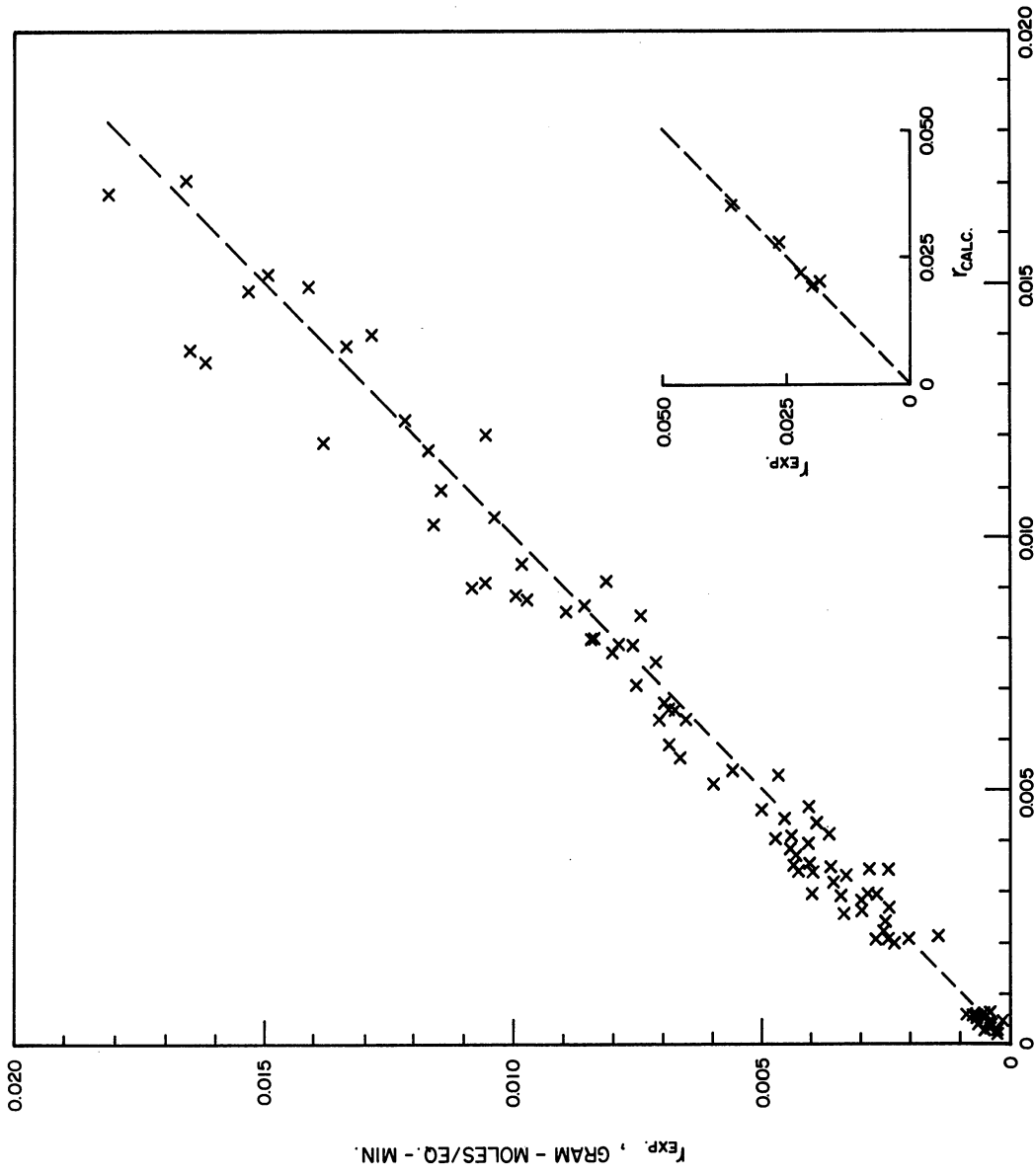Figure 25. Correlating Constants, 1440 psig.

Figure 26. r_{exp} vs. r_{calc}.

NOMENCLATURE

A through G   constants

C_p heat capacity, cal/gm-$^\circ$C

E   activation energy, cal/gm-mole

F   molal feed rate, moles/min.

H   enthalpy, cal/gm-mole

K   chemical equilibrium constant

N   equivalents of resin in reactor

P   atmospheric pressure, mm Hg

R   gas constant

T   absolute temperature, $^\circ$K

V   molal volume, liters/mole

a,b,c   constants

f   error of F

k   reaction rate constant

n   error of N

p   partial pressure, mm Hg

r   reaction rate, gm.-moles/eq.-min.

t   temperature, $^\circ$C; time

x   mole fraction

α phase distribution coefficient

δ error of Δx

Subscripts

A   alcohol

P   propylene

-81-

W	water
f	final
i	initial
p	products
r	reactants
s	surface
s.s.	steady state
v	volumetric

BIBLIOGRAPHY

1. Anonymous Chem. and Met. Eng., 23, (1920) 1230.

2. Astle, Melvin J., and Pinns, Murray L. J. Org. Chem., 24 (1959) 56-60.

3. Azarnoosh, Azarpoor, and McKetta, John J. J. Chem. Eng. Data, 4, (1959) 211.

4. Barker, G. E., and White, R. R. Chem. Eng. Prog. Symp. Series, No. 4, 48, (1952) 75.

5. Bauman, W. C., and Eichhorn, J. J. Am. Chem. Soc., 69, (1947) 2830.

6. Bent, Franklin A., and Wik, Simon N. U.S. 2,036,317 (April, 1936).

7. Brey, W. J. Anal. Chem., 26, (1954) 838-42.

8. Chambers, Robert R. U.S. 2,803,667 (August, 1957).

9. Cottle, Delmer L., and Young, David W. U.S. 2,810,759 (October, 1957).

10. Dale, C. B. Ph.D. Thesis, The University of Michigan (1955).

11. Douglas, W. J. M. Ph.D. Thesis, The University of Michigan (1958).

12. Friedman, Bernard S., and Morritz, Fred L. U.S. 2,830,091 (April, 1958).

13. Hamilton, G. E., and Metzner, A. B. Ind. Eng. Chem., 49, (1957) 838.

14. Ipatieff, V. N., and Monroe, G. S. J. Am. Chem. Soc., 66, (1944) 1627.

15. Katzen, R. Pet. Ref., 40, (1961) 161.

16. Keith, Carl D. U.S. 2,805,261 (September, 1957).

17. Kelly, J. T. U.S. 2,843,642 (July, 1958).

18. Klein, F. G., and Banchero, J. T. Ind. Eng. Chem., 48, (1956) 1278.

19. Kreps, Saul I., and Nachod, Frederick C. U.S. 2,477,380 (July, 1949).

20. Kressman, T. R. E. Ind. Chemist, 36, (1960) 3-8.

21. Langer, Arthur W., Jr. U.S. 2,861,045 (November, 1958).

22. Leffler, J. E. The Reactive Intermediates of Organic Chemistry, p. 137, Interscience Publishers, New York, 1956.

23. Levy, Norman, and Greenhalgh, Robert K. U.S. 2,683,753 (July, 1954).

24. Lukasiewicz, Sigmund, J., Denton, W. I., and Plank, Charles J. U.S. 2,658,924 (November, 1953).

25. Marberry, J. E. Ph. D. Thesis, The University of Michigan (1960).

26. Majewski, F. M., and Marek, L. F. Ind. Eng. Chem., 30, (1938) 203.

27. McDonald, D. W., and Hammer, W. F. Ind. Eng. Chem., 48, (1956) 1621.

28. McDonald, D. W., and Hamner, W. F. Ind. Eng. Chem., 49, (1957). 1518.

29. McDonald, D. W., and Hamner, W. F. Ind. Eng. Chem., 52, (1960) 962.

30. Muller, J., and Waterman, H. J. Brennstoff - Chem., 38, (1957) 357.

31. Reed, L. M., Wenzel, L. A., and O'Hara, J. B. Ind. Eng. Chem., 48, (1956) 205.

32. Reynolds, Peter W., and Pittwell, Laurence R. U.S. 2,755,309 (July, 1956).

33. Robinson, Ralph L. U.S. 2,769,847 (November, 1956).

34. Runge, Von Franz, Bankowski, Otto, and Hoffmann, Gerhart Brennstoff - Chem., 34, (1953) 330.

35. Saletan, D. I., and White, R. R. Chem. Eng. Prog. Symp. Series No. 4, 48, (1952) 59.

36. Sherwood, Peter W. Pet. Engr., 28, (1956), C33.

37. Sliepcevich, C. M., and Brown, G. G. Chem. Eng. Progress, 46, (1950) 556.

38. Sliepcevich, C. M. Ph.D. Thesis, The University of Michigan (1947).

39. Smith, Carl D. U.S. 2,797,247 (June, 1957).

40. Stanley, H. M., Youell, J. E., and Dymock, J. B. J. Soc. Chem. Ind., 53, (1934) 205.

41. Sussmann, Sidney, Ind. Eng. Chem., 38, (1946) 1228.

42. Teter, John W., Gring, John L., and Hettinger, W. P., Jr. U.S. 2,830,090 (April, 1958).

43. Wegner, C.   U.S. 2,876,266 (March, 1959).

44. Young, David W.   U.S. 2,813,908 (November, 1957).