RATE OF HYDRATION OF PROPYLENE

by

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B.S., Massachusetts Institute of Technology
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for the degree of Master of Science
from the Massachusetts Institute of Technology
1940

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Signature of Author...

Department of Chemical Engineering, May 16, 1940

Signature of Professor
in Charge of Research...

Signature of Chairman of Department
Committee on Graduate Students.............................

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The Graduate House
Mass. Institute of Technology
Cambridge, Massachusetts
May 10, 1940

Professor George W. Swett
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge, Massachusetts

Dear Professor Swett,

In partial fulfillment of the requirements for the degree of Master of Science, I submit to you this report on an investigation of the rate of hydration of propylene by sulfuric acid.

Yours very truly,

William A. Merritt

Acknowledgment

The author wishes to express his appreciation for the guidance of Professor E. R. Gilliland during the conduction of this investigation.

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I. SUMMARY

The purpose of this thesis was to study the rate of hydration of propylene under flow conditions, using 60% sulfuric acid, moderate pressures, and temperatures around 100° C. The desirability of obtaining accurate data on this subject is due to the fact that the established method of producing isopropyl alcohol from absorption of propylene in approximately 80% sulfuric acid, dilution, and subsequent rectification of the acid ester involves the expense of reconcentrating the sulfuric acid and also the loss of a considerable amount of the acid in the reconcentrating process due to the oxidation of organic substances left in the dilute acid after rectification.

At ordinary pressures and temperatures the rate of absorption of propylene in 60% sulfuric acid is negligible, and temperatures above 100° C. cause oxidation by the acid and polymerization. If the weak acid is to be used, the only alternative is to employ pressure, in order to obtain reasonable reaction rate.

This thesis work was performed at moderate pressures, ranging from 100-250 lbs./sq.in. gage, and temperatures from 94-160° C. Sulfuric acid about 60% in strength was charged to a copper-lined pressure reactor, and propylene continuously recirculated through the reactor, the gas from the reactor being sent through a condenser, from which the condensed

alcohol ran into a trap. Make-up propylene was supplied from a gas holder, and the gas was recirculated via the compressor which kept pressure on the reactor. Samples for analysis could be taken from the reactor and from the condensate trap, and the rate of flow of propylene was measured by a flow-meter. Complete details of the apparatus may be found under PROCEDURE.

Four runs were obtained, the first two at 120 and 100 lbs./sq.in. gage respectively and about 100°C., and the third and fourth at 150 and 250 lbs./sq.in. gage and 160°C. The propylene flow rates for the four runs were respectively 9.50, 7.02, 4.76, and 6.03 cu.ft./hr. at S.T.P. In spite of the comparatively high rates of gas flow in the first and second runs, practically no vapor condensate could be obtained from the condenser trap, due to the fact that the operating temperatures were too low. The alcohol content of the acid in the reactor at the end of the first two runs was 23.1% and 19.1% respectively, and in each case considerable organic material was found as a separate layer floating on top of the acid layer, although at the higher temperatures of Runs III and IV more of the organic material was formed. In the last two runs the equilibrium alcohol content of the vapor from the reactor was 15.2% and 18.2% respectively, the slightly higher concentration for Run IV apparently being due to the higher operating pressure. The equilibrium alcohol concentrations of the acid in the reactor for Runs III and IV were 28.4% and 29.1% respectively, a substantial increase over the corresponding concentrations for Runs I and II, which were operated at lower pressures and temperatures.

At the higher temperatures of Runs III and IV a considerable condensate rate was obtained, being 56.0 and 64.0 cc. per 15 minutes respectively (at equilibrium). From the condensate rate data and the flow of propylene to the reactor, the molal ratio of alcohol to propylene in the vapor from the reactor could be calculated for Runs III and IV, and also the per cent conversion at the dynamic equilibrium conditions, dynamic equilibrium conditions being defined as when the rate of increase of alcohol concentration in the condensate and reactor acid approached zero. The per cent conversions so calculated for Runs III and IV were 9.4% and 10.1%. The theoretical % conversions at equilibrium for these conditions as calculated from equilibrium and fugacity data are 16.1% and 17.3%. In spite of the comparatively low vapor rates employed in these runs it seems remarkable that the time of contact attained between gas and acid was sufficient to enable the true equilibrium conditions to be approached so closely. The faster flow rate in Run IV must be responsible for the shorter time required to reach dynamic equilibrium conditions, the higher alcohol concentration attained at equilibrium apparently being due to the higher pressure.

From this data it seems that for commercial operation probably the most advisable operating conditions would be not less than 120°C. and about 150 lbs./sq.in. pressure. Increasing the pressure would not appreciably increase the alcohol concentration obtained, which would be about 15%. As opposed to the present process of diluting the acid ester mixture, rectifying, and reconcentrating the diluted acid, the operation would be carried out by rectifying the dilute alcohol produced to the concentrated form, and adding water at intervals to the acid to replenish that which has been evolved as alcohol and water vapor. At times the acid would have to be changed, after the accumulation of too much organic byproduct.

It is recommended that more data be obtained using 60% sulfuric and other pressures, temperatures, and flow rates.

II. INTRODUCTION

The problem of the utilization of synthetic petroleum gas is becoming increasingly important because of the great development of the vapor and liquid phase cracking inductries, due to the demand for high anti-knock fuels. Refineries are overburdened with large quantities of gas of high olefin content, which at the present time are being burned as fuel, in spite of the fact that they constitute a source of raw material for the preparation of very valuable chemical products.(6)

About 2,000,000 barrels of oil are cracked daily, producing over one billion cubic feet of gas of high olefin content. The predominant olefin is the lowest one in the series, ethylene, and a gas obtained as the result of a normal liquid phase cracking process contains 12-14% ethylene, while gas from vapor phase cracking contains 14-18% of that olefin. The propylene content is somewhat lower.(2) Typical analyees of the gas from liquid phase and gas phase cracking units are as follows:

	Liquid Phase Cracking (Cross)	Gas Phase Cracking (Gyro)
Methane and Hydrogen	46.3 %	35.4 %
Ethylene	1.2	22.9
Ethane	16.6	13.3
Propylene	5.3	18.1
Propane	16.2	0.0
Butenes and Butadiene	4.3	5.5
Butanes	6.1	1.4
Pentanes and heavier	4.0	3.4
	100.0 %	100.0 %

The composition of the olefin fraction of a gas representing roughly 50% of a typical vapor phase cracking gas is in the order of 55% ethylene and 30% propylene.

Thus the problem of utilizing this vast source of olefins is commanding much attention at the present time, and most of the work to date has been directed toward the production of alcohols by a hydration process.

The most successful process in commercial operation depends upon the absorption of the olefin gas in strong sulfuric acid, resulting in the formation of the alkyl ester, which is then hydrolyzed to yield the alcohol.(6) In more detail, the gas containing a mixture of ethylene, propylene, and other olefin and hydrocarbon vapors is first treated with caustic to remove traces of hydrogen sulfide, and then with sulfuric acid of specific gravity 1.6, at a temperature of 30° C., to remove other olefin material, permitting the propylene to pass unabsorbed. In a second treatment, the propylene is absorbed in sulfuric acid of specific gravity 1.8, at a slightly higher temperature, and the solution of isopropyl acidsulfate is allowed to build up. The mixture is then hydrolyzed with water, in which process partial conversion to the alcohol takes place, and the diluted solution is then rectified, completing the hydrolysis and yielding an overhead product of the constant-boiling mixture 91% isopropyl alcohol by volume. The process is usually run continuously, the diluted sulfuric acid being reconcentrated and used over again.

Many patents have been taken out relating to this process, and much experimental work done to effect improvements in the olefin absorption, such as the addition of mineral oil to the acid in order to stimulate absorption of the olefin prior to actual esterification, the use of catalysts in the sulfuric acid, and the use of higher temperatures and pressures in order to increase the rate of reaction.

The cost involved due to the necessity of reconcentrating the sulfuric acid makes the desirability of using a weaker sulfuric acid, such as 60%, apparent. Also, acid is lost in the reconcentrating process due to the oxidation of organic substances left in the dilute acid after rectification.

The rate of reaction with 60% sulfuric acid is negligible at ordinary temperatures and pressures, and temperatures greater than 100°C. tend to cause oxidation by the acid. Several proposals have been made to raise the pressure, however. Some actual data have been obtained by the Standard Oil Company of New Jersey in several pressure tests.(20) A gas containing 18-20% propylene was shaken in a bomb with 60% sulfuric acid at 400-600 lbs./sq.in. pressure and 80-100°C. In two hours the absorption amounted to 1.5-2.4 mols of propylene per mol of acid. In flow experiments, however, the results obtained were not nearly as satisfactory. A semi-plant tower about fifty feet high, designed to provide a long time of contact between gas and acid, when operated on a gas containing 18% propylene gave a reduction only to 10-15% in the gas issuing from the top. In another flow experiment, a one-plate column was constructed with a twenty-foot acid depth. At entering gas rates of 30 cu.ft./min., the propylene content fell from

18% to 15%, while at entering rates of 150 cu.ft./min. the propylene content fell to 10%, presumably due to the fact that at the high gas rate a large quantity of small bubbles was produced rather than a few large ones, thus providing better gas to acid contact. In other words, while excellent results were obtained in the case of the batch experiments, for some reason the absorption was not nearly as satisfactory in the flow experiments.

It was the purpose of C. Lewis' thesis(20) to obtain more data on the mechanism of absorption under pressure, using a batch reactor. He made one three-hour run at a temperature of 100°C., pressure 500 lbs./sq.in., and using 60% sulfuric acid and pure propylene gas. Besides the acid layer, which contained dissolved propylene, isopropyl alcohol, the easily hydrolyzable mono-sulfate and the difficultly hydrolyzable disulfate, Lewis obtained 60 cc. of a yellow liquid insoluble in the acid layer and floating upon it, constituting side reaction products due to oxidation and polymerization. Taking liquid samples periodically he found that at the end of two hours the concentration of total (free and combined as ester) alcohol leveled off at about two mols of alcohol per mol of acid, rising to 2.1 within the next hour. From a curve of concentration vs. time, which rose in practically a straight line for the first two hours, he concluded that the mechanism was not one of rapid formation of ester at the surface followed by diffusion through the liquid, that is, that the rate of absorption is proportional to the concentration at saturation minus the instantaneous concentration, since if this were the case the concentration vs. time curve would have fallen off gradually instead of rising in a straight line. Lewis concluded that as the alcohol content of the acid increased, the solubility of the propylene was maintained due to the solvent action of the alcohol.

As opposed to this process using strong sulfuric acid and involving the intermediate formation of the alkyl ester before the production of the alcohol, much work has been done on the direct catalytic hydration of propylene and ethylene using as catalysts activated metals and dilute mineral acids.

Klever and Glaser (19) reported that in the absence of acid at 150°C. and 190 atmospheres pressure only 0.00011 mols of ethylene per mol of water were hydrated after 17 hours, and at 200°C. and 100 atmospheres only 0.0008 mols reacted, while for the same length of time but in the presence of 1.93% HCl more than a mol of ethylene was hydrated per mol of acid. They also state that even with two or three % mineral acid the reaction rate is too slow to be of commercial importance.

Apparently the first patent (5) on this phase of the work was granted in 1924 claiming the production of alcohols when olefins were heated with water at 150 -250°C. under pressures from 20-200 atmospheres. The water should preferably be acidulated, and the reaction assisted by "surface action."

A patent granted to Johannsen and Gross (17) in this country in 1927 specified pressures above 20 atmospheres and temperatures above the boiling point of water. In an example in the body of the patent it is claimed that by heating 2.0 grams of ethylene with 10 cc. of 4.3% HCl at 220°C. a 63% yield of ethard was obtained. The use of hydrochloric acid, sulfuric acid, and phosphoric acid as catalysts is specified.

Considerable work has been done using as catalysts the salts of heavy metals having a slightly acid reaction, and many "activated" metals, including gold, silver, copper, iron, cobalt, nickel, chromium, tantalum, vanadium, molybdenum, manganese, and compounds of these such as the oxalates and carbonyls. Metal oxides have been used, such as the oxides of aluminum, thorium, tilanium, tungsten, and chromium.

The work of Swann, Snow, and Keyes,(31) in 1930, on the hydration of olefins in the liquid phase is one of the most complete in this field. Using pressures from 600-800 lbs./sq.in. at a temperature of 135°C., and employing a 5% HCl catalyst, they showed that the highest concentration of isopropyl alcohol obtainable in the liquid phase after one hour was 0.63% by weight.

Gunness(14) investigated the system ethylene, ethanol, water, in the temperature range 174-307°C. and pressure range 82-264 atmospheres. His object was to find an expression for the free energy of hydration of ethylene in the gas phase from the equilibrium data, employing the relation $\Delta F = -RT \ln K$. The equilibrium constant was calculated from vapor phase data at equilibrium, although had data been available on the activity coefficients of the reactants in the liquid phase, the liquid phase data might have been used, since both phases were in equilibrium. Gunness performed batch experiments, using a 3 mol % sulfuric acid solution as catalyst, maintaining constant total pressure during each run, and providing means of constant agitation of the gas and liquid phases. When the concentration of the liquid phase reached a constant value, a vapor sample was condensed and analyzed.

The thesis of Majewski(24) was directed toward obtaining expressions for free energy change in the hydration of propylene in both phases, and also data on the rate of reaction, the effect of temperature and pressure, and the nature of the side reactions occurring.

Working in a pressure range 95-503 atm. and a temperature range 160-360° C., and using dilute phosphoric acid catalysts, he studied the rate of reaction in the liquid phase by periodic sampling. The vapor at equilibrium was analyzed for isopropyl alcohol, isopropyl ether, water, and polymer. The principal constituents analyzed for in the liquid were isopropyl aocohol and dissolved propylene. His results showed that the concentration of alcohol in bothphases increased as the temperature decreased and the pressure increased. No normal propyl alcohol was found in the liquid phase. The range of alcohol concentrations obtained in the liquid phase are: at 205° C. and pressure range 95-503 atm., 110-201 gms./liter, while in the vicinity of 280° C. and the same pressure range, only 19.9-48.4 gms./liter.

Isopropyl ether, due to its high vapor pressure, was found entirely in the vapor phase, and results indicated that lower temperatures were more conducive to its formation. Below 210°C. no polymer was formed, but above this temperature it became a more predominant reaction product as the temperature was raised. At 240°C. over one hour was required for its appearance, while at 290°C. 35 cc. were formed in the same time. The effect of pressure was to increase the amount of polymer formed and also its distillation temperature. The densities and indices of the polymers were found to resemble those of long-chain unsaturated hydrocarbons or cyclics rather than complex alcohols or ethers.

At low temperatures a catalyst was found essantial, and it was believed that the reaction took place almost entirely in the liquid phase. At least six hours were normally required to reach equilibrium. At low temperatures, when side reactions such as oxidation and polymerization were negligible, dilute sulfuric and hydrochloric acids were substituted and gave the same equilibrium conditions as did the phosphoric acid. The two concentrations of phosphoric acid used, 7.7% and 12.1%, gave the same equilibrium conditions but the initial rate was twice as fast in the latter case. In no run was any evidence found of the acid alkyl ester in the liquid phase.

Majewski concluded that the effect of increasing the pressure was to increase the solubility of the propylene in its liquid phase and its concentration in the vapor phase, and the net conversion to alcohol. The conversion to isopropyl ether varied as the second power of the propylene concentration, and the conversion to polymer by some power of the propylene concentration greater than one. Temperature affected the equilibrium, the rate of reaction, and the nature of the side reactions. Increasing the temperature increased the polymer formation. The duration of the runs varied with the conditions of operation, about 20 hours being required to reach equilibrium at 165° C., while at 280° C. several hours were sufficient. In the liquid phase, the principal reaction was the formation of isopropyl alcohol, and no normal propyl alcohol was formed. At temperatures from 160-165° C. and pressures from 95-503 atmospheres about 20 hours were required to attain equilibrium, but 45-65% of the reaction took place in the first two hours, the reaction rate then falling off. At the higher pressures he observed a characteristic falling off of the alcohol concentration with time after 30 hours, explained by the formation of large amounts of side reaction products in the vapor phase which decreased the partial pressure of the propylene in the vapor and hence its solubility in the liquid, causing the decomposition of the alcohol already formed.

At the higher pressures the time required to attain a given liquid concentration was shorter and the maximum liquid concentrations were greater than at the lower pressures. At 200-210° C. the concentrations attained were not so high as at 160-165° C., but the reaction rates were so high that 95% of the equilibrium conversion was obtained in two hours, the time required to reach complete equilibrium being about 14 hours. In a comparison of the reaction rates produced by various catalysts, Majewski tried 12.1% and 7.7% phosphoric acid, 2.2% sulfuric acid, 1.5% hydrochloric acid, and pure water. The 12.1% phosphoric acid doubled the initial reaction rate but did not change the final equilibrium concentration attained by the 7.7% acid.

Research has not been confined entirely to ethylene and propylene, however. Marck and Flege (25) investigated the catalytic vapor phase hydration of 2-butene at 427-528°C. under conditions of continuous flow and pressures from 3000-5000 lbs./sq.in. They obtained only low yields of butanal, and concluded that as the molal ratio of steam to butene is increased the conversion to the alcohol increases and polymer formation decreases. Increasing the pressure from 3000 to 5000 lbs./sq.in. increased polymerization to a greater extent than hydration. They employed as catalysts phosphoric acid and cuprous chloride supported on pumice.

Stanley, Youell, and Dymock (30) have determined equations for constants for the hydration reactions of ethylene and propylene as functions of temperature. They employed a flow method at atmospheric pressure, working in the temperature range 150-250°C. and using acid phosphates containing manganese and boron as catalysts. Equilibrium was approached from both the synthesis and decomposition sides. The olefin gas was passed first through a wet test meter, then a saturator, which in the case of the synthesis experiments contained pure water, and in the decomposition runs contained

5% aqueous alcohol, and then through a heated tube into the catalyst tube, which was of pyrex and 600 cc. in volume. The gases issuing from the reactor were condensed by an ice and salt cooling medium, and the excess olefin gas measured in a wet test meter and analyzed in a Bone-Wheeler apparatus.

In the experiments with ethylene, gas rates varied from one liter per hour at 145°C. to 20 liters per hour at 250°C., over 500 cc. of the catalyst. Employing a mean value of the equilibrium constants obtained from the synthesis and decomposition runs, the equation derived for the constant as a function of temperature was, in the case of ethylene, $\log K_p = \frac{2100}{T} - 6.195$ where T is absolute Kelvin, and Kp is the ratio of the partial pressure of ethyl alcohol to the product of the partial pressures of water and ethylene at equilibrium. Since the equilibrium constant decreases with increasing temperature, the hydration reaction is exothermic, the heat of reaction at constant pressure being 9600 calories per mol. In the experiments with propylene, the gas rates varied from 4.0 to 8.9 liters per hour per 500 cc. of catalyst, and the equation derived was $\log K_p = \frac{1960}{T} - 6.060$. The corresponding heat of hydration is about 9000 calories per mol. The dilute aqueous solutions of isopropyl alcohol produced in these experiments were analyzed by the method of Cassar (Ind. Eng. Chem. 1927, <u>19</u>, 1061).

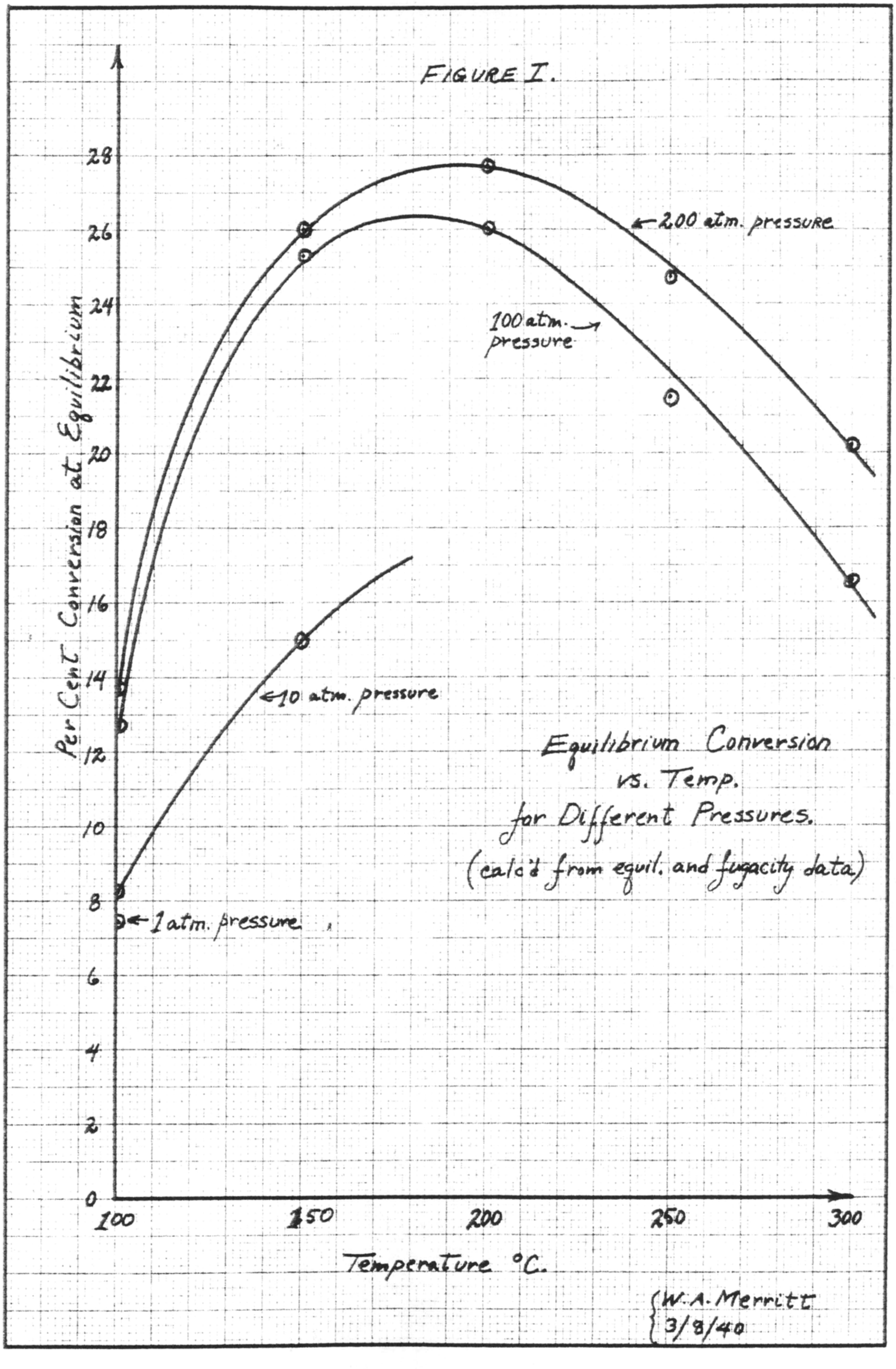
Quoting from an early paragraph in their article of July 1934 in the Journal of the Society of Chemical Industry:

> "With the exception of a few isolated determinations at somewhat elevated temperatures, little is known about the influence of temperature on the position of equilibrium in any of the reactions between olefin and water. This lack of data is no doubt primarily due to the fact that no really active catalysts have been found for the hydration of olefins, and accordingly it has so far not been possible to approach equilibrium except at high temperatures, where side reactions may become appreciable. In the course of a prolonged study of a large number of possible catalysts for the hydration of olefins, we have been fortunate in discovering active catalysts in the presence of which equilibrium may be approached at temperatures as low as 150°C."

The catalysts developed by them were acid phosphates containing manganese and boron, prepared by evaporating down manganese carbonate and boric anhydride in 2:1 molal ratio with a definite weight of phosphoric acid in excess water. The resulting solid was baked at 200-250°C., powdered, and pressed into tablets. The composition of this catalyst was represented by the formula MnO,BO,xH_3PO_4 where X varied between 2.4 and 3.6. For the experiments with ethylene at 145°C., the catalyst consisted of granules of pumice impregnated with 66% sulfuric acid containing about 5% silver sulfate.

Both from a commercial standpoint and as a logical sequence to what has been done previously, it seemed appropriate to study the rate of hydration of propylene in a flow process, at low pressures, using 60% sulfuric acid. Lewis(20) studied the mechanism of batch absorption of propylene in 60% sulfuric acid, but before this thesis no work had been done on the flow process at low pressures with the exception of the tower experiments of the Standard Oil Company of New Jersey. In this thesis the 60% acid was charged to a reactor, and propylene gas recirculated through the reactor via the compressor which maintained the pressure on the system. The vapor issuing from the reactor passed through a condenser, from which the condensed dilute alcohol ran into a trap and the excess olefin gas recycled, makeup propylene being supplied continuously from a gas holder which floated on the low pressure side of the system. The temperature of the reactor was controlled electrically, and the flow rate of the propylene measured by a flowmeter. Samples could be withdrawn from the reactor and condenser trap and analyzed for alcohol content. When the rate of increase of alcohol concentration in the reactor acid and condensed vapor became practically zero, dynamic equilibrium conditions were considered to have been reached, and from compositions and flow rates the per cent conversion of the propylene being sent through the reactor could be calculated and compared with the theoretical per cent conversion at equilibrium for the operating temperature and pressure as calculated from the

FIGURE I.



Equilibrium Conversion
vs. Temp.
for Different Pressures.
(calc'd from equil. and fugacity data)

W. A. Merritt
3/8/40

equilibrium data of Stanley, Youell, and Dymock(30) and the fugacity chart for hydrocarbon vapors. Figure I gives curves of theoretical per cent conversion at equilibrium versus temperature for different pressures, and it is apparent that for a given temperature increasing the total pressure increases the per cent conversion obtainable at equilibrium, but not by a great deal, particularly at the lower temperatures. The calculations involved in plotting the curves of Figure I are given in (A) of the APPENDIX. Since high temperatures are conducive to polymer formation, it was desirable to carry out this investigation at temperatures just high enough to provide a steady rate of alcohol evolution from the acid in the reactor.

III. PURPOSE

The purpose of this thesis is to provide some accurate data on the per cent conversion obtainable in a flow process for the production of isopropyl alcohol using 60% sulfuric acid, pressures from 100-250 lbs./sq.in., and temperatures from 100-150°C. As originally planned, the temperature was not to be carried above 100° C., but in order to obtain a steady evolution of alcohol from the acid in the reactor it was found necessary to raise the operating temperature to 160° C., with a corresponding increase in ~~polymer~~ byproduct formation.

It was planned to make a series of runs at different flow rates for each of several pressures, and compare the periods of time required to reach dynamic equilibrium, and also to compare the per cent conversions obtained at dynamic equilibrium with the theoretical per cent conversions at equilibrium for the given temperatures and pressures as read from the calculated curves of Figure I.

IV. PROCEDURE

Description of Apparatus: The apparatus is shown diagrammatically in Figure II. Details of the apparatus are given in (F) of the APPENDIX.

Essentially the apparatus consisted of a closed system, propylene being recirculated through the acid in the reactor via the compressor which held pressure on the system, and make-up propylene being supplied from a storage bottle maintained under a head of water on the low pressure side of the system.

Samples of the acid from the reactor could be withdrawn for analysis, and samples of the condensed vapor from the reactor could be withdrawn from the trap beneath the condensor.

Operating Technique: Before starting a run the acid was charged to the reactor, and the reactor slowly brought up to temperature. The quantity of acid charged was 120-150 cc., and it was introduced through the sampling valve at the bottom of the reactor by means of a funnel which served as a level indicator. The time required to bring the reactor up to temperature was usually about fifteen minutes. The control valve was then closed and propylene flushed through the system by allowing a slight pressure to build up and discharging the air-propylene mixture through the liquid sampling valve at the bottom of the trap. After several minutes of flushing it was considered that at least eighty per cent of the air had been expelled and the run was started.

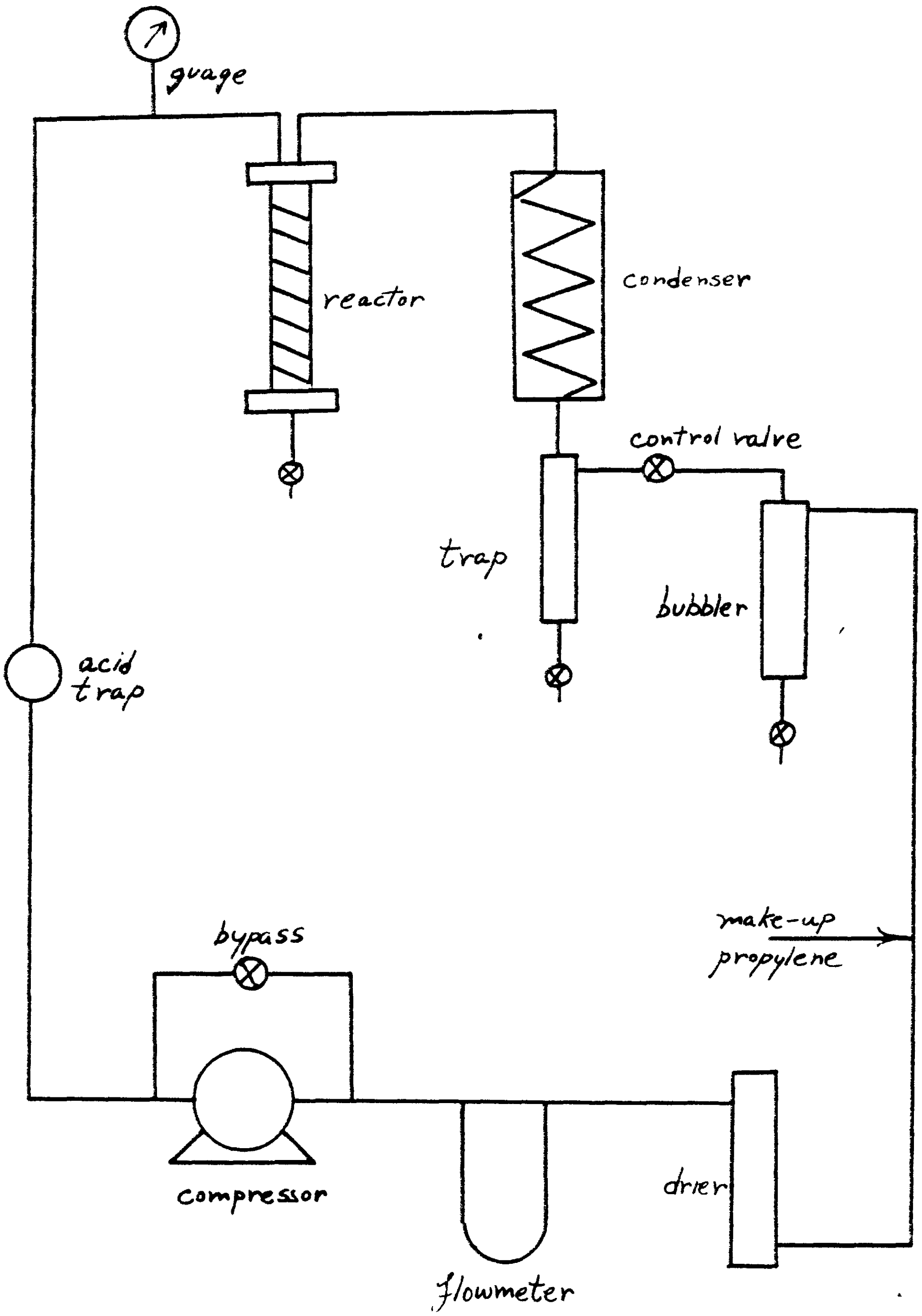
After the pressure had built up almost to the desired operating pressure, the control valve was cracked and care was taken not to permit the static pressure as indicated by the flowmeter static pressure gauge to rise above the mercury equivalent of the four-foot water head on the supply of propylene. A satisfactory flow rate was normally obtained without building up too great a static pressure on the low pressure side of the system. By regulating a bypass valve on the compressor in conjunction with the pressure control valve the flow rate could be varied independently of the pressure on the reactor.

The propylene in the supply bottle was replenished periodically, and at times it was found convenient to leave the cylinder valve cracked and continually bubble propylene into the storage bottle rather than fill it at intervals.

Samples were taken about every hour from the reactor and condenser trap, and occasional samples from the bubbler, although this was given up after it was apparent that the acid and alcohol concentrations were negligible. The acid and condensed vapor samples were analyzed for alcohol by the Pomndorf method of analysis as modified by Gunness (see Appendix), the acid samples being diluted with twice their volume of water and hydrolyzed by refluxing

FIGURE II

DIAGRAM OF APPARATUS

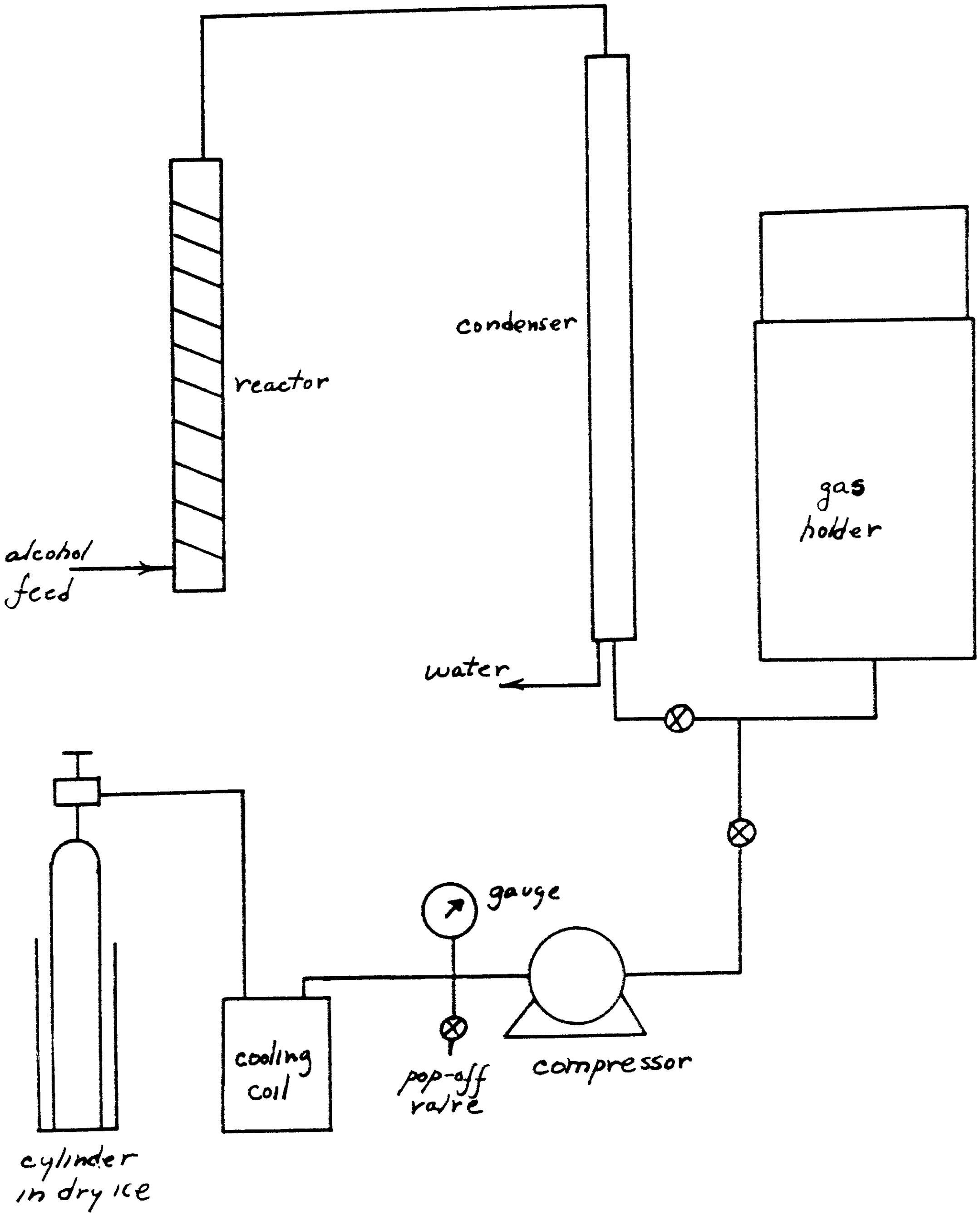


before being analyzed. Dynamic equilibrium conditions were considered reached when the alcohol content of the condensed vapor from the reactor failed to rise appreciably over a period of one-half hour. The rate of production of alcohol at dynamic equilibrium was found by allowing the condensate to accumulate for 15 minutes at the end of the run. The motor was then stopped, the pressure released from the system, and the acid in the reactor withdrawn and examined for polymer. The volume of acid and polymer were noted. During the run, normally about two times per run, the water in the reactor was replenished, and an attempt was made to keep the concentration of the acid at about 60%. The pressure was released each time this occurred and the make-up water introduced through the sampling valve at the bottom of the reactor.

Propylene Generator. Figure III is a diagrammatic sketch of the apparatus used to produce and liquefy the propylene used in the runs. The reactor contained alumina, and the propylene was produced by introducing liquid isopropyl alcohol (91%) at the bottom of the heated reactor and allowin g it to be dehydrated, the propylene-water vapor mixture being passed through a condenser which condensed out the water, the propylene being stored in a gas holder. The temperature of the catalyst was maintained at 300-350°C., and it was separated from the iron wall of the reactor by

FIGURE III

PROPYLENE GENERATOR



a layer of asbestos, since contact of the gas with the metal promotes polymerization of the propylene. The capacity of the gas holder was 35-40 cu.ft., and since this represents about 4.2 lbs. of propylene one full gas holder was considered sufficient for the runs, particularly in view of the fact that several pounds were already available in a discarded cylinder.

The propylene was liquefied in a high pressure cylinder, by combined compression and cooling. The cooling medium was dry ice in gasoline, and the compressor used during the runs was used to keep pressure on the sylinder. The gas was fed from the holder through calcium chloride drying tubes, then through the compressor, and before entering the cylinder it was cooled partially by passing through a coil immersed in an ice-salt bath. At the temperature attained by the dry ice the vapor pressure of the liquid propylene is about 40-50 lbs./sq.in., so when the pressure would slowly rise to about 80 lbs./sq.in. it was apparent that air was being compressed and by means of a pop-off valve the air and other inerts were periodically removed during the liquefaction. When the gas holder was emptied the cylinder was allowed to come up to room temperature, during which time the pressure of the propylene rose to about 180 lbs./sq.in., the existing vapor pressure. The cylinder was then connected to the five-gallon bottle as described above.

V. RESULTS

The results of this thesis are presented in the following table and Figures IV, V, VI, and VII, which are plots of alcohol concentration vs. time for the four runs.

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	RUN I	RUN II	RUN III	RUN IV
Pressure (lbs./sq.in.gage)	120	100	150	250
Flow rate (cu.ft./hr.at S.T.P.)	9.50	7.02	4.76	6.03
Temperature of reactor (°F.)	200	220	320	320
(°C.)	94	106	160	160
Per cent sulfuric acid used	60	60	60	60
Time required to reach equilibrium (hrs.)	5.00	4.67	5.75	4.17
Alcohol concentration in condensed vapor at equilibrium (wgt. %)	--	--	15.2	18.2
Alcohol concentration in reactor acid at equilibrium (wgt.%) (excluding organic layer)	23.1	19.1	28.4	29.1
Alcohol production at equilibrium (mg./hr.)	--	--	34000	46200
(mmols/hr.)	--	--	568	771
Propylene flow rate (mmols/hr.)	--	--	6020	7630
Molal ratio $\left(\frac{\text{alcohol}}{\text{propylene}}\right)$ in vapor from reactor at equilibrium	--	--	0.104	0.112
Per cent conversion at equilibrium	--	--	9.40	10.13
Theoretical per cent conversion at equilibrium calculated from equilibrium and fugacity date	--	--	16.1	17.3

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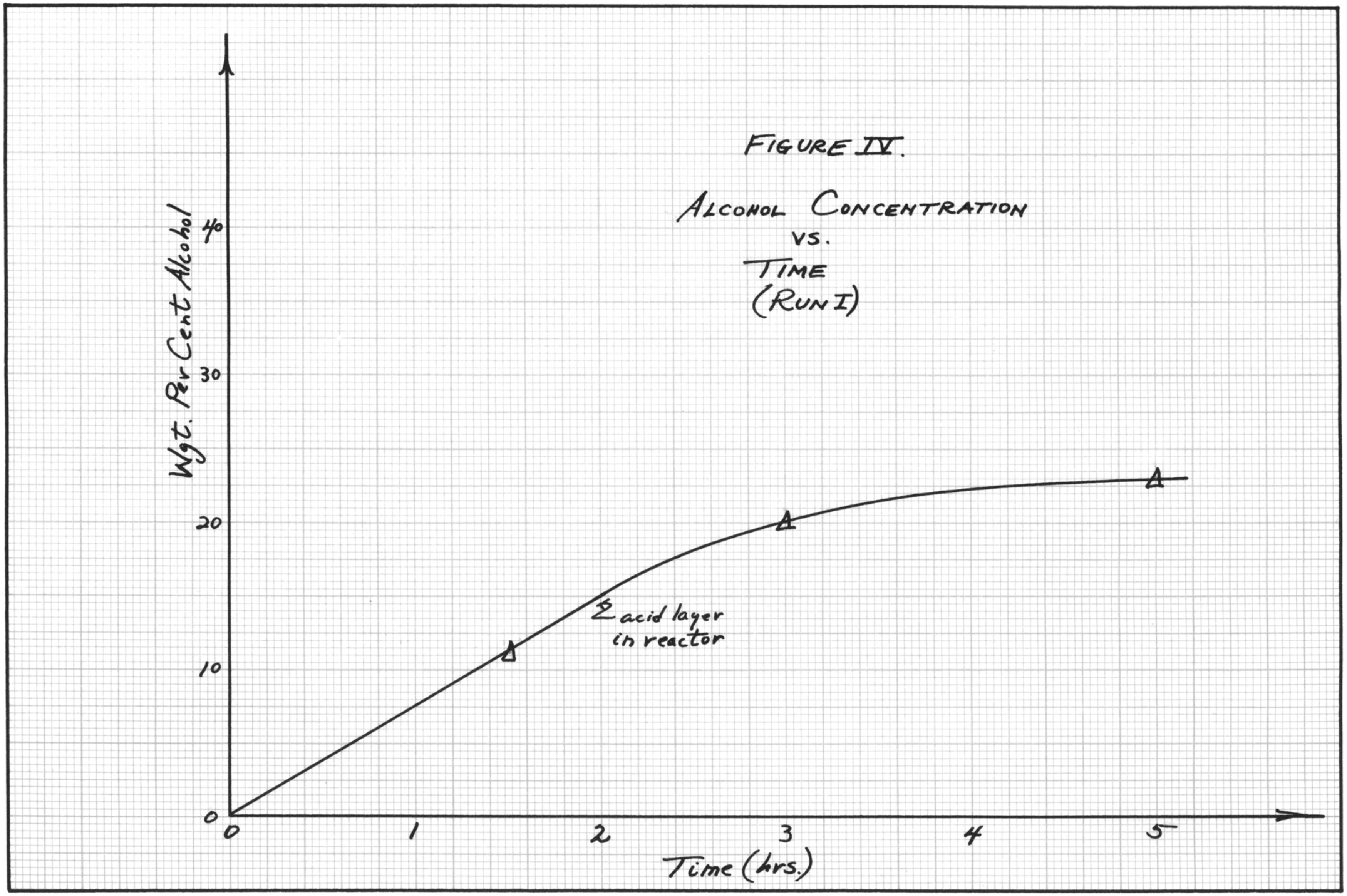

FIGURE IV.

ALCOHOL CONCENTRATION
VS.
TIME
(RUN I)

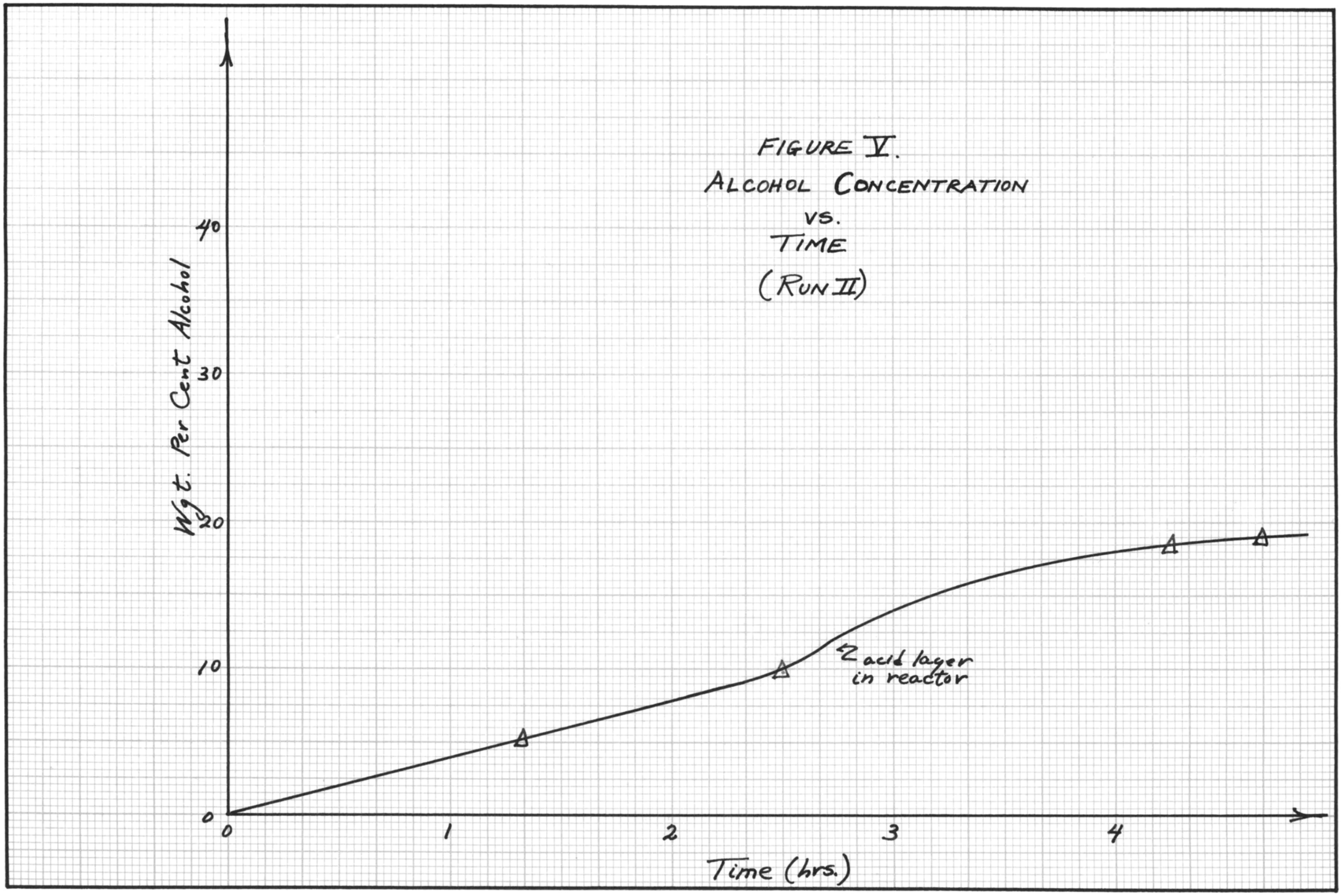

FIGURE V.
ALCOHOL CONCENTRATION
VS.
TIME
(RUN II)

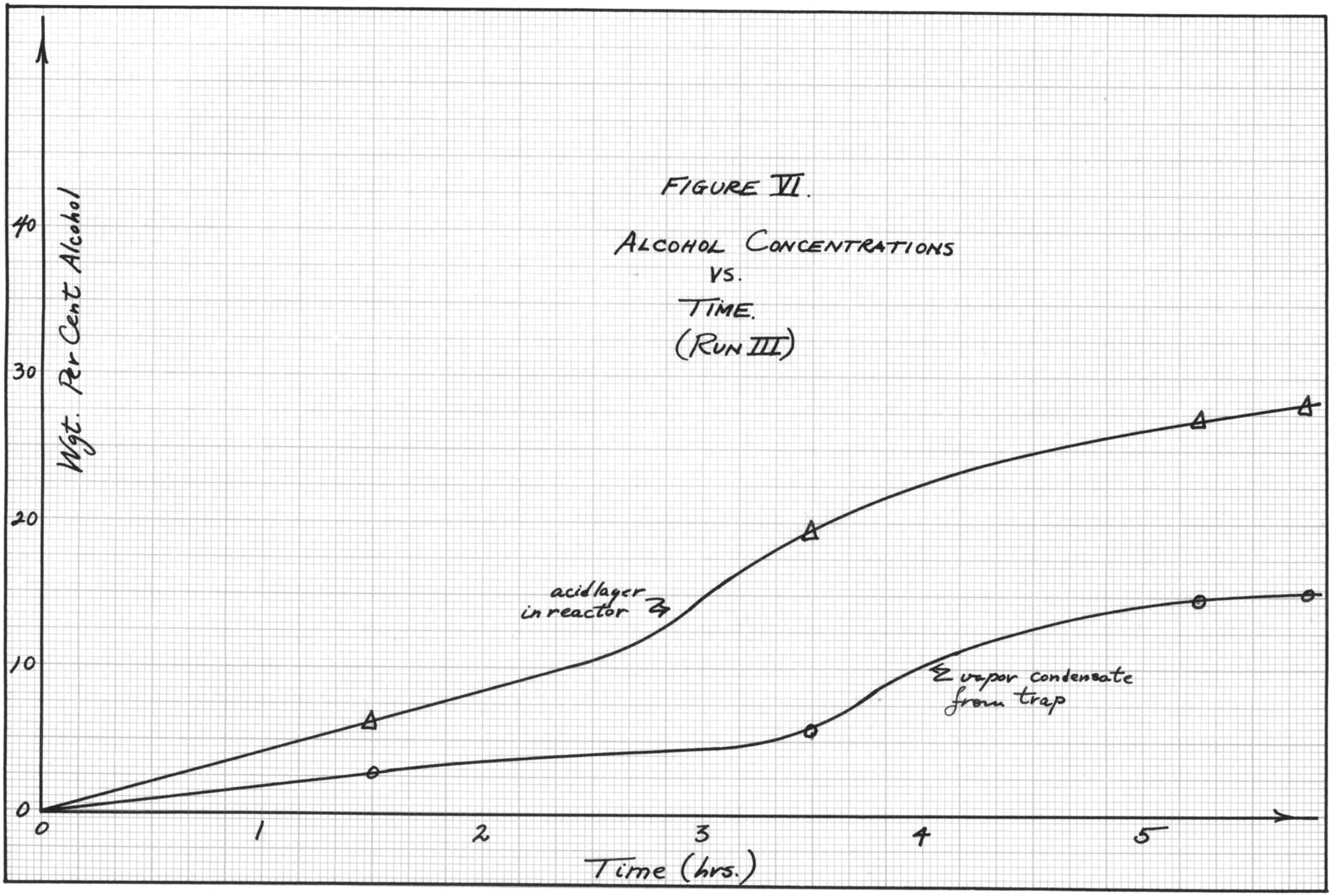

FIGURE VI.

ALCOHOL CONCENTRATIONS VS. TIME. (RUN III)

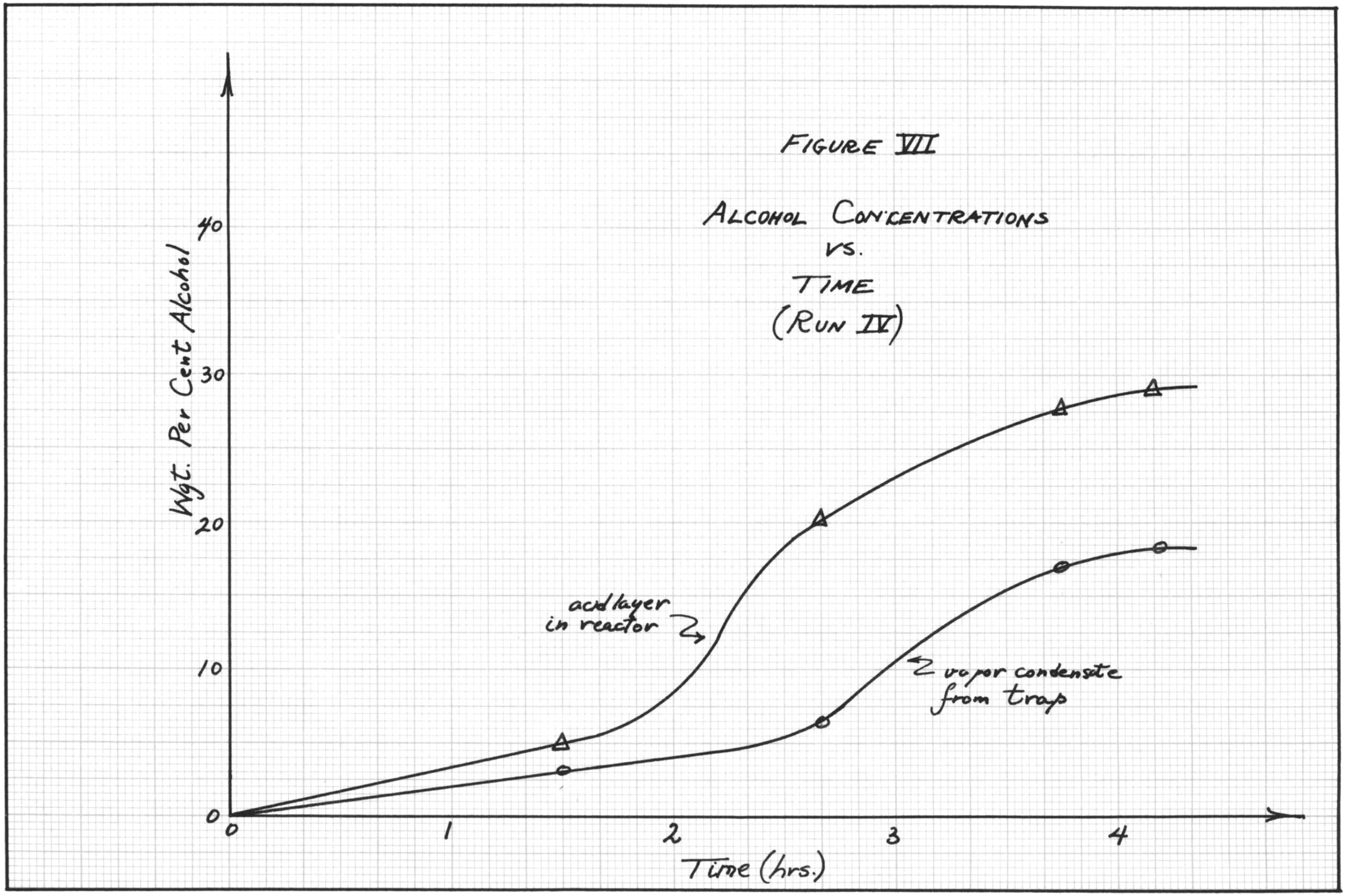

FIGURE VII

ALCOHOL CONCENTRATIONS
VS.
TIME
(RUN IV)

VI. DISCUSSION OF RESULTS

The most important single conclusion that can be drawn from the results of this thesis is that the conversion of propylene to isopropyl alcohol obtainable in a flow process employing 60% sulfuric acid at temperatures from 100-160° C., pressures from 100-250 lbs./sq.in., and the flow rates employed is a substantial proportion of the theoretically possible conversion at equilibrium.

No figures for per cent conversion could be calculated in Runs I and II due to the fact that steady evolution of alcohol from the reactor acid could not be obtained at the operating temperatures of 94° and 106°C. In Runs III and IV, however, operating at temperatures of 160°C., the per cent conversions obtained were 9.4% and 10.1% vs. the theoretical conversions of 16.1% and 17.3% respectively, indicating that conversions definitely in the range of those theoretically possible can be attained. Furthermore, from an inspection of the curves for Runs III and IV (Figures VI and VII) it is apparent that the alcohol concentration curves might have risen a few per cent higher in each case before becoming absolutely horizontal, that is, dynamic equilibrium might not have quite been completely reached.

The data of Runs III and IV. indicate that at higher pressures, 250 lbs./sq.in. as compared with 150 lbs./sq.in., the per cent conversion obtainable at dynamic equilibrium is slightly higher than at lower pressures. Runs III and IV were both run at the same temperature, 160 C., but the alcohol concentrations obtained in the condensed vapor from the reactor in the two cases, 15.2% and 18.2% were 3.0% apart, or a per cent difference of about 20%. In Run IV the alcohol concentration obtained in the reactor acid was also slightly higher than in Run III, the per cents being 29.1 and 28.4 respectively. The effect of flow rate is also brought out in Runs IIIand IV. The flow of propylene in Run III was 4.76 cu.ft./hr. as compared with 6.03 cu.ft./hr. in Run IV, and in the latter case equilibrium conditions were reached in 4.17 hrs. compared with 5.75 hrs. in Run III, shortening the time required at 27.5% for a 26.8% increase in the rate of gas flow. Also, the volumetric production of alcohol at equilibrium is higher at the higher velocity of Run IV than in Run II.

Comparing Runs III and IV with Runs I and II, it is apparent that increasing the pressure increases the alcohol concentration in the reactor acid at equilibrium, since for the four runs at pressures of 120, 100, 150, and 250 lbs./sq.in. respectively, the alcohol concentrations in the acid at equilibrium were respectively 23.1%, 19.1%, 28.4%, and 29.1%. It is interesting to compare the slope of the acid concentration curves for the four runs with the curve obtained by Clay Lewis(20) in the batch run with

60% sulfuric. Lewis made one three-hour batch run at 100°C. and 500 lbs./sq.in. pressure, using 60% sulfuric acid and pure propylene gas. By analyzing liquid samples from his reactor at intervals he was able to construct a curve of alcohol concentration (both free and combined as acid ester) versus time, which enabled him to study the mechanism of batch absorption. He plotted his data as mols alcohol per mol acid versus time, and the fact that his curve rose in a straight line for two hours led him to believe that the rate of absorption did not depend purely upon the difference between the instantaneous and saturation concentrations of alcohol in the acid, since in that case the rate of absorption would have fallen off with time. His conclusion was that the rate of absorption was maintained by the solvent action of the alcohol already formed. His data have been replotted in Figure VIII as per cent alcohol by weight in the reactor acid vs. time, and it is apparent that the straight line character of the curve is still retained.

Comparing this curve with Figures IV, V, VI, and VII it is seen that the curve for Run I is the only one which may be said to reproduce the general shape of Lewis' curve, and even in this case the per cent concentrations at all points are lower. In this respect all four runs are similar, for in no case do the maximum alcohol concentrations rise above thirty per cent, whereas Lewis' alcohol concentration leveled off at about 50%. This high per cent is undoubtedly due to the high pressure of 500 lbs./sq.in. which he employed, since the data of Runs III and IV clearly indicate this effect of increasing the pressure. The general shape of the curves for Runs II, III, and IV is to follow a straight line for a certain length of time and then rise to a greater slope before finally levelling off to the horizontal. This can be accounted for by Lewis' explanation that the solvent action of the alcohol already formed serves to increase the rate of propylene absorption.

Comparing the relative shapes of the vapor and acid concentration curves for Runs III and IV, it is apparent that in each case as the rate of increase in alcohol concentration in the acid begins to fall off the rate picks up in the vapor phase. This would seem to indicate that generally speaking the mechanism of the flow absorption of propylene in sulfuric acid is that the alcohol concentration in the acid continues to build up until a saturation value is reached corresponding to the operating pressure and temperature, and from then on alcohol is evolved from the acid as fast as it is formed, the distribution between alcohol, water vapor and propylene in the vapor leaving the reactor being dictated by the equilibrium constant for that temperature, the pressure, and the rate of gas flow. Until the acid is saturated the tendency is for the alcohol formed to remain in the acid rather than be evolved. It should be noted that in the case of the curves for alcohol concentration in the condensed vapor samples there is a

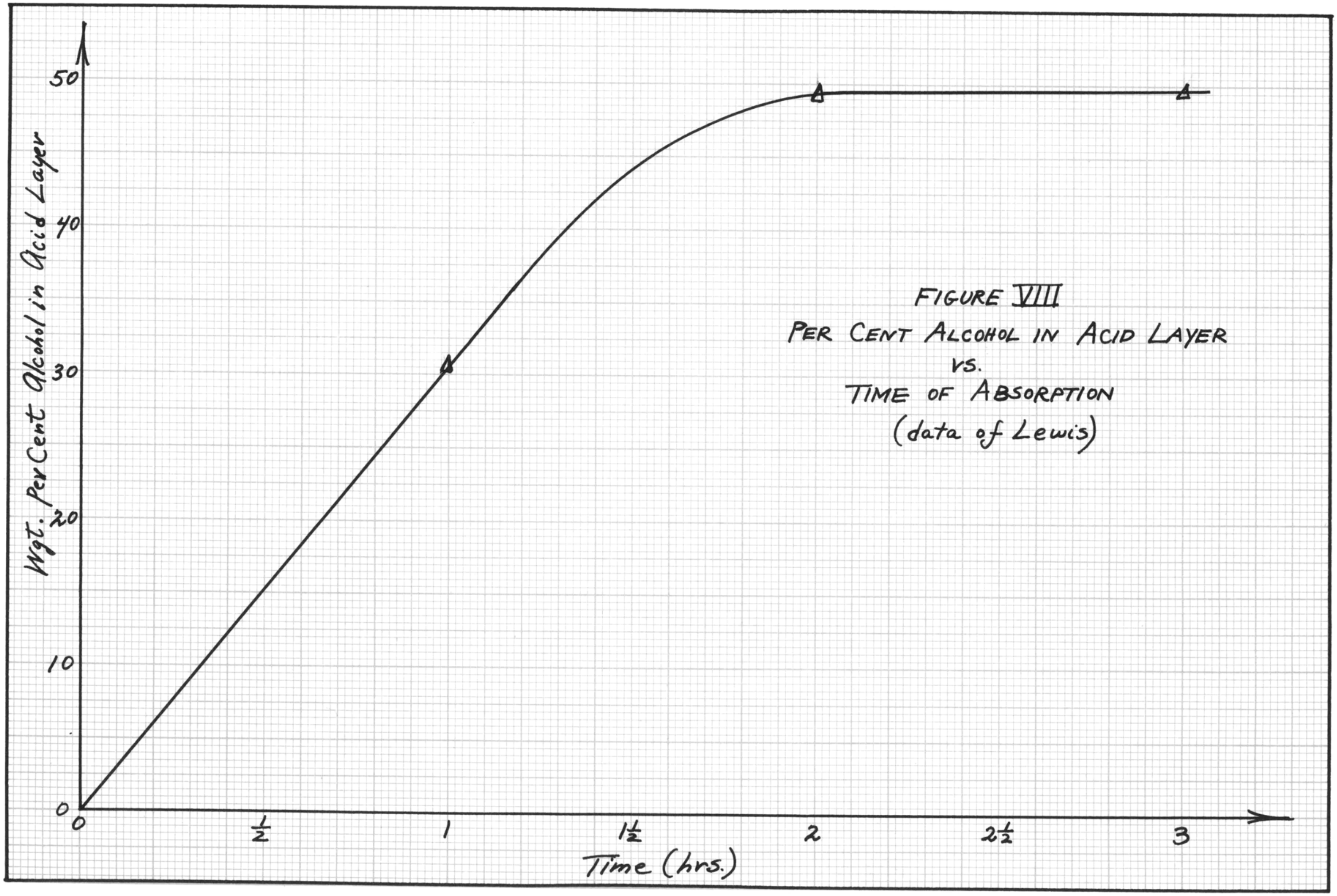

FIGURE VIII
PER CENT ALCOHOL IN ACID LAYER
VS.
TIME OF ABSORPTION
(data of Lewis)

lag involved, that is, the true instantaneous alcohol concentrations are somewhat greater than the curves would indicate due to the fact that the condensate samples analyzed actually represent an accumulation over a period of time.

The formation of organic byproducts was observed in all of the runs. In Runs III and IV byproduct formation was greater than in Runs I and II, due to the higher temperature and pressures employed, although temperature probably is the controlling factor. In Runs III and IV about 60 cc. of byproduct were found floating on the surface of 50 cc. of acid, while in Runs I and II the organic material formed was only about 60% of the acid present. Samples of the organic layer were analyzed in a Babcock-Wilcox bottle, using first a 10% salt solution to extract the alcohol, and then, using a fresh sample of polymer, 85% phosphoric acid was used to extract the ether. The results of these analyses indicated that the polymer contained about 3% alcohol and 80% ether. Evidences of other side reactions observed during the runs are the formation of cuprous oxide, which settled out as a red powder in the samples of condensed vapor taken from the trap, the formation of cupric sulfate in the reactor, and traces of sulfur dioxide in the gas stream. Blackening of the copper lining in the reactor and of the acid at the end of each run was caused by cupric oxide. Apparently the copper lining will be oxidized by the hot 60% sulfuric acid if any air is present in the system.

If no air at all is present there should be no oxidation of the copper by the acid, as can be shown experimentally by keeping a strip of copper wire submerged in hot 60% sulfuric acid over a period of time.

As a commercial process this flow method of making isopropyl alcohol by absorption in 60% sulfuric acid would seem quite feasible, provided too high temperatures would not have to be used to promote evolution of the alcohol from the acid. If this were the case losses would be incurred due to polymerization and oxidation. Neglecting loss of acid due to deterioration, the major cost involved in the flow process would be the rectification of the dilute (10%) alcohol-water mixture evolved from the reactor, while in the established method of making the alcohol not only is the cost of rectification involved but also the cost of reconcentrating the sulfuric acid up to the requisite strength. In the flow process the acid would remain in the contact chamber continually, water being added at intervals to replace that which was evolved as alcohol.

In view of the comparatively meagre data obtained in this thesis it would seem advisable that more work be done along the same lines. More data could be obtained at the operating pressures of this thesis but using other rates of flow, and investigations should be made of the minimum temperatures at each flow rate necessary to produce steady evolution of alcohol. In order to reduce the side reactions to ether formation alone work should be carried out in systems as completely free of air as possible. If it proves impracticable to remove all the air from the system, runs might be made in glass-lined reactors.

VII. CONCLUSIONS

From the results of this thesis it is concluded that:

(1) Alcohol concentrations approaching those theoretically obtainable at equilibrium can be attained in a reasonably short time in the production of isopropyl alcohol using 60% sulfuric acid in a flow process.

(2) The optimum conditions of operation are 100-160°C. and 150-250 lbs./sq.in. pressure, using propylene flow rates of about 10.0 cu.ft./hr. per sq.in. of acid surface in the contact chamber.

(3) Under these conditions alcohol concentrations from 15-18% may be expected within 4-5 hours in the condensate from the vapor evolved from the acid in the reactor.

(4) At temperatures much above 100°C. the formation of organic byproducts becomes appreciable.

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VIII. RECOMMENDATIONS

It is recommended that:

(1) More data be obtained on organic byproduct formation, maximum alcohol concentrations obtainable, and the time required to reach dynamic equilibrium under varying conditions of temperature, pressure, and rates of gas flow.

(2) In particular, runs be made at 100°C. at faster gas rates than those employed in Runs I and II of this thesis, to see if any improvement is effected in the evolution of alcohol from the reactor at this temperature.

IX. APPENDIX

A. Calculation of Theoretical Per Cent Conversion at Equilibrium vs. Temperature for Different Pressures

The equation of Stanley, Youell, and Dymock(30) is used to solve for K_p at a given temperature. Then, using the fugacity chart for hydrocarbon vapors and the fugacities for saturated water as calculated by Gunness(14) from data given in Keenan and Keyes Steam Tables(18), the per cent conversion obtainable at that temperature and a given pressure may be calculated.

As an example, consider $P = 100$ atmospheres and temp. $= 250^{\circ}C$.

$$\log_{10} = K_p = \frac{1950}{T} - 6.060$$

$$T = 250 + 273 = 523$$

$$\log_{10} K_p = 3.725 - 6.060 = -2.335$$

$$K_p = \underline{0.00463}$$

$$K_p = \frac{\left(\frac{f\pi}{\pi}\cdot\pi\right)_{alc} y_{alc}}{\left(\frac{f\pi}{\pi}\cdot\pi\right)_{wat} y_{wat} \left(\frac{f\pi}{\pi}\cdot\pi\right)_{prop} y_{prop}}$$

$$= \frac{\left(\frac{f\pi}{\pi}\cdot\pi\right)_{alc} y_{alc}}{(\alpha f_P X)_{wat} \left(\frac{f\pi}{\pi}\cdot\pi\right)_{prop} y_{prop}}$$

$$= \frac{(f\pi)_{alc}\, y_{alc}}{(f_P)_{wat}\, (f\pi)_{prop}\, y_{prop}}$$

$$\text{whence, } \frac{y_{alc}}{y_{prop}} = \frac{K_p (f\pi)_{prop} (f_P)_{wat}}{(f\pi)_{alc}}$$

$(T_R)_{alc} = \frac{523}{508} = 1.04$, $(P_R)_{alc} = \frac{100}{53} = 1.88$, whence

$\frac{f\pi}{\pi} = 0.46$ and $f\pi = 46$ atm.(22)

$$(T_R)_{prop} = \frac{523}{365.3} = 1.44\ , \ (P_R)_{prop} = \frac{100}{45.0} = 2.22,$$

whence $\frac{f\pi}{\pi} = 0.81$, $f\pi = 81$ atm.$^{(22)}$

$(f_P)_{wat}$ at 250°C. = 33.4 atm. $^{(14)}$

$$\frac{y_{alc}}{y_{prop}} = \frac{0.00463 \times 81 \times 33.4}{46} = 0.271 = R$$

$$\% \text{ conversion} = \frac{\frac{y_{alc}}{y_{prop}}}{1 + \frac{y_{alc}}{y_{prop}}} \times 100 = \frac{y_{alc}}{y_{prop} + y_{alc}} \times 100 = \frac{R}{1+R} \times 100$$

$$= \frac{0.271}{1.271} \times 100 = \underline{21.4}\ \%$$

B. Calibration Plots and Calculations therefor

Data for flowmeter calibration (wet test meter):

temp. of air to flowmeter	static pressure	flowmeter differential	cu.ft./hr. at inlet conditions
70°F., saturated with water vapor.	0.28 in.Hg.	0.24 in.Hg.	4.15
	0.51	0.42	5.65
(70°F.=21.2°C.)	0.83	0.69	7.65
	0.88	0.74	8.12
	1.21	0.97	9.4
	1.53	1.24	10.8
	1.98	1.64	12.4

These data are plotted on semilogarithmic paper as feet of fluid flowing vs. volumetric rate of discharge at S.T.P. As an example in converting the test data, consider the first set at $\Delta h = 0.24$ in. Hg:

p.p. water at 70°F. = 0.74 in.Hg.

barom. = 29.90 in.Hg.

static pressure = 0.28 in.Hg.

total pressure on gas to flowmeter = 30.18 in.Hg.

to find the density of the gas, its molecular weight is first calculated:

$$\% \text{ water} = \frac{0.74}{30.18} \times 100 = 2.45$$

$$\% \text{ air (dry)} = 97.55$$

$$(.0245 \times 18) + (.9755 \times 28.9) = 28.5 = \text{M.W.}$$

Let x = density of the saturated air in gm./cc.

then $\left(\frac{30.18}{29.92}\right)(1) = \left(\frac{x}{28.5}\right)(82)(294)$

whence x = 0.00120 gm./cc.

density of mercury = 13.6 gm./cc.

hence h as feet of fluid flowing (i.e., feet of saturated air)

$$= \left(\frac{0.24}{12}\right)\left(\frac{13.6}{0.00120}\right) = 227 \text{ ft.}$$

volumetric rate of discharge at S.T.P. (1 atm., 32°F.):

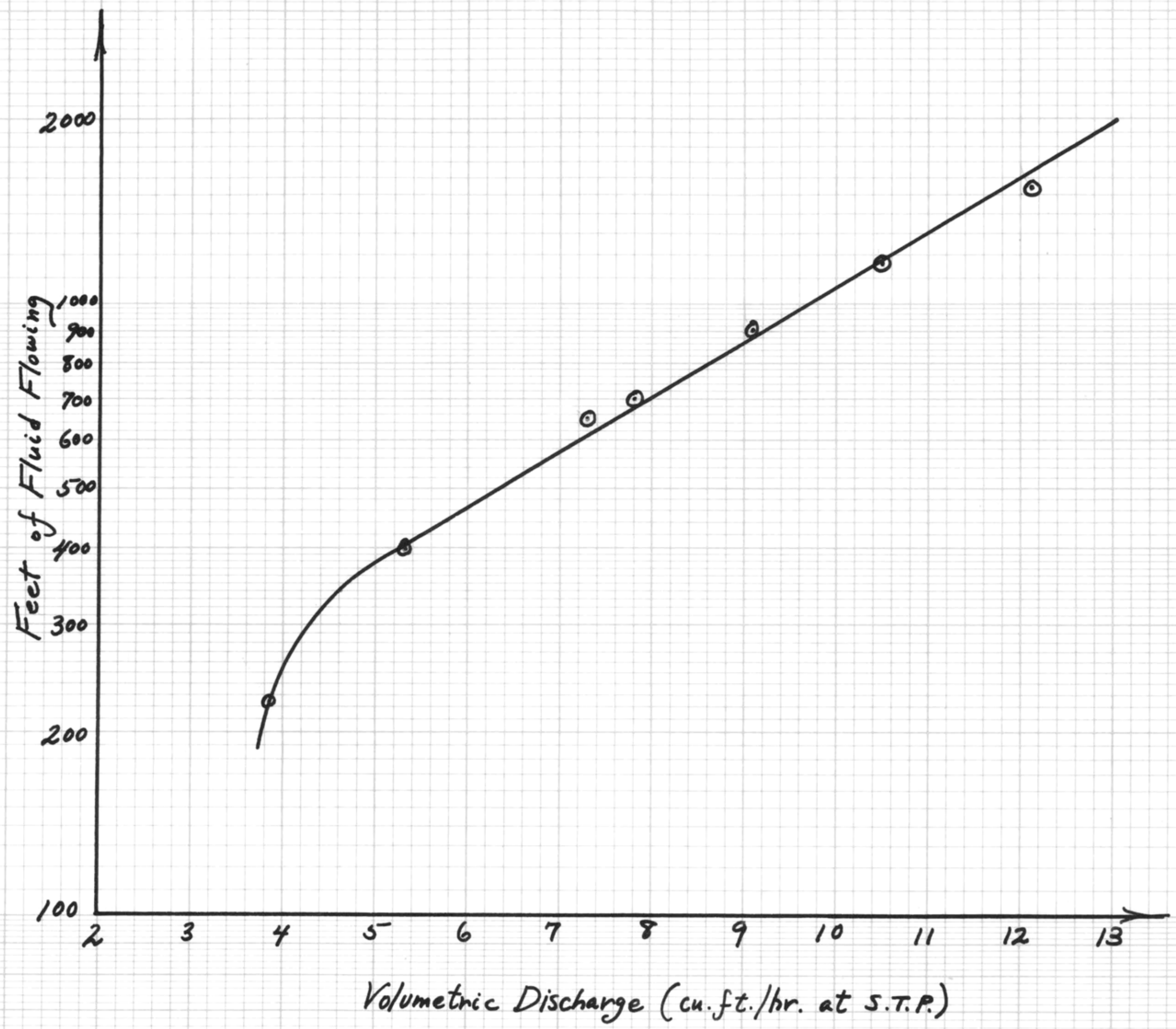
$$(4.15)\left(\frac{273}{294}\right)\left(\frac{30.18}{29.92}\right) = 3.90 \text{ cu.ft./hr.}$$

The other six points are calculated in this manner and the calibration plot (Figure IX) drawn. With the exception of the first two points, at low discharge rates, the other points lie along a fairly straight line of slope about 0.53. That is, for the capillary tubing used the flow rate is proportional to the 0.53 power of the differential pressure.

The calibration plot constructed in this way can be used for any fluid being metered (See Sample Calculations).

FIGURE IX

FLOWMETER CALIBRATION PLOT



Thermocouple Calibration: The calibration of the copper-constantan thermocouple was done using the steam point and the naphthalene point, the cold junction being maintained at 0°C. by ice water in a thermos bottle. These two points provided sufficient calibration over the temperature range at which the runs were being made.

Data

point	corrected temperature	mv.obs'd	stand.mv.	deviation
steam	100.10°C.	3.975	4.280	-0.305 mv.
naphthalene	218.26	9.680	10.265	-0.585

The temperatures corrected for barometric pressure, which was 76.27 cm.Hg., were calculated from the equations:

$$\text{steam: } t_p = 1000.000 \quad 0.03686(p-760) - 0.0000202(p-760)^2$$

$$\text{naphthalene: } t_p = 217.96 \quad 0.207(t_p \quad 273.1)\log_{10} \frac{p}{760}$$

A calibration plot, Figure X, and a deviation plot, Figure XI, were constructed for the thermocouple.

As explained under PROCEDURE, a 400°F. thermometer was used more often than the thermocouple during the runs.

FIGURE X

THERMOCOUPLE CALIBRATION PLOT

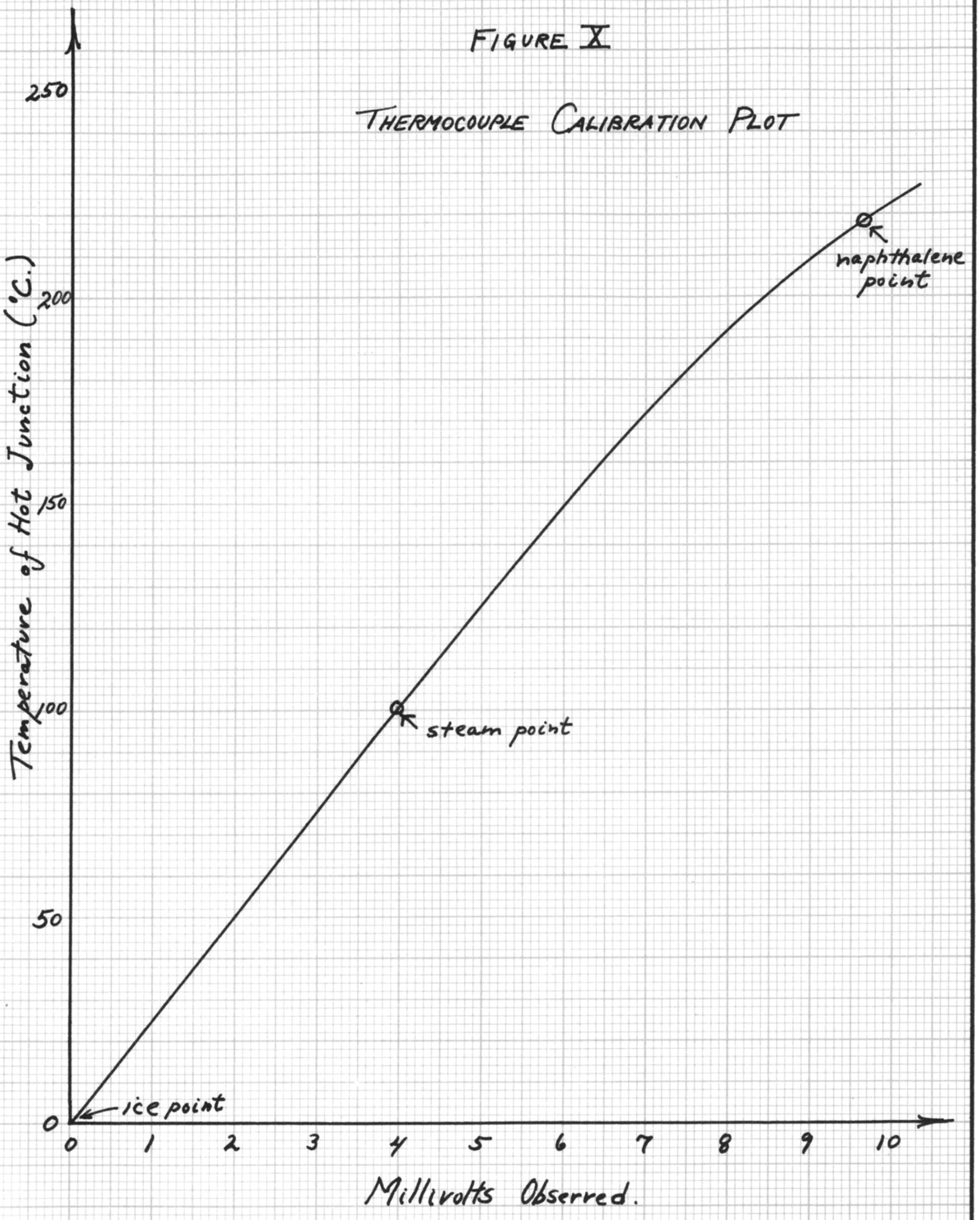
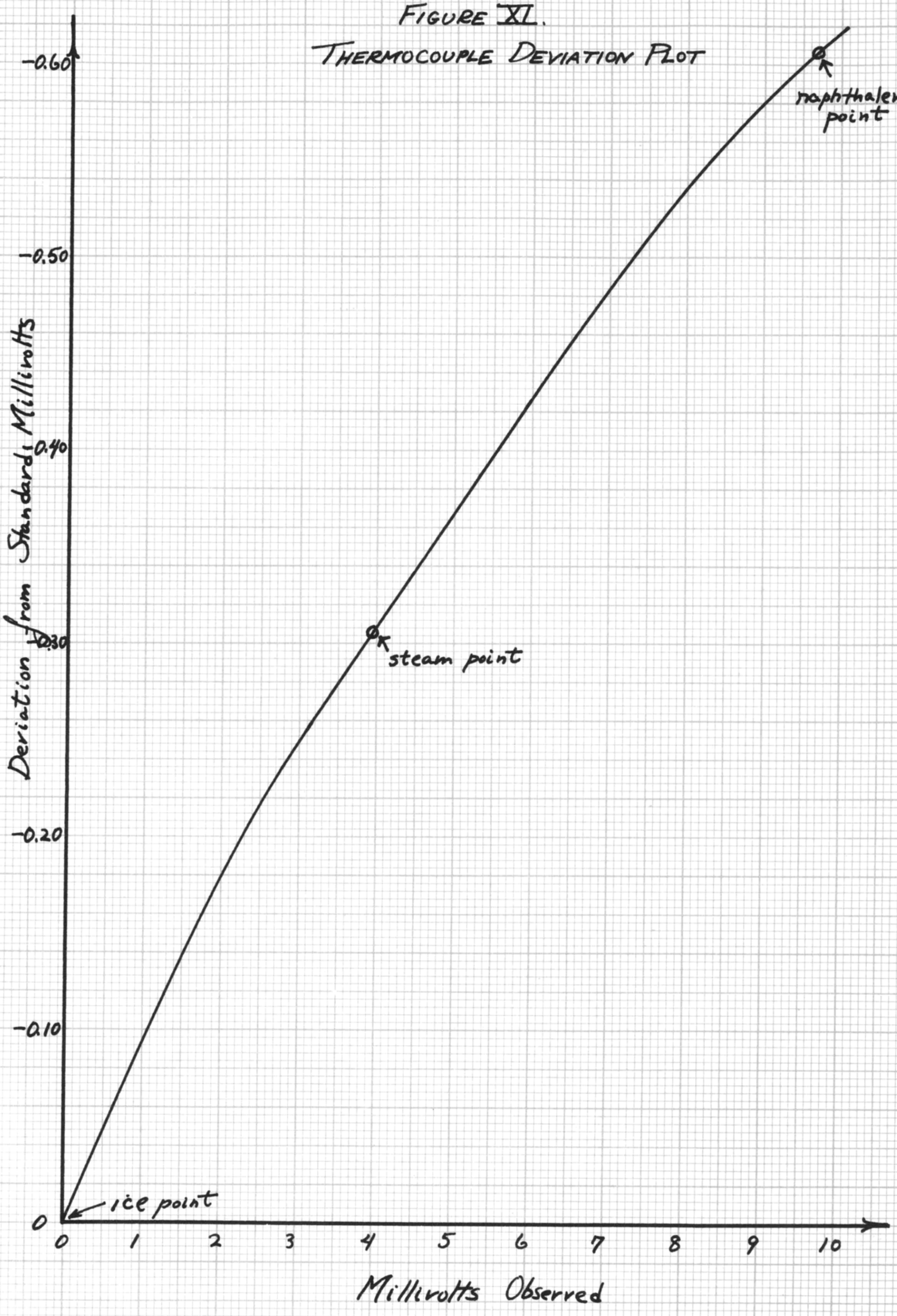


FIGURE XI.

THERMOCOUPLE DEVIATION PLOT



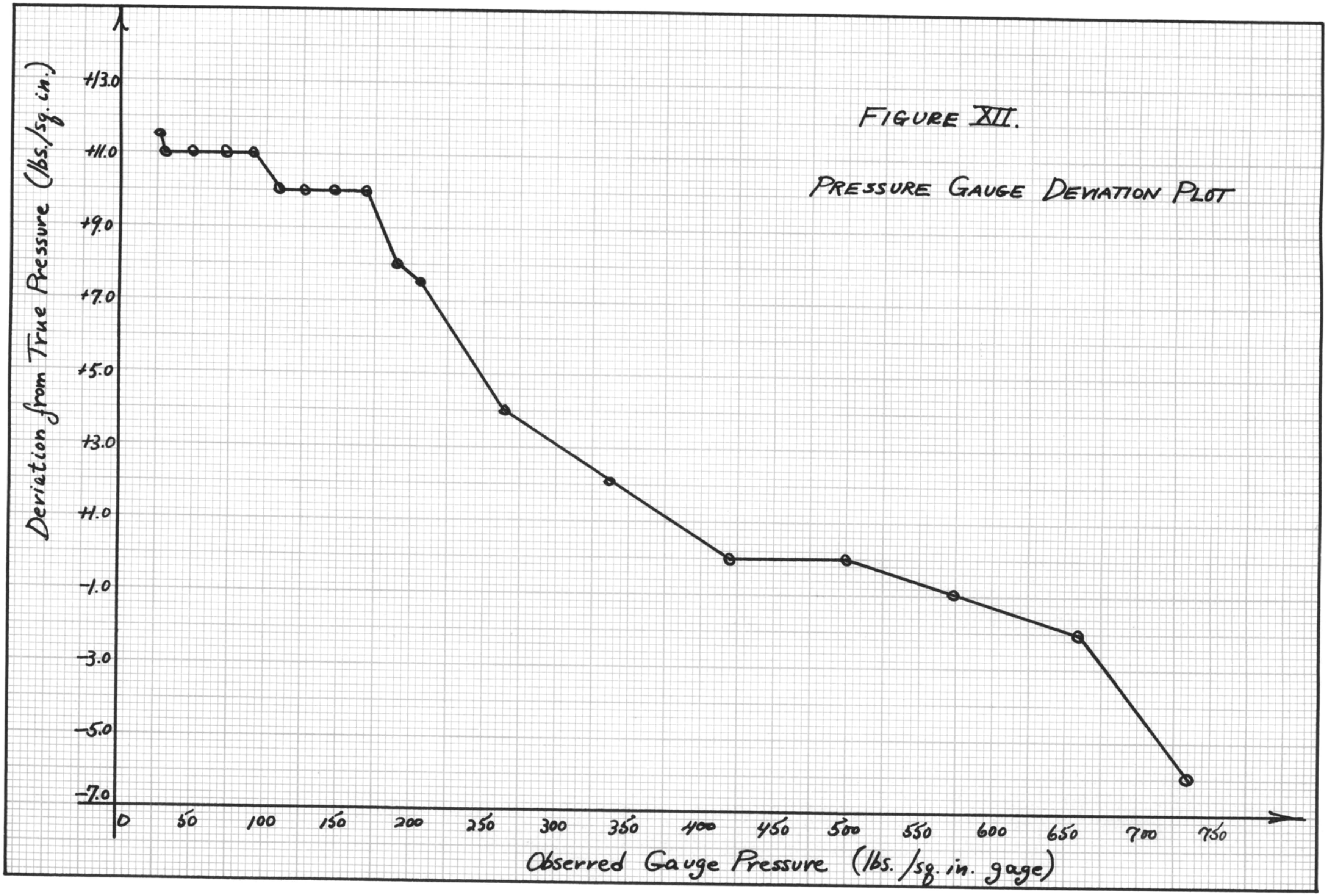


FIGURE XII.

PRESSURE GAUGE DEVIATION PLOT

C. Method of Analysis

The analytical procedure outlined below is the modified Pondorf(27) procedure used by Gunness.(14) By this procedure very small amounts of isopropanol can be detected, and it is unaffected by the presence of dissolved propylene or acids. Essentially the procedure consists in nitriting the alcohol with nitrous acid, extracting the nitrite with three extractions of carbon tetrachloride, oxidizing it to nitric acid and the alcohol with standard permanganate, and back titrating the excess permanganate with standard thiosulfate. In the analysis only about 92% of the alcohol is determined, so it is necessary to introduce a correction factor.

Two 150-cc. separatory funnels, a 250-cc. glass-stoppered titrating bottle, pipettes, and burettes are used. Into one funnel, hereafter called no. 1, are run 40 cc. of carbon tetrachloride and 20 cc. of water, while 20 cc. of wash solution is put into funnel no. 2 (the wash solution contains 50 gm. sodium bicarbonate and 4 gm. sodium nitrite per liter of water). Next, 3 cc. of a 30% sodium nitrite solution is added to no. 1, plus 5 cc. of 7.5% hydrochloric acid, and then a one-cc. portion of the sample pipetted in.

Funnel no. 1 is shaken for 15 seconds, the carbon tetrachloride layer is drawn off, and shaken in no. 2 for 30 seconds, and then drawn off into the glass-stoppered titrating bottle.

The extraction of the alcohol nitrite in no. 1 is repeated, using first 30 cc. and then 20 cc. of carbon tetrachloride. In each case the extraction is washed in funnel no. 2 before being put into the titration bottle.

To the 90 cc. of carbon tetrachloride in the titrating bottle is added 20 cc. of one-normal sulfuric acid and 20 cc. of the same acid containing 20% manganous sulfate. Tenth-normal permanganate is next added in 5 cc. portions until further addition results in the persistence of brown manganese oxide after shaking. Potassium iodide solution is then added and the solution titrated with standard thiosulfate until the rose color in the organic layer has disappeared.

The permanganate is standardized by running an analysis on pure alcohol, and expressing the strength of one cc. of the permanganate in terms of milligrams of alcohol. This will not be quite the theoretical amount. Since the carbon tetrachloride is not absolutely pure, it is necessary to run a blank on it, which usually amounts to about 3% of the permanganate used. The analysis is good to ½%.(14)

D. Sample Calculations (Data of Run III)

In the standardization of the permanganate (approx. 0.1 N) against alcohol of known concentration, 1 cc. of isopropyl alcohol of sp.gr. 0.81 (87.2%) was diluted to 10 cc. with distilled water and one cc. taken for analysis.

mg. alcohol in sample $= 0.81 \times 0.872 \times \frac{1}{10} \times 1000 = 70.9$ mg.

cc. $KMnO_4$ used = 23.6 cc.

blank on reagents used - 0.30 cc. $KMnO_4$

thiosulfate for titration of excess $KMnO_4$ = 0.6 cc.

10 cc. $KMnO_4$ are equivalent to 11.9 cc. thiosulfate.

net $KMnO_4$ used $= 23.6 - 0.3 - (\frac{10}{11.9})(0.6) = 22.8$ cc.

strength of permanganate $= \frac{70.9}{22.8} = \underline{3.10}$ mg. alcohol per cc.

In the blank test on the reagents, 5 cc. $KMnO_4$ were used and 5.6 cc. thiosulfate were required to titrate the excess. Blank $= 5.0 - (\frac{10}{11.9})(5.6) = 0.30$ cc. $KMnO_4$.

In Run III, the average flowmeter differential was 0.61 in.Hg.

gas metered assumed to be pure dry propylene at 70°F.(21.2°C.)

static pressure = 2.25 in.Hg.

total pressure $= 29.90 + 2.25 = 32.15$ in.Hg.

Mol. wgt. of propylene $= 42_m$

density of gas being metered

$$= \left(\frac{32.15}{29.92}\right)\left(\frac{1\times42}{82\times294}\right) = \underline{0.00188} \text{ gm./cc.}$$

feet of fluid flowing $= \left(\frac{0.61}{12}\right)\left(\frac{13.6}{0.00188}\right) = \underline{367}$

volumetric rate of flow at S.T.P. corresponding to f.f.f. = 367

= 4.76 cu.ft./hr.(S.T.P.)

$\frac{4.76}{359} \times 454 \times 1000 = \underline{6020 \text{ mmols/hr.}}$

alcohol concentration in condensed vapor at equilibrium:

$53.5 - 0.3 - \left(\frac{10}{11.9}\right) \times 5.0 = 49.0$ cc. net $KMnO_4$ for

1 cc. sample.

1 cc. $KMnO_4$ is equivalent to 3.10 mg. alcohol.

per cent alcohol in sample

$\frac{49.0 \times 3.10}{1000} \times 100 = \underline{15.2\%}$

rate of alcohol production at equilibrium = 56.0 cc. per 15 minutes.

$56.0 \times \frac{60}{15} \times 0.152 \times 1000 = \underline{34000 \text{ mg}}$. alcohol/hr.

$\frac{34000}{60} = \underline{568}$ mmols alcohol/hr.

molal ratio $\frac{\text{alcohol}}{\text{propylene}}$ in vapor from reactor at equilibrium:

$\frac{568}{6020-568} = \underline{0.104}$

per cent conversion at equilibrium $\frac{568}{6020} \times 100 = 9.40\%$

theoretical % conversion obtainable at 160 C. and 150 lbs./sq.in. is <u>16.1%</u> as read from Figure I.

E. Summarized Data

Run I (May 2):

time begun	9:00 P.M.
pressure	120 lbs./sq.in. gage
temp. of reactor	200°F.
flowmeter differential	1.5 in.Hg.
static pressure	0.2 in.Hg.
volume of 60% acid charged	120 cc.
water replenished in reactor at	11:15 P.M. and 12:30 A.M.
equilibrium conditions reached at	2:00 A.M.

Sampling:

location	time	cc.taken	cc.analyzed	$KMnO_4$	thiosulfate	% alcho
reactor*:	10:30 P.M.	4.0 cc.	0.5 cc.	19.4 cc.	1.3 cc.	11.2%
	12:00	4.0	0.5	33.2	1.1	19.9
	2:00 A.M.	4.0	0.5	39.5	2.5	23.1
condenser trap:	10:30 P.M.	4.0	not analyzed			
	12:00	1.0	not analyzed			
	2:00 A.M.	2.0	2.0 cc.	5.0	12.0**	0.10
bubbler:	11:00 P.M.	10.00	not analyzed, negligible acidity and alcohol content.			

Volumetric production of alcohol from trap at equilibrium (cc. per 15 min.)	negligible
Approximate concentration of reactor acid at end of run	60%
Approximate volumes of acid and organic layers in reactor at end of run	80 cc.acid 50 cc.organic

---

* organic layer not included in reactor samples

** in this case 3.0 cc. thiosulfate equivalent to 1.0 cc. $KMnO_4$

Summarized Data (contd)

Run II (May 5):

time begun.............. 4:00 P.M.

pressure................ 100 lbs./sq.in gage

temp. of reactor........ 220°F.

flowmeter differential.. 1.0 in.Hg.

static pressure......... 2.5 in.Hg.

volume of 60% acid charged.............. 150 cc.

water replenished in reactor at......... 6:00 P.M. and 7:45 P.M.

equilibrium conditions reached at............ 8:40 P.M.

Sampling:

location	time	cc.taken	cc.analyzed	$KMnO_4$	thiosulfate	% alcohol
reactor:	5:20 P.M.	10 cc.	0.5 cc.	10.7 cc.	2.4 cc.	5.2%
	6:30	12	0.5	19.8	4.4	9.8
	8:15	10	0.5	34.5	5.0	18.5
	8:40	10	0.5	34.7	4.3	19.1

condenser trap: no samples large enough to analyze obtained at any time during run.

bubbler: not analyzed, negligible acidity and alcohol content.

Volumetric production of alcohol from trap at equilibrium (cc. per 15 min.).................... negligible

Approximate concentration of reactor acid at end of run.............................. 60%

Approximate volumes of acid and organic layers in reactor at end of run.................. 90 cc.acid
60 cc.organic

Summarized Data (contd)

Run III (May 7):

time begun	6:00 P.M.
pressure	150 lbs./sq.in. gage
temp. of reactor	320° F.
flowmeter differential	0.61 in.Hg.
static pressure	2.25 in.Hg.
volume of 60% acid charged	150 cc.
water replenished in reactor at	8:00 P.M. and 10:00 P.M.
equilibrium conditions reached at	11:45 P.M.

Sampling:

location	time	cc.taken	cc.analyzed	$KMnO_4$	thiosulfate	% alcohol
reactor:	7:30 P.M.	10. cc.	0.5 cc.	12.6 cc.	2.5 cc.	6.3%
	9:30	10.	0.5	37.0	5.6	19.8
	11:15	5.	0.5	45.6	2.1	27.0
	11:45	5.	0.5	51.0	5.7	28.4
condenser trap:	7:30	5.	1.0	13.4	4.9	2.8
	9:30	5.	1.0	20.0	3.9	5.1
	11:15	5.	1.0	51.9	4.5	14.8
	11:45	5.	1.0	53.5	5.0	15.2

bubbler: not analyzed, negligible acidity and alcohol content.

Volumetric production of alcohol from trap at equilibrium (cc. per 15 min.).................... 56.0 cc.

Approximate concentration of reactor acid at end of run............................ 60%

Approximate volumes of acid and organic layers in reactor at end of run.................. 50 cc.acid
60 cc.organic

Summarized Data (contd)

Run IV (May 9):

time begun.............. 4:30 P.M.

pressure................ 250 lbs./sq.in. gage.

temp. of reactor........ 320° F.

flowmeter differential.. 0.84 in.Hg.

static pressure......... 2.25 in.Hg.

volume of 60% acid
charged................ 120 cc.

water replenished
in reactor at.......... 6:30 P.M. and &:45 P.M.

equilibrium conditions
reached at............ 8:40 P.M.

Sampling:

location	time	cc.taken	cc.analyzed	$KMnO_4$	thiosulfate	% alcohol
reactor:	6:00 P.M.	5.0 cc.	0.5 cc.	12.0 cc.	4.5 cc	4.9%
	7:10	5.0	0.5	36.7	5.0	20.1
	8:15	5.0	0.5	50.3	6.2	27.7
	8:40	5.0	0.5	51.1	4.5	29.1
condenser trap:	6:00	5.0	1.0	14.5	5.0	3.1
	7:10	5.0	1.0	23.5	3.8	6.2
	8:15	5.0	1.0	59.1	4.5	17.1
	8:40	5.0	1.0	62.3	3.8	18.2

bubbler: not analyzed, negligible acidity and alcohol content.

Volumetric production of alcohol from trap at
equilibrium (cc. per 15 min.).................. 64.0 cc.

Approximate concentration of acid in reactor
at end of run................................ 60%

Approximate volumes of acid and organic
layers in reactor at end of run................ 50 cc.acid
60 cc.organic

F. Details of Apparatus

The details of the apparatus shown in Figure II are given in this section.

Pressure was supplied to the system by an air compressor driven by a 1/3 H.P. motor, and the compressor was capable of maintaining a pressure of 450 lbs./sq.in. gage on the system, which was well above the desired operating pressure of 100-250 lbs./sq.in.

The reactor was a copper-lined length of heavy iron pipe, about thirty inches long and 3/4 in. inside diameter, and the head pieces were bolted to flanges at each end. At the bottom of the reactor a brass needle valve was located for the purpose of withdrawing samples of the acid from the reactor during a run and also to provide a means of charging the reactor with acid prior to a run. The outlet tube from the bottom of the reactor to this valve was 3/16 in. medium wall copper tubing, as was most of the other tubing in the apparatus, and extended up into the reactor about three inches. It was silver-soldered through a thin disc of copper, and the copper disc held tightly against the bottom flange in the manner of a gasket between the bottom head and flange, so that only copper and silver solder were exposed to the acid in the reactor. The use of a needle valve for withdrawing the acid samples was considered advisable in view of the better control obtained under pressure. The propylene entered at the top of the reactor through quarter-inch copper tubing which extended down into the reactor to a point about six inches from the bottom. Since the reactor was usually charged with acid to a depth of about 17-18 inches, the depth of acid through which the propylene bubbled was probably in the neighborhood of 14 inches, allowing a few inches for the velocity of the gas as it issued from the inlet pipe. A thermocouple well also extended down from the top to a point about eight inches from the bottom of the reactor, that is, to a point about at the middle of the column of acid. This well consisted of quarter-inch medium wall copper tubing, plugged at the end, and in most of the runs it was found more convenient to use a thermometer in place of a thermocouple, the readings differing by only about three degrees Fahrenheit. The thermocouple originally constructed for measuring the temperature was copper-constantan, and its calibration and deviation plots are given in the APPENDIX. At the top of the reactor an outlet was provided for the gas through quarter-inch copper tubing, extending into the reactor about i/8 inch. The three tubes at the top of the reactor were silver-soldered through a copper disc as in the case of the sampling line at the bottom of the reactor. Heat was supplied to the reactor by means of i/16 inch Chromel-A heating ribbon supplied with 110-volt D.C. current, which also ran the motor for the compressor. A variable resistance afforded a means of varying the temperature in the reactor. Asbestos tape was used to insulate the reactor and the vapor line leading to the condenser.

The condenser was a spiral of quarter-inch copper tubing in a vertical position, the cooling medium being water. Soldered to the line leading from the condenser was a trap for catching the condensate, and from which samples of the condensate could be withdrawn through a brass needle valve. The trap consisted of a piece of 3/4 inch brass pipe about eleven inches long, a vapor exit being provided from the top of the trap about one inch above the bottom of the inlet tube from the condenser. The gas from the trap then passed through a brass needle valve which controlled the pressure on the reactor, and then through a water bubbler and calcium chloride drying tube to the flowmeter, from which it was recycled to the compressor. The water bubbler was similar in construction to the trap, except that a pinchclamp could be used instead of a needle valve for withdrawing liquid samples since the bubbler was on the low pressure side of the system. The inlet tube to the bubbler extended down to about an inch from the bottom, and ordinarily about six inches of water were maintained in the bubbler.

The flowmeter used to measure the rate of flow of propylene to the reactor consisted of a piece of capillary glass tubing about three inches long with a capillary between 1/32 and 1/64 inch in diameter, connected at each end to a U-tube of mercury and one of water (for low flow rates), and connected at the inlet end to a static pressure gauge containing mercury. A thermometer well was not installed as it was felt that the gas being metered would be substantially at room temperature. The meter was calibrated in the standard way with a wet test meter, and the calibration curve is given in the APPENDIX.

The pressure gauge located just before the reactor was of the Bourdon type, and had a range of 750 lbs./sq.in. It was calibrated by the dead weight method, and the calibration is given as a deviation plot in the APPENDIX.

The unit for supplying make-up propylene to the system consisted of a five-gallon bottle connected to the cylinder of propylene, the gas in the bottle being maintained under a constant head of four feet of water. A connecting line entered the system at a point before the flowmeter, the storage propylene being dried by the same calcium chloride drier as was the gas coming through the bubbler. The four foot head of water was necessary due to the fact that at the operating pressures and flow rates desired it was necessary to crack the control valve so far that an appreciable static pressure existed on the low pressure side of the system.

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