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The Catalytic Vapor Phase Alkylation of Phenol by Alcohols

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By Robert Lemieux

Approved by H E Sheffer

January, 1949

THE CATALYTIC VAPOR PHASE ALKYLATION OF PHENOL BY ALCOHOLS

INTRODUCTION

The object of this research is to study the reactions between phenol and various alcohols, using an activated alumina catalyst, at a temperature of 325 °C. The alcohols, which are studied, are methyl, ethyl, and benzyl alcohol, respectively.

It is futher desired to study methods of analysis of products. The reaction products are so numerous and varied, that adapting appropriate methods of analysis becomes a major problem. It is also desired to attempt to uncover some information which may shed some light upon an explanation of the mechanism of the reactions. Many mechanisms have been proposed and all are highly disputed by workers in the field.

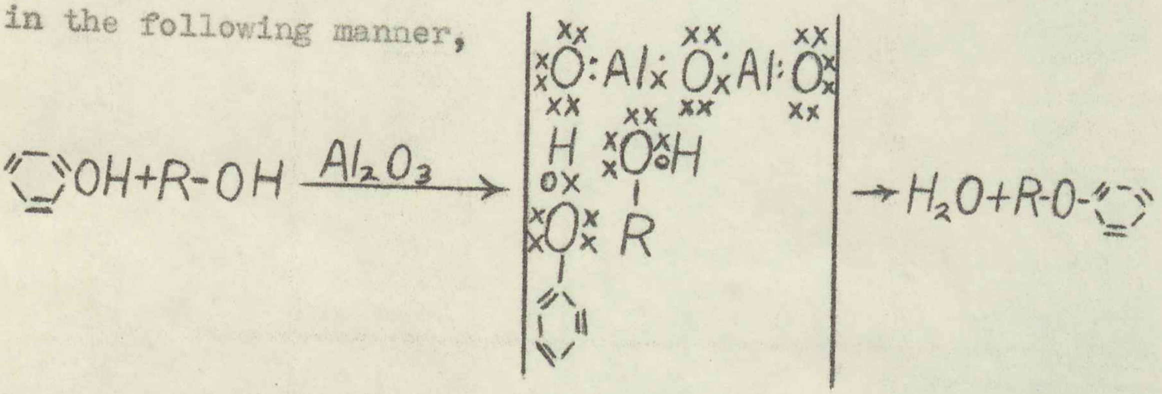
Sept. 14, 1949

Thesis

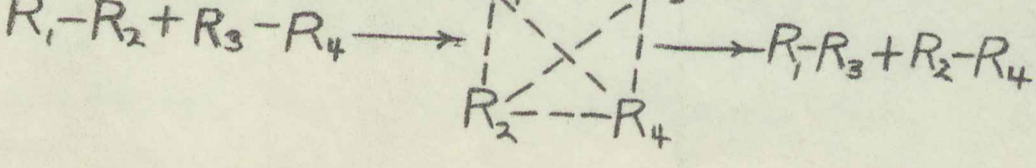
THEORETICAL AND HISTORICAL REVIEW

The principal components of converted products consist of mono alkyl phenols, alkyl phenyl ethers, and higher boiling components consisting of poly substituted phenols and phenyl ethers. Of these, the mono substituted products are obtained in greatest yield.

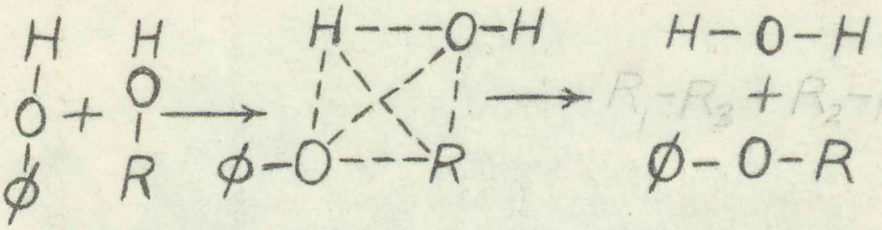
From the information obtained in these reactions, it would be sheer folly to be dogmatic about any proposed mechanism. However, some insight into the problem may be obtained from the following considerations. It is supposed that all of the above reaction products form a phenyl ether, and the corresponding phenols are formed as a result of the rearrangement of the phenyl ethers. This may come about in the following manner,



Such an explanation is in accordance with Eyring's theory of the activated complex.[1] Thus, bonding is represented by him as being half way between that for the reactant and that for the resultant, as,

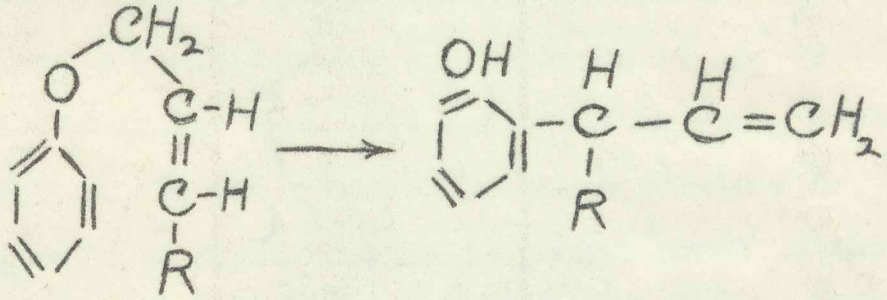


More specifically,



The activation and proximity of the reacting molecules is accomplished by the alumina catalyst through hydrogen bonding.

Much more information is available, concerning the rearrangement of alkyl phenyl ethers. Claisen[2] found that allyl phenyl ethers rearrange to allyl phenols. He has also shown that the allyl group does not attach itself to the phenyl nucleus through the carbon atom originally linked to the oxygen atom of the ether, but rather, through the gamma carbon atom, as,

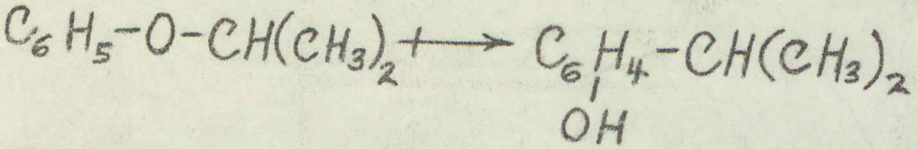


Iso-butyl, sec. butyl, and tert. butyl phenyl ethers give the same para tertiary butyl phenol, when aluminum trichloride is used as the rearranging agent.[3] This would appear to indicate that the reaction is intermolecular rather than intramolecular as supposed in the case of the allyl phenyl ether rearrangement.

The absence of any ortho product may be attributed to steric hindrance. Because of this effect, two alpha, beta, gamma shifts to a para position appears to be somewhat unlikely.

Olefins are generally produced as by-products in those reactions which involve an intramolecular rearrangement of an alkyl group. For example, butylene and phenol are formed in the rearrangement of sec. butyl phenyl ether.[4] It is also of significance to note that butylene and phenol react to produce sec. butyl phenol under conditions which are similar to those which prevail in the rearrangement of the ether.

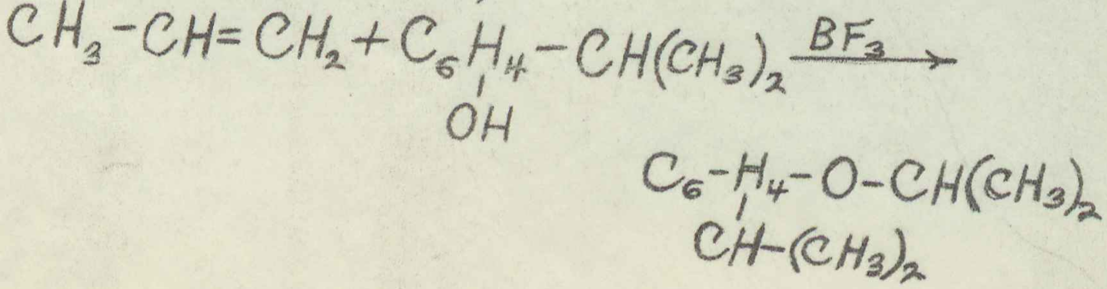
In their studies on the mechanism of this change, Niederl and co-workers[5] have shown that the first product of the reaction of unsaturated hydrocarbons with phenol is not a substituted phenol, but an ether. The formation of phenols constitutes a second stage in the reaction process. These conditions have been confirmed by Sowa, Hinton, and Nieuwland.[6] In the presence of boron trifluoride, phenol and propylene first produce isopropyl phenyl ether, and the ether rearranges to a corresponding phenol, as,



$$C_6H_5-O-CH(CH_3)_2 \longrightarrow \underset{\underset{OH}{|}}{C_6H_4}-CH(CH_3)_2$$

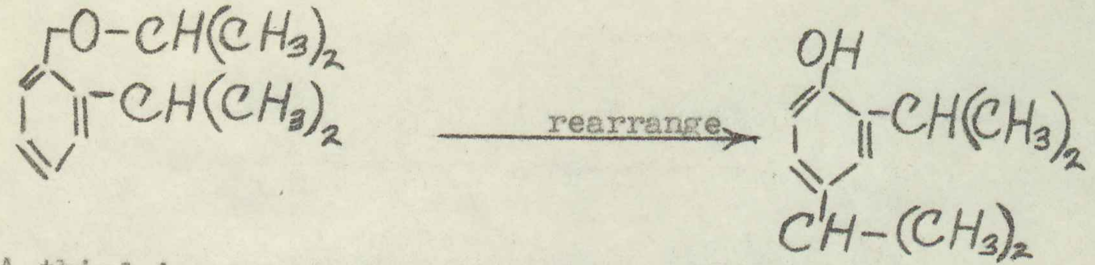
ortho

The process may continue,



$$CH_3-CH=CH_2+\underset{\underset{OH}{|}}{C_6H_4}-CH(CH_3)_2 \xrightarrow{BF_3} \underset{\underset{CH-(CH_3)_2}{|}}{C_6-H_4}-O-CH(CH_3)_2$$

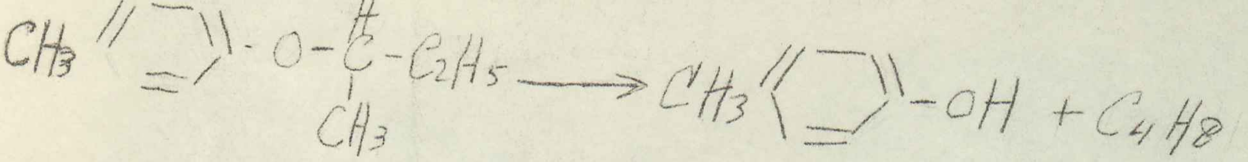
and,

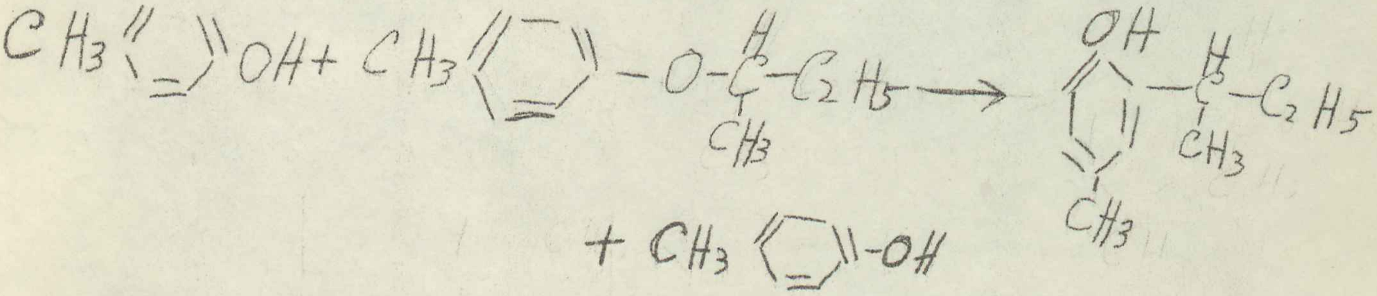


A third isopropyl group may be introduced in this manner. This rearrangement is considered to be intramolecular. However, Short and Stewart[7] have shown in their study of the rearrangement of phenyl benzyl ether that, in the presence of anisole, more than one half of the benzyl radicals have become attached to the anisole nucleus. These investigators believe that the rearrangement is intermolecular. Sowa, Hinton, and Nieuwland[6] have submitted facts which are best explained on the assumption that the rearrangements are intermolecular in nature.

Sprung and Wallis[4] have also considered the possiblity that the phenols are not produced by an intramolecular rearrangement, but are formed as a result of a reaction between two molecules of the ether. These workers have prepared sec. butyl phenyl ether, sec. butyl meta cresyl ether, and sec. butyl para cresyl ether, in optically active modifications, and have studied their rearrangements under different conditions. The principal side reaction was a scission into butylene and the corresponding phenol. In each case, the alkylated phenols, formed in the rearrangement retained their optical activity. The intermolecular rearrangement proposed by Sprung and

Wallis is,





Such a formulation easily explains the presence of unsaturated hydrocarbons, and unsubstituted cresols or other phenols. This mechanism can also explain the presence of poly substituted phenols. Sprung and Wallis have also suggested the possibility of an intra molecular rearrange- based on the concepts of Whitmore.[8] They suggest that the rearrangement can take place in such a manner, that the group, in its migration from the oxygen atom to the phenyl nucleus, although never free, leaves behind its shared pair of electrons. This fragment is now in such an electronic state, that it may do either of three things. It can give normal rearrangement products. It can lose a proton to the potential phenol fragment, and form the corresponding unsaturated hydrocarbon. Or, the fragment can isomerize during the rearrangement process. If the fragment isomerizes, tertiary butyl derivatives are formed, as obtained by Smith,[3] in the presence of aluminum trichloride.

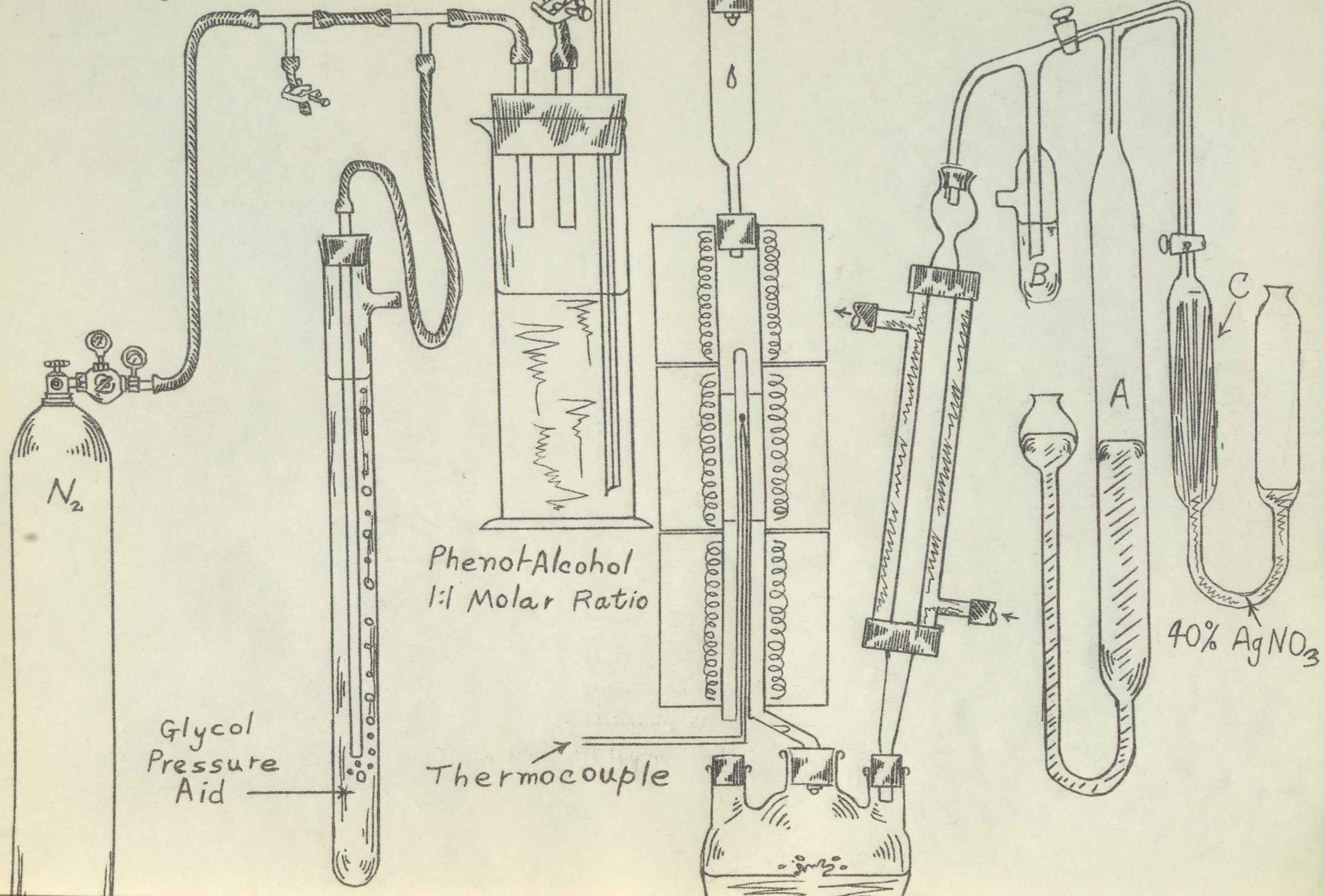
EXPERIMENTAL

Reaction Runs.

A diagram of the apparatus is illustrated in Figure one. Nitrogen pressure is applied to the surface of the ~~phenol~~ phenol and alcohol solution. This pressure forces the liquid up through a capillary and over to the converter, where a drop rate is started. These drops fall into a stainless steel tube, which contains a bed of eighth inch activated alumina pellets. After the reactants pass through the catalyst, the resultants are collected in a Grignard flask, at the bottom of the converter. The gas analysis apparatus is used only in the phenol ethyl alcohol reaction and is discussed in connection with ethylene analysis.

The converter autoclave is divided into three sections; the temperature is maintained constant throughout the catalyst bed by careful regulation of the electrical power fed to these sections, by means of two variacs and a rheostat. The temperature, throughout the catalyst bed, is measured by means of a copper-constantin thermocouple. The hot junction is placed at predetermined positions, in the catalyst bed, through a small tube which is concentric with the reaction tube. The EMF developed by the thermocouple is measured by a Leeds and Northup student potentiometer. The variacs and rheostat are adjusted to maintain a temperature of 325 °C, as nearly as possible.

Fig. 1


N_2
Glycol
Pressure
Aid
Phenol+Alcohol
1:1 Molar Ratio
Thermocouple
B
A
C
40% $AgNO_3$

Each run requires three hours time; during which, approximately 200 ml. of equimolar phenol and alcohol solution are passed through the converter. This rate results in a catalyst contact time, which is approximately three seconds. Exactly thirty two grams of catalyst are used in each three hour run.

Ethylene Gas Analysis.

In the phenol ethyl alcohol reaction, a large volume of gas was observed to be evolved. Since activated alumina is an excellent dehydration catalyst for ethyl alcohol, it was decided to analyze for ethylene. The method which is used is discussed in the following paragraphs and results are recorded in the Appendix.

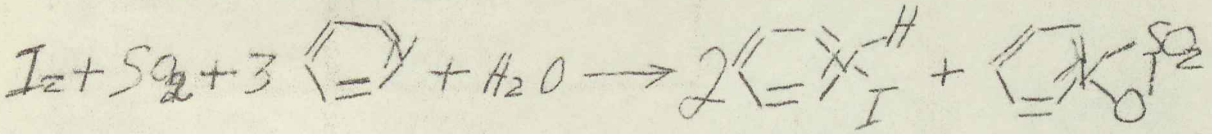
A sample of the gas is collected in the gas buret (A) (see Fig.1), and the time required to collect the sample is recorded. This time is determined, with a stop watch, by starting with the mercury level in the buret at zero. The level of the mercury is dropped at a rate which just maintains atmospheric pressure within the system. This is accomplished by observing the trap (B). The level of water in the inner tube is retained at a level with the water in the outer closed tube, by dropping the mercury bulb on the gas buret. It is assumed that the temperature of the catalyst tube is maintained constant throughout a run. The sample, once collected, is passed from the buret into an ethylene absorption tube (C), which contains 40% silver nitrate, a specific solvent for ethylene.[9] This tube also contains a number of lengths of glass tubing, in order to increase the surface area of the silver nitrate solution. The ethylene is dissolved, and the remaining gas is returned to the buret. The difference in buret readings, before and after absorption, yields the amount of ethylene in the sample. Samples are collected and analyzed at 15 minute intervals in each run.

Since the rate ofreaction on the surface of a catalyst is constant at constant temperature, it would appear that a plot of the rate of ethylen production versus time would give a straight line parallel to the time axis. That is, $\frac{dx}{dt}$ equals k. Further, the area under such a curve would be equal to the total amount of ethylene produced. Thus, $x = \int_0^t k\,dt = kt$.

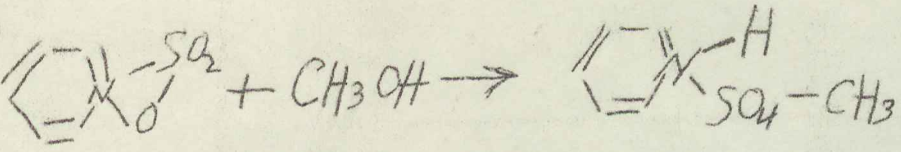
In practice this is not quite true. The system contains only air at the start of the reaction. But, as the reaction is continued, the ethylene produced sweeps out the air, and ar the end of the run, the ethylene rate approaches an asymptotic value. Thus, the last sample contains only ethylene, as shown by analysis. A straight line, parallel to the time axis is extrapolated from this point to time zero. The area under this line gives the total volume of ethylene which is produced.

Determination of Water.

In all reaction runs, no unreacted alcohol was ever recovered. In the phenol ethyl alcohol reaction, it was decided to analyze the product for water. Since, in almost all the possible reactions, one molecule of water is produced for each molecule of ethyl alcohol converted, it becomes desireable to compare the mols of water, produced in the reaction, with the mols of alcohol passed through the converter. The method used, is that described by Fischer.[10] The reagent, which is used, is known commercially as Karl Fischer reagent, and consists of a solution of iodine and sulfur dioxide in pyridine. A known weight of sample is added to this solution, of known water equivalence. The excess reagent is titrated with a water in methanol standard. The stoichiometric relations[11] for the reactions are,



and,



It was necessary to analyze both the product and the reactants for water, because of the hygroscopic nature of phenol. Water is also present in ethyl alcohol. Water, determined in this fashion, gives a result which corresponds to the total ethyl alcohol reacted, within the limits of experimental error. The phenol ethyl alcohol product was the only product a water analysis was carried out for, using this method.

Separation of Phenolic and Ethereal Components.

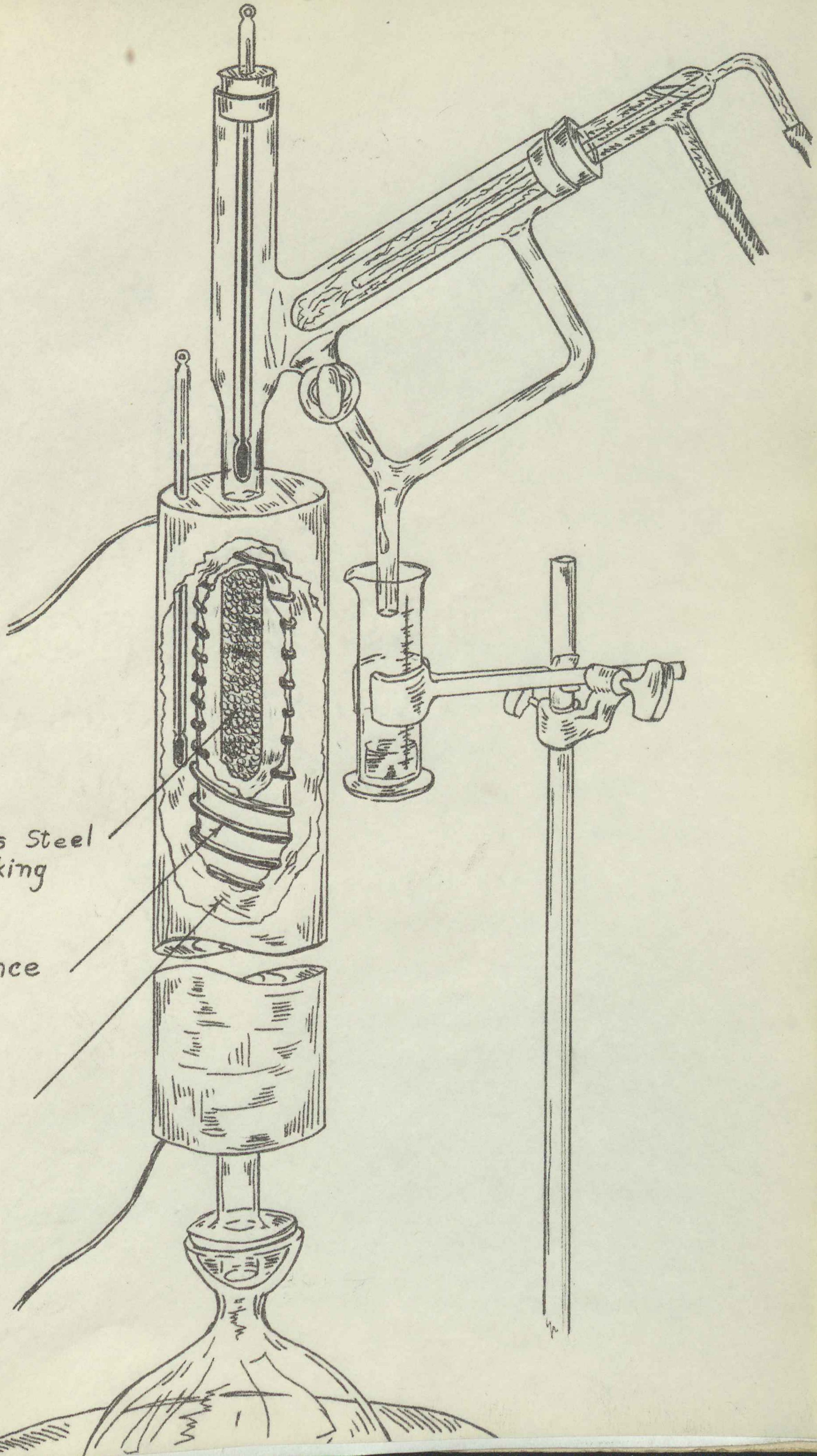
It was found by Adamsvich[12] that much better separation of products by frational distillation was obtained if the phenols and phenyl ethers were separated, and each distilled separately. This is accomplished by treating the product with 20% sodium hydroxide, and extracting the phenyl ethers with diethyl ether. The phenols are recovered by neutralization with hydrochloric acid, and consequent extraction of dissolved phenols with benzene from the water solution.

Distillation Runs.

The phenolic and ethereal components are separated by fractional distillation. A column of approximately thirty theoretical plates, at total reflux, is used. This column is illustrated in figure 2. It is approximately five feet tall, and the packed section consists of half inch glass tubing, packed with stainless steel helices. This still is operated at a reflux ratio of anywhere from 10:1 to 30:1 during one distillation, depending on the conditinns predominating during any one part of the distillation. The column and pot are heated electrically. The heat supplied is carefully controlled by the same variacs used in

Fig. 2

Fractionating Column



reaction runs. Data and graphs of typical distillations are given in the Appendix. This large column is used only to fractionate the phenolic components. The ethereal components are fractionated in a smaller column of the same type. A smaller column is used because the hold up of the larger column is so great as to prevent an efficient distillation of smaller quantities of material. In the distillation of the phenol benzyl alcohol reaction product, the alkylated phenol fractions are distilled the the smaller column which has been adapted for vacuum distillation. These high boiling components (300°C and up at 760 mm) are distilled in vacuo to prevent unnecessary decomposition.

Analysis of Phenol and O-cresol Mixtures.[B]

In the fractionation of the phenolic component of the phenol methyl alcohol reaction product, a good separation between unconverted phenol and o-cresol was not accomplished. Thus, it became necessary to analyze these unresolved fractions, in order to determine more accurately the amount of unconverted phenol and o-cresol.

A mixture containing 65% water and 35% of the phenol sample is placed in an eight inch test tube, and is heated until the immiscible components become miscible. The tube is then placed in a larger tube, which serves as an air jacket, and both tubes are placed in a thermostat, maintained at about 65 °C.

This thermostat consists of nothing more than a large beaker of water. A thermometer, with .1 degree divisions, calibrated for 3 inch immersion, is placed in the solution, which is then stirred vigorously. As the solution cools, a faint turbidity sets in, which serves as a warning of the approach of a cloud point. Finally, there is an abrupt increase in the opacity of the mixture. This is taken as the cloud point, and the thermometer is read to the nearest .05 of a degree. This procedure is repeated, and the mean of several averages is taken. For cloud points up to 70.25 °C, the % of o-cresol is given by the equation,

$$\% \text{ o-cresol} = \frac{\text{C.P.}(^{\circ}\text{C}) - 66.40}{1.326}$$

and for cloud points from 70.25-73.50 °C by,

$$\% \text{ o-cresol} = \frac{\text{C.P.}(^{\circ}\text{C}) - 66.81}{1.167}$$

In some samples the % of o-cresol is beyond the range of these equations. They are brought into range by adding pure phenol, so that a mixture results which contains 90% of added phenol. This method works very well, but of course it increases the experimental error.

Identification of Products.

The various distillation fractions of the phenolic components are identified by preparing phenoxyacetic acid derivatives, as directed by Shriner and Fuson[14], and by taking the melting points of these derivatives.

Ethers are identified by preparing the 2, 4, di-nitro derivatives. A sample of the ether is treated with equal volumes of concentrated nitric and sulfuric acids. The reaction is allowed to run for five minutes, at a temperature of 45 °C. The reaction mixture is then poured onto cracked ice. The derivative which separates is recovered by suction filtration. It is then recrystallized from dilute alcohol, and a melting point is taken. Other means of identification are used, such as boiling points, and indices of refraction. Such measurements also indicate the degree of purity of the sample. It was impossible to find a value for the indes of refraction of o-ethyl phenol in the literature. The value obtained from the purest sample is $n^{23} = 1.5334$.

RESULTS

The results of the various reactions are recorded in the table on the following page. The run numbers refer to the alcohol which is reacted. Thus PA-3 refers to methyl alcohol, PA-2 to ethyl alcohol, and PA-1 to benzyl alcohol. The phenyl ethers refer to anisole,in PA-3, phenetole in PA-2, and to phenyl benzyl phenyl ether in PA-1. The alkyl phenols refer to the cresols, ethyl phenols, and benzyl phenols respectively. It might be well to mention that some meta ~~alkyl~~ phenols are produced in these reactions, but they are in such insignificant quantities, as not to warrant recording.

The analysis of the phenol benzyl alcohol reaction was never completed because of insufficient time. The products of this reaction contained an unusually large quantity of decomposition products, in the form of tars and residues. Further, the amount of benzylated phenols which were recovered form a minor part of the reaction product. Yet, 52.5% of the phenol was converted. The ethereal components of the product were obtained in greatest yield. These components consisted principally of decomposition products. It was a very viscous, sticky liquid, which became even more viscous upon heating. In the light of these facts, it appears that the phenol and alcohol reacted to a large extent, but the products decomposed immediately, because of the high temperature.

RESULTS

Run Number	PA	3	2	1
Time	Hrs.	3	5	6
Temperature	°C	325	318	325
Contact Time	Sec	2.72	2.84	5.62
Catalyst: Number		A-1	A-1	A-1
Feed: Phenol Rate	mol/mol	1:1	1:1	1:1
Alcohol Rate				
P/A Ratio				
Analysis: Alcohol	Wt. %	0.0	0.0	-
Alkene	"	0.0	1.8	-
Water	"	~~11.8~~	11.8	-
Phenyl Ether	"	6.5	1.8	-
Other Ethers	"	7.3	10.9	-
Phenol	"	40.3	31.4	23.1
o-alkyl phenol	"	13.6	11.7	2.7
p-alkyl phenol	"	7.1	6.0	1.4
Higher phenols	"	8.4	5.5	-
Residue	"	0.0	7.3	-
Losses	"	16.0	12.2	-
Alcohol Converted	Mol %	100	100	-
Alcohol converted to alkene	"	0.0	9.6	-
Convertible phenol converted	"	46.4	54.0	52.5
Convertible phenol to ether	"	7.6	2.0	-
Convertible phenol to other ethers	"	9.4	-	-
Convertible phenol to o-alkyl phenol	"	15.7	13.1	2.8
Convertible phenol to p-alkyl phenol	"	8.2	6.8	1.5
o-alkyl phenol/p-alkyl phenol ratio		1.9	1.9	1.9

SUMMARY

The catalytic vapor phase alkylation of phenol by alcohols is studied. The alcohols which are reacted with phenol are methyl, ethyl, and benzyl alcohol, respectively. In all reaction runs, approximately 50 % of the phenol is converted. Ortho, and para alkyl phenols are formed in a two to one ratio. This indicates that both the ortho and para positions are equally vunerable to attack. Other products consist of alkyl phenyl ethers~~s~~, poly substituted phenols and phenyl ethers.

In the case of the phenol benzyl alcohol reaction it is believed that phenol and benzyl alcohol react to form products which are unstable at the temperature studied.

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APPENDIX.

1. Typical reaction run data. This is the benzyl alcohol, phenol reaction run. This run consists of two 3 hour runs. Fresh catalyst is used in the second 3 hour run.

Time	Feed Ml.	Drop Rate	Temperature of Cat. Bed					Preheater Variac	Bed Variac
			Top	1"	2"	3"	4"		
3:00	370	28	326	325	324	320	318	74	63
3:15	335	28	330	325	328	325	325	74	63
3:30	325	28	336	340	340	336	330	70	70
3:45	300	28	325	328	330	326	325	60	60
4:00	287	20	320	322	324	325	325	60	60
4:15	275	20	306	320	325	325	320	60	60
4:30	270	20	310	310	310	310	310	60	60
4:45	260	20	310	315	320	320	310	60	60
5:00	250	20	310	326	326	326	328	60	60
5:30	230	20	325	330	330	330	330	60	60
5:45	220	20	326	327	327	327	325	60	50
6:00	210	20	326	330	327	325	325	off	off
1:20	200	20	300	300	300	300	300	60	60
1:45	185	24	320	325	330	330	320	62	62
2:00	173	20	310	320	320	320	310	70	62
2:15	165	20	310	320	320	320	310	70	64
2:30	153	20	305	314	320	320	310	70	64
2:45	140	20	310	320	325	325	320	74	68
3:00	123	20	320	328	335	335	333	74	68
3:35	97	20	320	322	328	328	325	74	64
4:04	70	20	322	330	330	330	330	74	64
4:30	46	20	315	320	325	328	324	74	63

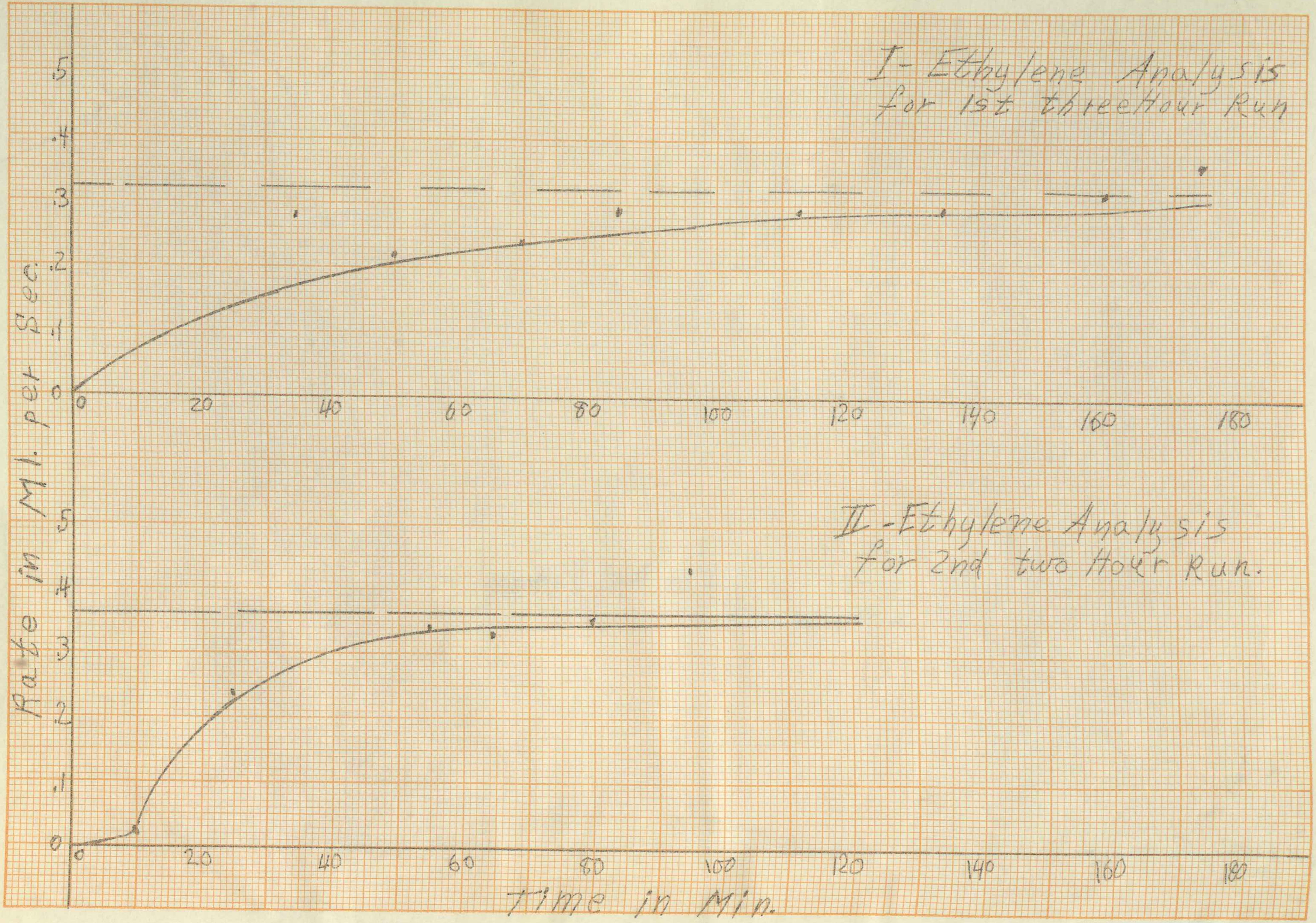
2. Results of Ethylene Gas Analysis.

The products from a three hour run and a two hour run are composited into one reaction product. Thus data and graphs for two ethylene determinations are given.

Data for Curve I

Time	v_1	v_2	Δv	Δt	$\Delta v/\Delta t$
0 min.	50 ml.	50 ml.	0 ml.	75 sec.	0 ml./sec.
35	50.0	26.6	23.4	85	0.28
50	50.0	18.8	31.2	145	0.22
70	49.8	12.4	37.6	159	0.24
85	50.0	8.0	42.0	146	0.29
113	50.0	7.3	42.7	147	0.29
135	49.4	7.3	42.1	145	0.29
160	51.0	10.0	41.0	128	0.32
175	51.8	10.4	41.4	113	0.36
		Data for Curve II			
0 min	50 ml.	50.ml.	0 ml.	104 sec	0 ml./sec.
10	50.2	48.4	1.8	81	0.02
25	50.0	20.8	29.2	120	0.24
55	50.0	12.0	38.0	110	0.34
65	51.0	10.8	40.2	130	0.33
80	49.8	7.6	42.2	120	0.35
95	49.6	6.8	42.8	100	0.43

The perfect gas laws are used to calculate the weight of ethylene. This gives a value of 5.97 gms. for a produce which weighs 329.42 gms.



I- Ethylene Analysis for 1st three Hour Run

II -Ethylene Analysis for 2nd two Hour Run.

3. Data and Calculations for Water Determination.

The first determination, in using Karl Fischer reagent consists in finding the number of milliliters of reagent which is equivalent to one milliliter of water in methanol standard. This is accomplished by titrating a sample of the reagent with the water in methanol standard. The end point is observed by a disappearance of the reddish brown color of iodine, and the appearance of the light yellow color of the resulting solution. The value obtained is called the R factor. This factor is 7.14 for the reagents, which are used.

The next determination is the F_{KF} factor. This factor represents the grams of water equivalent to one milliliter of the reagent. This absolute equivalence is determined by adding a known amount of water to a 50 ml. sample of the reagent, and titrating the remainder with the water in methanol standard.

Thus, $$F_{KF} = \frac{\text{Wt. of Water}}{(\text{ml. KFR} - \text{ml. of } H_2O \text{ in meOH STD. x R.}}$$

This value is .001875 gm./ml.

It is now possible to compute the absolute water equivalence of the water in methanol standard, which is denoted by F_{Alc}

Thus, $F_{Alc} = F_{KF} \times R.$

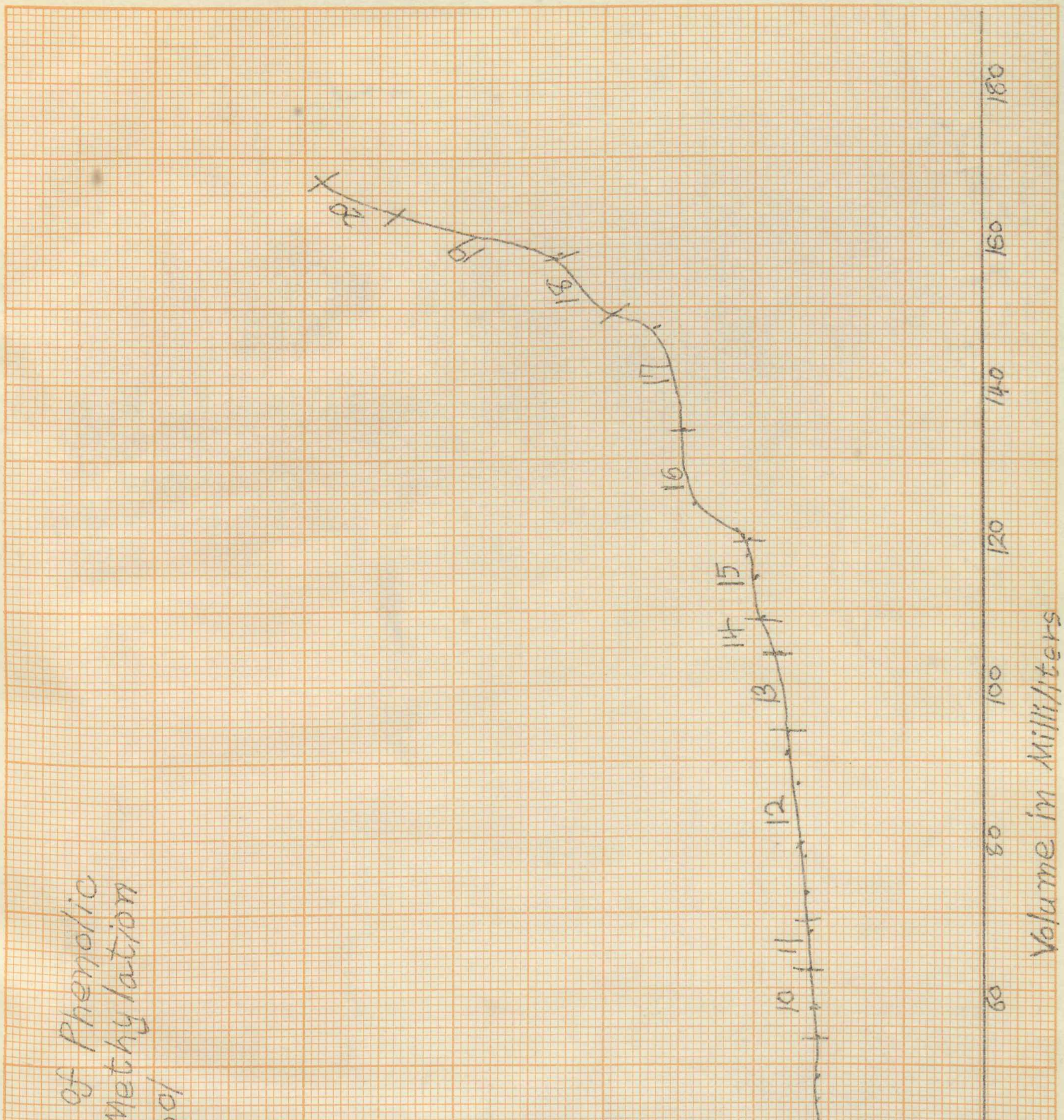
and $F_{Alc} = .001875 \times 7.14 = .0134$ gms. of water per ml. of water in meOH Std.

The average of two unknowns minus the average of two reactant samples give a value of 12.28 %. This figure represents the percentage of water formed in the reaction This corresponds to 40.13 gms. of water in a product which weighs 329.42 gms. The theoretical value of water is 43.25 gms.

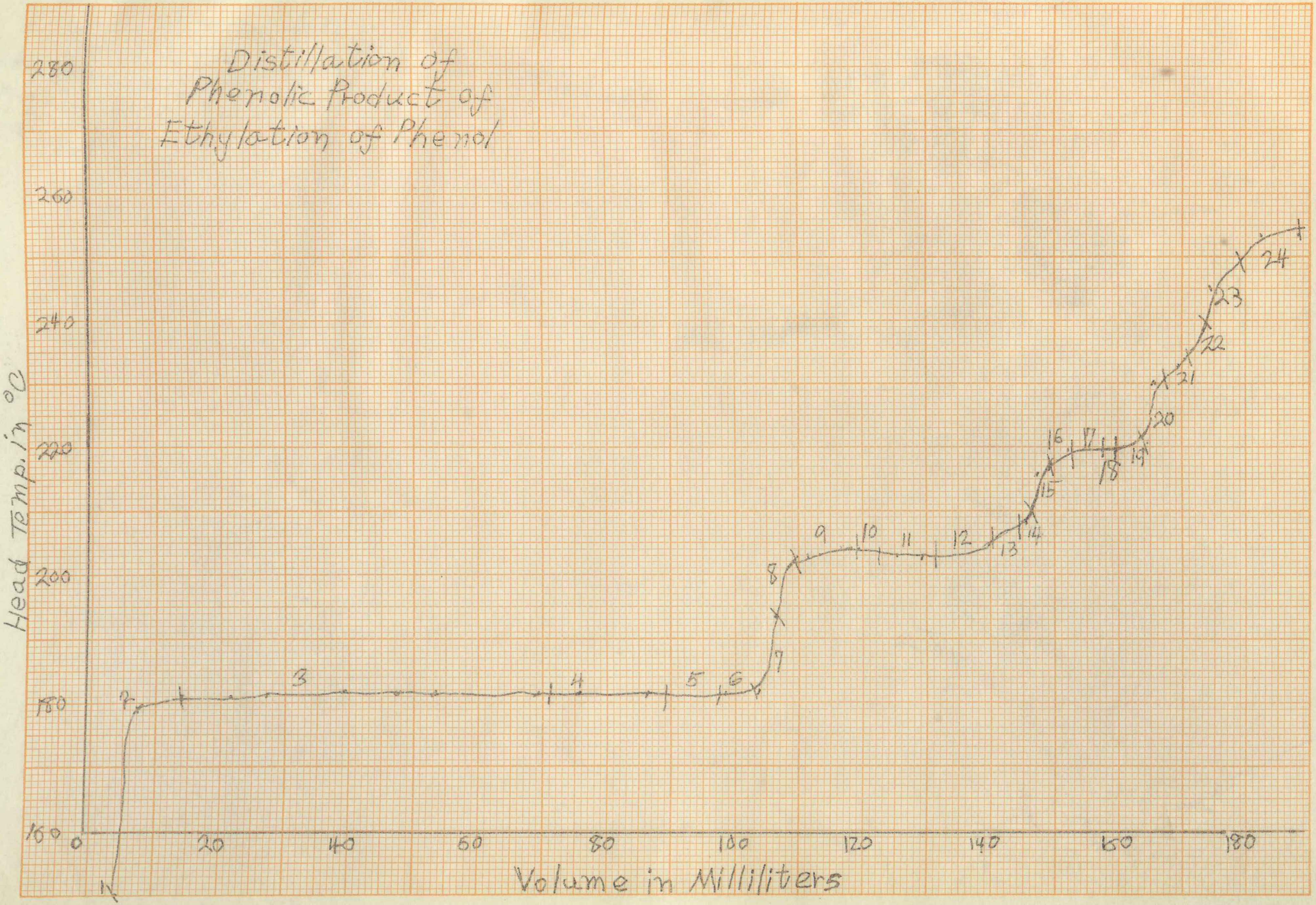
4. Distillations.

A part of the distillation of the phenolic component of the phenol ethyl alcohol reaction product is given in the following table. Only part is given, since it would serve no useful purpose to tabulate several pages of repetitious numbers. Several distillation curves are given in the following pages. The numbers along the curves refer to cut or fraction numbers. Those fractions which appear at the middle of a plateau are used for identification. Most of the figures which appear at the table of results have been determined from these distillation curves.

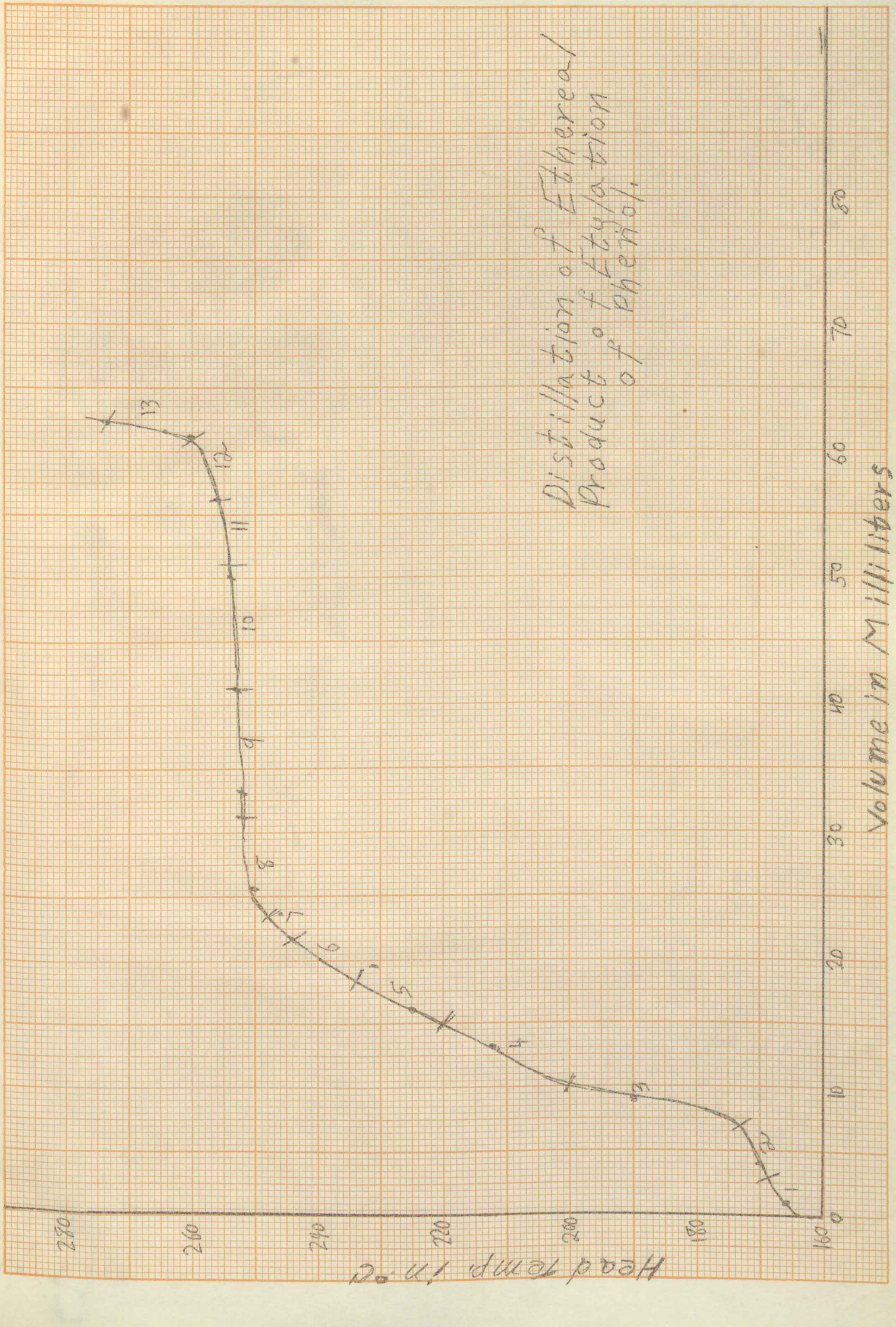
Time	Temperature		Variacs		Product			
	Col.	Head	Pot	Col.	Tot.Vol	Cut Vol	Cut No	Cut Wt.
4:00	205	202.5	130	110	110.2	3.6	8	3.65
4:10	210	203	130	112	113	3.0	9	
4:15	212	203	130	112	114	4.0	9	
4:30	212	204	130	110	120	10.0	9	9.66
11-22-48.								
3:30	215	202	110	114	121	1.0	10	
3:50	212	203	110	110	123	3.0	10	3.23



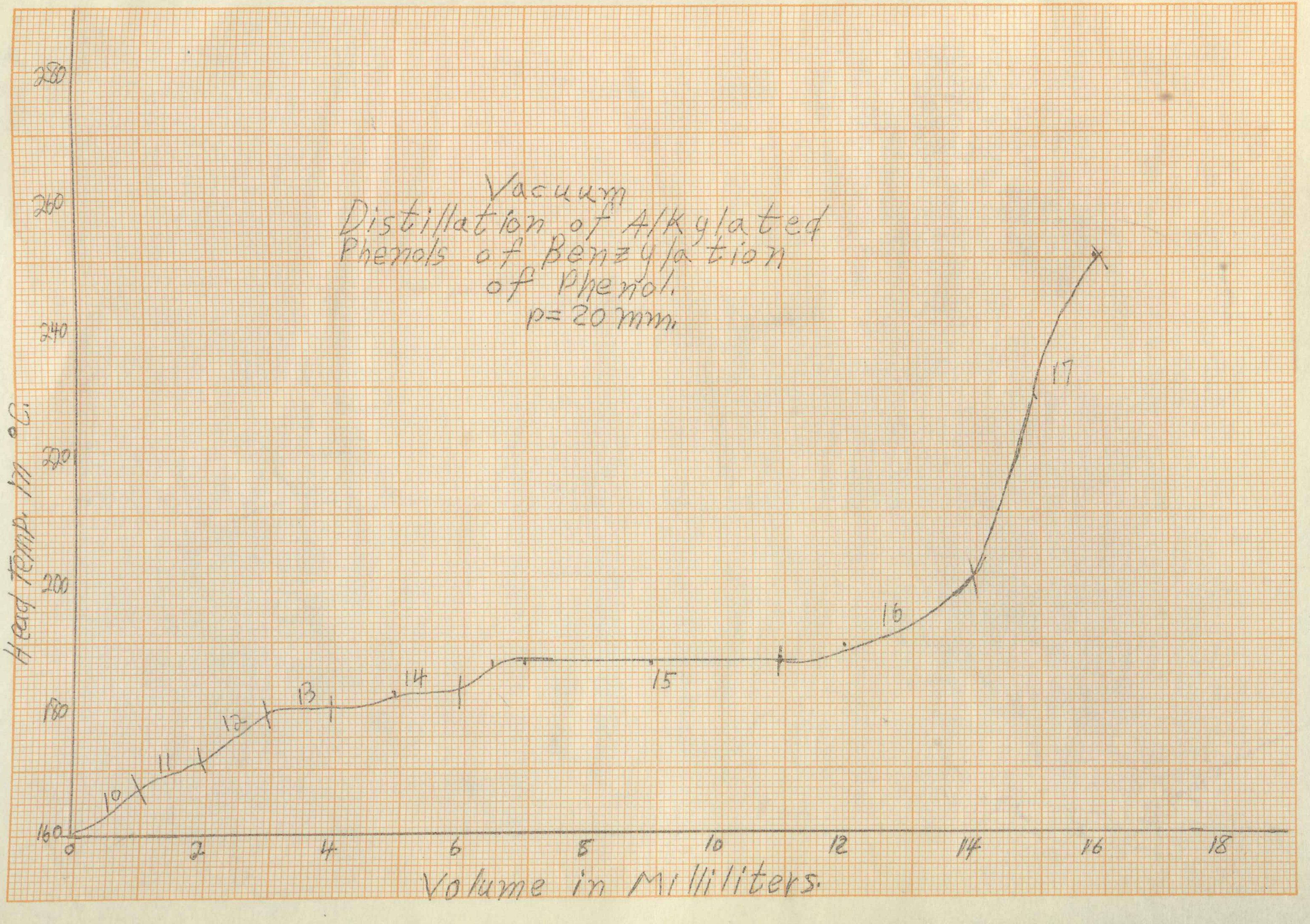
Distillation of Phenolic Product of Methylation of Phenol



Distillation of
Phenolic Product of
Ethylation of Phenol



Distillation of Ethereal Product of Ethylation of Phenol.



Vacuum
Distillation of Alkylated
Phenols of Benzylation
of Phenol.
p= 20 mm.

5. Determination of o-Cresol in Phenol.

o-Cresol is determined for Cuts numbered, 9, 10, 11, 12, 13, and 14, of the phenolic component in the distillation of the phenol methyl alcohol reaction product.

The thermometer is calibrated by observing the cloud points of samples of pure phenol and water. Thus, a cloud point of 66.40 °C indicates zero % o-cresol. The average deviation of the thermometer from three samples is 0.48 °C.

The analysis of Cut no. 9 is given.

Cut no. 9 weighs 49.68 gms. 9.00 gms. of pure phenol are added to 1.00 gms of cut no. 9, thus reducing the % of o-cresol by 10 times.

Of this, 7.00 gms. are added to 13.00 gms. of water, which results in a mixture which contains 65% water and 35 % of phenol sample. Observed Cloud Points are:

(1) 66.65
(2) 66.70
(3) 66.70
Average 66.70

adding the thermometer correction, gives 67.18 °C.

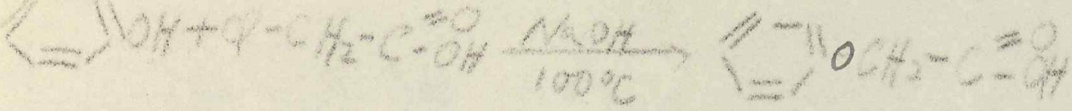
$$\% \text{ o-cresol} = \frac{67.18 - 66.40}{1.326} = \frac{.78}{1.326} = .588\ \%$$

% o-cresol in cut no. 9: .588 % x 10 = 5.88 %

or a total of .0588 x 49.68 gm. = 2.92 gms of o-cresol

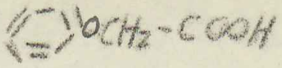
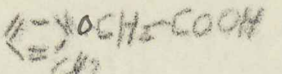
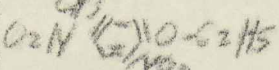
6. Preparation of Derivatives and Identification of Products.

a. Phenoxy-acetic acid derivatives of phenols are prepared.



b. 2-4- di-nitro derivatives of ethers are prepared.

Identification Data.

Run	Cut No.	n^{25}	B.P. °C	Derivative	% Yield	m.p.
PA3	9	-	181.5		74.6	98.8
3	17	-	199		88.3	151
2	2	1.5079	171		85	84
2	3	-	181.5		40	99
2	11	1.5835	205		80	140