



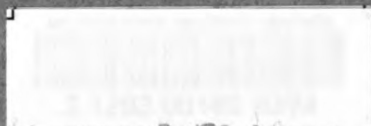
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THE HYDROLYSIS OF AROMATIC HALIDES
AND THEIR HOMOLOGUES IN A
CLOSED SYSTEM

THESIS FOR THE DEGREE OF M. S.

Loyd Harold Rowe

1933



Hydrolysis
Halides

Chemistry

THE HYDROLYSIS OF AROMATIC HALIDES AND THEIR
HOMOLOGUES IN A CLOSED SYSTEM

A Thesis

Submitted to the Faculty of Michigan State
College of Agriculture and Applied Science
in partial fulfillment of the requirements
for the Master of Science Degree.

by

Loyd Harold Rowe

JUNE 1933

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INTRODUCTION

The work described in this paper is an entirely new type of organic research to be carried on at Michigan State College. Therefore, it has been the most earnest desire of the author to attack those phases of the problem which will help most in the continuity of this particular field of research by some of those men who choose to do major work in organic chemistry at this institution in the future.

The purely chemical phase of the work constitutes primarily the hydrolysis of those halogen derivatives of aromatic compounds and their homologues in which the halogen is attached directly to the aromatic ring. The majority of such hydrolyses cannot be carried out at temperatures which are available when working at atmospheric pressure. Therefore, it has been necessary to build apparatus by means of which these reactions can be carried out in a closed system so that any desired temperature can be obtained. The design of a rotating bomb was obtained from the Organic Research Department of the Dow Chemical Company through the courtesy of Dr. E. C. Britton, assistant director of organic research for that company.

The only extensive research of this type which is being carried out at the present time is at the Dow Chemical Company. It was through an interest in that work that Dr. R. C. Huston, director of organic chemistry at Michigan State College, decided to try and introduce some of the same type of work as part of his curriculum of organic research, and to carry it out, if possible in conjunction with Dr. Britton.

Therefore, the author wishes it to be understood that the work described in this paper has been carried out principally upon the suggestions of and with the permission of Dr. Britton.

Due to the newness in this laboratory of the type of work herein described, the author has been obliged to include, as a very important part of his work, the building of apparatus and the development of technique of operation of this apparatus. He is hopeful, therefore, that his description of the more mechanical phases of his work, as given in the following paper will be of some help to those who succeed him.

The Problem Defined

There are three definite parts to the problem:

1. The building of an apparatus consisting of a rotating bomb and a furnace in which the bomb can be heated to and maintained at any desired temperature up to 360° centigrade.
2. The development of technique of operating the above apparatus.
3. The hydrolysis of iodobenzene.

HISTORICAL (1)

Ever since the announcement by Kekule in 1865 of his ring formula for benzene, chemists have been endeavoring to more thoroughly determine and understand its chemical properties through a study of replacements among its substituents. Thus the replacement in benzene of halogen by the hydroxyl group occupied the attentions of many of our early investigators. The comparatively great resistance to chemical action displayed by aryl halides added to the zest for such accomplishment. In spite of the great interest shown in this type of work, we find numerous inconsistencies exhibited in the work done by these early investigators.

Laurent and Gerhardt⁽²⁾ reported the preparation of chlorbenzene by the action of phosphorus pentachloride on phenol and, furthermore, the hydrolysis of this chlorbenzene into phenol when heated with aqueous caustic potash. Again Church⁽³⁾ reported the action of alcoholic potash upon chlorbenzene as leading to a reaction mass which could be made to yield phenol on acidification. The work of Riche⁽⁴⁾ would indicate that the apparent hydrolysis observed by Laurent, Gerhardt, and Church was due to an employment of an impure chlorbenzene. Riche heated a mixture of carefully purified chlorbenzene and alcoholic potash for fifteen hours in a sealed tube at boiling temperatures and observed no apparent indication of hydrolysis. Fittig⁽⁵⁾ attempted to bring about the decomposition of chlorbenzene by the action of silver acetate and by alcoholic potassium acetate in sealed tubes, but with negative results even after heating for a week. Later, Fittig⁽⁶⁾ varified the results of Riche⁽⁴⁾.

The first actual accomplishment of the hydrolysis of chlorbenzene was reported by Dusart and Brody⁽⁷⁾ where only brief mention is made of

heating chlorbenzene and caustic soda in aqueous solution to 300°C . in closed vessels and isolating phenol from the reaction product. This result as commented upon by Henninger⁽⁸⁾ was not generally accepted. At least no particular interest was aroused and the research lay untouched for many years.

Fritz Blare⁽⁹⁾ 1886, attempted to replace the halogen on benzene by methoxy. He heated brombenzene with sodium methylate in a sealed tube for 24 hours at a temperature varying between 230 and 270°C . The reaction proceeded only slowly. The reaction product was found to contain not only anisol but considerable amount of phenol and diphenyl oxide, the sum total indicating a 40 per cent conversion of the original brombenzene.

The use of copper as a catalytic agent for the splitting off of halogen from its position as a substituent in the benzene molecule was first announced by Ullmann in 1900. Ullmann and Sponagel⁽¹⁰⁾ thus proved the order of retention of chlorine, bromine and iodine by the aromatic nuclei decreased with an increase in atomic weights, respectively of the substituents. These same men investigated the reaction of a large number of reagents on benzene halides in the presence of copper or some salt of copper, and under pressure.

A patent granted to Akten Gesellschaft⁽¹¹⁾ indicates that when chlorbenzene was heated with an excess of aqueous ammonia and copper sulphate at 180 – 200°C . for 20 hours, an 80 per cent yield of aniline was obtained.

The distinct advantage of metallic copper in aiding the hydrolysis of derivatives of benzene was evidenced in a patent to F. Bayer⁽¹²⁾ in which the hydrolysis of halogenated phenols by aqueous solutions of alkaline-earth hydroxides, with or without the addition of alkali hydroxides, was

carried out in closed copper vessels heated to 170-200°C. under pressure and with stirring. Mention is made of the use of alkali iodide as catalyst, the principle underlying its use having been previously observed by Wohl⁽¹³⁾.

In 1913 Torley and Motter were granted British and French patents^{(14), (15)} for the preparation of polyhydric phenols from o- and p-dichlorobenzenes by the action of caustic alkali in 15 per cent aqueous solution under pressure, at 300-350°C. and in the presence of metallic copper. These investigators were granted further patents^{(16), (17)} for the preparation of phenyl ether by the action of alkali alcoholates or phenates upon halogenated aromatic hydrocarbons at 320°C. and in the presence of copper. The effectiveness of temperatures higher than 300°C. was made apparent in these last two patents.

At about this same time (1913) Meyer and Bergius were at work in Hanover upon a study of hydrolytic agents at higher temperatures on benzene halides. A United States patent⁽¹⁸⁾ was granted to them on a process for heating, under pressure, chlorbenzene or -chlornaphthalene with caustic alkali in 10 per cent aqueous solution at a temperature of 300°C. The researches of Meyer and Bergius⁽¹⁹⁾ as published in 1914 constituted the most exhaustive presentation of hydrolytic studies upon chlorbenzene that had as yet appeared. The tendency of chlorbenzene and caustic alkali mixture to form tar at temperatures around 300°C. drove these investigators to the use of dilute alkali solutions. Water alone upon chlorbenzene at 300°C. gave only a trace of phenol. Equimolar proportions of chlorbenzene and caustic alkali did not affect more than a 70 per cent hydrolysis, with quantity of diphenyl oxide almost equal to that of phenol in the final product; but in the presence of two moles of caustic alkali to one of chlorbenzene they were able to obtain almost complete hydrolysis, or

conversion, and a product consisting of about two parts phenol to one of diphenyl oxide.

Again, when one mole of chlorbenzene was mixed with four moles of caustic alkali in 15 per cent aqueous solution and heated for 20 hours in a stationary bomb at 300°C . these investigators obtained a 92 per cent yield of phenol. The long reaction time contributed to a lesser amount of diphenyl oxide in the reaction product. This was interpreted as due to the action of excess of alkali at high temperatures upon the diphenyl oxide intermediately formed. When they heated $2\frac{1}{2}$ moles of caustic alkali to one mole of chlorbenzene in a rotating autoclave for 26 hours at 300°C . they obtained almost 100 per cent conversion, 90.8 per cent phenol, and 4.7 per cent diphenyl oxide. The residue, 4.5 per cent, consisted of tar.

Meyer and Bergius extended their investigations upon the chlorbenzene to determine the effect of a catalyst upon the hydrolysis, and also to include the hydrolytic action of substances other than caustic soda, such as milk of lime, sodium carbonate, borax, and ammonia solution.

In 1917 Aylsworth was granted a United States patent⁽²⁰⁾ in which was set forth a new procedure for effecting organic chemical reactions at high temperatures and pressures and in a continuous system. Chlorbenzene as well as benzenesulfonic acid, was here brought into action with fairly strong caustic alkali solutions for the production of alkali phenate and, in turn, phenol.

In this country also, and at approximately the same time, Herbert H. Dow took up the investigation of the hydrolysis of brombenzene⁽²¹⁾. He showed that an aqueous caustic soda solution is effective in the hydrolysis of brombenzene at a temperature as low as 250°C . with a yield of phenol amounting to 85 per cent.

In 1920 Rosenmund and Harms⁽²²⁾ reported the action of several salts of strong bases and weak acids upon benzene halides. Brombenzene was brought together with an aqueous alcoholic solution of sodium acetate, together with a little calcium carbonate and copper acetate, and heated under pressure at 240°C. for 15 hours, and finally at 280°C. for 5 hours. The reaction product, extracted with ether, yielded a halogen-free oily product. The aqueous residue, upon acidification, gave a yield of 50 per cent in phenol.

Up to 1922 the only paying commercial method of synthesizing phenol was the "benzenesulphonic acid - sodium hydroxide fusion process".

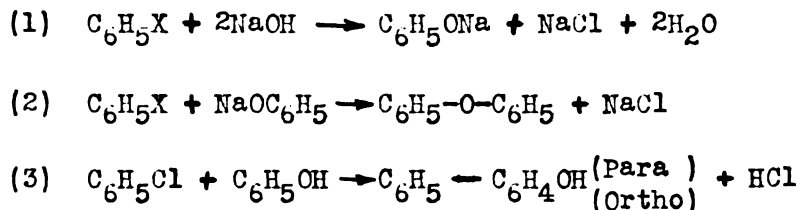
In 1922 the Dow Chemical launched an extensive program of research upon the study of the production of phenol from benzene halides, under the direction of William J. Hale and Edgar C. Britton.

They placed in operation a type of rotating bomb which will be described later, since the same type of apparatus was used in accomplishing the hydrolyses to be described in this paper.

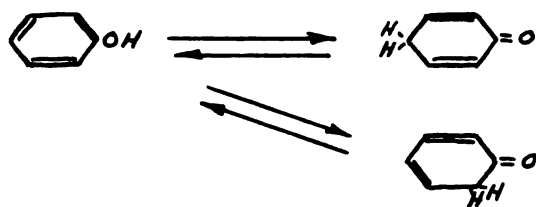
They established very definitely and conclusively the conditions under which chlorbenzene can be converted on a paying commercial basis into phenol, and also established the optimum conditions for the hydrolysis of brombenzene.

To better appreciate the splendid piece of work accomplished by Hale and Britton, the reader is urged to study carefully the account of their researches on chlorbenzene and brombenzene as published in the Journal of Industrial and Engineering Chemistry, Vol. 20, pp. 114-124 (1928).

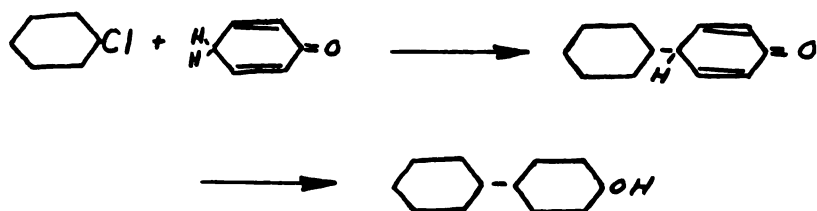
It may be stated in brief form that their researches led to the following important conclusions: They found that by heating the benzene halide with aqueous caustic soda in rotating bombs three principal competing reactions would take place.



Equation (1) depicts the main trend of reaction when a benzene halide is hydrolyzed by caustic soda. Equation (2) shows the possible mechanism of the formation of diphenyl oxide which is found in very appreciable quantities (6-10%) in the reaction mixtures. Equation (3) depicts the formation of ortho and para phenylphenols which are the principal constituents found in the tar residues. It might be well to discuss briefly the theory upon which Dr. Britton accounts for the formation of these phenols. Glenz⁽²²⁾ has offered a theory upon which he considers that phenol undergoes a tautomeric change and exists in two possible keto forms. In aqueous solution he considers phenol as existing in an equilibrium having the following structures:



Under such an interpretation, the hydrogens in positions ortho and para to the oxygen in the keto forms would be more reactive, and hence condensation with benzene halide might easily proceed under the influence of alkali according to the following equation:



Hale and Britton found that from 20 to 25 per cent of the tar waste was made up of these monohydroxydiphenyl compounds, of which at least three-fourths consists of p-hydroxydiphenyl.

The affect of alkali concentration was carefully studied to determine what concentration would affect the greatest possible formation of phenol, as compared with the total hydrolysis of the benzene halide used. They found that at concentrations over 11-12 per cent they were confronted with extremely high formation of undesired materials. Concentration as low as 3 per cent required a higher temperature, but clearly demonstrated a lesser formation of undesired materials. Their experiments pointed to an optimum concentration of caustic soda as lying between 6 and 10 per cent.

The tendency for hydrogen formation when using metal bombs was noticed, and its effect assumed to be active in the formation of the derivatives that constituted a large percentage of the tar residues. It was noted, however, that the continued use of the bombs led to the formation of a mat of magnetic iron oxide on the walls which greatly reduced the continued formation of hydrogen.

A very careful study of the affect of temperature and time upon hydrolysis of chlorbenzene and brombenzene was made from which data a time-temperature curve and a time in minutes vs. per cent yield of phenol curve were plotted for chlorbenzene. These curves are shown reproduced in Figures 1 and 2.

When the value used to plot the curves shown in Figure 2 were substituted in formula for unimolecular reaction:

$$K = \frac{1}{t} \log_e \frac{A}{A-X}$$

where: A = quantity of chlorbenzene used

X = quantity of phenol produced.

t = time in minutes.

a constant (K) = 0.0095 to 0.0098 was obtained.

Performance Curve for the Hydrolysis of Chlorbenzene from the Research of W.J. Hale and E.C. Britton at the Dow Chemical Company

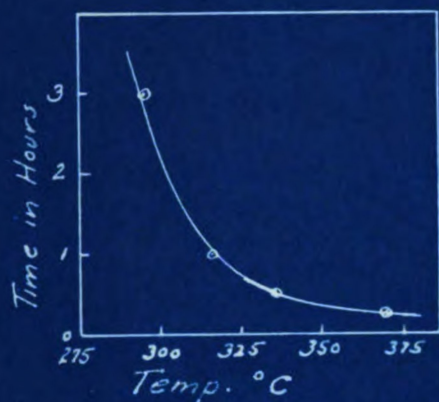


Fig. 1

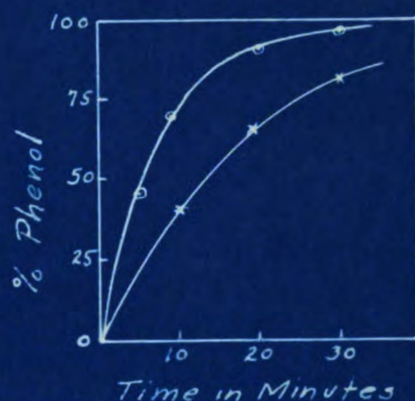


Fig. 2

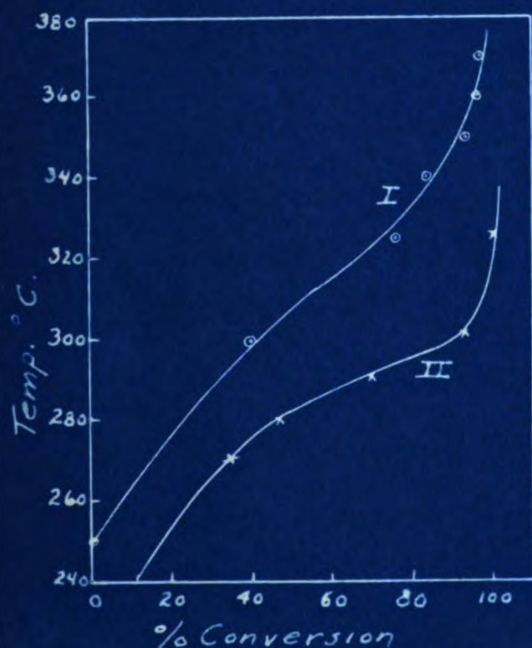


Fig. 3.

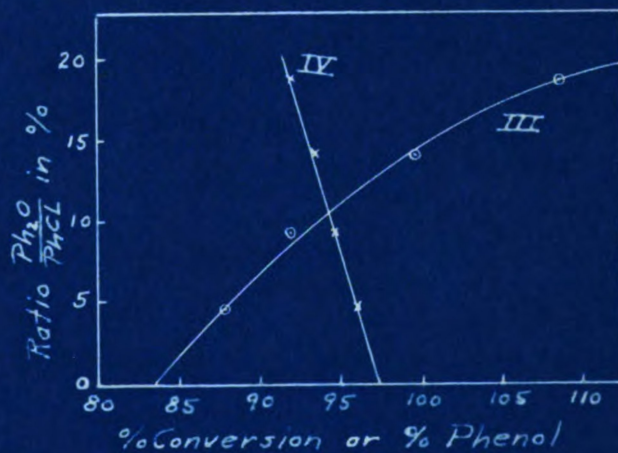


Fig. 4.

When the same values were substituted in the formula for bimolecular reaction, no constant was obtained. Therefore, the reaction had to be considered as one of simple hydrolysis of chlorobenzene by water - an exact parallel to the hydrolysis of ethyl acetate by water.

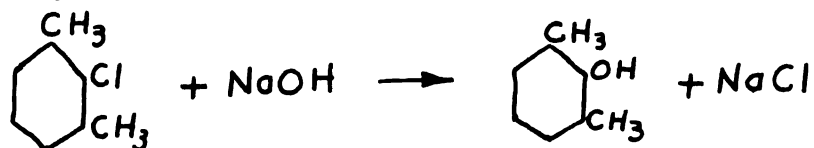
The affect of catalysts was studied, and it was found that metallic copper gave the best results. This conclusion led to the use of copper bombs in place of iron bombs. An interesting phenomenon, however, was noticed in this connection. It was found when copper was placed in an iron bomb that it would not act as a true catalyst unless it was insulated electrically from the iron. Several materials were tried out for use as insulator, but marble was the only one that would successfully withstand the corrosion of the reaction mixture. From the data obtained by hydrolysis in iron and copper bombs, the curves shown in Figure 3 were plotted. It was found that the catalyst had a marked effect in speeding up the reaction. Curves I and II, Figure 3 represent the relations when using iron and copper bombs respectively. It was found that at the higher temperatures and longer periods of reaction the action of the catalyst was much less pronounced. In all cases the degree of hydrolysis must be taken as indicative of the affect of the catalyst; that is, the production of diphenyl oxide is just as much catalyzed as the production of phenol in the hydrolysis of benzene halides, and in most cases the diphenyl oxide produced amounted to 6-10 per cent of the benzene halide used. It was shown, however, that iron acted as a negative catalyst on the formation of phenylphenols.

An investigation into the possibilities of decreasing the yield of diphenyl oxide was undertaken, and with much success. This was finally

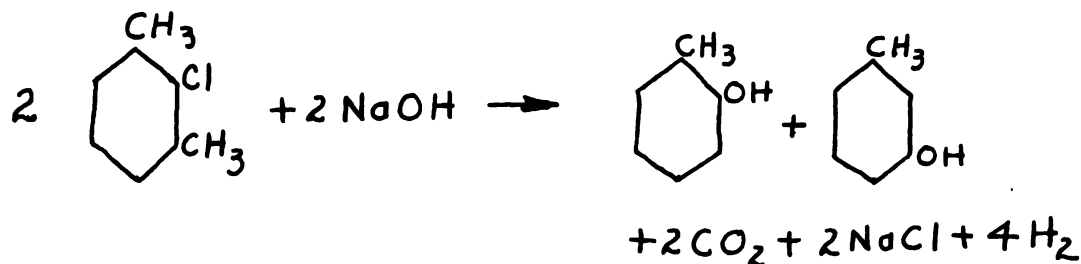
accomplished by the addition of diphenyl oxide to the system in various amounts. From the data thus obtained the curves shown in Figure 4 were plotted, Curve III, based upon the diphenyl oxide introduced as against the yield in phenol, and Curve IV based upon the diphenyl oxide introduced as against total conversion of the chlorbenzene. The point at which the two curves intersect represents the conditions under which the yield of phenol is equal to the total conversion. Thus it was possible to establish a definite ratio of diphenyl oxide to chlorbenzene that would affect the maximum yield of phenol. The diphenyl oxide was assumed to produce a condition of equilibrium in the system which tended to retard its further formation. Inspection of Curve IV Figure 4 shows that when high ratios of diphenyl oxide to chlorbenzene were used, the total conversion exceeded 100 per cent. This fact indicates that some of the diphenyl oxide introduced was hydrated into phenol. This phenomenon was investigated, and it was found possible to obtain commercial yields of phenol from its anhydride - i.e. diphenyl oxide.

These investigations have paved the way to a commercial process now in operation at the Dow Chemical Company which leads the world in the production of phenol.

In more recent years these same investigators for the Dow Chemical Company have worked up the hydrolysis of some of the more complex halogen derivatives of aromatic compounds such as: mono-chlortoluenes, mono-chlornaphthalene, mono-bromtertiarybutylbenzene, mono-chlorcymene, and mono-chlorxylene. An interesting phenomenon in connection with the hydrolysis of mono-chlorxylene (2-6 dimethyl chlorbenzene). When the reaction was carried out in a copper bomb, the hydrolysis proceeded as would be expected, thus:



However, when the reaction was carried out in an iron bomb without a catalyst the hydrolysis proceeded very slowly, and one of the CH_3 groups was split off as CO_2 ; the reaction mixture yielding a mixture of ortho and meta cresol.



The choice of a compound suitable for the purpose of initiating this type of hydrolytic work into the chemical research curriculum at Michigan State College was made by Dr. Huston at the suggestion of Dr. Britton. Among the compounds suggested by the latter was "iodobenzene". This was chosen, and the conditions of its hydrolysis are described in a portion of this paper.

- (1) The material for this historical was taken largely from the article: "Development of Synthetic Phenol from Benzene Halides" by William J. Hale and Edgar C. Britton of the Dow Chemical Company, as published in the Journal of Industrial and Engineering Chemistry, Vol. 20, p. 114-124 (1928). The following references are those given in the article.
- (2) Compt. rend., Vol. 28, p. 170 (1849); Pharm. Zentralblatt, p. 314, (1849)
- (3) J. Chem. Soc. (London) Vol. 1, p. 76 (1863)
Ann., Vol. 128, p. 216 (1863)
- (4) Ann., Vol. 130, p. 256 (1864)
- (5) Ibid., Vol. 121, p. 363 (1862)
- (6) Ibid., Vol. 133, p. 49 (1865)
- (7) Compt. rend., Vol. 74, p. 1051 (1872)
- (8) Ber., Vol. 5, p. 389 (1872)
- (9) Monatsh., Vol. 7, p. 626 (1886)
- (10) Ann., Vol. 350, p. 83 (1906)

- (11) D.R.P. 204,951, (1908)
- (12) D.R.P. 249,939, (1912)
- (13) Ber., Vol. 39, p. 1951 (1906)
- (14) British Patent 9450, (April 22, 1913)
- (15) French Patent 458,136 (April 23, 1913)
- (16) British Patent 9451 (April 22, 1913)
- (17) French Patent 458,843 (April 23, 1913)
- (18) U. S. Patent 1,062,351 (May 20, 1913)
- (19) Ber., Vol. 47, p. 3155 (1914)
- (20) U. S. Patent 1,213,142 (1917)
- (21) U. S. Patent 1,274,394 (1918)
- (22) Ber., Vol. 53, p. 2226 (1920)

APPARATUS

Rotating Bombs

A design of the bomb used in the present work is shown in Figure 5. This bomb was made from 0.4% carbon steel and was designed to operate with a reasonable factor of safety at temperatures as high as 400 degree centigrade. Since a temperature of 360°C. is as high as can accurately be measured with a mercury thermometer, it is of course impossible to operate at higher temperatures without the use of pyrometer equipment. It will be noticed from the design that the bomb is equiped with a baffle on each side of the inner wall which increases the agitation of the reaction mixture. The bomb is closed by means of a ground joint which must be kept carefully ground and should be greased whenever it is not in use to prevent rusting.

Figure 6 is a design of a copper bomb. For the present work a copper bomb was not available. However, it is hoped that for future work one may be added to the equipment. Therefore, it was deemed advisable to obtain as much information as possible concerning the use of a copper bomb and include the same along with the design shown in Figure 6 in this paper. This bomb is, of course, designed to operate in the same rotating apparatus (Figure 7) as is the iron bomb. Its design, however, had to be altered somewhat due to certain operating conditions. Notice that the large nut which holds the cap of the iron bomb, Figure 5, in place is made of one solid piece of metal, and that each time the bomb is dissembled this nut must be unscrewed. In the case of a copper bomb, such frequent use of the threads would soon cause excessive wear due to the softness of the metal.

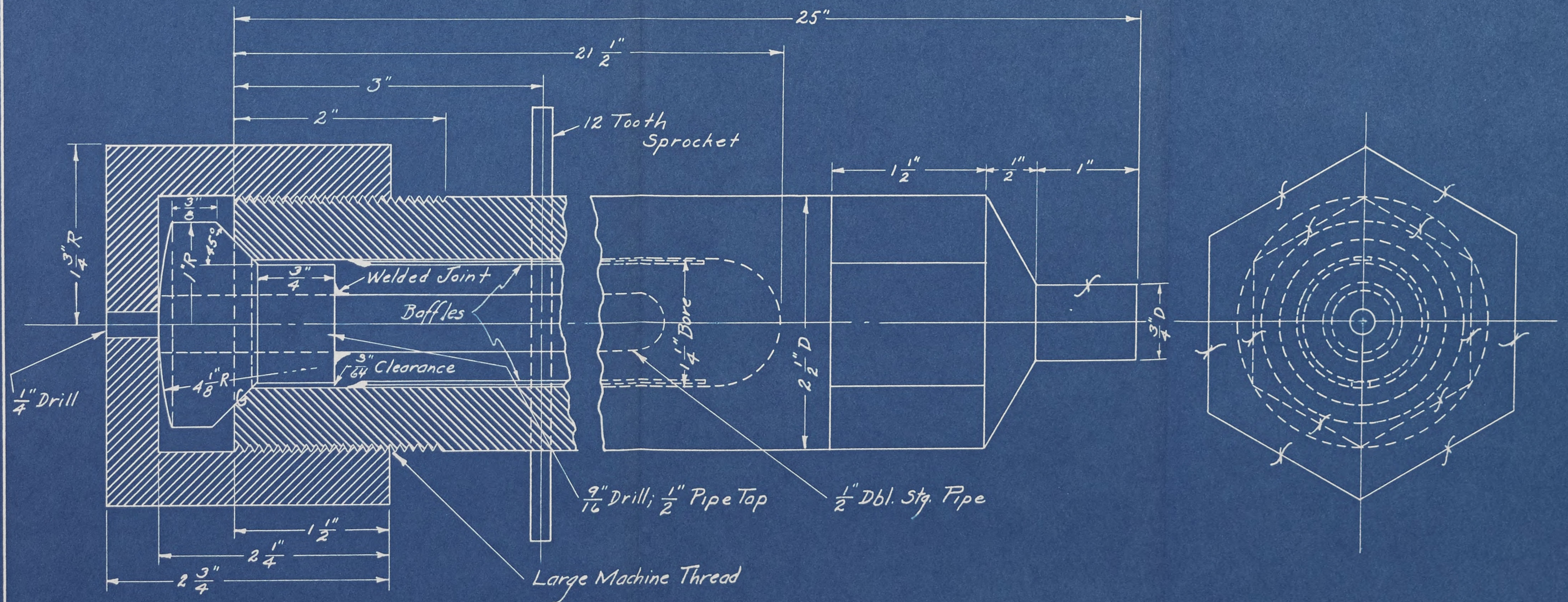
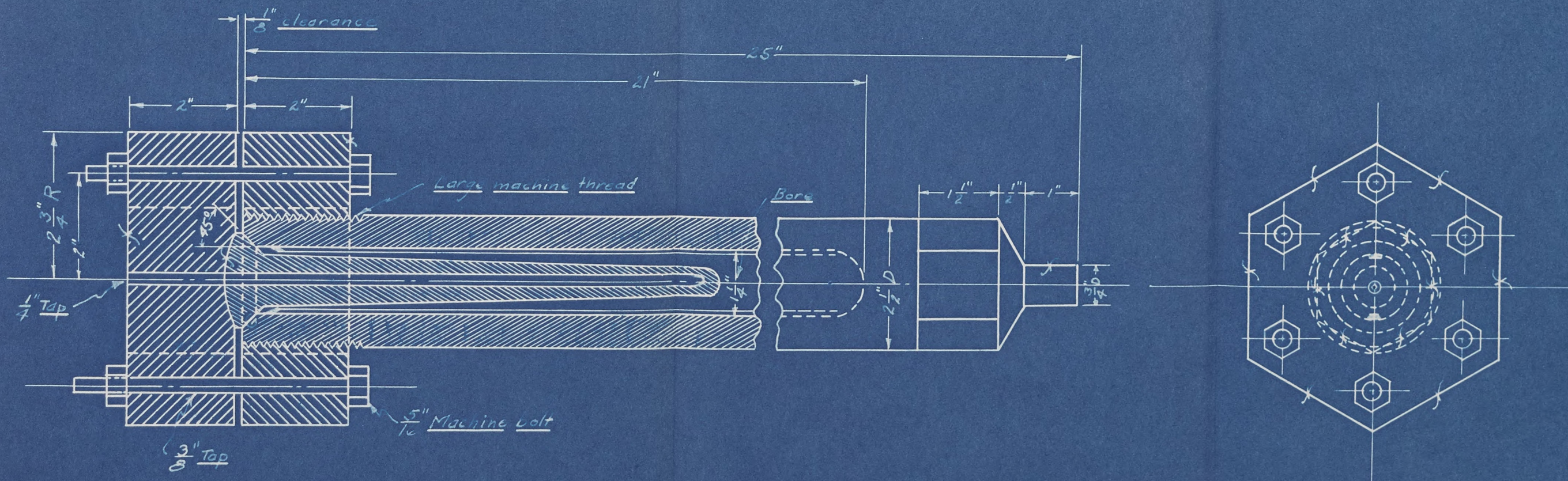


Fig. 5.

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DEPT. OF CHEMISTRY
BOMB ASSEMBLY
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MATERIALS:

-  COLD ROLLED COPPER OR ENDURO
-  STEEL

Fig. 6.

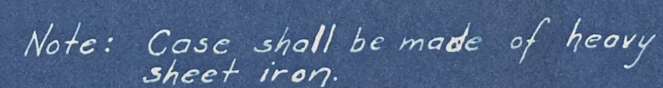
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BOMB ASSEMBLY
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DATE: 7/4/32 J. H. Rowe.

Therefore, this large nut on the copper bomb was designed in two parts. The lower half may be screwed onto the barrel of the bomb and then left in place. The top half then rests on the cap and is held in place by means of six bolts which extend through the bottom half of the nut.

Another slight alteration in design was found advisable due to information obtained in the present work. In the iron bomb the joint which holds the thermometer well to the cap was originally brazed. After operating the bomb a few times it was found that the brazed joint had been attacked to such an extent by the caustic soda that excessive leaking soon resulted. The brazing metal had, therefore, to be removed and the joint welded with steel. In the case of the copper bomb there must be no iron surfaces in contact with the reaction mixture, so it is advisable to turn the cap and thermometer well out of one solid piece of metal.

Due to the low tensile strength of copper, a further safety precaution is necessary. This is not shown in the design, but consists simply of turning out a steel ferrule having a wall three-eighths of an inch in thickness and an inside diameter such as will permit it to fit snugly over the barrel of the bomb. It may be turned out in several short sections which may in turn be spot welded in place. Such a ferrule increases greatly the resistance of the walls of the bomb to pressure from the inside, and thus increases its factor of safety.

In operating with copper bombs, it was found by Dr. Britton at the Dow Chemical Company that the two surfaces of contact at the ground joint had a tendency to stick together. He found a simple means of preventing this in sprinkling the two surfaces with talcum powder before sealing the bomb.



The Rotating Device and Heating Element.

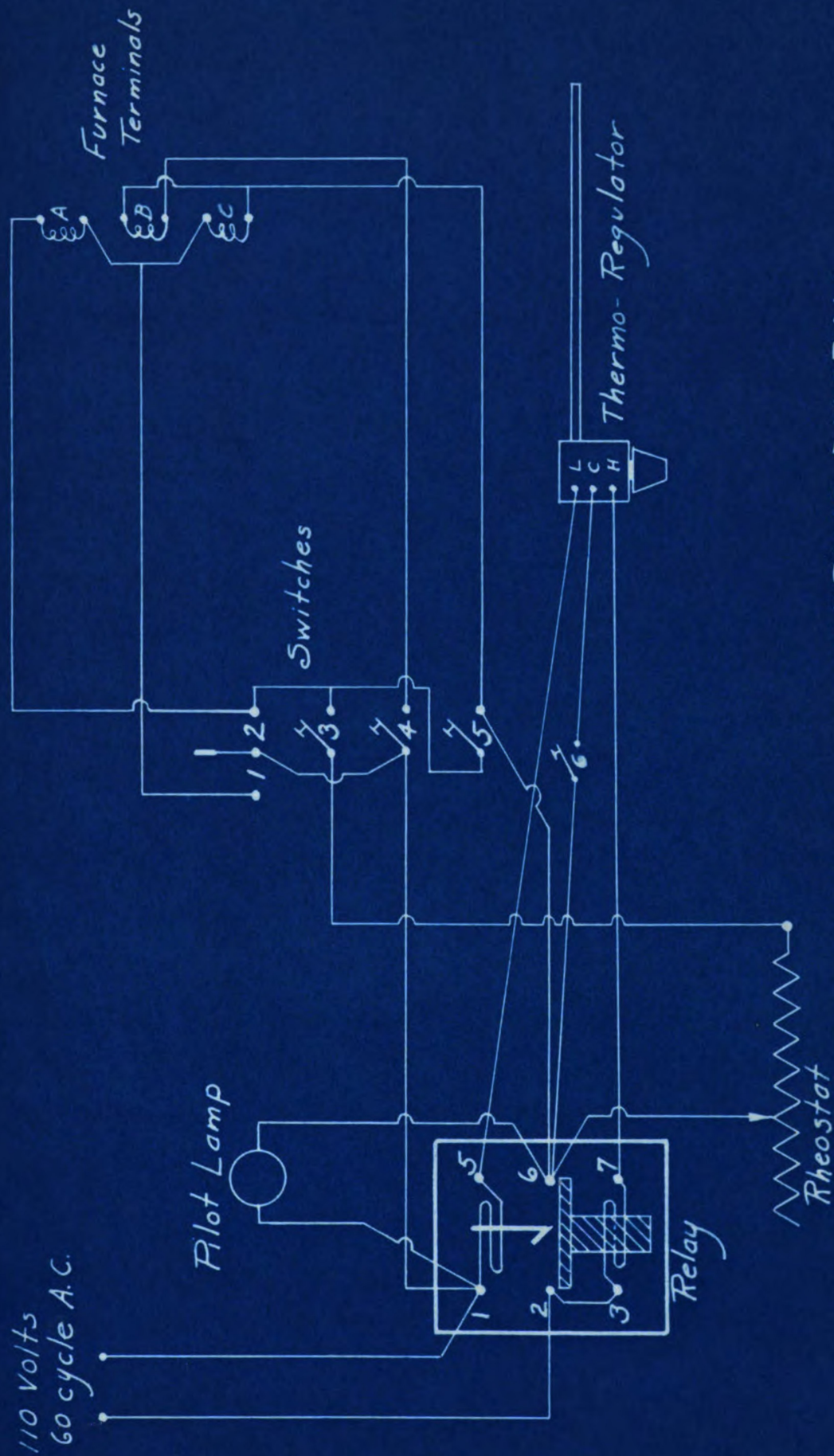
In Figure 7 is shown a three view drawing of the sheet metal case enclosing the rotating mechanism and the heating element. The bomb hangs horizontally through the heating element suspended at the back by a brass bearing and at the front by a sprocket chain. This sprocket chain is, in turn, linked to the driving motor through a large sprocket wheel, a worm gear, and a pulley. The ratio of the mechanism is such as will turn the bomb at about 12 R. p.m. when driven by a motor which runs at 1800 R p.m. A $1\frac{1}{6}$ H.P. motor is of sufficient strength to drive the mechanism.

The heating element is built up as follows: The inner core is made from a section of three inch pipe. Sections are removed from each side, as shown in the drawing, leaving a complete circumference at each end and also at a point slightly in back of the center. These sections are removed to better permit the heat to pass into the center of the unit where the bomb is rotating. Over this metal core are placed two sections of alundum clay cores which have grooves around the outside in which to place the resistance windings. These resistance windings are composed of number 17 and number 22 nichrome wire. On the back core is wound 45 feet of number 17; on the back portion of the front core is wound 25 feet of number 22, and the balance of the front core is wound with number 17. These windings are then covered to a thickness of about $\frac{1}{4}$ inch with a refractory clay plaster to prevent them from becoming loose due to expansion when heated. A stack made of a section of one inch pipe in which to place a thermo-regulator is made to lead down to the inside of the unit. Finally, a section of ordinary steam pipe covering is placed around

the entire unit and held in place by means of sheet metal straps. The ends of each resistance winding are led to binding posts on the outer wall of the apparatus.

The heating element as thus designed will produce much more heat than is necessary to maintain a temperature in the bomb of 360°C . In fact when all three units are hooked in parallel, the entire inner surface of the element can be made to glow red. However, this large heating capacity is made use of, as will be shown presently.

The wiring diagram - In Figure 8 is shown a diagram of the wiring hook-ups. The temperature control mechanism consists of a thermo-regulator of the spiral bimetal type, and a relay. With a change of temperature the thermo-regulator makes or breaks the relay circuit which is directly across the main line. A pilot lamp is hooked up so that it will light when the relay circuit "makes" and goes out when the relay circuit "breaks". It was found experimentally that the temperature in the bomb could best be controlled when the input of heat was but little greater than the radiation. It was necessary, therefore, to hook up the three units of the element (designated by A, B, and C, Figure 8) in such a way as to get as large a variation of inputs as possible. Thus, the wiring diagram shows that when switches 1, 4, and 5 are closed, all three units are in parallel, and this condition gives the maximum heat. It will be remembered that unit A, the front unit of the heating element (27 feet of #17 nichrome) is much shorter than unit C, the back unit (45 feet of #17 nichrome). Therefore, unit A will get much hotter than will unit C when both are placed in parallel across the main line. By



WIRING DIAGRAM

Fig. 8.

J H K

opening switch 5 and closing switch 3 a rheostat is placed in series with unit A and may be used to cut down the current which passes through that unit. The heat input may be cut down a little more by opening switch 4 which throws unit B out of the circuit entirely. A further decrease may be facilitated by closing only switches 2 and 4. This places units A and C in series and the combination in parallel with unit B. The lowest possible heat input is produced by having only switch 2 closed, which places units A and C in series.

Experimentally it was found that certain settings of the switches gave the best results when operating within the different temperature ranges. Thus it is possible to show in tabulated form the settings to use for operating at different temperatures.

Table I - Switch Setting for Operating Temperatures.

Temperature °C.	Switches	
	Open	Closed
Below 200	1,2,3,5	4
200 to 250	1,3,5	2,4
250 to 300	2,4,5	1,3,
300 to 360	2,5	1,3,4

Precautions - Close examination of the wiring diagram reveals the fact that when switches 2 and 5 are both closed at the same time there is a dead short circuit across the main line. Therefore, these two switches must never both be closed at the same time. Switch 6 connects the thermo-regulator to the relay and should always be closed when the apparatus is left under heat, because the thermo-regulator "makes" and "breaks" the relay circuit. Precuation must always be taken to prevent the temperature in

the bomb from exceeding that which the thermometer in use will stand. Never remove or replace the thermo-regulator cover, or clean, handle or adjust the thermo-regulator contacts without first disconnecting the electric power. The regulating temperature may be varied, however, by turning the regulating knob in the proper direction without disconnecting the electric power.

Technique of Operation

Leaks - Make sure that the welded joint joining the thermometer well to the cap of the bomb is in good condition, because this is the point at which the bomb is most liable to leak. Even though this joint appears alright it may, under the tremendous pressure developed in the bomb, leak slightly. If this is found to be true, the piece should be mounted on a lathe, the old welding metal turned off, and the joint re-welded. This joint should always be welded - not brazed. Brazing metal is a copper alloy and will be quite readily attacked by the strong caustic soda solutions employed, which will soon cause the joint to leak. Furthermore, the copper acts as a catalyst, and very often it is desirable to make runs in which there is no catalyst present. Next make sure that the ground joint is kept thoroughly ground. Ordinary valve grinding compound is suitable for this purpose.

Capacity of the bomb - The capacity of the iron bomb is approximately 415 cc. The volume of the charge placed in the bomb should never exceed 55 per cent of the total volume. This leaves a reasonable amount of space in the bomb to allow for the hydrostatic expansion of the liquid charge. Continual use of the bomb causes a coating of magnetic iron oxide to form on the walls. This may become thick enough to materially decrease the total volume. Therefore, it is well to measure the volume occasionally to

make sure that the charge employed does not exceed 55 per cent of the total volume.

Conditioning the bomb - The bomb and strips of copper, if any are employed as a catalyst, should first be conditioned by placing a charge of 20 per cent caustic soda solution in the bomb and heating it at a temperature of about 325-350°C. for a period of about 4 to 8 hours. This period of heating is usually sufficient but should be repeated until the bomb will yield duplicatable results under a given set of conditions.

Charging the bomb - The weight of the constituents which are put into the bomb should always be known. If all constituents are liquids, their specific gravities can be respectively determined, and then the proper amounts of each added by means of pipettes. Then wipe the ground joint surfaces with a soft cloth to make sure that there are no gritty particles on them, and finally put the cap in place and screw the large nut on tight by means of a wrench.

Heating the bomb to the operating temperature - It is evident that a certain amount of reaction will take place in the bomb while it is being heated up to the temperature at which it is desired to run. To diminish this as much as possible the bomb should stand idle during this period of preliminary heating, and should be brought up to the desired temperature as quickly as possible. The main difficulty is in getting the heating element too hot such that the temperature rise cannot be checked at the desired point. It is evident from the construction of the system that heat will not pass rapidly from the heating units into the bomb. That is, there is a certain amount of lag between the temperature of the heating element and the temperature in the bomb. Therefore, in raising

the temperature of the bomb from that of the room it is necessary to have the heating element much hotter than is necessary to maintain the desired temperature in the bomb in order that the temperature in the bomb may be reached in a reasonable length of time. Then when the temperature in the bomb has reached a point somewhere between 50 and 100 degrees of the desired temperature, the electric power must be greatly diminished or in some cases entirely cut off so that the heating element and the bomb may come to an equilibrium temperature. The process of making this equilibrium temperature coincide with the desired operating temperature proves to be more or less a matter of personal technique on the part of the particular operator. However, a few suggestions may be of use. For raising the temperature to 250 degrees or less, close switches 1, 3, and 4, Figure 8; connect the electric power and allow the element to heat for about 15 minutes before inserting the bomb. Leave switch 6 open so that the thermostat will not break the relay circuit during this preliminary heating period. Then insert the bomb and leave it standing idle until the temperature is about 8-10 degrees lower than the operating temperature. The temperature seems to rise rapidly by about 10 degrees within a few seconds after rotation begins. Record the time when the bomb is set in rotation. When the temperature has reached a point about 50 degrees below the operating temperature set the switches according to Table I and permit the temperature to rise 25-30 degrees higher. Then cut off the electric power entirely and permit the system to come to equilibrium. This equilibrium point will usually be very close to the desired temperature. Finally, close switch 6 and adjust the thermostat to maintain the desired temperature. This adjustment requires

minor changes over a period of about one hour after which it will maintain a regulation within 5 or 6 degrees. When heating to temperatures over 250 degrees, close switches 1, 4, and 5 and insert the bomb within 10 minutes. Then follow the same procedure as before. The particular operator may find that minor variations from this procedure will give better results.

Removal of the contents of the bomb - At the end of the reaction time the bomb is removed from the apparatus and quickly quenched. Then it is dissembled and the contents well drained into a tared beaker and weighed. The object of weighing the charge before and after reaction is to detect any leakage. If the operator is reasonably sure that the bomb is not leaking he need not make this weighing for every run, but it is advisable to check up on a leakage occasionally by this method. All surfaces which have been exposed to the reaction mixture are then washed into the vessel containing the bulk of the mixture with warm water from a wash bottle. The reaction mass is then ready for laboratory investigation. The empty bomb should be thoroughly washed with acetone and dried, preparatory to further use.

The Static Bomb

In Figure 9 is shown a design of a bomb of somewhat larger capacity than the rotating bomb, but which has no means of agitating the reaction mixture. It has, however, a threaded tap on the side to which may be attached a pressure gauge. This bomb might be mounted on a cradle of some sort which could be made to rock by means of a crank-arm from the power of a small electric motor.

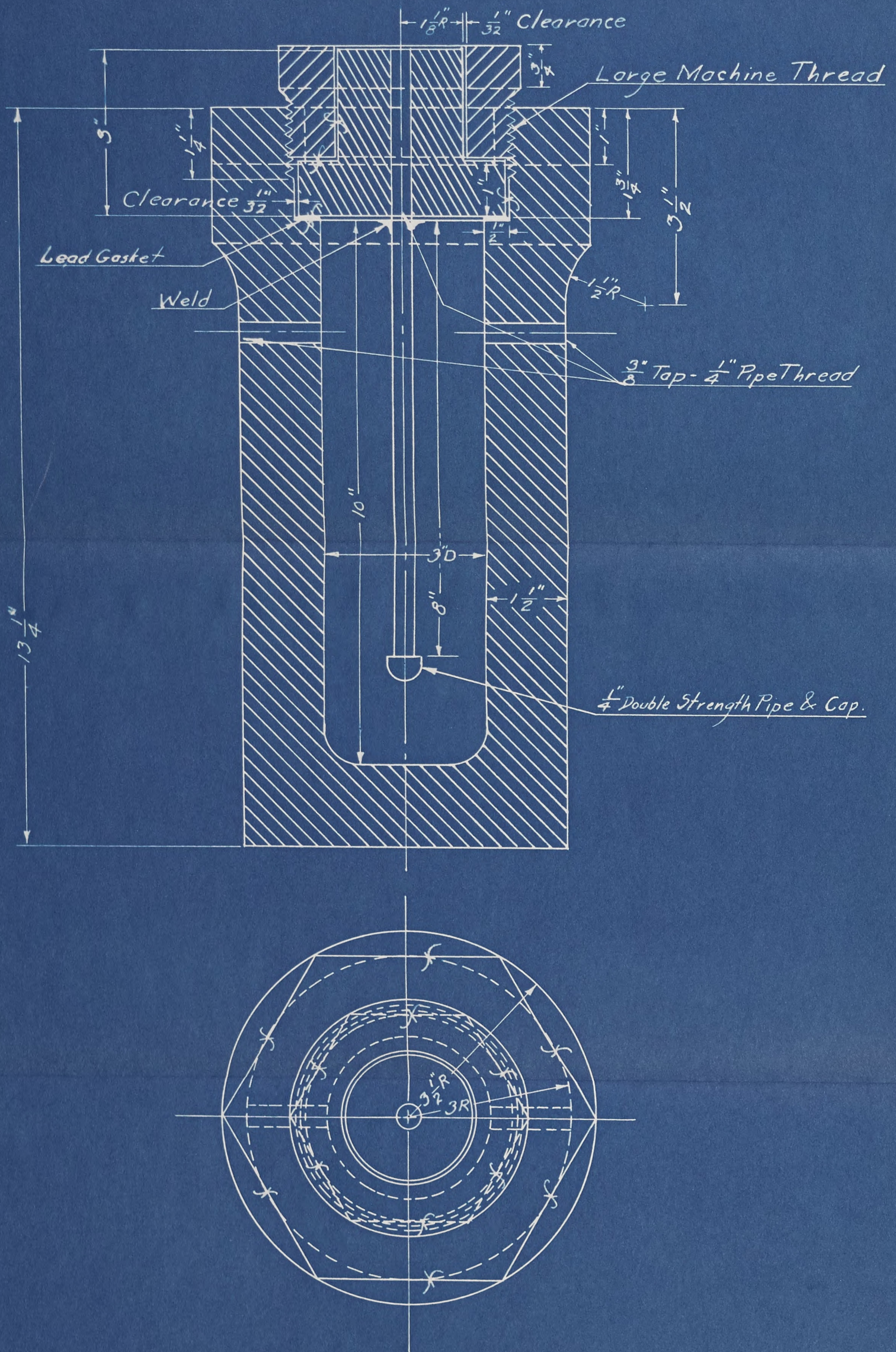


Fig. 9.

MICH. STATE COLLEGE
DEPT. OF CHEMISTRY
BOMB ASSEMBLY
SCALE: 1" = 2"
DATE: 4/10/33 L. H. ROWE.

LABORATORY INVESTIGATION

Constitution of the Reaction Mixture

The reaction mixture as taken from the bomb may contain the following substances in varying amounts. Unreacted iodobenzene, excess caustic soda, sodium phenate, diphenyl oxide, sodium iodide, and tar. Hale and Britton have been able to show in their researches on chlorbenzene and brombenzene by working with large volumes of accumulated tar that 20 to 25 per cent of the tar is made up of ortho and paraphenylphenol and that the balance is a mixture of various dephenyl condensation products each of which is formed only in minute quantities. If diphenyl oxide is present in any appreciable quantities it can be seen as an oily substance floating on the surface of the reaction mixture. Any unreacted iodobenzene will settle to the bottom as an oily layer. The phenol and tar are alkali soluble, so they will be held in the aqueous layer.

Methods of Analysis

Determination of total conversion - For every molecule of iodobenzene that is hydrolysed, regardless of the organic product formed, one molecule of sodium iodide is formed. Therefore, determination of the total inorganic halogen is a measure of the amount of conversion which has taken place. This is accomplished by means of the Volhard method. The alkaline reaction mixture is first extracted with benzene to remove the unreacted iodobenzene and diphenyl oxide, and is then made up to any convenient volume, one litre usually proves to be the best. Two different sized aliquots are then acidified with nitric acid and titrated by the Volhard method.*

* * * * *

* "Analytical Chemistry" by Treadwell and Hall - page 605.

Determination of phenol - The method used in this work for the most part was that of W. Koppeschaar. The following discussion of that method was copied directly from the text book "Analytical Chemistry" by Treadwell and Hall, page 591.

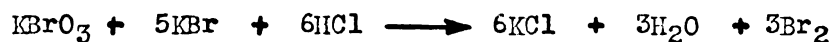
Principle: - If an aqueous solution of phenol is treated with an excess of bromine, the phenol is converted quantitatively into tribromophenol:



The tribromophenol is a pale yellow crystalline substance which is quite insoluble in water (43.7 litres of water dissolves one gram of tribromophenol). If after the reaction has taken place, KI is added to the solution, iodine is liberated corresponding to the excess of bromine, and by titrating this iodine with $\text{Na}_2\text{S}_2\text{O}_3$ solution, it is possible to calculate how much bromine reacted with the phenol.

Requirements: - 0.1 N bromine solution and 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution.

On account of the volatility of free bromine, Koppeschaar uses a solution of KBrO_3 and KBr which, when acidified gives a known amount of free bromine in accordance with the equation:



Thus to obtain 0.1 N bromine which will keep indefinitely, dissolve exactly 2.784 grams of pure KBrO_3 (dried at 100°) and about 10 grams of KBr in water and dilute the solution to one litre at 20°C . An excess of bromide (KBr) does no harm.

The use of the above described method in the present work requires a slight modification due to the presence of NaI in the reaction mixture,

which would liberate free iodine in the presence of bromine unless first removed from the solution.

The procedure is as follows: - Pipette two aliquots of the unknown solution of different volumes into labeled glass-stoppered flasks (Iodine flasks of 300 cc. capacity are best). Acidify each with as little amount as possible of nitric acid, and precipitate the iodine by addition of an excess of a solution of AgNO_3 with vigorous shaking until the yellow precipitate of AgI collects together and the supernatant liquid appears free of any cloudiness. Then add about 10 cc. of concentrated HCl and again shake vigorously to remove the excess AgNO_3 . Finally add standard bromine solution until the mixture is distinctly yellow which indicates an excess. The HCl added above is sufficient to liberate the bromine from its salts. Shake the mixture vigorously; then add about 25 cc. of 8 per cent KI solution and titrate the free iodine with standard $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch indicator.

To check up on the accuracy of this procedure, a solution of pure phenol and water was made up such that the percentage of phenol was approximately equal to that found in the bomb liquor and this solution titrated for phenol. Then NaOH and NaI were added to an aliquot of this solution in about the proportions that they are present in the bomb liquor and this new solution titrated for phenol by the modified method described above. It was found that the error introduced by the modification was negligible.

Another source of error introduced by the use of Koppeschaar's method lies in the fact that many of the compounds in the tar are phenolic and are thus subject to bromination the same as is phenol. Britton found that this error is minimized by back-titrating the liberated iodine within a minute or two after the precipitation of the tribromophenol.

It was surmised that possibly the extraction of the alkaline bomb liquor with benzene to remove any diphenyl oxide and unreacted iodobenzene might introduce error in the phenol titration. So a portion of the above known solution containing phenol, NaOH, and NaI was extracted and then titrated. No appreciable difference in the phenol titration was observed.

Determination of excess caustic soda - The determination of excess caustic is a good check on the Volhard titration for per cent conversion, since for every molecule of NaOH that is removed one molecule of NaI is formed. This determination is made by diluting a rather large aliquot of the bomb liquor, acidifying it with an excess of standard H_2SO_4 and then back-titrating with standard NaOH to a cochineal end point. Cochineal changes color at a ph. of about 5 which is approximately the ph. at the true neutral point in a solution containing phenol.

Distillation methods - The amount of diphenyl oxide must be determined by the distillation of the benzene extract. It was isolated in the present work by the use of a six inch fractionating column sealed onto the side arm of a 50 cc. Claisen distilling flask. The extract was introduced into the flask by allowing it to drip from a separatory funnel into the flask about as fast as the benzene would distill off. The appearance of the reaction mixture will indicate roughly the presence of any appreciable amount of tar. The alkaline reaction mixtures which are comparatively free of tar will have a reddish-purple color when first removed from the bomb, but upon being exposed to the air will rapidly turn to a dirty gray. If appreciable quantities of tar are present, the mixture will have a dark tarry appearance when first removed from the bomb.

To determine the extent of tar formation the entire reaction mixture must be acidified, with dilute acid to prevent the liberation of free iodine due to the oxidation of NaI, and then distilled as in the case of the extract containing diphenyl oxide. All substances up to and including diphenyl oxide (B.p. 259°) may be distilled at atmospheric pressure. Above that it is advisable to distil under vacuum.

Effect of Concentration of Caustic Soda

From the work of Hale and Britton on chlorbenzene and brombenzene it was to be expected that a wide variation of the caustic soda concentration would lead to somewhat variable difference between percentage yield in phenol and total hydrolysis, as based on the iodobenzene used. They found that at concentrations so low as 3 per cent comparative results required a higher temperature, but clearly demonstrated a lesser formation of undesired material. At concentration over 11-12 per cent they were confronted with an extremely high formation of undesired material. Their experiments in general pointed to an optimum concentration as lying between 6 and 10 per cent.

Table II shows the effect on the hydrolysis of iodobenzene of varying the caustic soda concentration. It is interesting to note that even over a wide difference of concentration little difference between the yield in phenol and total conversion was noticed. A concentration of 10 per cent was chosen for this work.

Table II - Effect of Concentration of Caustic Soda
(Rotating Iron Bomb - Copper Present)

Exp. No.	C_6H_5I : grams	NaOH : Normality	($2\frac{1}{2}$ moles) : %		Temp. : $^{\circ}C.$	Time : hours	Phenol : %	Conver- sion : %
			: cc.					
1	18.12	3.51	14.0	57.0	240	1	88.5	94.0
2	18.12	2.95	11.8	67.5	240	1	94.3	97.0
3	18.12	2.50	10.0	80.0	240	1	95.5	98.0
4	18.12	1.575	6.3	127.0	240	1	94.0	97.0
5	18.12	1.43	5.72	140.0	240	1	89.0	97.5
6	9.06	0.615	2.46	162.0	240	1	97.0	97.5
7	18.12	3.51	14.0	57.0	300	1/2	96.0	97.0
8	18.12	2.5	10.0	80.0	300	1/2	96.0	97.0
9	9.06	0.69	2.76	145.0	300	1/2	94.0	95.5

Effect of Copper Catalyst

The presence of a catalyst has been shown by Hale and Britton to have a definite effect in speeding up the reaction in the hydrolysis of benzene halide, Figure 3. In Table III is given the results of a few characteristic runs which show that the effect of a catalyst on the hydrolysis of iodobenzene coincides with the effect that it has on the hydrolysis of chlorbenzene and brombenzene - namely, that at lower temperature the effect is very marked (compare runs 10, 11, 14 and 16, Table III), but that at higher temperatures its effect is not easily registered (compare runs 13, and 18).

Table III - Effect of Copper Catalyst in Rotating Iron Bomb

Exp. No.	Catalyst	C ₆ H ₅ I : grams	NaOH (2½ moles) : Normality	NaOH (2½ moles) : %	NaOH (2½ moles) : cc.	Temp. : °C.	Time : hrs.	Phenol : %	Conversion : %
10	absent	18	2.5	10	80	150	2½	none	none
11	"	18	2.5	10	80	170	2	"	"
12	"	18	2.5	10	80	250	2	-	25.4
13	"	18	2.5	10	80	360	¼	97.0	98.6
14	present	18	2.5	10	80	150	2	31.0	31.5
15	"	18	2.5	10	80	160	1	28.5	28.8
16	"	18	2.5	10	80	170	2½	82.8	83.5
17	"	18	2.5	10	80	190	1¼	92.2	92.5
18	"	18	2.5	10	80	250	½	95.0	97.1

Extent of Reaction While Heating Without Rotation

It was considered advisable to obtain some idea of the amount of reaction which took place while the bomb was being heated up to the temperature at which it was to operate. It was found that the minimum time in which this temperature could be conveniently attained was between 30 and 45 minutes. In Table IV is given the results obtained when heating to various temperatures, the time in each case being approximately 40 minutes. These results are shown graphically in Figure 10.

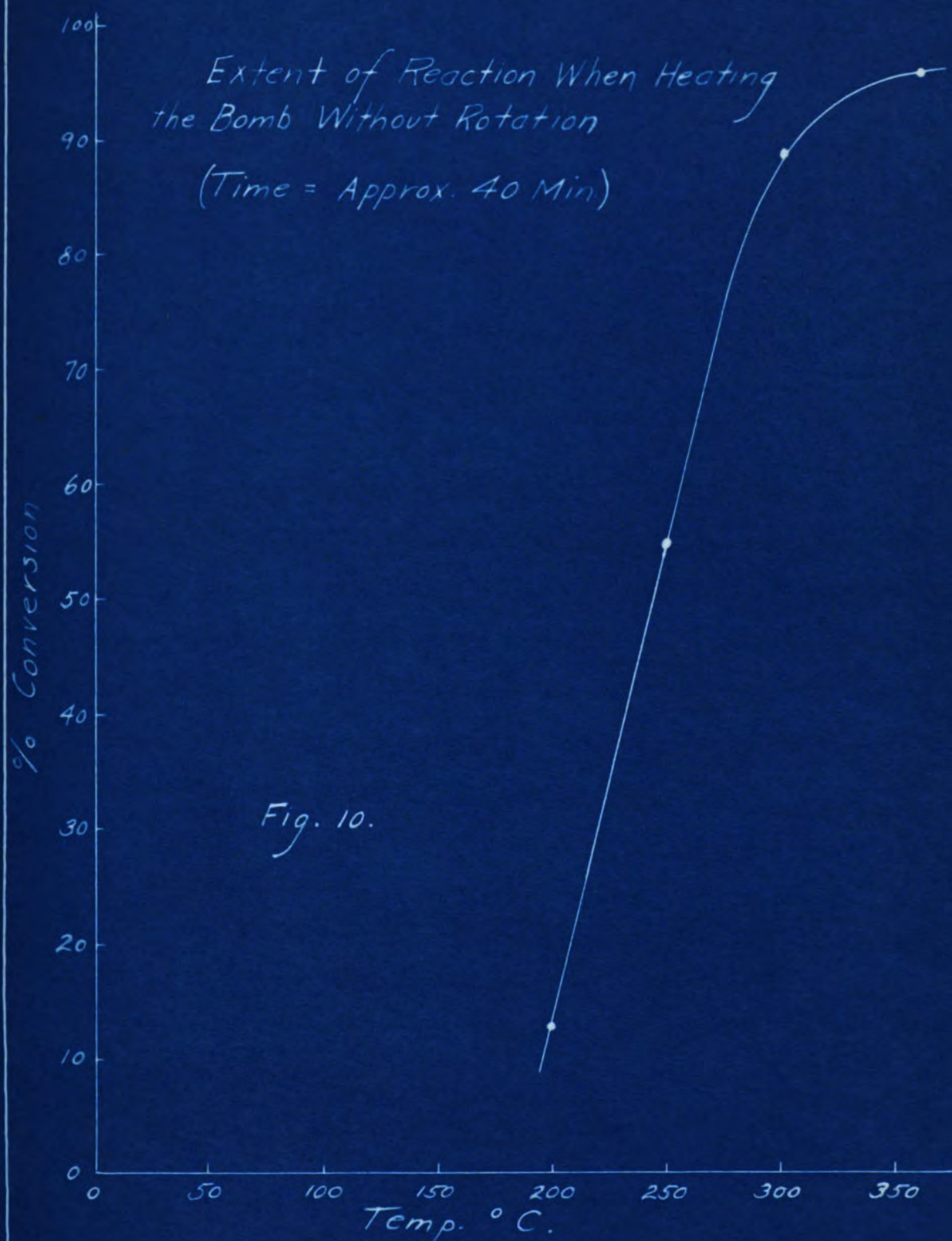


Table IV - Extent of Reaction While Heating Bomb
Without Rotation.

(Approximate Time: 40 minutes)
(Rotating Iron Bomb - Copper Present)

Exp. No.	C_6H_5I grams	NaOH ($2\frac{1}{2}$ moles) Normality	%	cc.	Temp. °C.	Phenol %	Conver- sion %
19	18.12	2.48	9.93	85	360	92.7	96.7
20	18.12	2.48	9.93	85	300	87.0	98.6
21	18.12	2.19	8.76	90	250	55.0	55.0
22	18.12	2.19	8.76	90	200	13.0	13.0

The above results show conclusively that it is practically impossible to obtain very accurate time and temperature relations under the conditions employed. It is suggested that if a furnace could be built that would heat the bomb to the required temperature very rapidly (say in about 3 to 5 minutes) and the bomb then placed in the rotating furnace which had been previously heated to the proper temperature, much more accurate results could probably be obtained.

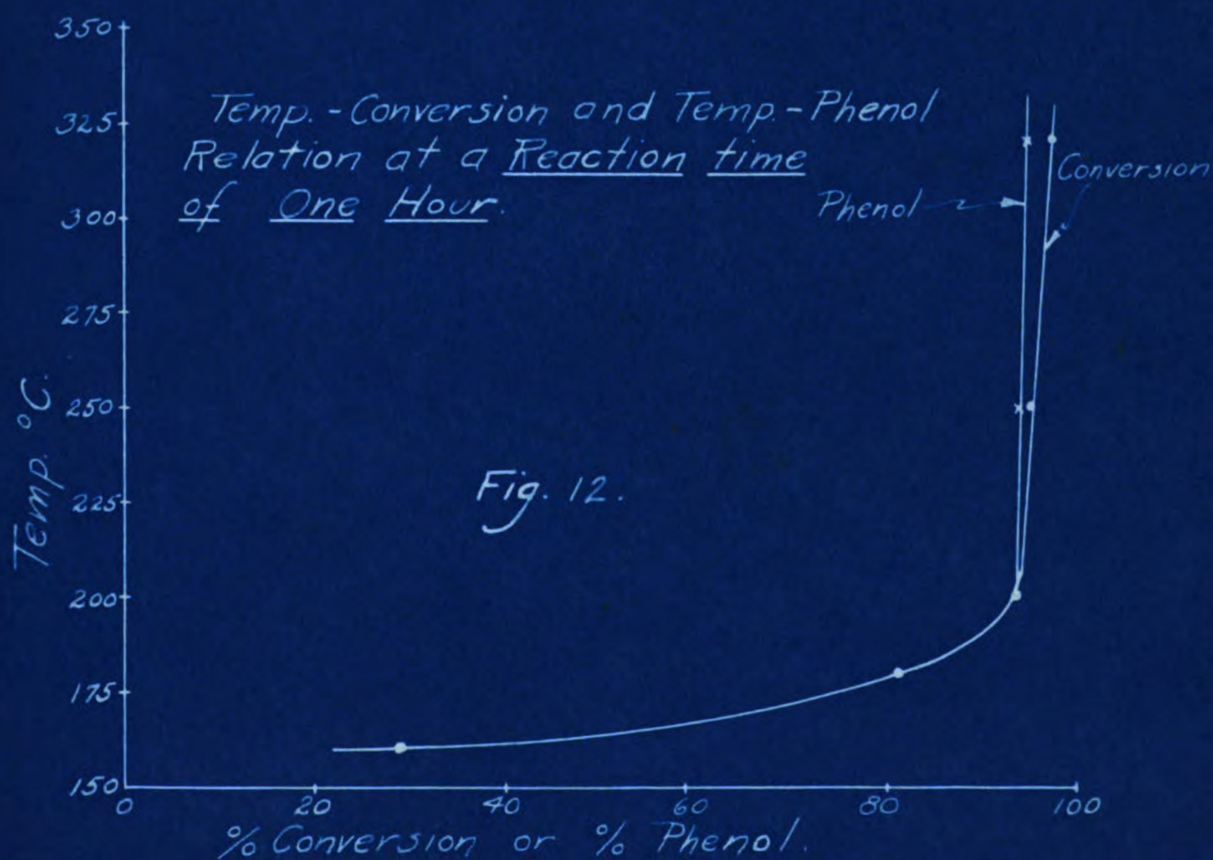
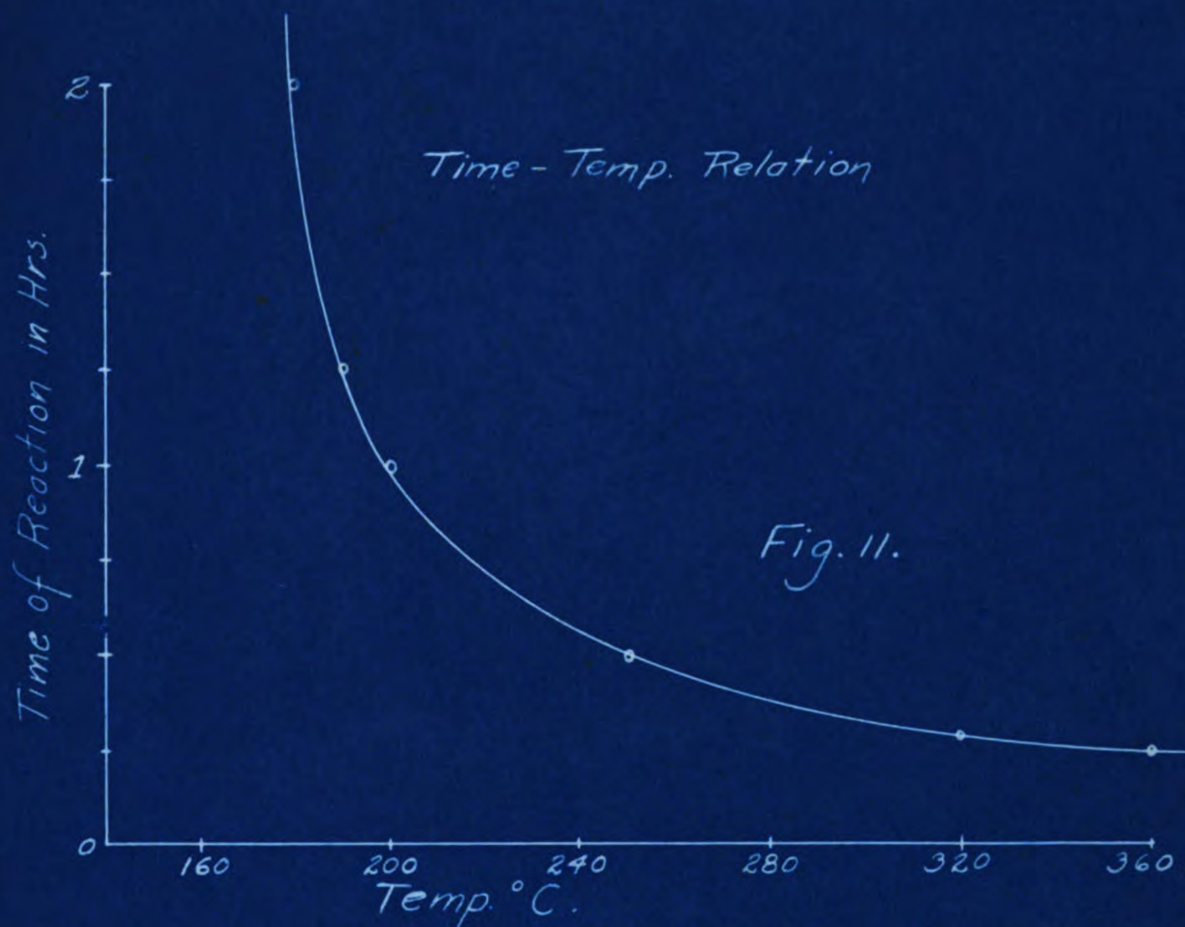
Time-Temperature Relation

The results from some of the experiments involving the hydrolysis of iodobenzene with variations of time and temperature are given in Table V. From these results the time-temperature curve, Figure 11, was drawn. The total conversion for all points on this curve is not necessarily a constant value, but is in all cases greater than 92 per cent.

Table V - Time-Temperature Relation
(Rotating Iron Bomb -
Copper Present)

Exp. No.	C ₆ H ₅ I : grams	NaOH (2½ moles) : Normality	: %	: cc.	Temp. : °C.	Time : Hours	Phenol : %	Conversion : %
23	18	2.5	10	80	360	0 ⁽¹⁾	72.2	88.1
24	18	2.5	10	80	360	$\frac{1}{4}$	72.0	99.1
25	36	2.5	10	160	320	2	96.8	97.9
26	36	2.5	10	160	320	1	95.2	97.5
27	36	2.5	10	160	320	$\frac{1}{2}$	93.1	94.8
28	36	2.5	10	160	320	$\frac{1}{4}$	91.6	93.3
29	36	2.5	10	160	320	0	55.2	62.0
30	18	2.5	10	80	250	$\frac{1}{2}$	95.0	97.1
31	18	2.5	10	80	220	$\frac{2}{3}$	95.0	96.5
32	18	2.5	10	80	200	2	97.0	98.4
33	18	2.5	10	80	200	1	93.4	93.9
34	18	2.5	10	80	200	$\frac{1}{2}$	88.4	88.7
35	18	2.5	10	80	200	$\frac{1}{4}$	70.9	70.9
36	18	2.5	10	80	190	$1\frac{1}{4}$	92.3	92.4
37	18	2.5	10	80	180	2	93.0	93.0
38	18	2.5	10	80	180	1	81.2	81.6
39	18	2.5	10	80	180	$\frac{1}{2}$	50.0	50.0
40	18	2.5	10	80	170	$2\frac{1}{2}$	82.8	83.5
41	18	2.5	10	80	170	2	80.7	81.0

(1) Zero time indicates that the bomb was removed from the furnace as soon as the desired temperature was reached.



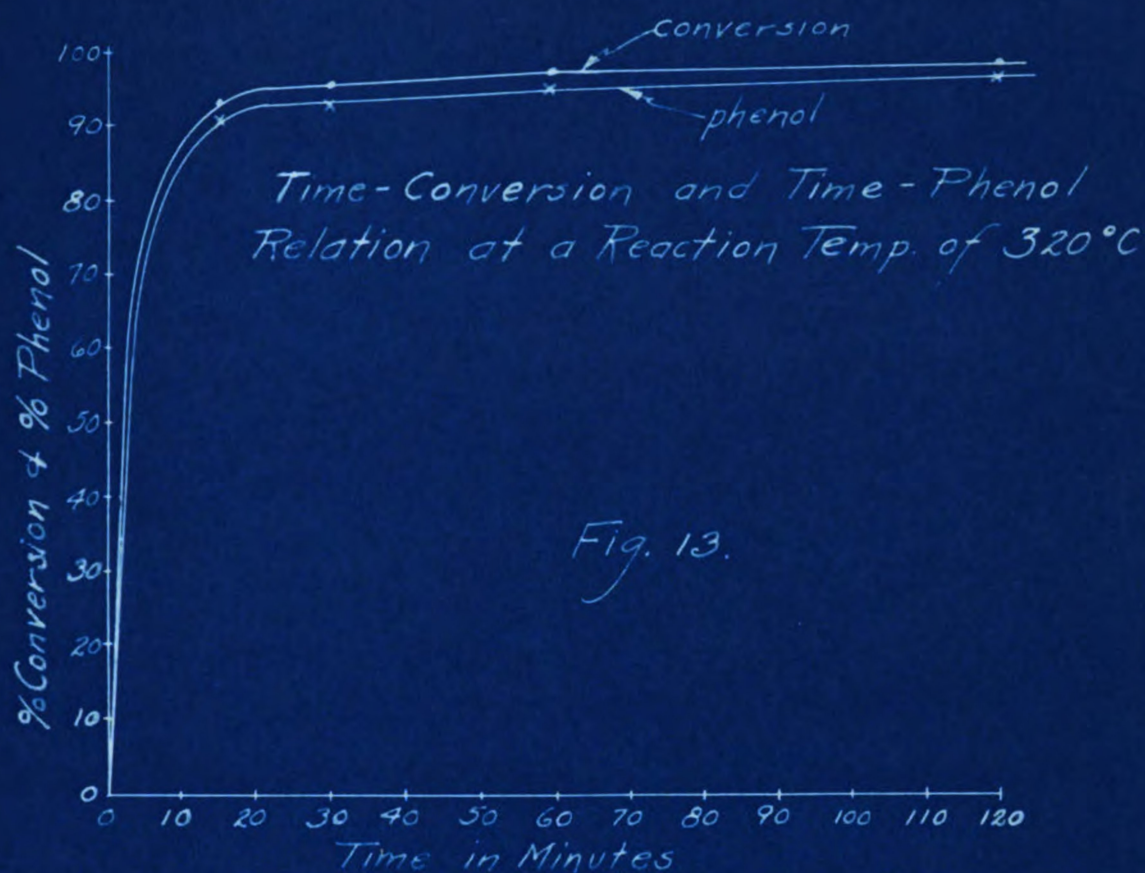


Fig. 13.

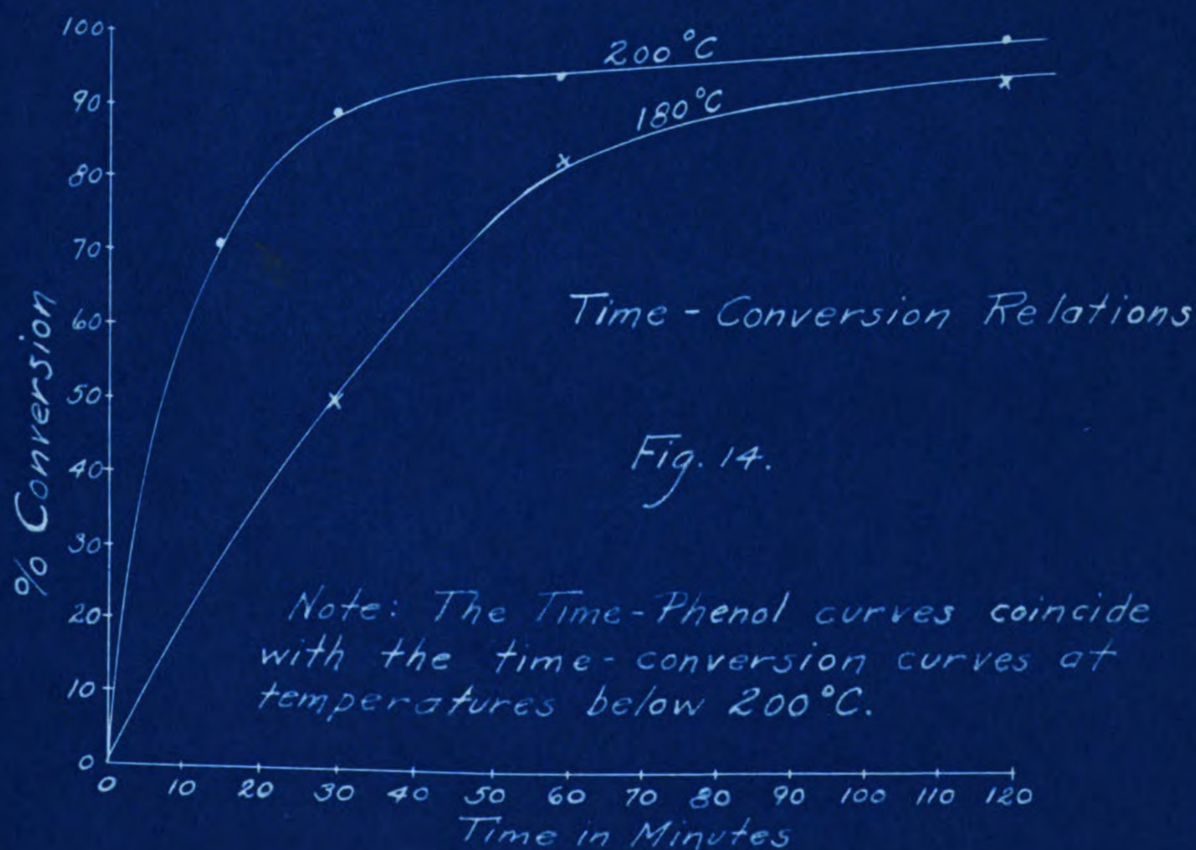


Fig. 14.

In Table VI are the results obtained at various temperatures while keeping the time of reaction constant at one hour. These results are shown graphically in Figure 12. These two curves show the very slight, but very definitely marked differences between the percentage yield in phenol and the total conversion at the higher temperatures. This difference was found to be due almost entirely to the formation of diphenyl oxide.

Table VI - Temperature Conversion, and Phenol
Relation at Constant Time of Reaction
(Rotating Iron Bomb - Copper Present)

Exp. No.	C ₆ H ₅ I	NaOH (2½ moles)	Temp. °C.	Time Hrs.	Phenol %	Conversion %		
	grams	Normality						
42	36	2.5	10	160	320	1	95.2	97.5
43	18	2.5	10	80	250	1	94.8	94.0
44	18	2.5	10	80	200	1	93.4	93.9
45	18	2.5	10	80	180	1	81.2	81.6
46	18	2.5	10	80	160	1	28.5	28.8

Constant of Unimolecular Reaction

When values from Table V were substituted in the equation for unimolecular reaction.

$$K = \frac{2.303}{t} \log_{10} \frac{A}{A-X}$$

Where: t = time in seconds

A = mole fraction of iodobenzene used

X = mole fraction of phenol produced.

Values for K were obtained which showed conclusively how impossible it is to get accurate time-temperature data under the conditions employed. At the lower temperature (170-190°C.) where, of course, the minimum amount of reaction would take place before the bomb reached the operating temperature, fairly constant values were obtained for K. Its value ranged from about 0.00020 at 170°C. to 0.00057 at 190°C.

Tar Formation

A series of runs were made employing the conditions that should favor the formation of tar so that the constitution of the tar could be investigated. These conditions, according to Britton, are the use of concentrated alkali and the carrying out of the reaction in an iron bomb without copper catalyst, since copper acts as a negative catalyst in the formation of diphenyl condensation products such as phenylphenols and others. The bomb was thoroughly cleaned with nitric acid, and then a number of runs made using 20 per cent NaOH and a reaction temperature of 250-300°C. The reaction mass in each case was acidified and extracted with benzene. These extracts constituting the hydrolysis of about 100 grams of iodobenzene were accumulated and then distilled. Out of the entire mass only a fraction of a gram of tar was obtained. This exceedingly small formation of tar led to the assumption that perhaps not all of the copper had been removed from the bomb, thus catalyzing the formation of phenol. To determine if this was true two points were picked from the time-temperature curve and runs made in an attempt to duplicate the results there recorded, without the addition of a catalyst. In both cases it was found that the per cent conversion was much smaller, which indicated that there was little or no copper left in the bomb to catalyze the reaction. From these results it was concluded that

even the most favorable conditions for the formation of tar failed to affect its formation in any appreciable quantities.

It was, therefore, impossible to accumulate a quantity of tar sufficient to determine anything about its constitution.

CONCLUSIONS

By comparing the results obtained in this work on iodobenzene with those obtained by Hale and Britton on chlorbenzene and brombenzene, a few general conclusions may be drawn:

1. The performance curves for the hydrolysis of iodobenzene are similar to those for the hydrolysis of chlorbenzene and brombenzene.

2. Hydrolysis of iodobenzene at high temperatures causes the formation of very appreciable quantities of diphenyl oxide, but to a much lesser extent than in the hydrolysis of chlorbenzene.

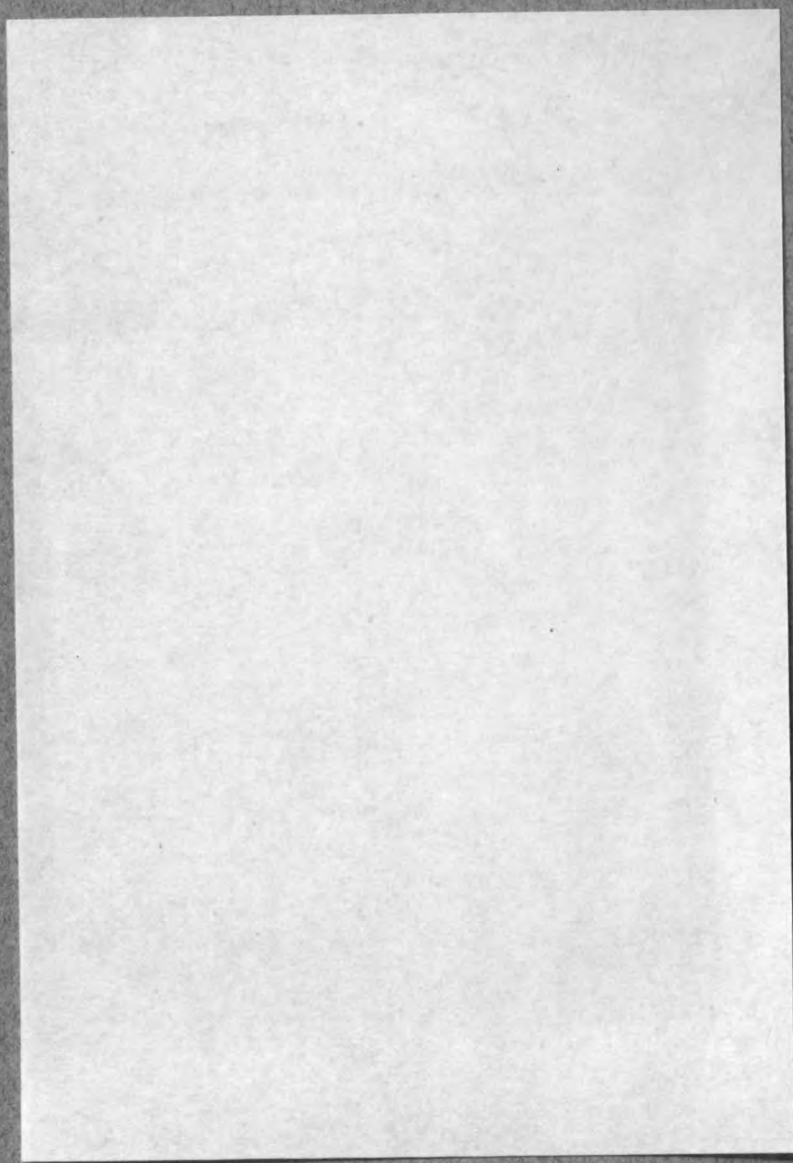
3. Wide variation in the concentration of alkali causes much less variation between total conversion and per cent phenol in the hydrolysis of iodobenzene than it does in the hydrolysis of chlorbenzene.

4. Conditions favoring an 8 per cent production of tar in the hydrolysis of chlorbenzene fail to affect its formation in any appreciable quantities in the hydrolysis of iodobenzene.

5. The hydrolysis of iodobenzene will take place at much lower temperatures than will the hydrolysis of chlorbenzene or brombenzene.

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