PARTIAL OXIDATION IN THE LIQUID PHASE

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THESIS

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I. INTRODUCTION.

The partial oxidation of organic compounds using air as the oxidizing agent, and in the presence of a catalyst, has been the foundation of several successful commercial reactions.

Oxygen may be substituted for hydrogen in a hydrocarbon for example, by a process involving several steps and utilizing relatively costly oxidizing agents. It is apparently difficult to make the substitution directly. Examples of such a reaction are the well known partial oxidation of naphthalene to phthallic anhydride, and the partial oxidation of anthracene to anthraquinone[1]. In these cases specially prepared catalysts are used, and the reactions are carried out in the vapor phase.

Since all oxidations are exothermic, it is necessary to maintain very precise temperature control. Otherwise the oxidation would continue and only the end products of the reactions be obtained, namely carbon dioxide and water. Experience has shown that temperature control is an exceedingly important factor in this type of reaction.

If such a reaction is carried out in the vapor phase and a solid catalyst is used, the heat is presumably liberated at the surface of the catalyst, because this is where the reaction is supposed to take place. The heat is transmitted to the walls of the reaction tube by means of the gases, the solid catalyst, or both. Since the heat capacity of the reacting gases is small, usually an inert, diluting gas is added to make up for this deficiency. Steam is often used because of its relatively high specific heat. The solid catalyst, though it may have a fairly high heat capacity, is often a poor conductor of heat, and as it is usually stationary, is of little value. Once the heat reaches the walls of the reaction tube, it is a relatively simple matter to conduct it away and maintain any desired temperature gradient by means of boiling or molten baths.

On the other hand, if the reaction could be run in the liquid phase, the relatively high heat capacity and better heat conductivity might make the matter of temperature control more simple. However, it is difficult to obtain good contact between a gas and a liquid, especially when that gas is usually not very soluble in the reacting liquid, as in the case of air and organic liquids.

There are many processes involving the oxidation of an organic liquid by means of air, some of which are commercial, and others which might well become commercial processes if the general problem of bringing the two phases into contact efficiently were solved. The oxidation of acetaldehyde to acetic acid is an example of such a reaction which is already carried out on a commercial scale. The importance and use of acetic acid is ever increasing with the growth of industrial organic chemistry. Acetic acid is used in the manufacture of lacquers, cellulose acetate, and various solvents. Another example is the preparation of acetophenone by the Friedel-Craft's reaction which is quite expensive. Its use in the preparation of resins and as a reagent in the preparation of various organic compounds is increasing.

In order to make comparative tests on the efficiency of the stirring apparatus, the reaction of ethylbenzene with oxygen, without a catalyst, was studied. It was further believed that certain substances might be found which would accelerate the reaction. It was also thought that the type of stirring apparatus used would be effective in carrying out the oxidation of acetaldehyde to acetic acid. Since acetic acid is of such great industrial importance, this reaction was studied in the presence of various catalysts, making use of the stirring apparatus. The use of alcohol as a possible source of acetic acid was tried in a continuous process for the oxidation of alcohol by means of air to acetic acid in two steps.

II. HISTORICAL

There has been a great deal of investigation on oxidation in the liquid phase by means of air, but not nearly so much as on vapor phase oxidation. In the case of the reaction, ethylbenzene plus oxygen to give acetophenone, Stephens[2], by bubbling oxygen through different liquid aromatic hydrocarbons, at an elevated temperature for as long as 24 days at 100° C., obtained 9.5 grams acetophenone from 50 grams of ethylbenzene without a catalyst. In the presence of acetic anhydride[3], 25 grams of ethylbenzene yielded 8.0 grams of acetophenone in eleven days. The efficiency of the acetic anhydride in promoting the reaction seemed to be due to the property which the acetic anhydride has in combining with the water which is a product of the reaction and which has an inhibitory effect.

A large number of investigators have studied the oxidation of alcohol to acetic acid by means of air, and a great number of methods for carrying out the reaction have been suggested, as well as many catalysts for hastening the reaction. Although some investigators have obtained acetic acid in the direct oxidation of alcohol by means of air in the presence of various catalysts in one step[4], nevertheless it seems to be generally granted that the direct oxidation of alcohol to acetic acid is not practicable. Judging from the patent literature, the immediate source of synthetic acetic acid is acetaldehyde, using oxygen or air as the oxidizing agents, and various salts of cerium[5], manganese[6,7], iron[8], vanadium[9], and others as catalysts. Glacial acetic acid alone, also catalyzes the oxidation of acetaldehyde.

There are various sources of acetaldehyde, one being the hydration of acetylene[11] in the presence of a mercury salt. The technical application of this method involves the following difficulties: (1) A diminution in yield due to the polymerizing action of the hot acid on the acetaldehyde. (2) The deterioration of the mercury catalyst which is gradually converted into an inactive slime containing organic mercury compounds. (3) The selection of suitable materials for the apparatus to be employed. Another source of acetaldehyde is ethyl alcohol which can be oxidized in the vapor phase by means of air with various catalysts, including copper and silver gauze, with varying yields, 60%[12] and as high as 78%[13] conversion being mentioned in the literature. Well below 10% of the alcohol is lost as carbon dioxide and other unrecoverable products, while the remaining unconverted alcohol can be recovered.[14] Recently another possible commercial source of acetaldehyde has been discovered in the partial oxidation products of natural gas and petroleum gases.

In view of the great industrial significance of acetic acid, and since the supply as furnished by the distillation of wood is inadequate, attention has been turned very extensively to synthetic methods. The sources of acetaldehyde, which is necessarily an intermediate product in the industrial synthesis of acetic acid, are becoming more numerous. There are two general methods available for oxidizing acetaldehyde to acetic acid by means of air or oxygen in the presence of a catalyst. Either the acetaldehyde vapor mixed with air or oxygen can be passed over the catalyst or the reaction can be effected at a relatively low temperature by passing air or oxygen into a solution containing the acetaldehyde and a catalyst. The high temperature method is liable to losses due to over-oxidation, while the low temperature method favors the production of peracetic acid, a compound which decomposes with explosive violence. Judging from the patent literature the low temperature, liquid phase method seems to be preferred[15]. Manganese[16] seems to be the most popular catalyst, particularly the acetate.

Oxygen under pressure[17] or air under higher pressure has been used for the oxidation of acetaldehyde, but the difficulties involved are great. The reaction is strongly exothermic, so a very efficient cooling system has to be employed, and at the same time a sufficient depth of liquid is necessary for sufficient aeration. Also all metals sufficiently strong to stand the pressure employed are attacked by the combined influence of oxygen and acetic acid, thus entailing a heavy repair bill. Besides, of course, there is the danger of explosion due to the formation of peracetic acid. In the presence of manganese acetate, an excess of acetaldehyde decomposes the peracetic acid, but on the other hand, over-aeration in a deficiency of acetaldehyde causes the formation of peracetic acid.

The more recent patents describe processes in which the air and aldehyde are passed through packed towers with glacial acetic acid, with or without catalysts present in the acetic acid[18].

III. THEORETICAL.

A. General Theory of Oxidation.

In general, oxidations can be divided into three groups:

(1) Oxidations which take place spontaneously as soon as the oxidizable material is brought into contact with oxygen or air under the proper conditions of temperature and pressure.

(2) Oxidations which are brought about by the simultaneous oxidation of certain substances called auto-oxidizers.

(3) Oxidations effected by substances which are apparently unchanged, called oxidation catalysts.

Various theories have been proposed to explain oxidations of types (2) and (3). Schonbein[19], a proponent of the dualistic theory, believed cases of auto-oxidation could best be explained by Brodie's[20] hypothesis in which he contends that oxygen is split up by the process of auto-oxidation. Van't Hoff[21], as a result of his experiment on phosphorus, said that atmospheric oxygen is already normally dissociated.

The intermediate compound theory has been developed by M. Traube[22], H. Bach[23], C. Engle and V. Wild[24] and others. Bodländer[25] and Baeyer and Villiger[26], in researches on oxidation by air, the actor, of benzaldehyde the inductor, with indigo as an acceptor, gave additional support to Bach's theory by the isolation of an intermediate compound, benzoyl hydrogen peroxide.

$$C_6H_5CHO \text{ plus } O_2 = C_6H_5\ CO:O(OH)$$

which peroxide could then react in 2 distinct ways:

(a) with another molecule of benzaldehyde,

$$C_6H_5CHO \text{ plus } C_6H_5CO{:}O(OH) = 2C_6H_5\,COOH$$

(b) With the acceptor indigo,

$$C_6H_5CO{:}O(OH) \text{ plus indigo} = C_6H_5CHO \text{ plus isatin.}$$

The hypothesis of the formation of an unstable peroxide of the inductor has been further strengthened by the isolation of such salts as in the case of cerium oxide by Job[27], and in the case of ferric and ferrous salts by Manchot[28], Goard and Rideal[29], and Bohnson and Robertson[30].

In the case of cerium studied by Job, he found that a cerium salt dissolved in the presence of K_2CO_3 is a colorless auto-oxidizer. We have,

$$Ce(OH)_3 \text{ plus } O_2 \text{ plus } Ce(OH)_3 = Ce(OH)_3\text{-O-O-}Ce(OH)_3$$

Water reacts with this compound,

$$Ce(OH)_3\text{-O-O-}Ce(OH)_3 \text{ plus } H_2O = Ce(OH)_4 \text{ plus } Ce(OH)_3\,O{:}OH$$

This blood red peroxide $Ce(OH)_3\,O{:}OH$ when brought into contact with an oxidizable substance such as potassium arsenite, oxidizes it, returning to the yellow ceric hydrate. There has been no catalysis. But, if glucose is added the ceric hydrate oxidizes the glucose, being itself reduced to the cerous hydrate which can recommence the cycle of reactions.

B. Theory of Oxidation Applied to Acetaldehyde and Ethylbenzene

Job has studied the effects of cerium[37] and cobalt[35] in alkaline solution for the oxidation of glucose with air. He found that each of these salts acts both as a catalyst and as an auto-oxidizer. Bertrand[31] found that manganese also acted as a catalyst for the oxidation of pyrogallol and hydroquinone. He found that contrary to expectation nickel promoted the oxidation. Ferric and ferrous[28, 29] salts have been reported as being active promoters of certain oxidation reactions.

There is some evidence that acetaldehyde itself may form a peroxide at very low temperatures[32]. But the temperatures maintained in this investigation exclude that possibility. Wielands[33] work indicates that the oxidation of acetaldehyde may be a dehydrogenation process, especially in the presence of water,

$$2CH_3CH(OH)_2 \text{ plus } O_2 = 2CH_3CO_2H \text{ plus } 2H_2O.$$

He showed that if moist aldehyde is shaken with palladium black, hydrogen combined with the palladium is obtained. If air is admitted, the hydrogen is used up and the dehydrogenation proceeds further. It is well known that the velocity of oxidation of acetaldehyde is decreased in the presence of water. This may be due to the fact that of the anhydrous and hydrated forms in equilibrium, only the anhydrous aldehyde undergoes rapid oxidation, while the dehydrogenation of the hydrated aldehyde is slower.

It was the belief at the beginning of this investigation that the activity of an accelerator in a given oxidation reaction depended upon at least two factors. First, it would be necessary that the oxidizing agent or catalyst be capable of oxidizing the organic compounds. In so doing the oxidizing agent would change from a higher state of oxidation to a lower state of oxidation. Second, it would depend upon whether atmospheric oxygen would continuously cause the oxidation of the oxidizing substance or catalyst. The rate of oxidation then would be determined by the slower of these two processes.

Creighton and Fink[38] list the normal oxidation potential of several metallic ions in acid solution. One would predict that if gaseous oxygen would cause the reformation of the ion in the higher state of oxidation and acetaldehyde in acetic acid solution would reduce that ion to the lower state of oxidation, then from this table, cobalt should be the most active accelerator, and manganese, cerium, iron and chromium would follow in the order mentioned. With this in mind the above mentioned catalysts and others were tried as accelerators in the oxidation of acetaldehyde to acetic acid by means of air.

Ethylbenzene[3] has been found to be oxidized by air or oxygen very slowly to acetophenone without the presence of a catalyst. In the presence of a substance such as acetic anhydride, the rate of oxidation was increased. It was believed that the slowness of the rate of oxidation was partially due to lack of intimacy of contact between the liquid and oxygen. Hence, it was believed that efficient stirring would accelerate the reaction some, and the presence of a catalyst should accelerate the reaction more.

IV. EXPERIMENTAL

A. Preparation of Catalysts.

1. Acetate of Cobalt[34]

The acetate of cobalt was prepared by precipitating the carbonate from a solution of the nitrate, filtering, washing well, and then dissolving the carbonate in 80% acetic acid. The 80% acetic acid solution was evaporated down and glacial acetic acid added to make the solution the proper acetic acid concentration for the test to be made.

2. Acetate of Nickel[36]

The acetate of nickel was prepared by dissolving the pure carbonate obtained from stock, in 80% acetic acid. The 80% acetic acid solution was evaporated down and glacial acetic acid added to make the solution the proper acetic acid concentration for the test to be made.

3. The Acetate of Manganese[37]

The acetate of manganese was prepared by precipitating the carbonate from a solution of the nitrate, filtering rapidly, washing well, and dissolving the carbonate in 80% acetic acid. The solution was then made to the proper acetic acid concentration for each test.

4. The Acetate of Vanadium

The acetate of vanadium was prepared by precipitating the hydroxide from a solution of vanadium trichloride with ammonium hydroxide, and dissolving the hydroxide in glacial acetic acid. A green solution was obtained which was filtered quickly and used immediately, either by adding acetaldehyde first and oxidizing, in which case, the solution stayed green; or if the green solution was treated with oxygen in the stirring apparatus before the acetaldehyde was added it turned brown and showed a greater oxidizing activity.

5. Acetate of Cerium.

Cerous oxalate of better than 99% purity was dissolved in boiling nitric acid and the solution of the nitrate was treated with sodium carbonate, filtered, washed well, and the carbonate dissolved in 80% acetic acid. The acetic acid solution was then made up to the required acetic acid concentration for each test.

6. Acetates of Chromium and Iron.

The acetates of chromium and iron were prepared by precipitating the hydroxide, filtering, washing well and dissolving the precipitate in glacial acetic acid.

B. Development of Apparatus.

The original form[39] of the apparatus used in an effort to obtain good contact between a reacting gas and liquid was a nickel tube with a slit halfway across the center. This tube was used for hydrogenating acetone in the presence of finely divided nickel by means of hydrogen gas. Although the employment of such a slit seemed to help obtain more intimate and greater rapidity of contact than the usual methods, its use was difficult and discontinuous. Next, a slit was used which was formed by two circular plates[39] about an inch in diameter. One was stationary, the other rotated. The reacting gas and liquid were forced, in the form of a spray, through an opening at the center of the stationary plate. This type of slit was found to be quite effective, and the efficiency was found to be improved in attaining a large surface in the slit by making it cone shaped. This greater surface allowed better temperature control of the slit by permitting it to be surrounded by a cooling bath.

The mechanical difficulties involved in the use of the large cone shaped slit are very great. First, a high speed of the rotating element is necessary, and since the two parts of the slit must be within 0.005 of an inch apart, the greatest precision is necessary in the support and bearing of the shaft carrying the rotating element. This precision can be obtained by skilled mechanics in the working of iron or steel for such an apparatus, but where corrosive liquids are used, non-corroding metals must be employed, the working of which involves even greater expense and skill. Therefore, since a very corrosive mixture was used in making the greater number of tests in this investigation, a glass container with an Illium[39] rotating stirrer was used.

The Illium stirrer was obtained from the Burgess-Parr Company. It was found to be entirely unattacked by any concentration of acetic acid in the presence of oxygen.

This Illium stirrer consists of a shaft about 8 inches long, tapering from a diameter of 5/8 inch at one end to a diameter of 3/8 inch at the other end. The large end of the shaft is screwed into the air turbine, while the smaller end of the solid shaft is enlarged from a diameter of 3/8 inch to form a solid flat circular plate of 3 1/4 inches in diameter. In the center of this flat surface is a threaded opening by means of which the lower plate is fastened to the upper plate. The lower plate contains an opening from the bottom leading into the space between the plates. Through this opening the gas and liquid are drawn between the plates from the bottom by centrifugal force and expelled through the peripheral opening. In this rotating stirrer the entire slit turns, and circulation through the slit takes place by centrifugal force.

The oxidation of ethylbenzene was carried out in an apparatus of the form shown on Plate No. 1, except, that no wash bottles were attached to the condenser. The container used was a 250 c.c. pyrex beaker just large enough for the stirrer and the tube introducing the oxygen. This beaker was supported as shown, inside a 600 c.c. beaker upon some flat pieces of rubber stopper. An air turbine rotated the stirrer at a rate of 5,000 revolutions per minute. The inner beaker was fitted with a stopper of rubber, covered with latex, with a central opening for the stirrer. A bearing, with graphited asbestos cord packing closed the opening about the stirrer practically gas-tight under the pressure maintained in the apparatus. The stopper was also fitted with openings for a filling funnel, a reflux condenser, the oxygen tube, a siphoning tube and a thermometer which was bent to fit under the turbine, and then calibrated. The oxygen came from a cylinder equipped with a Hoke reducing valve, and was measured by an accurate flowmeter.

The tests on various catalysts in the oxidation of acetaldehyde to acetic acid in water-acetic acid solution was carried out in an apparatus of the form shown in Plate No. 1. The solution was contained in a liter beaker of the tall type. It was 7 1/2 inches tall and 4 inches in diameter. This beaker was supported inside a 1.5 liter beaker by means of flat pieces of rubber stopper. The 1.5 liter outside beaker, was fitted with an inlet for steam and another for cold water and an overflow. The inner beaker was fitted with a large rubber stopper through which openings were cut for the bearing which closed around the stirrer, the filling funnel, the oxygen tube, the thermometer, bent as described above, and the siphon for emptying. There was also an opening for the condenser which was connected to wash bottles.

The apparatus for the continuous oxidation of alcohol to acetic acid is shown in Plate No. 2. This apparatus was used to effect the oxidation in two steps, so the same apparatus was used for the acetaldehyde to acetic acid step, as is shown in Plate No. 1. In addition, there was a unit attached for the oxidation of alcohol to acetaldehyde which consisted of a flowmeter to measure the air, connected to a tube leading into the alcohol flask of 350 c.c. capacity. The alcohol flask was heated by a hot plate to control the ratio of air to alcohol vapor. Connected to the flask was the catalyst tube, 10 m.m. inside diameter and 40 cm. long filled with copper gauze catalyst. The catalyst tube was heated by means of an electric furnace in series, with a bank of 10 lamps with an arrangement whereby any number of the lamps could be connected in parallel,or two banks of five each in parallel connected in series. This allowed temperature control accurate to within 10 degrees centigrade. The temperature in the reaction tube was measured by means of a chromel-alumel thermoelectric pyrometer.

A glass tube of 5 m.m. inside diameter, led from the catalyst tube to a flask above which was connected a water-cooled bead condenser equipped with a thermometer at the top and connected by a long glass tube to the oxygen tube leading into the aldehyde-acetic acid apparatus. The bottom of this flask was connected to the bottom of another smaller flask by a 5 m.m., inside diameter, pyrex glass tube fitted with a stopcock. This smaller flask was on a lower level than the larger flask, and it was fitted with a drain cock. To the top of this smaller flask was connected an air-cooled bead column equipped with a thermometer and leading through a total water condenser into the filling funnel of the acetic acid apparatus.

C. Procedure

1. The oxidation of ethylbenzene.

The ethylbenzene used was prepared by ethylation of benzene with ethylene in the presence of aluminum chloride as described by Milligan and Reid[40]. The ethylbenzene fraction was allowed to stand over calcium chloride for several weeks and then fractionated again. The fraction, boiling between 136 degrees and 137 degrees C. (corrected), was taken. One hundred grams of ethylbenzene was placed in the reaction beaker with the catalyst, if any was used, and the steam was turned on. The oxygen was passed in at a rate calculated to oxidize all the ethylbenzene in twenty-four hours. The stirrer was run at a rate of about 5,000 revolutions per minute and the reaction was allowed to go continuously for twenty-four hours. At the end of this time the products were removed and 10 c.c. tested for acetophenone with phenylhydrazine and semicarbazine. The semicarbazone of acetophenone was weighed to determine the amount of acetophenone present.

2. The tests on catalysts for oxidation of acetaldehyde

Before each series of runs on a given catalyst enough catalyst was made for the series. The most concentrated acetic acid solution was used first, with a concentration of catalyst present of from 1% to 2% in all cases. Four hundred c.c. of this solution were put into the reaction vessel and the surrounding water bath heated to 70 degrees C. with steam. The acetaldehyde to be oxidized was obtained by the hydrolysis of paraldehyde with dilute sulphuric acid. The acetaldehyde was distilled over a long bead column and the temperature of the vapor coming off was kept below 35 degrees C. and condensed under ice. There was a small amount of water in the acetaldehyde, but the acetaldehyde content was determined by titration, with sodium bisulphite. About 30 grams of acetaldehyde was added and the stirrer started at a rate of about 5,000 revolutions per minute. The oxygen was turned on by means of the Hoke reducing valve so that as the absorption capacity of the solution increased more oxygen would be released. By practice, it was possible to set the valve so that there would be no pressure in the wash bottles at all and the gas still would be fed in as fast as the solution would absorb it. As the oxidation proceeded the acid concentration and acetaldehyde concentration was determined at intervals by withdrawing a portion by means of the siphon. The acetic acid concentration was kept constant to within 1% and the acetaldehyde concentration was kept between 1.5 to 1.75 molal.

The test was run for at least an hour after the oxygen absorption became constant. The pressure inside the system was watched by means of the level of the water inside the glass tube in the first wash bottle. Under ordinary circumstances this stayed level with the water in the flask. On rare occasions, the Hoke valve would stick, when there was a change in the rate of absorption of the oxygen and some excess gas would bubble thru, or more often when there was a sudden increase in absorption, water would be sucked up in the tube. It was necessary to keep the temperature constant to within one degree. Otherwise there would be an expansion of the gas in the system causing the Hoke valve to close, or a contraction causing more gas to flow than was really being used, in either case causing the reading on the flowmeter to fluctuate. This close temperature control was rather difficult without a thermostat, but since the reaction was exothermic and the rate was reasonably constant the temperature could be controlled to plus or minus one degree by controlling the flow of cooling water. The temperature control was facilitated by the stirring since a slight change in temperature of the bath was almost instantly recorded by the thermometer in the reaction vessel. The problem of comparing rates of oxidation is discussed by Job[41].

After the absorption had remained reasonably constant for at least an hour, the stirrer was stopped, and the system swept out with oxygen through the wash bottles. The increase in acid was determined, and the remaining acetaldehyde was determined both in the solution and that absorbed in the absorption flasks. The carbon dioxide absorbed in the sodium hydroxide wash bottles was determined, by acidifying the aliquot part and heating and measuring the volume in an Orsat apparatus. After all the data had been obtained on the preceding test the solution was diluted to a lower acid concentration and another similar test made. This was repeated until the acid concentration was so low that the absorption was scarcely detectable. This data was then checked at another time and the curve plotted.

3. Tests on the continuous oxidation of alcohol to acetic acid.

Only two tests were made on the continuous oxidation of alcohol to acetic acid in two steps. The procedure was identical in both tests except that manganese acetate was used as the catalyst in the acetaldehyde to acetic acid section of the process in one test and cobalt acetate was used in the other test. Referring to Plate No. 2, the air was passed through the flowmeter at a rate of about 80 liters per hour. The temperature of the 95% alcohol in the alcohol flask was kept at a temperature of 50 to 55 degrees by means of the hot plate in order to maintain a ratio of about 5 mols. of air to one mol. of 95% alcohol. The alcohol-air mixture then passed into the catalyst tube filled with highly activated copper gauze which was kept at a temperature of 310 degrees C. plus or minus 10° C. Forty to fifty percent conversion of the alcohol to acet~~ic~~aldehyde ~~acid~~ took place in the catalyst tube as was found by preliminary tests on this part of this process. The reaction products then passed into a large flask where most of the alcohol and water condensed while the unused air and vapors passed up through the bead column cooled with water at about 15° C. In this column the greater part of the remaining alcohol and water condensed out with some of the acetaldehyde. Some acetaldehyde and the unused air passed on into the gas tube leading into the acetaldehyde-acetic acid solution where about twice the calculated amount of oxygen was added from the oxygen cylinder, the rate being indicated by the flowmeter. The condensate in the first flask was transferred to the second flask through the tube connecting them by opening the stopcock. The acetaldehyde was distilled over by means of the hot plate below the second flask and was condensed into the filling funnel of the acetaldehyde-acetic acid system. The purity of the acetaldehyde distilled over was controlled by watching the temperature of the vapor coming over from the air-cooled bead column.

The concentration of this acetic acid solution used in the acetaldehyde oxidation was maintained at about 50% acetic acid. This was necessary to keep the rate of oxidation fast enough to prevent an accumulation of acetaldehyde in the stirring apparatus, when manganese acetate was used as the catalyst. In the case of the test in which cobalt acetate was used the acid concentration remained nearly constant without the addition of extra acid. A run of six hours was made at the end of which the amount of alcohol used was determined. The acid formed was determined by measuring the volume of the acetic acid solution before and after each test and titrating each time with standard sodium hydroxide solution. The quantity of acetaldehyde unconverted was determined by adding the quantity found absorbed in the wash bottles, the amount left in the acetic acid solution and the amount left in the dilute alcohol-water solution. The dilute alcohol-water solution left was fractionally distilled to obtain 95% alcohol, the weight of which recovered was subtracted from the initial weight used.

V. DISCUSSION OF RESULTS

A. The oxidation of ethylbenzene

The oxidation of ethylbenzene with oxygen gas has been carried out by means of the stirring apparatus at 102 to 104° C. without a catalyst, and also the effects of many substances as catalysts have been tried. Four runs of 24 hours each were made. The most significant data are given below.

TABLE I.

Catalyst used	Grams of ethylbenzene	Grams acetophenone yielded	Grams ethylbenzene evaporated.
none	150	2.5	27
100 grams acetic anhydride	100	18.0	30
3 grams manganese acetate	150	31.0	35
3 grams cerium oxide	150	3.0	33

Comparing the results of Stephens[3] with those of Table I, it seems the stirrer did not increase the efficiency of the oxidation without the presence of a catalyst very much. Stephens obtained 9.5 grams of acetophenone from 50 grams of ethylbenzene in 24 days. Referring to Table I, the oxidation in one day without a catalyst was about 1.67%. Stephens obtained a yield of 19% in 24 days or a yield of less than 1% per day. It might appear that the result without a catalyst in Table I was better than that of Stephens, but it is reasonable to believe that the oxidation is more rapid at first due to the absence of water, which is an inhibitor. However, the difference in yield per day is large enough to assume that the stirrer helped to accelerate the rate of reaction slightly at least. Comparison of the results shown in Table I and those of Stephens, in which acetic anhydride was present gives a better indication of the efficiency of the stirrer. Referring to Table I, the yield, using acetic anhydride, was 18 % per day, while Stephens' yield was 36 % for 11 days or about 3.3 % per day. This indicates clearly that the absorption of oxygen was facilitated by the stirrer. It appears too, that the more reactive the substance is toward oxygen, the more the stirrer facilitates the absorption of the oxygen.

Several substances were tried as catalysts for the reaction. Manganese acetate was found to act as an accelerator, giving a yield of acetophenone of 20.6 % in 24 hours. This is better than in the case of acetic anhydride. Since only about 2 % manganese acetate was used, it seems that the effect of the manganese acetate was more that of a true catalyst than that of removing the inhibitor, water. Various oxides were tried as accelerators. Ceric oxide showed the best activity which was little better than no catalyst at all. Other acetates than that of manganese were tried but with little success.

It was found that the results of the oxidation using freshly prepared ethylbenzene were not nearly so good as the results obtained by using ethylbenzene which had been allowed to stand for several weeks over calcium chloride. The best results were obtained with ethylbenzene that had stood over calcium chloride all summer. This indicates quite clearly the inhibitory effect of the presence of even small amounts of water.

Comparison of tests made by treating ethylbenzene with oxygen in an ordinary bubbling tube, and using a centrifugal stirrer under conditions which were otherwise the same, shows that the stirrer is effective in bringing the gas and liquid into good contact more rapidly. However, the comparative efficiency of the stirrer is proportional to the speed of the reaction. Where the rate of reaction of gas and liquid is slow, the comparative efficiency of the stirrer is low.

B. The Oxidation of Acetaldehyde using Various Catalysts.

The tests on the various substances used as catalysts for the oxidation of acetaldehyde to acetic acid were run under as nearly identical conditions as possible. There were some losses due to leakage of the apparatus at the bearing, around the stirrer. However, this loss was between 1 and 3 % and was quite constant. The tests made on the catalysts were mainly of comparative value. The results of the tests are given below in Table II. The substances used as catalysts in the various tests are as follows:

Test No.1, the acetate of cobalt.

Test No.2, the acetate of nickel.

Test No.3, the acetate of manganese.

Test No.4, the brown acetate of vanadium.

Test No.5, the acetate of cerium.

Test No.6, the green acetate of vanadium.

Test No.7, the acetates of iron and chromium.

Test No.8, glacial acetic acid.

TABLE II.

% by weight acetic acid	oxygen absorption liters per hour	% yield acetic acid	% yield CO_2	% lost
Test No. 1				
93	25	98.0	10	1.0
88	15	97.5	1.3	1.2
81	6	97.0	1.8	1.2
77	4	97.0	1.8	1.2
70	2	97.0	1.9	1.1
60	0.5			

TABLE II. (cont.)

% by weight acetic acid	oxygen absorption liters per hour	% yield acetic acid	% yield CO_2	% lost
Test No.2				
93	12	97.0	1.7	1.3
86	10	97.0	1.6	1.4
77	7	97.0	1.7	1.3
70	3.4	97.0	1.5	1.5
67	0.5			
Test No.3				
93	8.4	97.5	1.5	1.0
91	7.0	97.5	1.4	1.1
86	4.6	97.0	1.8	1.2
81	2.4	96.0	2.5	1.5
75	0.5			
Test No.4				
93	7.0	97.0	1.5	1.5
90	6.3	97.0	1.5	1.5
86	5.8	97.5	1.4	1.1
80	4.0	97.0	1.4	1.6
70	3.4	96.0	1.9	2.1
60	0.7			
Test No.5				
92	5.0	97.5	1.5	1.0
90	4.0	97.5	1.4	1.1
83	3.0	97.0	1.9	1.1
70	1.0	97.0	1.8	1.3
60	0.4			

TABLE II. (cont.)

% by weight acetic acid	oxygen absorption liters per hour	% yield acetic acid	% yield CO_2	% lost
Test No.6				
93.	4.0	96.0	2.5	1.5
90	3.6	96.0	2.0	2.0
83	1.0	95.0	2.4	1.6
75	0.4			
Test No.7				
93	3.0	95.0	3.0	2.0
90	1.6	95.0	2.5	2.5
85	1.0	94.0	2.8	3.2
80	0.5			
Test No.8				
93	2.0	95.0	3.0	2.0
91	1.0	95.5	3.0	1.5
84	0.2			

The rate of oxidation was found to decrease with the concentration of acetic acid in the solution in every series of tests. In the presence of certain catalysts, the decrease in rate of oxidation was not as great for a given decrease in acetic acid concentration, as in the presence of others. The decrease in rate of oxidation with the decrease in acetic acid concentration in the presence of cobalt, manganese and nickel was very great. On the other hand, the decrease in rate of oxidation with decrease in acetic acid concentration in the presence of cerium and vanadium was not nearly so great. This general decrease in rate of oxidation with decrease in acetic acid concentration seems to agree with Wieland's results.

Cobalt was found to be the greatest accelerator of the oxidation of acetaldehyde to acetic acid, with nickel second, and manganese third. The activity of cobalt was demonstrated by the fact that if all the oxygen was passed into the cobalt acetate solution that could be absorbed, the solution became dark brown, and the oxygen absorption was a maximum. But if only a deficiency of oxygen was added, for instance, by decreasing the flow of oxygen into the stirring apparatus, the solution became lighter rapidly and finally was a light pink, the color of the cobaltous ion. This would seem to indicate that the oxidation is catalyzed by the presence of the cobalt ion, as shown by a fair amount of absorption in the presence of the pink color, and by both the cobalt ion and an intermediate oxide as shown by the presence of the dark brown color and higher rate of absorption.

The absorption in the presence of manganese was not as rapid as the absorption in the presence of cobalt, but the same color changes were evident, which seems to indicate that manganese acts in the same way that cobalt does in the acceleration of the reaction. The slope of the curve of nickel differs from all the other curves, which is no more surprising than to find that nickel works at all as a catalyst for oxidation. No color changes were evident in the nickel solution under varying conditions of oxidation.

The activity of cerium and vanadium did not decrease as rapidly with decreasing acid concentrations as the activities of the other catalysts. No color changes were evident in the cerium solutions. A brown acetate of vanadium was obtained if the solution was treated with oxygen before acetaldehyde was added. The solution then stayed brown throughout the test. If acetaldehyde was added immediately, the solution would stay green if an excess of acetaldehyde remained present, and the rate of oxidation was consistently less than the rate of oxidation of the brown solution.

Iron and chromium showed slightly better activities than glacial acetic acid alone. Various combinations of catalysts were tried but in no case did any combination show an activity greater than the most active one of the group. Other substances, such as turpentine, xylene, oxides of nitrogen, Fehlings solution, and various insoluble oxides were tried, but either they had little effect, or else the effect was too small compared to the complications involved in their use, so that they were not practical as accelerators for the reaction.

Various substances were found to have an inhibitive effect. It was found that iron decreased the effect of manganese and cerium. Substances dissolved by acetic acid splashing up on the rubber stopper had a poisoning effect upon the catalyst. This was remedied by covering the stopper with a layer of latex, letting it dry, and then treating with acetic acid. Also care was taken to keep the solution from splashing up to the stopper.

Tests on the oxidation of acetaldehyde to acetic acid in the presence of the various catalysts were made using air. The general shape of the curves were the same. However, the yields of acetic acid were slightly lower, and the yield of carbon dioxide higher due to acetaldehyde being carried over by the excess air and vapor phase oxidation of the aldehyde taking place. Tests made using manganese acetate, and cobalt acetate are typical.

Basis one hour runs.

TABLE III.

Catalyst	% by weight acetic acid	% yield of acetic acid	% yield of CO_2	% acetaldehyde carried over
manganese acetate	93	94.0	5.0	21
" "	90	93.5	5.0	20
" "	80	93.0	5.5	18
cobalt	93	95.0	4.5	20
"	88	94.5	5.0	18
"	81	94.0	5.0	16

The percentage of the acetaldehyde carried over decreased slightly with the decrease in acetic acid concentration, being held in solution by the high percentage of water.

C. The Effects of Varying Conditions.

The effect of temperature on the rate of reaction was studied. It was found that the optimum temperature under the best conditions otherwise was about 70° C. The effect of raising the temperature on the reaction, increased the rate of reaction, other variables being kept constant, but it also decreased the solubility of the acetaldehyde in the solution. It increased the amount of acetic acid distilled over, and the percentage of carbon dioxide was also increased. Hence the optimum temperature was determined by balancing these effects.

The best concentration of acetaldehyde was found to be between 1.5 and 1.75 molal. The rate of reaction was lower for lower concentration of acetaldehyde, but higher concentrations of acetaldehyde did not increase the rate of reaction, and it was impossible to maintain a higher concentration of acetaldehyde under the conditions of temperature and pressure used.

The best rate of oxygen applied to the solution, was found to be the maximum rate at which the oxygen was totally absorbed. If an excess was passed through the solution, acetaldehyde was carried over, and the amount of carbon dioxide increased very much by the reaction of the excess oxygen with the acetaldehyde in the vapor phase.

Under the condition used, the maximum rate of stirring possible was about 5,000 revolutions per minute. It was found that when the rate of reaction was slow, the rate of stirring could vary from 3,000 to 5,000 revolutions per minute without a noticeable change in rate of absorption. But when the rate of reaction was rapid as in the case of oxidation catalyzed by cobalt, the rate of stirring affected the rate of absorption very appreciably. When the rate of stirring was 5,000 revolutions per minute, as in one case, the rate of absorption was increased to 25 liters per hour. In all tests of this investigation, the maximum rate of 5,000 revolutions per minute was used.

D. The Continuous Oxidation of Alcohol to Acetic Acid

Tests were made using cobalt acetate as the catalyst for the acetaldehyde to acetic acid step one time, and using manganese acetate as the catalyst the second time. The test was made for six hours. The most successful results were as follows:

TABLE IV.

1. Test using cobalt acetate in 90% acetic acid solution.

mols. alcohol used per hour	% converted to acid	% CO_2	% recovered as aldehyde	% alcohol unacc. for	% yield
0.72	62.1	7.8	27.8	2.3	89.9
2. Test using manganese acetate in 90% acetic acid solution.					
0.57	50.2	8.2	38.2	3.4	88.4

The percent yield is calculated on the basis of recovered products.

These results show that it is possible to oxidize alcohol continuously to acetic acid in two steps with a yield of 90%. With the present stage of development of non-corroding metals, the necessary equipment for such a process on an industrial scale seems possible.

VI. CONCLUSIONS.

The acetate of cobalt was found to be the most active accelerator for the oxidation of acetaldehyde to acetic acid in acetic acid solution. It was found that as the water content was increased, the rate of reaction decreased until at a concentration of acetic acid of 60%, the rate of oxidation of acetaldehyde was very small.

The acetate of nickel, contrary to expectation, was an accelerator of the oxidation of acetaldehyde to acetic acid. The acetate of manganese resembled cobalt in its effect as a catalyst. However, the rate of oxidation was not as high in the presence of manganese. Two acetates of vanadium were used which were of different activity. The acetate of cerium was also found to accelerate the reaction. The acetates of iron and chromium had a very slight catalytic activity. The rate of oxidation in glacial acetic acid is less than the rate of oxidation in the presence of any of the catalysts mentioned. No combinations were found which gave better results than single catalysts.

The continuous oxidation of alcohol to acetic acid in two steps was found to yield 80% of the theoretical amount of acetic acid.

Manganese acetate and acetic anhydride were found to accelerate the rate of oxidation of ehtylbenzene in the liquid state. High speed stirring in the presence of these catalysts was found to accelerate the rate of oxidation still more. Manganese acetate was found to accelerate the rate of oxidation of ethylbenzene more than acetic anhydride.

Various substances were found to inhibit the oxidation of both ethylbenzene and acetaldehyde. Water was found to decrease the rate of oxidation of both. The presence of iron was found to decrease the activity of other catalysts, as manganese, cerium and vanadium.

Substances dissolved from the rubber stopper decreased the oxidation of acetaldehyde and ethylbenzene.

The effect of high speed stirring on the rate of absorption, was found to be most marked where the rate of reaction was most rapid, and almost imperceptible where the rate of reaction was low. In the case of the rate of reaction of the gas and liquid being high, the rate of stirring was found to affect the rate of absorption, for example, doubling the rate of stirring alone, increased the rate of oxidation 50 %. The rate of stirring was found to accelerate the oxidation of ethylbenzene also. However, again the effect of the stirring apparatus was greatest when the reaction between the gas and liquid was most rapid. It is concluded that the efficiency of stirring is due to bringing the gas and liquid into good contact where the rate of reaction would be faster if good contact were established rapidly enough. The high speed stirring cuts down the gas film which is always present in absorption processes.

PLATE NO. 1

Apparatus for Catalyst Testing

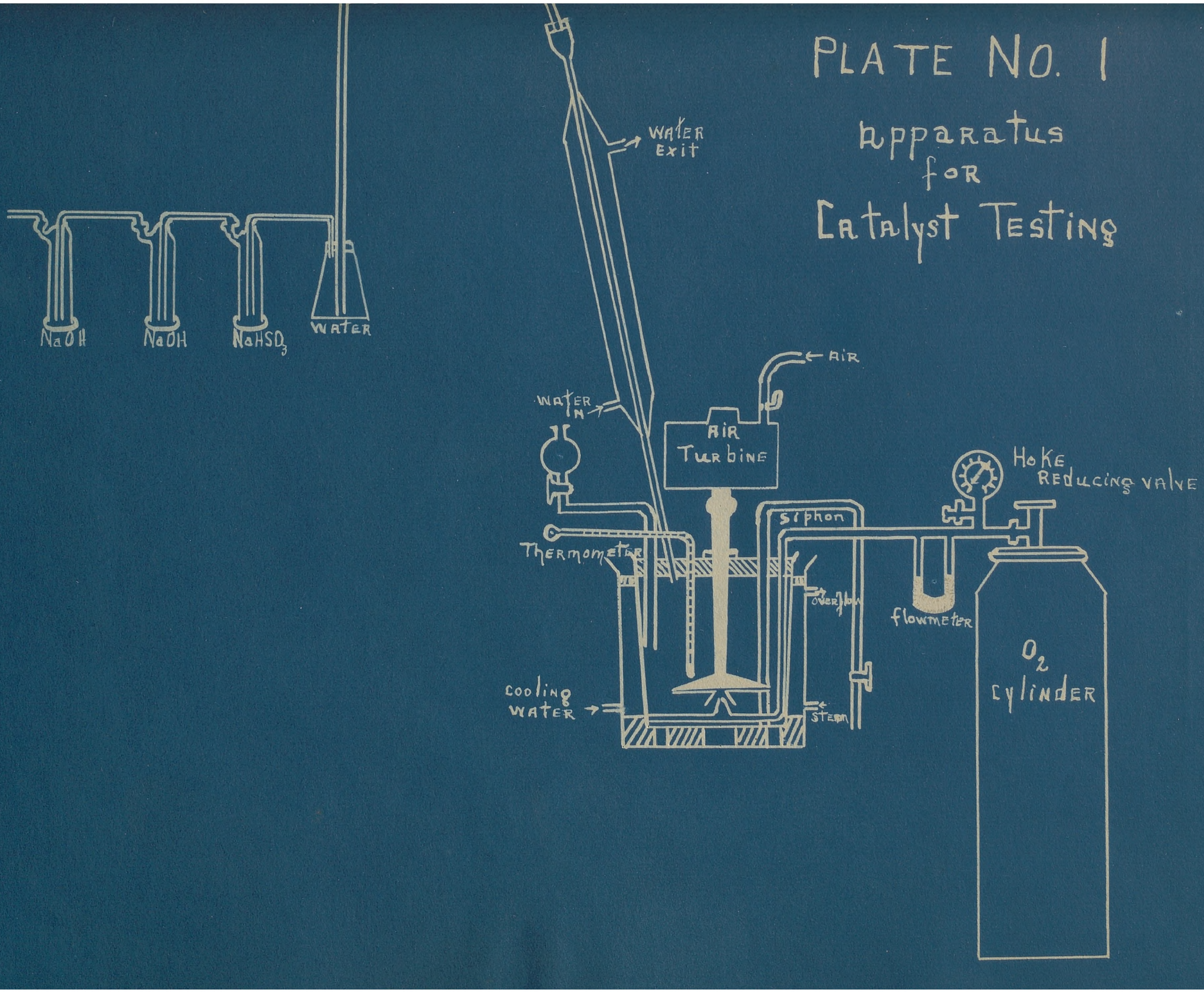
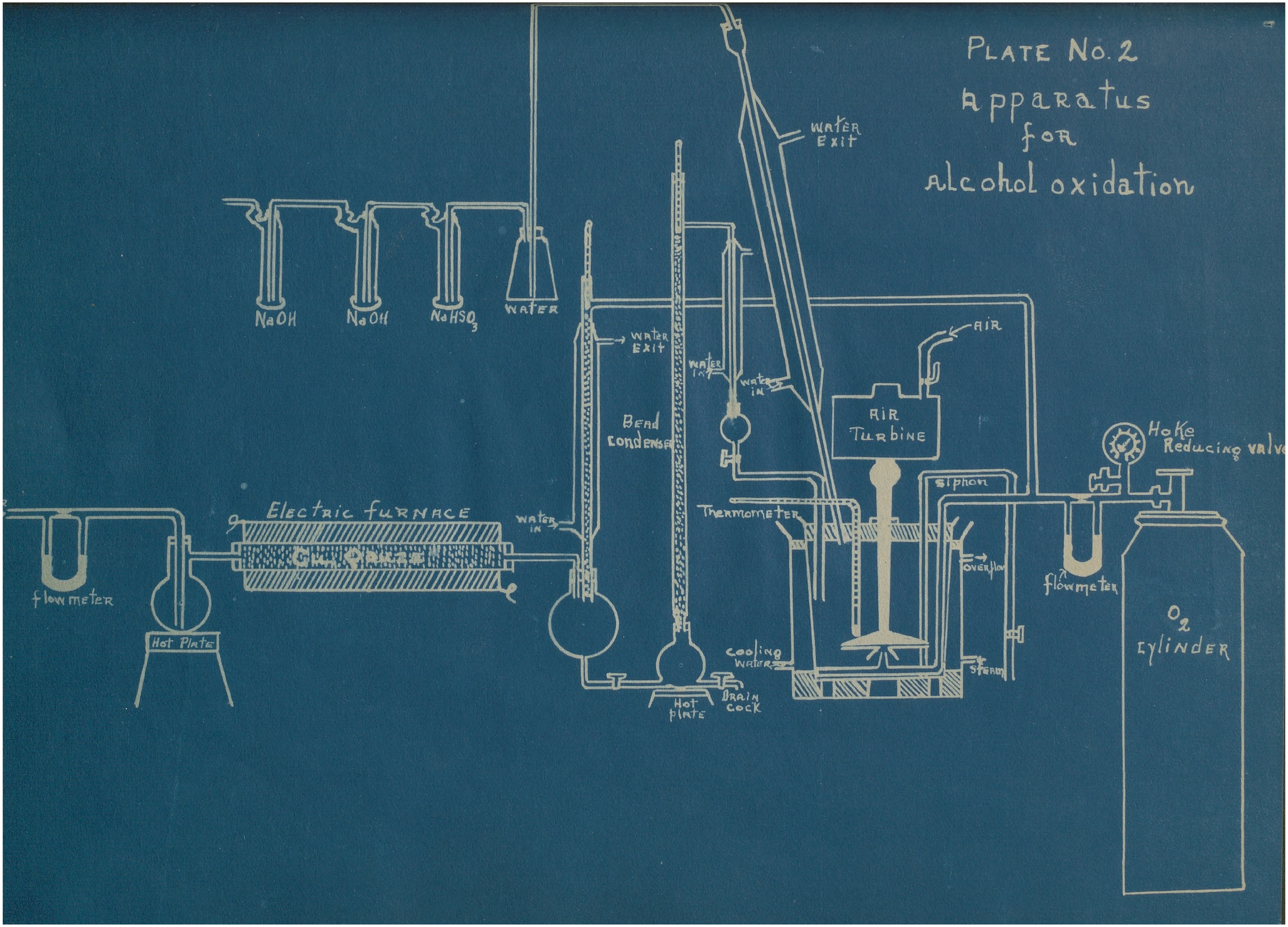


PLATE No. 2

Apparatus for alcohol oxidation



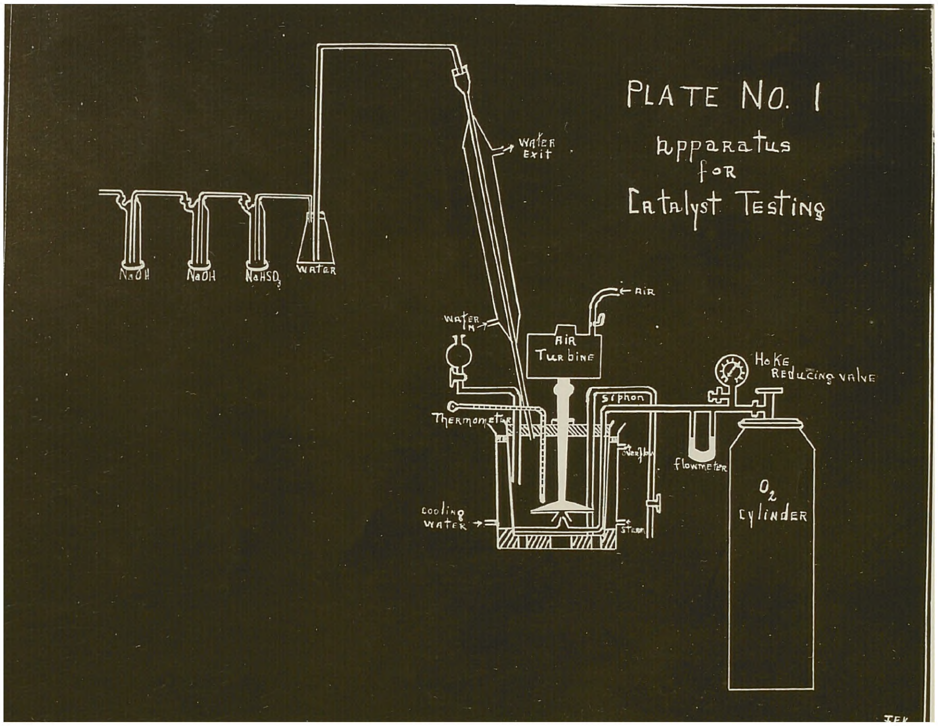
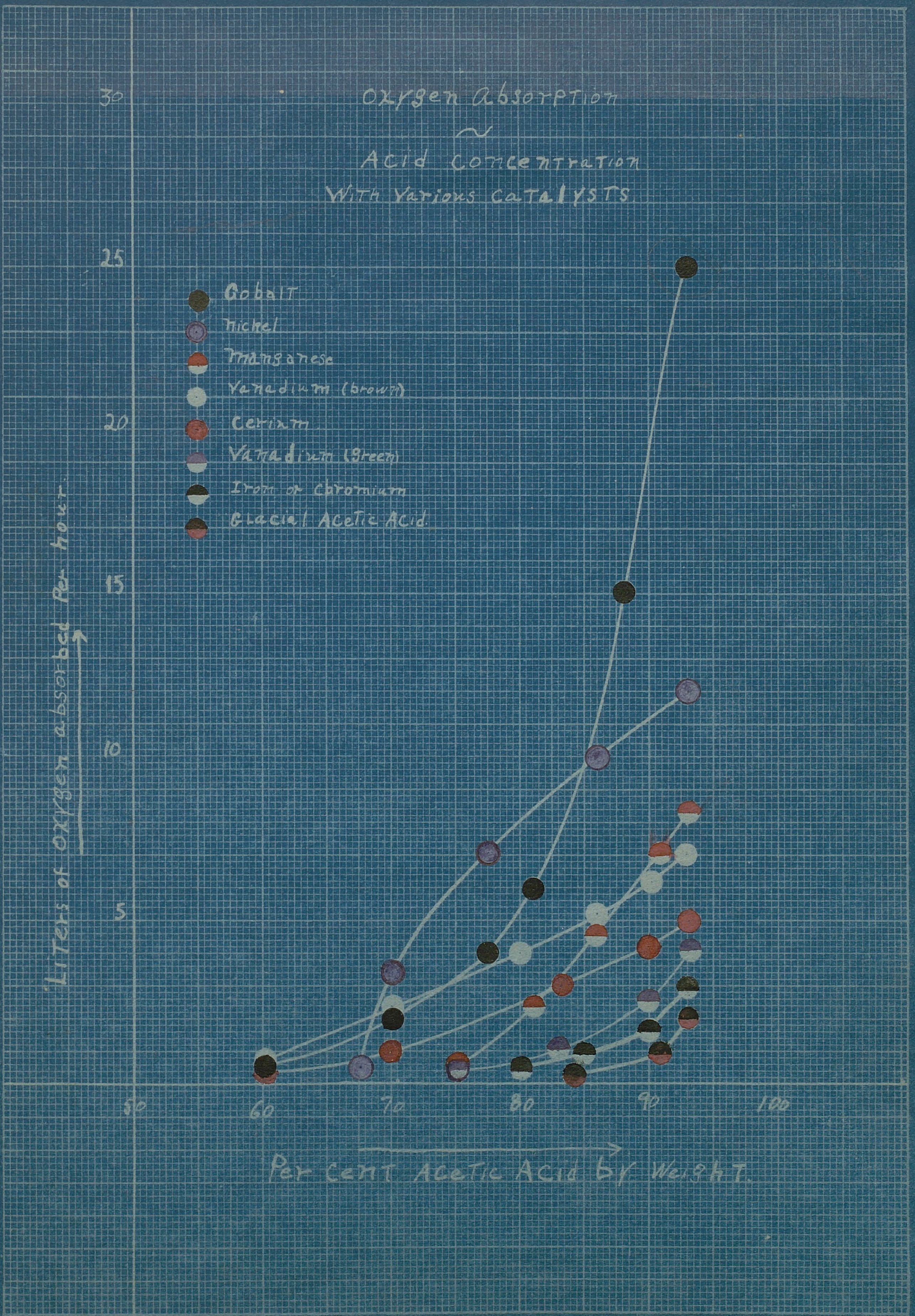
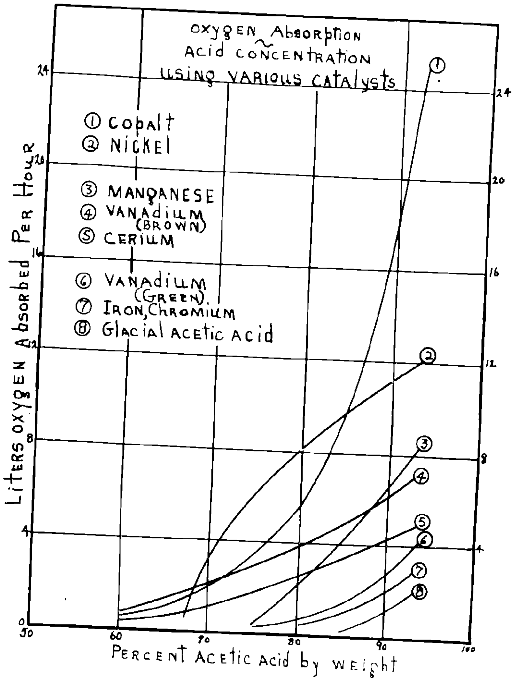


PLATE NO. I
Apparatus for Catalyst Testing

~~[illegible]~~

Fig. I


Oxygen absorption
~
Acid concentration
With various catalysts
Cobalt
nickel
manganese
Vanadium (brown)
Cerium
Vanadium (Green)
Iron or Chromium
Glacial Acetic Acid
Liters of oxygen absorbed per hour
30
25
20
15
10
5
50
60
70
80
90
100
Per cent Acetic Acid by Weight.


OXYGEN Absorption ~ Acid CONCENTRATION
USING VARIOUS CATALYSTS
① Cobalt
② NICKEL
③ MANGANESE
④ VANAdium (BROWN)
⑤ CERIUM
⑥ VANAdium (GREEN)
⑦ IRON, CHROMIUM
⑧ Glacial Acetic Acid
Liters Oxygen Absorbed Per Hour
Percent Acetic Acid by weight
0
4
8
12
16
20
24
50
60
70
80
90
100
①
②
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⑧

Fig III

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