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Oxygen Problem--Report XXXI
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I. Abstract

1. The recommended procedure for the preparation of di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt is reproduced.
2. Further studies of the temperature of activation of the hydrate first formed in the preparation of di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt indicate that the material requires temperatures of about 125-130° for rapid activation.
3. The rate of oxygenation of di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt was measured at various temperatures and humidities. The rate of oxygenation is more or less independent of the temperature and is affected somewhat by the moisture content of the air. When the moisture content of the air is above 1 mg. of water per liter the competing absorption of oxygen and moisture becomes apparent, and the amount of oxygen decreases as the moisture content of the air increases.

II. Review and Objective.

The early work dealing with the preparation of di-(3-nitrosalicylal)ethylenediimine cobalt is described in the Report XIV. Studies on the method of preparing the material and the early difficulties experienced are described there. The steps in the preparation of the material are : (1) the nitration of salicylaldehyde, (2) the separation of the 3-nitro and 5-nitrosalicylaldehydes so obtained, (3) the condensation of 3-nitrosalicylaldehyde with ethylenediamine, (4) the conversion of the latter compound to its hydrated cobalt derivative, and (5) the activation of the latter to yield an oxygen-carrying material. The various steps in the procedure have now been well worked out (see Reports XV and XXIV for the nitration step) and the yields are excellent, the major disadvantage being in the loss of about half of the salicylaldehyde to the useless 5-nitrosalicylaldehyde. The temperature of activation, that is of eliminating the water from the hydrate first formed, to yield an oxygen-carrying material, was not completely determined in the earlier work.

As implied in the earlier reports, the rate of oxygenation of di-(2-hydroxy-3-nitrobenzaldehyde is influenced by the humidity of the air. This subject is of importance and requires further study. The principal object of the work, therefore was to study the rate of oxygenation of di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt as it is affected by temperature, pressure, and humidity.

III. Recommended Procedures for the Nitration of Salicylaldehyde, the Separation of 3-Nitro- and 5-Nitrosalicylaldehyde, and the Preparation of Di-(2-hydroxy-3-nitrobenzal)ethylene-diimine Cobalt.

- (1) The Nitration of Salicylaldehyde. In a 5 liter, 3-neck flask, equipped with a motor driven stirrer, a dropping funnel, a thermometer, and a vacuum line to carry off the fumes, place 2000 g. of glacial acetic acid and 500 g. of salicylaldehyde (technical). Cool this solution in an ice bath to 25° and then start the slow addition of the nitric acid. During the next 2.5 hours add 400 g. of 98 per cent nitric acid, sp. gr. 1.50. This acid must be added slowly and after the first 100 g. has been added the temperature should be reduced to less than 15° and held below 15° until the addition is complete. After all of the acid has been added, remove the solution from the ice bath and allow it to warm to about 45°. This will take from 1-2 hours. When the temperature reaches 45°, immediately pour the material into 10 liters of water containing some cracked ice. Let the material stand at least 5 hours, then filter off and dry. The yield from this procedure is about 92 per cent, calculated on the basis of the technical grade salicylaldehyde as 85 per cent pure.
- (2) The Separation of 3-Nitro from 5-Nitrosalicylaldehyde. Dissolve 4 parts of the mixture of isomers in 30 parts water and 1 part of sodium hydroxide. Heat until all of the material is in solution, and allow it to cool slowly by standing overnight. Filter off the crystalline sodium salt of the 5-nitro salicylaldehyde and treat the filtrate with 1:1 sulfuric acid until no more material is precipitated on further addition of acid. Filter off the pure 3-nitro salicylaldehyde.

In order to further purify the 5-nitro salicylaldehyde recrystallize the sodium salt of 5-nitro salicylaldehyde twice from 6 times its weight of water. Dissolve the resulting pure sodium 5-nitro salicylaldehyde in 6 times its weight of water and acidify with 1:1 in sulfuric acid until no more precipitate appears. Filter off and dry the pure 5-nitro salicylaldehyde.

In order to obtain the isomer of 3-nitro salicylaldehyde which will give an oxygen carrier dissolve the 3-nitro salicylaldehyde prepared above in twice its weight of hot alcohol and place the resulting solution in a well insulated container. Allow the solution to stand 2 or 3 days without disturbing and then filter off the large dark brown crystals of the high melting isomer, m.p.: 108-110°.

- (3) The Preparation of Di-(2-hydroxy-3-nitrobenzal)ethylenediimine Cobalt. Dissolve 2 moles of 3-nitrosalicylaldehyde (m.p.: 108-110°) in 1500 ml. of hot 95 per cent alcohol. To this solution add 1 mole of ethylenediimine. Cool the solution and filter off the orange-yellow precipitate. Mix the Schiff's base without drying into 10 liters of hot water. Add 2 moles of sodium hydroxide and 2 moles of sodium acetate dissolved in 1 liter of water. To the resulting material add 2 moles of cobalt chloride dissolved in 1 liter of water. Digest the mixture on a steam bath for 6-8 hours. Filter and dry the material at 100°. Activate the dried compound either in a vacuum oven at 120° or under infra red lamps.

IV. The Activation of Di-(2-hydroxy-3-nitrobenzal)ethylenediimine Cobalt.

The compound Di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt is obtained by the usual method of preparation in the form of a hydrate. The loss of water upon drying is gradual and there seems to be no definite temperature at which the hydrate begins to decompose.

Studies on the activation of the 3-nitro compound have shown that the material may be activated in air at a temperature of 125-130°. At this temperature no apparent decomposition results but the rate of activation is not rapid, about

24 hours being required. Under a vacuum the 3-nitro compound may be activated at a somewhat lower temperature. There does not seem to be a definite optimum temperature for the activation. Experiments have shown that the activation will occur at a temperature of 90-95° under a high vacuum but only very slowly. Only at a temperature of 120-125° under a vacuum can the rate of activation be considered rapid.

In another experiment a sample of 3-nitro compound was partly activated at room temperature in a vacuum desiccator over phosphorus pentoxide. A sample activated in this manner carried 2 percent oxygen, however, activation in this manner required several days.

V. The Rate of Oxygenation of Di-(2-hydroxy-3-nitrobenzal)ethylenediimine Cobalt.

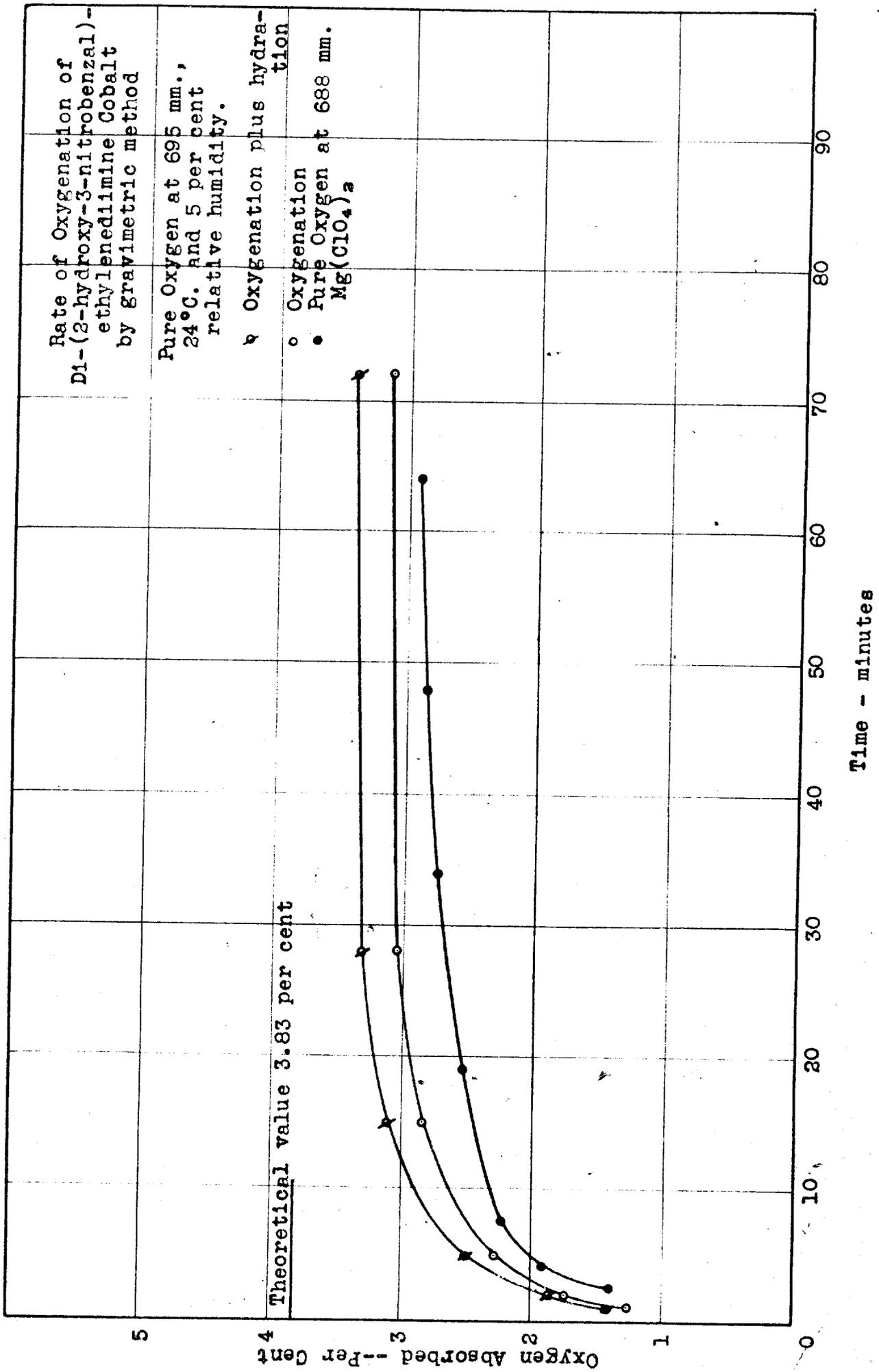
A number of the earlier determinations of the rate of oxygenation of di-(3-nitrosalicylal)ethylenediimine cobalt were made by measuring the increase in weight of a glass stoppered U-tube containing the compound on the passage of air or oxygen through the tube. This method was quite satisfactory, although the compound would often plug the glass wool filters and thus prevent an adequate gas flow through the U-tube. The oxygenation rates were determined at various temperatures by placing the U-tube in a water bath at the temperature desired. The glass stoppered U-tubes used in these rate determinations had cross section of about 0.5 in. The temperature of the compound was probably not maintained very constant during these determinations since no provision was made for controlling the temperature of the gas moving through the compound and since the temperature of the bath was often quite removed from room temperature. This method was also very time consuming.

It was found that di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt absorbed water as well as oxygen if the air or oxygen used was not thoroughly dried. Therefore a study was made to determine the correlation between the quantity of water present in the gas and the rate of oxygenation, the oxygen pressure and temperature being held constant. The humidity of the in-going gas was adjusted by passing the gas through sulfuric acid solutions of various concentrations or through suitable saturated salt solutions. The gain in weight of the U-tube was measured and the oxygen evolved and its volume determined. The weight of oxygen

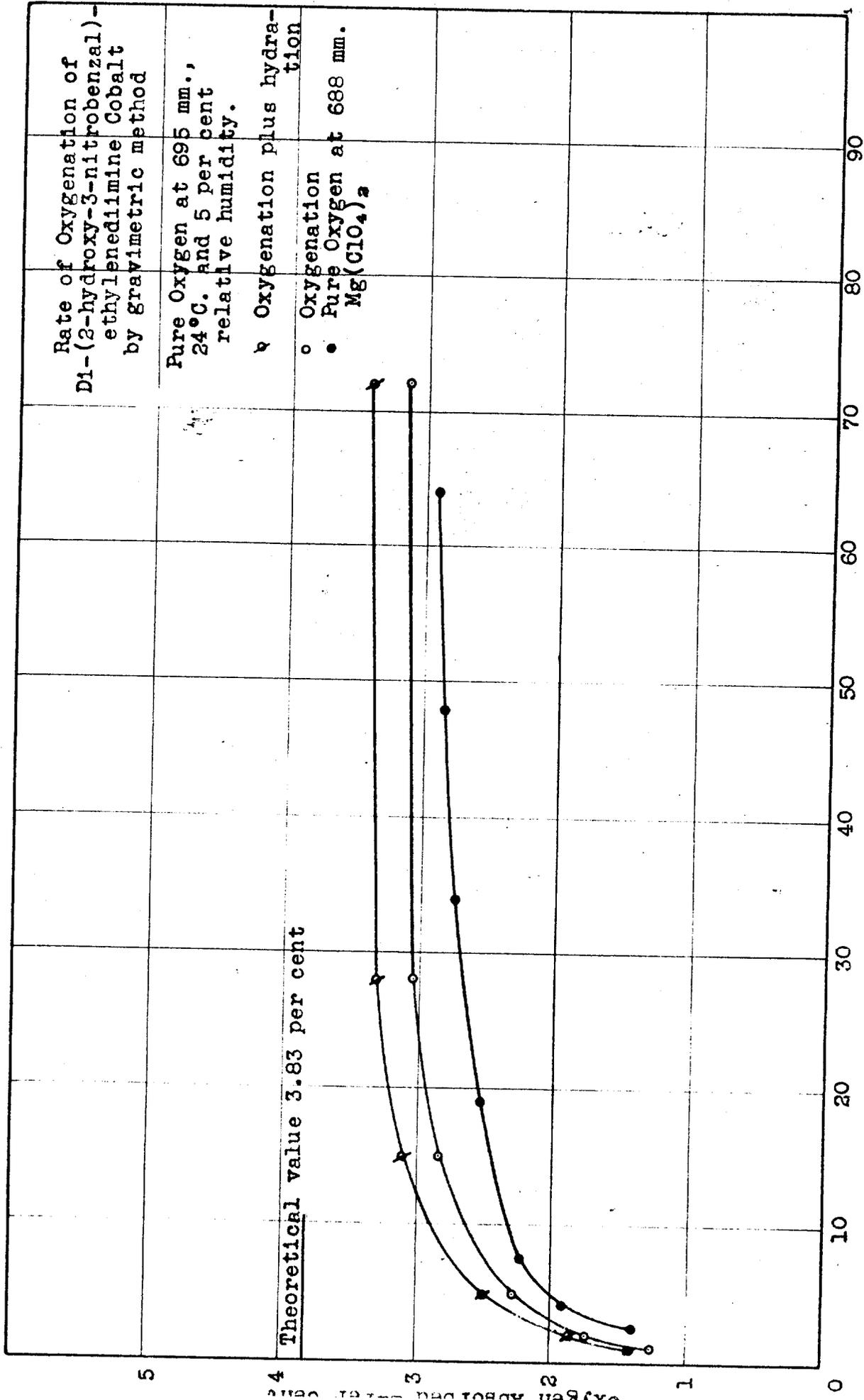
absorbed was then calculated and this weight of oxygen subtracted from the gain in weights of the U-tube. The difference in weight was then equal to the weight of water absorbed. The rate of absorption of water was assumed to be linear during the period of oxygenation, the rate of absorption of water per minute was calculated, and this value was applied as a correction to the weight of the U-tube at each interval during the oxygenation. There was thus obtained the rate of oxygenation plus hydration and the rate of oxygenation alone. Although this method may not be absolutely correct since the absorption of water may not have been linear, it is felt that any error involved could only be very small.

The data obtained for the rate of oxygenation plus hydration and the rate of oxygenation alone at atmospheric pressure and room temperature at relative humidities of 0, 5, 10 and 56 per cent are shown in the accompanying three graphs. A saturated zinc chloride solution was used to adjust the humidity of the air to 10 per cent; sulfuric acid of sp. gr. 1.67 was used to adjust the humidity to 5 per cent; the atmosphere as used directly had a humidity of 56 per cent.

The gravimetric method, described above, for determining the rate of oxygenation of the compounds under study was rather tedious to carry out and subject to certain disadvantages. The following volumetric method for determining the rate of oxygenation was also used although it could be adapted only to measuring the rate of oxygenation in pure oxygen. The apparatus is pictured in the accompanying drawing. The U-tube was filled with a weighed sample of the compound. The sample was then deoxygenated and activated by immersing the U-tube in a bath of boiling saturated salt solution. At the same time a stream of dry nitrogen was passed slowly through the U-tube to sweep out the oxygen and water. As soon as the deoxygenation and activation was complete, in approximately 15 minutes, the stopcocks on the U-tube were closed and the U-tube installed in the rate apparatus. Ample time was allowed for the compound to come to the temperature of the bath. Then the U-tube and train up to the oxygen tank evacuated. The buret was filled with oxygen from the cylinder. A salt solution was used as retaining liquid in the buret so as to give the oxygen contained in it the desired humidity. When the evacuation was complete, the vacuum pump was stopped and the stopcock on the U-tube was closed. Then the stopcock on the buret was turned in such a manner as to admit the oxygen to the U-tube. The leveling bulb was so handled that the pressure of the oxygen remained as desired through the run. Buret readings were taken at timed intervals and from the volume of oxygen absorbed and the weight of the sample the weight per cent of oxygen absorbed was calculated.

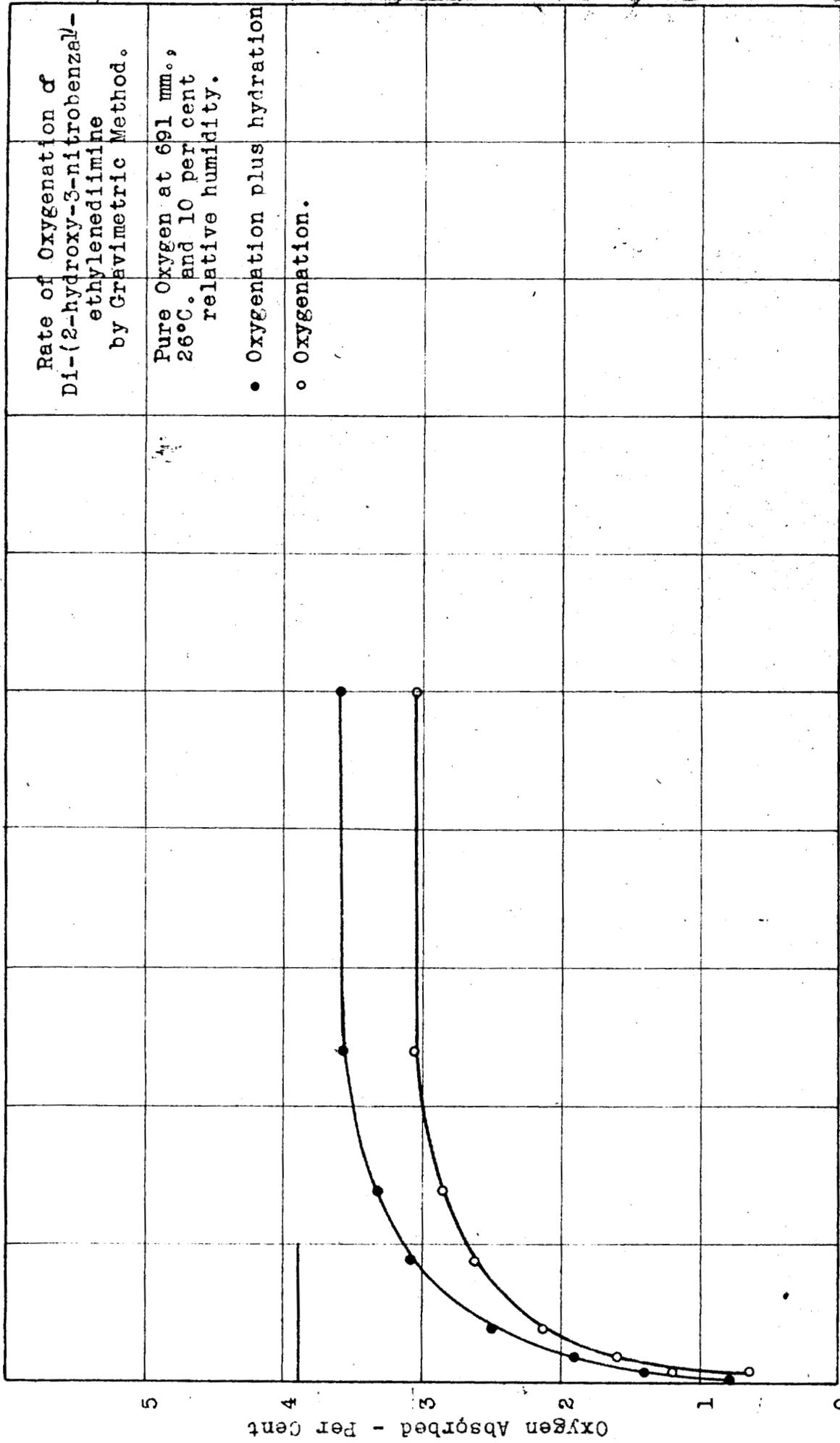


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Time - minutes

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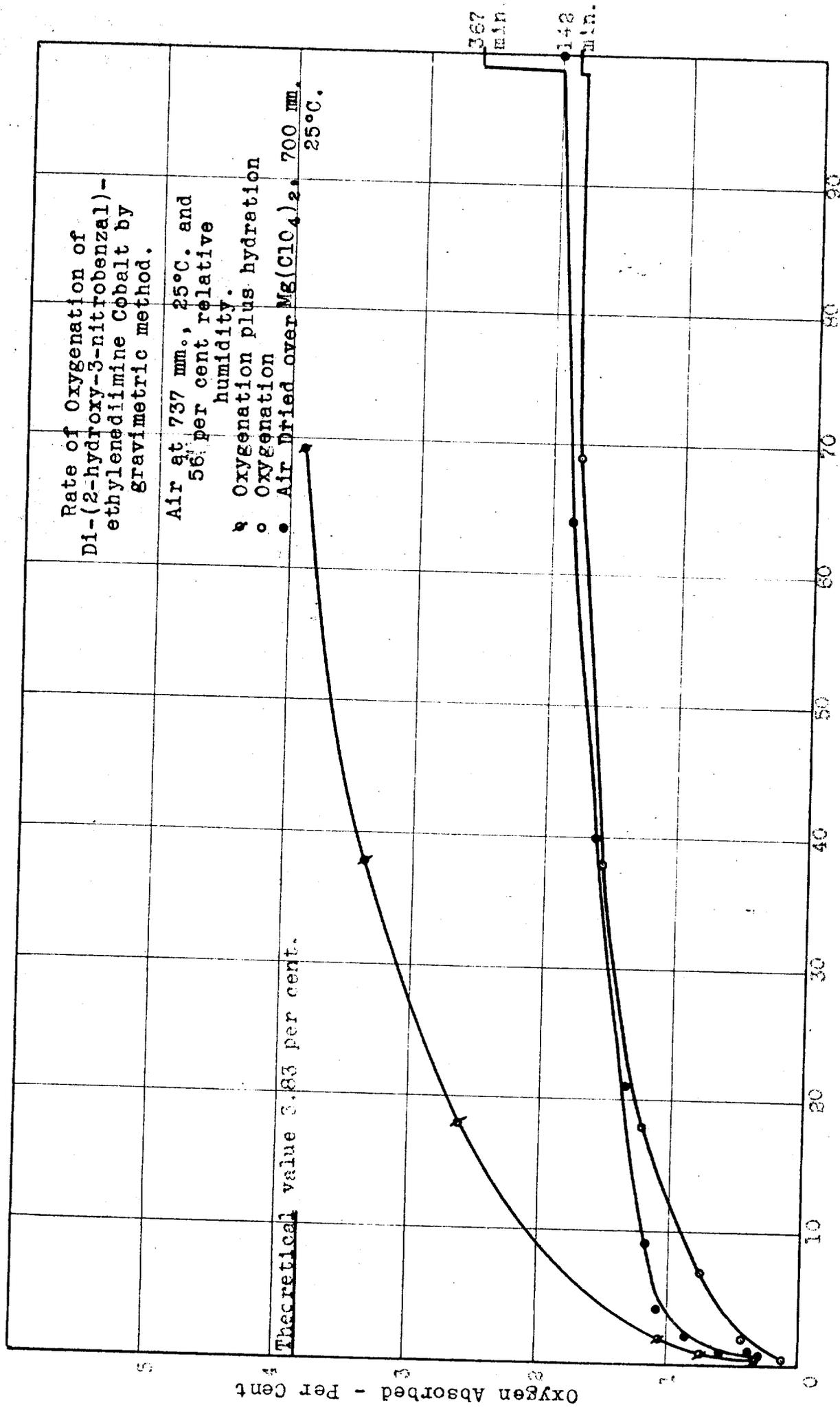
Rate of Oxygenation of Di-(2-hydroxy-3-nitrobenzyl)-ethylenediamine by Gravimetric Method.

Pure Oxygen at 691 mm., 26°C. and 10 per cent relative humidity.

- Oxygenation plus hydration
- Oxygenation.

Time - Minutes

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Time - Minutes

1262205

RATE OF OXYGENATION
OF

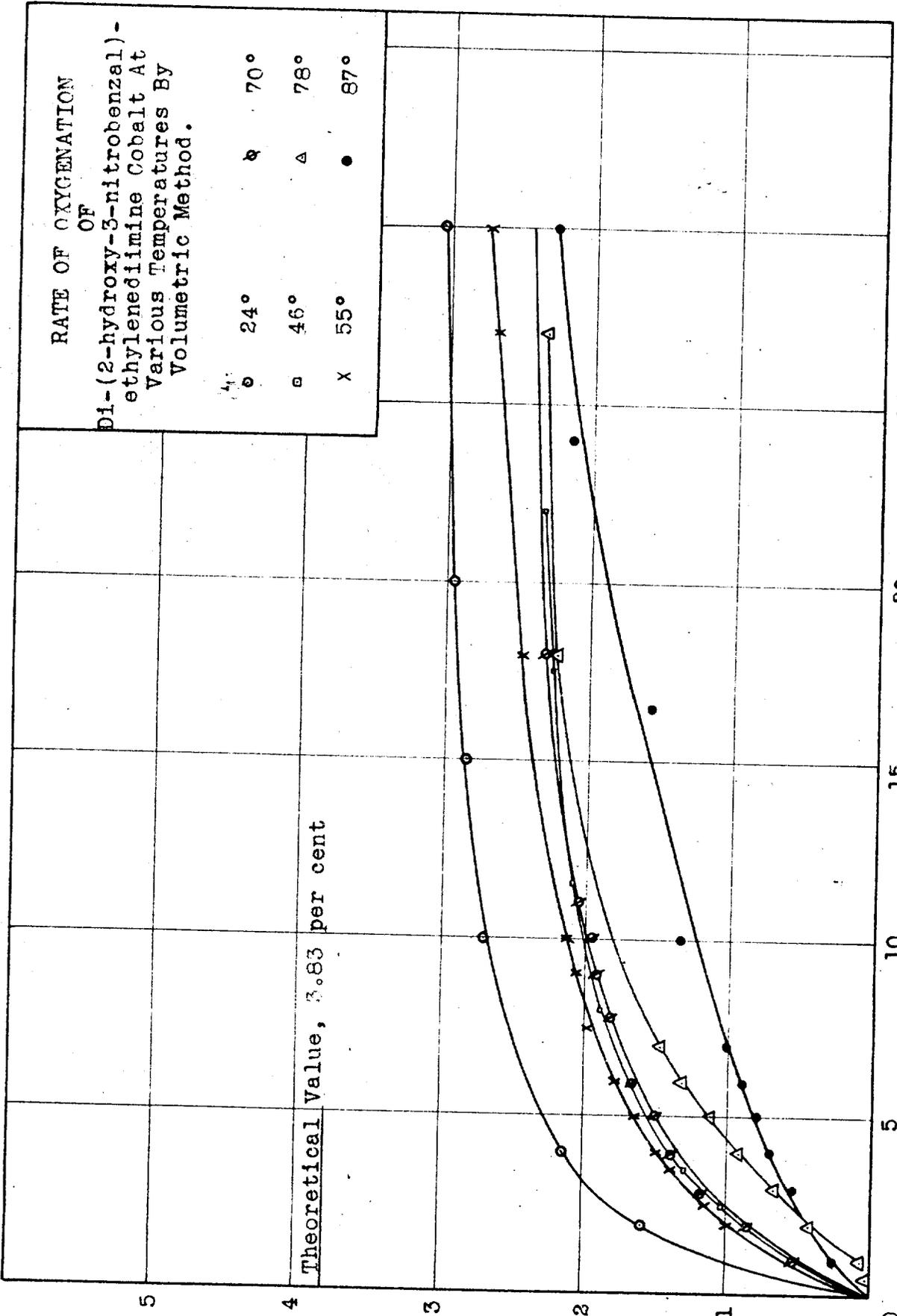
Di-(2-hydroxy-3-nitrobenzal)-
ethylenedimine Cobalt At
Various Temperatures By
Volumetric Method.

○	24°	⊙	70°
□	46°	△	78°
×	55°	●	87°

Theoretical Value, 3.83 per cent

Per Cent Oxygen Absorbed

0 5 10 15 20 25 30 35



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The rate of oxygenation of di-(2-hydroxy-3-nitrobenzal) ethylenediimine cobalt was determined using this apparatus at 24°, 46°, 55°, 70-72°, 76-77°, and 87°. The results are shown graphically in the accompanying figure. The rate of oxygenation of di-(2-hydroxy-3-nitrobenzal) ethylenediimine cobalt changed only slightly with temperature. This is particularly interesting since the rate of oxygenation of the parent, oxygen-carrying compound varies greatly with temperature.

The point at which the rate curve levels off depends markedly upon the oxygen pressure, that is, the higher the oxygen pressure the nearer to the theoretical, oxygen carrying capacity the rate curve approaches before leveling off.

Even when deoxygenated, di-(2-hydroxy-3-nitrobenzal) ethylenediimine cobalt was placed in an oxygen bomb at 200 psig., it did not quickly become entirely saturated with oxygen. In fact approximately 30 minutes was required for the last few tenths per cent of oxygen to be absorbed. However, when the compound was saturated with oxygen at 200 psig. it did not lose oxygen when the oxygen pressure was released.

The role that water plays in the rate of oxygenation of di-(2-hydroxy-3-nitrobenzal) ethylenediimine cobalt is not entirely clear. Apparently the rate of oxygenation is slightly faster in air or oxygen containing a small amount of water, that is, at relative humidities of 10 per cent or less. At the same time the compound is rendered inactive by the absorption of water. The deoxygenated compound upon absorption of water immediately turns yellow.

VI. The Absorption of Moisture and of Oxygen by Di-(2-hydroxy-3-nitrobenzal) ethylenediimine Cobalt.

A series of weighed samples of the activated di-(2-hydroxy-3-nitrobenzal) ethylenediimine cobalt were exposed to air at controlled humidities and allowed to come to oxygen and water equilibrium. The moisture content of the air ranged from 25 mg. to 0.2 mg. per liter, attained by the proper concentration of sulfuric acid in the humidifiers. At the end of 72 hours each sample was weighed, then deoxygenated and dehydrated by placing in an electrically heated tube at 130° and passing dry nitrogen over the sample. The moisture evolved was collected in a

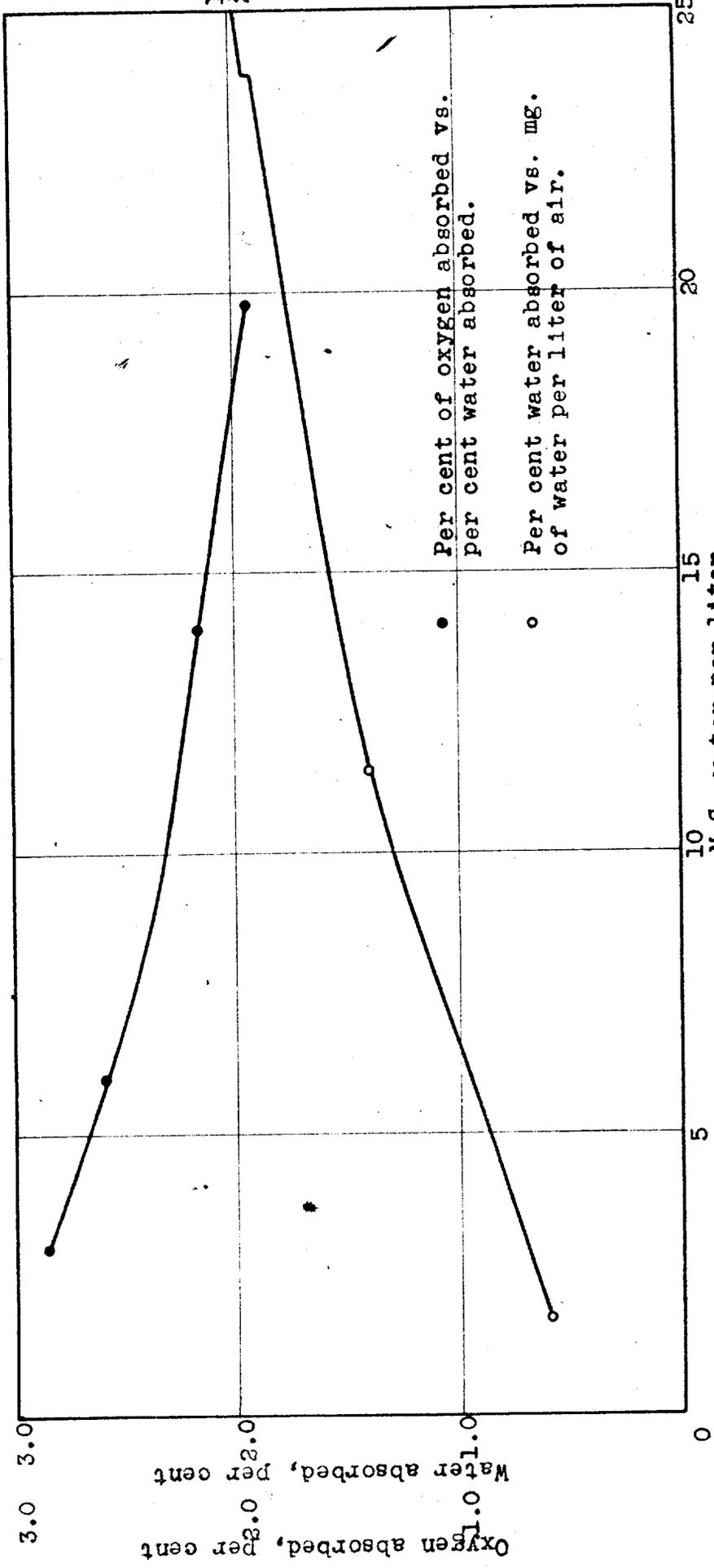
U-tube filled with magnesium perchlorate. The sample was then cooled in a vacuum desiccator and weighed to obtain the total loss in weight which is equivalent to both the oxygen and moisture absorbed. From the weight gained by the U-tube and the total loss in weight, the amount of moisture and the amount of oxygen absorbed at each humidity was calculated. The table below summarizes the results obtained.

	Density H_2SO_4	Per Cent H_2SO_4	Mg. Water per Liter air	Per Cent Oxygen Absorbed	Per Cent Water Absorbed
I	1.299	39.6	25.4	1.93	1.98
II	1.450	55.5	11.4	2.16	1.40
III	1.521	62.1	6.4	-----	-----
IV	1.629	71.6	1.7	2.6	0.6
V	1.740	81.2	0.24	2.85	0.3

*Sample 3 was lost during the course of this run.

From the graph in the accompanying figure it is apparent that the absorption of oxygen decreases markedly with increasing water content in the air. However, by comparison with the graph found for the compound Co-Ox M, Report XXXVIII, Section V, it will be evident that the effect of moisture on the 3-nitro compound is much less. However because of this competing absorption of water and oxygen, the air employed to oxygenate the compound when used for production of oxygen should be thoroughly dried.

In every case upon deoxygenation and dehydration at 130° the samples returned to their original weight showing that all of the moisture had been removed at this temperature. The possibility of entirely removing absorbed moisture at a much lower temperature has not as yet been definitely ascertained.



1.98
25.4
M.G.

• Per cent of oxygen absorbed vs. per cent water absorbed.

○ Per cent water absorbed vs. mg. of water per liter of air.

15
M.G. water per liter
1.0 2.0
Water absorbed per cent