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# Studies on oxygen-carrying cobalt compounds

George Carol Harrison  
*Iowa State College*

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STUDIES ON OXYGEN-CARRYING COBALT COMPOUNDS

by

George C. Harrison

A Thesis Submitted to the Graduate Faculty  
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry



Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

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## INTRODUCTION AND HISTORICAL REVIEW

Of the many chemicals adapted by nature to the processes of life, among the most ingenious are the materials which perform the vital respiratory function of animals, absorbing and releasing oxygen reversibly with ease. These materials, particularly hemoglobin, have been extensively investigated, and the literature has been well summarized [Barcroft (1), Harrow and Sherwin (2)]. The conditions for the absorption of oxygen are those normally found in the respiratory organs of animals, a relatively high oxygen pressure, and the conditions for the release of absorbed oxygen are those normally found in the tissue, a relatively low oxygen pressure. These oxygen-carrying compounds are extremely complex in composition and chemical and physico-chemical behavior. Their transport of oxygen is complicated by a similar transport of carbon dioxide in the reverse direction.

The possibility of separating from each other the oxygen and nitrogen of the atmosphere using hemoglobin is indeed interesting. The demand for the separated gases is great while the slaughter of animals in the meat packing industry would appear to furnish all the required hemoglobin. Unfortunately, hemoglobin is too unstable to be used in such a scheme to compete economically with the liquid air

process, although some attention has been paid to it (3).

The possibility of using purely synthetic metallo-organic compounds of the chelate ring type that are similar to hemoglobin was considered a feasible solution to the problem. Materials of this type are little known, only two are mentioned in as many articles in the literature; neither article is devoted entirely to the oxygen-carrying property. This field is truly virgin.

The first synthetic oxygen-carrying material was prepared by Kunz and Kress (4) by heating iron carbonyl with indigo in pyridine solution, thus expelling carbon monoxide. This material, an iron-indigo compound, yielded a red solution in pyridine which, on exposure to air, absorbed one mole of oxygen for each iron atom present. The solution turned green in the process. The oxygen was only loosely held for it could be removed by applying a vacuum, the color reverting to the original color as the oxygen was released. This material also absorbed carbon monoxide thereafter being inactive toward oxygen. The material was quite unstable toward oxygen undergoing gradual oxidation so that the solution lost its oxygen-carrying property after a few cycles. These properties are the same as those of hemoglobin; thus, the iron compound of indigo is a most unique respiratory model.

During the period 1920-1935 Pfeiffer and coworkers (5)

prepared a large number of metallo-organic coordination compounds possessing a cyclic or "chelate ring" structure. Many of these were quadridentate in character, that is the metal in them was attached to the organic portion of the molecule forming a tricyclic ring system with the metal at the center. One compound, a cobalt derivative of salicylaldehyde and ethylenediamine, was reported to become black on exposure to the atmosphere.

This material was investigated in more detail by Tsumaki, one of Pfeiffer's students, on his return to Japan (6). By the simultaneous interaction of cobalt acetate, salicylaldehyde and ethylenediamine Tsumaki obtained a brown material which he recrystallized from benzene and from chloroform. The red-brown crystals so obtained became dark brown in dry air, taking on weight at the same time. In a vacuum desiccator the crystals remained red-brown indefinitely. By first allowing these crystals to stand in air until dark brown and then heating to 100° Tsumaki was able to obtain oxygen and cause the crystals to return to their original weight and color.

Tsumaki recognized the character of the reaction as an oxygen addition to the cobalt atom itself and indicated that the linkage was quite in analogy with the bonds in oxyhemoglobin. From a number of determinations he concluded that the material combined with one-third of an oxygen



molecule per cobalt atom. Tsumaki devoted some further work to the measurement of the absorption spectra of various solutions of this material but otherwise evidenced little interest in the material either to prove definitely its composition by careful analysis or to determine if the cycle could be repeated.

During the spring of 1932 Diehl, working at the University of Michigan, prepared the copper, nickel and ferrous iron derivatives of disalicylaldehydenediamine, the condensation product of salicylaldehyde and ethylenediamine. Unfortunately he did not prepare the cobalt compound being primarily interested in the possibility of using the compounds in the analytical chemistry of copper and nickel, elements of coordination number four. On the appearance of the Pfeiffer, Breith, Lübke and Tsumaki paper (7) he abandoned this work. He returned to this field in the spring of 1938, following the publication of the Tsumaki paper, having in the meantime published a review of the general field of the chelate ring compounds (8).

The possibility of using metallo-organic compounds of the chelate ring type for the recovery of oxygen from the atmosphere occurred to Diehl in 1938 and he secured funds for such work from the Purdue Research Council. Although the iron-indigo compound described by Kunz and Kress and the metal phthalocyanine compounds were first marked for

investigation, the publication of the Tsumaki work diverted attention to the cobalt derivative of disalicylaethylene-dimine.

During the fall of 1938 at Purdue University Chao and Diehl (9) investigated disalicylaethylenediimine cobalt and a great number of closely related compounds. This work is embodied in seven reports which are at present being prepared for publication. Chao and Diehl showed that the oxygen-carrying capacity was well above the value obtained by Tsumaki, that the material had an oxygen-carrying capacity approaching one-half molecule of oxygen per cobalt atom. They also showed that the absorption of oxygen and the subsequent release of oxygen could be repeated many times without apparent decomposition of the cobalt compound. Their chemical analysis showed that the material they obtained might contain one-half molecule of water per cobalt atom. Their method of preparation was essentially that of Tsumaki but they showed the benzene recrystallization was unnecessary, in fact, undesirable for material of high capacity. Their preparative methods gave better but still erratic results.

The work of Chao and Diehl was continued by Hach and Diehl (10) at Iowa State College. They used the same method as did Chao and Diehl for the preparation but obtained better materials principally through practice and better equipment.

They developed a new oxygen-carrying compound from 3-nitrosalicylaldehyde, ethylenediamine and cobalt acetate, and showed that 5-nitrosalicylaldehyde when used similarly did not give an oxygen-carrying material. They developed new methods for the measurement of the capacity of these materials to absorb oxygen and began work to determine the rate of oxygen absorption from atmospheres of air and of oxygen. They studied the effect of light of various wave lengths on the material and showed that absorbed oxygen could be liberated by infra-red radiation. They also made several mechanical devices using these materials for the recovery of oxygen from the atmosphere.

Hach and Diehl adopted the simplified name Co-Ox for disalicylaalethylenediimine cobalt and Co-Ox N3 for di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt. These names and similar ones for new compounds will be used for convenience throughout the remainder of this paper. The chemical name will be used only to establish the constitution of the oxygen-carrying compounds as they are developed.

## EXPERIMENTAL WORK

### Object of the Work

The object of this work was to expand and develop the knowledge on synthetic oxygen-carrying materials. As the work unfolded three major phases of the problem developed: the development of new methods for the synthesis of disalicylalethylenediimine cobalt, Co-Ox, which would produce a material of high oxygen-carrying capacity in high yield from cheap and available materials; the investigation of those chemical and physical properties which would establish its exact chemical constitution or aid in applying Co-Ox to the recovery of oxygen from gaseous mixtures; and finally, the development of new oxygen-carrying materials.

### Methods for the Synthesis of Disalicylalethylenediimine Cobalt (Co-Ox)

The methods in use or under consideration by Hach and Diehl were three in number and differed in the order of addition of the three reagents used to form disalicylalethylenediimine cobalt.

Method A involved the simultaneous mixing of cobalt acetate, ethylenediamine and salicylaldehyde, each dissolved in an alcohol-water mixture in such concentrations that the

solutions could be well mixed in the time required for the precipitation of disalicylaethylenediimine cobalt to take place. This method was considered ideal in that it was a one-step procedure. It gave good yields but the oxygen-carrying capacity varied greatly.

Method B involved the preliminary preparation of the condensation product of salicylaldehyde and ethylenediamine (Schiff's base) and thereafter the conversion of the condensation product into the oxygen-carrying cobalt compound by reacting a solution of it in alcohol with a solution of cobalt acetate in water. The two steps in this procedure made it considerably longer than method A, but it assured that equivalent amounts of salicylaldehyde and ethylenediamine were reacted.

Method C involved the preliminary preparation of cobalt salicylaldehyde and thereafter its conversion to the oxygen-carrying cobalt compound by causing it to react with ethylenediamine. Like method B this was a two-step process but also assured that equivalent amounts of salicylaldehyde and cobalt would be brought together.

A systematic investigation of the following factors was conducted:

1. The purity of the reagents used.
2. The effect of an excess of any one of the three reagents in method A and of an excess of one of the two reactants in methods B and C.

3. The order and rate of additions of the reagents in method A and in the final step of method B.
4. The temperature of the solutions at the time of mixing in method A and the final step of method B.
5. The amount of solvents and the ratio of alcohol to water in the solvent in method A and the final step in method B.
6. The presence of air at the time of mixing for methods A and B and during the subsequent period of standing.
7. The time of standing between mixing and centrifuging.
8. The effect of cooling the reaction mixture before centrifuging.
9. The composition of the liquid employed in washing the material after centrifuging the mother liquor.
10. The extent and manner of washing the material.
11. The manner of drying the material after washing.

This investigation showed that method C was quite impractical as a suitable solvent for cobalt salicylaldehyde could not be found. The investigation of each factor was carried out holding all other factors as constant as possible. Each will now be discussed separately.

Factor 1. The investigation of the three reactants showed that the cobalt acetate and ethylenediamine were sufficiently pure for the preparations but that the salicylaldehyde as received from the manufacturers contained as high as 12 per cent impurities consisting of a strong acid (probably hydrochloric) in small amounts, salicylic acid and chlorosalicylaldehydes. Invariably the best

preparations were obtained when freshly distilled salicylaldehyde was used.

Factor 2. An excess of any reagent but cobalt acetate in the preparations was found to be detrimental to the oxygen-carrying capacity. The cobalt acetate was found to be easily washed from the cake in the centrifuge during the washing step by either alcohol or water.

Factor 3. The order of addition of reactants in method A found to give the best yields and highest oxygen-carrying capacities was ethylenediamine to the cobalt acetate followed without delay by the salicylaldehyde. For method B the addition of the cobalt acetate to the alcoholic solution of the condensation product, disalicylaethylenediimine, at a moderate rate with vigorous stirring was found to be best.

Factor 4. The reactions for both method A and method B were found to proceed best when the solutions were near their boiling points.

Factor 5. A general statement only can be made about the amount of solvent: As the amount of solvent was increased, the yield was reduced but the product had a slightly better oxygen-carrying capacity for both methods. The important fact that an oxygen-carrier cannot be formed in non-aqueous solvents was found in the study of the ratio of alcohol to water in these preparations. Best results were obtained when the final alcohol concentration was 60

to 70 per cent by volume.

Factor 6. Air in contact with the material when wet with water and more so with an alcohol-water mixture was found to produce a black oxidation product. This black material was not an oxygen-carrier. Its composition could not be determined.

Factor 7. The material could be allowed to stand out of contact with air over long periods of time without apparent change.

Factor 8. Cooling the reaction mixture before centrifuging slowed the filtering process and hindered the removal of soluble impurities.

Factors 9 and 10. It was found that a rapid washing with boiling water on the centrifuge gave the best product and aided in the final drying step.

Factor 11. Vacuum drying of the material after washing was found to be ideal although later studies showed that a satisfactory product could be obtained by rapidly drying the material in air by means of infra-red lamps.

Using the above investigation to produce materials under ideal conditions for each factor studied still resulted in materials of widely varying oxygen-carrying capacity and in variable yields. The factors were reviewed and each product examined. From the observations another factor was added to the list. It might be called the acidity factor arising



from the acetic acid liberated by the reaction.

The general methods of preparation A and B were changed to include sodium hydroxide to neutralize the acid giving five methods allowing for the order of addition of reagents. Briefly the general methods were as follows:

A (a). Cobalt acetate, ethylenediamine and salicylaldehyde were made to react and the acidity due to the acetic acid formed was removed by adding sodium hydroxide.

A (b). The sodium hydroxide and salicylaldehyde were mixed and added to the cobalt acetate and ethylenediamine.

A (c). The sodium hydroxide and ethylenediamine were mixed and added simultaneously to the cobalt acetate with the salicylaldehyde.

B (a). The condensation product, disalicylaethylenediimine was dissolved in alcohol and water, reacted with cobalt acetate, and the resulting acidity reduced by the addition of sodium hydroxide.

B (b). The condensation product, disalicylaethylenediimine, was dissolved in alcohol and water along with the sodium hydroxide and the cobalt acetate (as found later any cobalt salt will do) dissolved in water was added slowly to this solution.

Of these methods the one designated as B (b) proved to be the most successful, producing an oxygen-carrying material in good yields, 60-70 per cent, with an oxygen-carrying

capacity of 4.80 per cent by weight. This method has been developed and used widely in later studies for the preparation of new oxygen-carrying materials. It has been modified for the production of disalicylalethylenediimine cobalt to eliminate the necessity of using alcohol. The aqueous preparations resulted in increased yields, to as much as 95 per cent of the theoretical. Both methods for the synthesis of disalicylalethylenediimine cobalt will be given using the directions for each as found to give the best results.

Recommended procedure for the preparation of disalicylal-ethylenediimine.

An amount of 244 g. of salicylaldehyde is dissolved in 1 l. of 95 per cent ethyl alcohol and heated to 50°. To this solution is added while stirring vigorously 78.0 g. of ethylenediamine hydrate dissolved in 100 ml. of water. A yellow precipitate forms hardening the whole solution into a solid cake. It is allowed to cool at will to room temperature. The cake is then broken up and the liquid filtered off. The precipitate is dried in air. M.p.: 123°. Yield: about 240 g., 90 per cent.

Recommended procedure for the preparation of Co-Ox by the alcohol method.

An amount of 26.8 g. (0.1 mole) of disalicylaethylene-diimine is dissolved in 500 ml. of hot 60 per cent ethyl alcohol solution containing 7.5 g. of sodium hydroxide and 2-3 g. of sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ ). To this is added while stirring vigorously 24 g. of cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ). A red-brown precipitate forms immediately hardening the whole solution into a thick gel. The gel is covered with water and broken by stirring. The precipitate is best filtered on a basket type centrifuge in such a manner that the cake is not exposed to air until all the alcohol is thoroughly washed out with hot distilled water. The cake is allowed to centrifuge as dry as possible and then removed and dried in thin layers in a high vacuum oven at  $100^\circ$ . This material carries 4.79 per cent oxygen. Yield: 26 g., 80 per cent.

Recommended procedure for the preparation of Co-Ox in aqueous media.

An amount of 26.8 g. of finely powdered disalicylal-ethylenediimine is dissolved in 1500 ml. of water heated to  $95-100^\circ$  containing not less than 7.5 g. and not more than 7.9 g. of sodium hydroxide and from 2 to 3 g. of sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ ). The solution should be complete in

five minutes and should not be boiled unless the vapors are refluxed. To this solution is added 24 g. of reagent grade cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) dissolved in 100 ml. of warm water. This solution is added slowly with vigorous stirring. An orange precipitate that changes to a red-brown precipitate is first formed. This mixture is stirred for five minutes then filtered while still hot, preferably on a basket type centrifuge. The precipitate is washed with boiling water in such a manner that the cake is covered at all times, and is centrifuged as dry as possible. The cake is then removed and dried in thin layers in a high vacuum oven at  $100^\circ$ . The material carries 4.79 per cent oxygen. Yield: 31 g., 94-96 per cent.

Either of these procedures results in a brick red isomer of the oxygen-carrier if an excess of alkali is used. This material will be considered more extensively in the section on stereochemical considerations.

#### Properties of Co-Ox

The property of Co-Ox that makes it a most interesting material is its thermo-regenerative reaction with oxygen and the physical changes associated with this reaction. Co-Ox as it comes from the vacuum drying oven following its preparation is cinnamon-brown in color. When exposed to air

it absorbs oxygen, turning black simultaneously. If this black material is heated, oxygen is evolved and the Co-Ox is obtained again. Since this process is like the common hydration-dehydration process of hygroscopic materials it has been properly termed as an oxygenation-deoxygenation process.

The amount of oxygen absorbed has been found to depend upon a number of factors; the first is obviously the composition of the material and the remainder: the amount of oxygen in contact with the material, the temperature, the pressure and the length of time of exposure to oxygen. If the gas from which oxygen is extracted or if the material is not dry then moisture is an added factor. Under proper conditions the amount of oxygen absorbed reaches a maximum, this value being known as the oxygen capacity. The accurate evaluation of oxygen capacity has been instrumental in finding better methods of preparing the oxygen-carrying materials.

The measurement of oxygen capacity.

The method used by Chao and Diehl and later by Hach and Diehl furnished one of the best methods for the measurement of the oxygen capacity of Co-Ox. This method was not directly adaptable to materials developed later in this work but served as a standard for developing apparatus for testing

those materials.

Co-Ox is sufficiently unreactive toward oxygen in air at atmospheric pressure and room temperature so that it may be weighed in the deoxygenated form. Furthermore, if oxygenated it retains its oxygen when exposed to air at room temperature. Thus, it may be weighed, oxygenated and deoxygenated, and the gain in weight determined. It is only necessary to subject Co-Ox to conditions between these weighings that will assure complete oxygenation.

Recommended procedure for the oxygen capacity of Co-Ox.

A sample of Co-Ox is heated to 100° in a good vacuum to constant weight. For this purpose the Co-Ox may be carried in an appropriate boat holding about 10.0 g. placed in a steam or electrically heated vacuum drying pistol. The boat is then transferred to a vacuum desiccator and allowed to cool for 30 minutes. It is then removed from the vacuum desiccator and weighed rapidly in air. The boat is then transferred to a screw cap bomb and an oxygen pressure of about 200 p.s.i.g. (pounds per square inch gage) applied. This operation should take at least ten minutes. The pressure is then released, by means of a valve provided for the purpose, at a reasonably slow rate, otherwise, some of the Co-Ox may be blown from the boat. The material is then transferred to a desiccator and allowed to stand for at least 15 minutes. This step is very important and has been

overlooked as a source of error. The boat is then removed from the desiccator and weighed as before in air. The gain in weight divided by the sample weight times 100 is the per cent oxygen capacity. A good preparation of Co-Ox will absorb 4.8 per cent of its weight in oxygen.

The value so obtained is a correct one as was shown by several experiments. The oxygenated material was heated to 40° in a good vacuum (in other experiments to 50° in dry air or to 60° in oxygen), cooled to room temperature and reweighed; no change in weight was observed. This is sufficient evidence that an apparent loss in weight observed between weighings made immediately following removal from the bomb and weighings made after 15 minutes was due to causes other than slight deoxygenation. In fact, this difference was traced to two causes. The expansion of the oxygen in the bomb from 200 p.s.i.g. to atmospheric pressure was found to cool both the material and the boat, and to lead to a weighing error. The oxygen occluded in the freshly oxygenated material, having a greater weight than air, was found to affect the weight.

#### Constitution of Co-Ox.

The amount of oxygen absorbed by the best preparations of Co-Ox was 4.80 per cent. The theoretical capacity is 4.94 per cent assuming that one molecule of oxygen was

absorbed by each two molecules of cobalt compound, that is an atomic ratio of cobalt to oxygen of one to one. The most obvious explanation is that the deoxygenated compound probably contained water, perhaps in such a manner as to couple the two cobalt atoms and arrange them in such a manner as to absorb the oxygen. This would require a half molecule of water per cobalt atom and decrease the oxygen capacity to 4.79 per cent.

Hach and Diehl made many unsuccessful attempts to prove the presence of this water by heating the material in a high vacuum and passing the gases through dehydrite but only managed to obtain a yellowish oil due to decomposition at high temperature.

Following the researches that resulted in consistent preparations of 4.80 per cent oxygen capacity, complete analyses were made to fix the constitution of the oxygen-carrying material. A sample of Co-Ox made from recrystallized disalicylaethylenedimine and nickel free cobalt sulfate was analyzed for nitrogen by the Kjeldahl method, cobalt by ferrocyanide electrometric titration, carbon and hydrogen by the macro Liebig combustion method, and oxygen capacity by the method given earlier in this thesis. The average of six results for each constituent are given in Table I.



Table I  
Analysis of Co-0x

Constituent	Found	Molecular Weight Calculated from Analyses
	Per Cent	
Nitrogen	8.39 $\pm$ .03	334
Cobalt	17.69 $\pm$ .05	333
Carbon	58.01 $\pm$ .10	331
Hydrogen	4.30 $\pm$ .05	328
Oxygen Capacity	4.79 $\pm$ .01	333

The molecular weight of the material from the combination of cobalt with disalicylalethylenedimine would be 325.23 indicating that there are approximately 8 molecular weight units unaccounted for. It has been found convenient to consider this portion as one-half molecule of water per cobalt atom even though the hydrogen analysis is considerably low. This topic will be undertaken again in a later section entitled, Stereochemical Considerations.

The reaction of disalicylalethylenedimine and cobalt chloride in non-aqueous solvents.

In an effort to prove the presence of water in the molecule, a number of attempts were made to produce the oxygen carrier in non-aqueous solvents. For this purpose absolute alcohol, the only solvent found in which cobalt

chloride and disalicylaethylenediimine are both soluble, was chosen. Three materials were obtained in this study: the first and by far the most important was a very brilliant orange material. The second, an equally brilliant green material, was obtained from the orange by reacting it with hydrogen chloride gas or by boiling the solution in which the orange material was prepared. The third was a deep purple, crystalline material which proved to be identical to the red isomer obtained by using too much alkali in the preparation of the oxygen-carrying material (Co-Ox).

The orange material was studied thoroughly for its preparation and analyses.

Recommended procedure for the preparation of the orange material. An amount of 26.8 g. of disalicylaethylenediimine is dissolved in 600 ml. of absolute alcohol and to this is added 13. g. of anhydrous cobalt chloride dissolved in 200 ml. of absolute alcohol. The solution is stirred vigorously during the addition and then for about a minute. Best results are obtained in an etched beaker when the walls are rubbed vigorously with the stirring rod. The mixture is poured into a Buchner funnel, filtered rapidly, and, as soon as the mother liquor has been removed, washed with hot absolute alcohol. The material dries on the funnel in several minutes and should be a very brilliant orange in color. Yield: about 1.5 g., or less than 5 per cent.

The criterion of purity for this material is its color. No method of further purification was found. This material formed in the alcoholic solution with the generation of considerable hydrogen chloride which reacted with the remainder of the material in solution producing a green material of unknown composition. It was obtained by heating the solution and filtering. The green material was also obtained by exposing the orange material to dry hydrogen chloride gas. It turned dark green even for very small amounts of hydrogen chloride absorbed.

The orange and green compounds possessed some very interesting reactions. The orange material reacted with hot water producing an oxygen-carrying material of high oxygen capacity. This reaction was never carried out in amounts large enough for exact determinations of the oxygen-carrying capacity of the product resulting from treatment with water since the orange material was too difficult to prepare. The oxygen-carrying capacity of the material so produced was at least 4.6 per cent, however. Accompanying the formation of this active material there was formed cobalt chloride which passed into the filtrate.

The green material reacted with water in somewhat the same manner as the orange material giving an oxygen-carrying material that carried only 3.3-3.4 per cent oxygen. The filtrate was distinctly acid and contained some cobalt and

some organic material.

The analyses of the orange and green materials were made for cobalt by ferrocyanide electrometric titration, nitrogen by the Kjeldahl method, and chlorine by the Thompson-Oakdale method. The results obtained on the orange material were good enough to assume that the ratio of nitrogen to cobalt to chlorine was four to three to two.

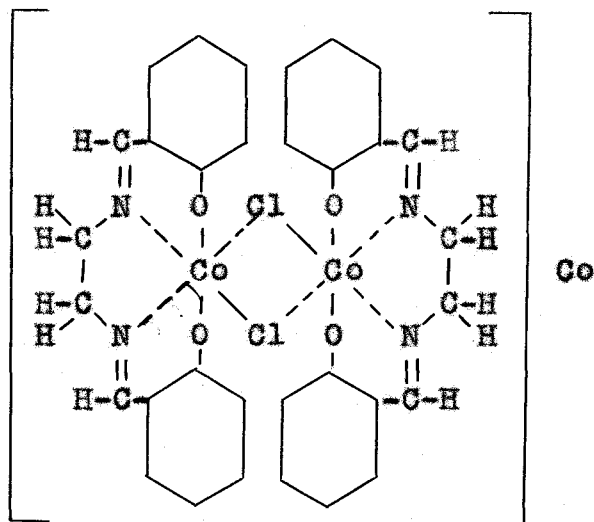
Table II

Analysis of the Orange Material

Analysis for	Found Per Cent	Theoretical for $C_{22}H_{25}O_4Co_2Cl_2$
Cobalt	20.90 21.01 20.92	22.62
Nitrogen	7.25 7.14 7.10	7.17
Chlorine	9.14 <sup>a</sup> 9.14 8.75	9.12

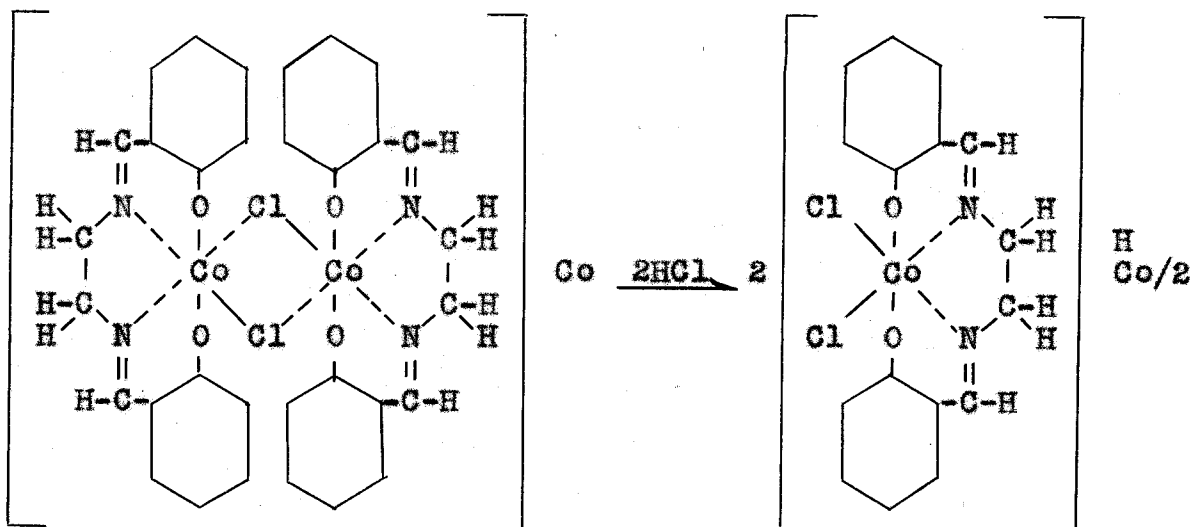
<sup>a</sup> A blank of .75 per cent has been applied. It was found for the reagents and a 1.0 g. sample of disalicylaethylenediimine.

The composition corresponding most closely to the results given in Table II is:



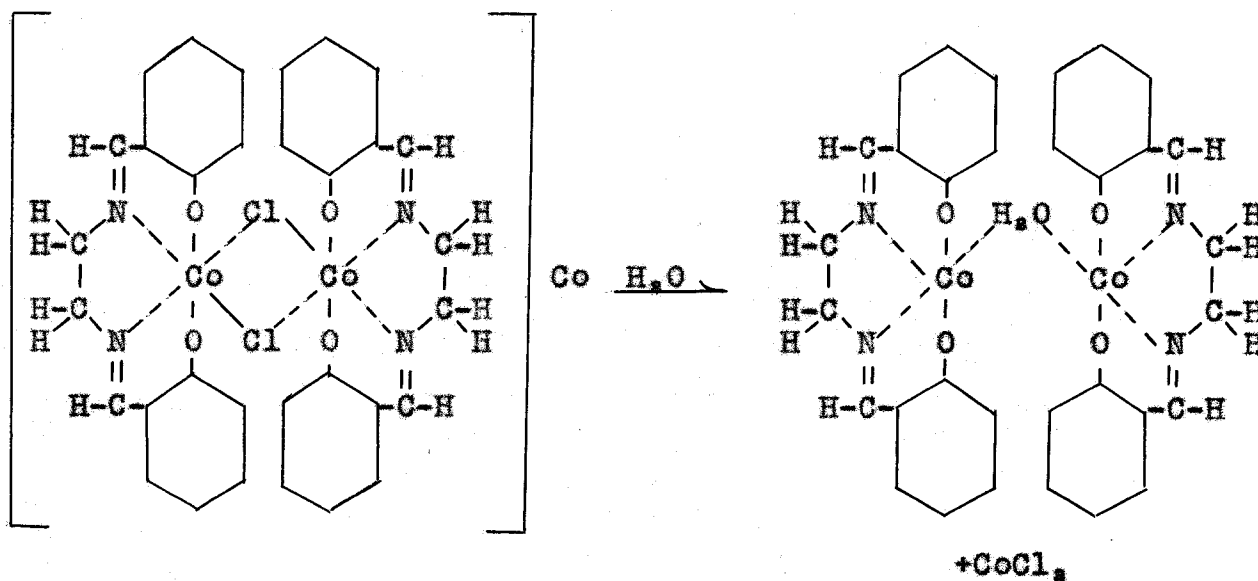
Similar compounds in which metal atoms are joined through bivalent chlorine atoms are well known in the coordination compounds of platinum and palladium but have not been previously extensively reported with cobalt.

The formation of the green compound from the orange is probably due to the reaction:



Cobalt compounds in which two halogens are attached in this manner are green.

The reaction of water on the orange material is probably:



The product is thus the same as the oxygen-carrying compound obtained in aqueous media, i.e., Co-Ox.

Other chemical properties of Co-Ox.

Co-Ox was found to display several other thermo-regenerative reactions besides that with oxygen. In much the same manner Co-Ox reacted with water, chloroform and pyridine forming a hydrate, a chloroformate and a pyridinate respectively. The hydrate is not particularly

stable, the water being eliminated at atmospheric pressure below 100°. Such a dehydration occurs during the preparation of Co-Ox and is known as the "activation" step. Tsumaki described the chloroformate and its regeneration while Calvin (11) described the pyridinate prepared by directly mixing water, pyridine, salicylaldehyde, ethylenediamine and cobalt chloride and recommended it as a good method of preparing Co-Ox. This method has been found unsatisfactory in this laboratory. The compounds with chloroform and pyridine are of some academic interest but impossible to work with practically on a large scale.

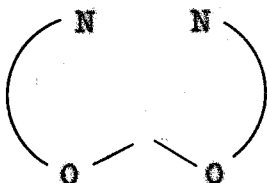
Co-Ox reacts with dilute alkali to form a bright red material that has been found by Hach and Diehl to have the same chemical analysis as either the oxygen carrier or the material obtained when too much alkali is used in the preparation. This material is important in that it is undoubtedly a second stereo form of the oxygen-carrying material. Therefore, the facts indicate that two pure stereo forms of disalicylaethylenediimine cobalt may be prepared by simply controlling the final pH of the reaction mixture.

#### Stereochemical considerations.

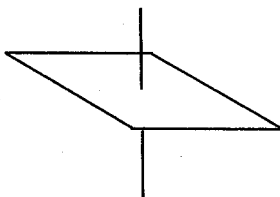
In the compound disalicylaethylenediimine cobalt, there exist three ways in which the organic molecule,



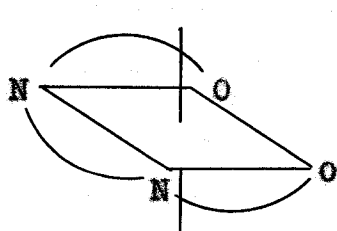
disalicylaethylenediimine, can be distributed about the cobalt atom. Adopting for the disalicylaethylenediimine molecule the shorter symbol



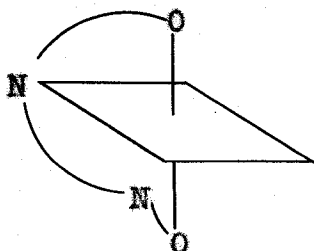
and utilizing the usual picture for designating a metal having a coordination number six



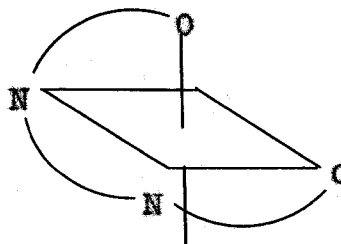
these arrangements are as follows



I

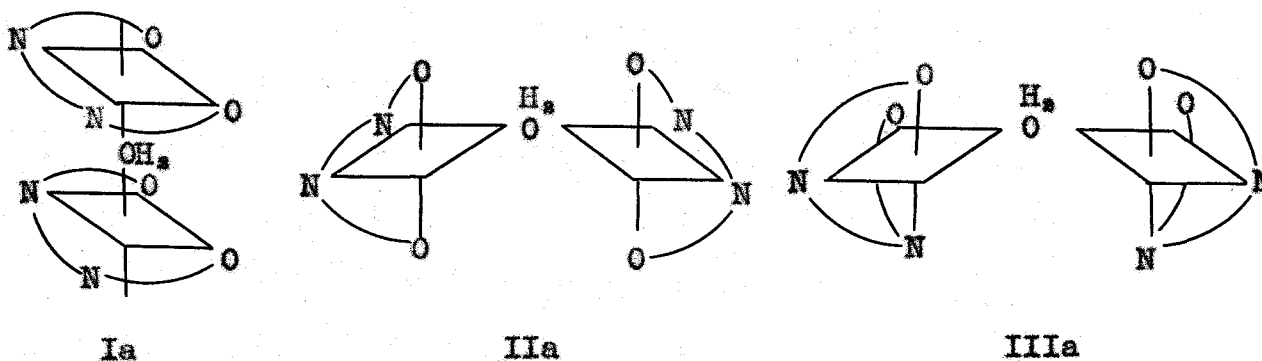


II

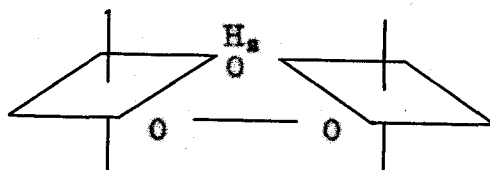


III

All of these forms are more or less strain free as shown by models, but form I is perhaps the most stable. Considering the half molecule of water present in the compound to function as a bridging group between two cobalt atoms, the structure of the various forms then becomes



In each of the three structures, Ia, IIa and IIIa, the sixth coordination position of each of the cobalt atoms is left vacant. In structures IIa and IIIa these positions are adjoining and there is just sufficient room for an oxygen molecule to slip into the empty space to form a peroxo bridge.



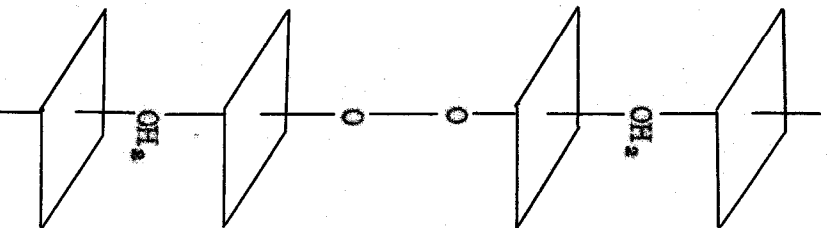
Such peroxo bridges are well known (12). In structure Ia there is no such convenient space provided for the oxygen molecule and oxygen absorption could only then occur intermolecularly which requires that the crystal structure be

so arranged that this may occur.

This structure is much less probable for the oxygen-carrying compound than structures IIa and IIIa, in which the favorable orientations are forced by the cis-arrangement of the bridging water molecule and the vacant coordination positions.

These stereochemical considerations thus indicate that there should exist three isomeric forms of disalicylateethylenedimine cobalt, two of which should carry oxygen and one of which should probably be inactive. It was at one time thought that the three forms of the oxygen-carrying compound were obtained by preparing the oxygen-carrying compound by different

methods. As a result of X-ray diffraction and absorption spectra studies (13), it is now known that the oxygen-



carrying material prepared in an aqueous media is identical with the material prepared in aqueous-alcohol media. The bright red inactive material is unquestionably a second isomeric form. It, therefore, appears that the three isomers predicted have not as yet been found.

From preliminary examinations of the X-ray diffraction patterns and a consideration of the density and density changes on oxygenation, Professor R. Rundle believes that the only possible stereochemical arrangement of the organic molecule about the cobalt atom is that represented by I and that the crystal arrangement is essentially a layer pattern with two cobalt atoms, each surrounded by the large organic molecule lying in parallel planes and separated by a relatively small distance, and that this pair of parallel molecules is separated from the next pair by a distance just sufficient to permit an oxygen molecule to slip in.

Such a picture implies that the property of carrying oxygen is dependent entirely upon a particular lattice arrangement, the occurrence of which is a matter of chance. From such a viewpoint, the discovery of new oxygen-carrying compounds has luck as a major element and research under such circumstances is discouraged at the outset. Structures IIIa and IIIb are still held to be distinctly possible and are favored in that they offer a definite reason for the absorption of oxygen and for the particular ratio of oxygen

to cobalt observed. Moreover, they are in accord with the knowledge of a branch of inorganic chemistry founded in the early years of this century by Alfred Werner (14) and neglected since his death, namely the field of the polynuclear compounds.

The magnetic susceptibility of Co-Ox and a few related compounds.

The object of measuring the magnetic susceptibility of Co-Ox and related compounds, of the inactive red isomer, and of disalicylaethylenediimine, was to gain knowledge that would help to explain the structure of the compounds, the mechanism of the oxygen-carrying process, and to assist in locating new oxygen-carrying materials. Hemoglobin is known to exhibit a change in magnetic character on oxygenation, the oxygenated form being diamagnetic. This phenomenon is related to the structure of the material, the oxygen absorption mechanism, and the change in color on oxygenation. Co-Ox was expected to show a corresponding shift in its magnetic behavior.

Apparatus to measure paramagnetism. One of the better methods of measuring magnetic susceptibility of solid materials is that used by Freed (15); this method has been used repeatedly by many investigators and has been found to give accurate and consistent results. The apparatus used

in this work was essentially that of Freed but lacking in many of the refinements and employing a weaker magnet. No provision was made to obtain the magnetic susceptibility at other than room temperature. A glass tube was made of uniform 3 mm. pyrex glass tubing with a thin uniform partition exactly in the center. The tube was placed between the poles of an electro-magnet in such a manner that the field and tube above the partition was a mirror image of the field and tube below the partition. The tube extended well beyond the field in both directions. The tube was fitted at the top with glass ears, by which it could be suspended from the arm of a balance by a fine wire, a hook, and a stirrup. The balance used was an ordinary analytical balance in good condition and capable of fourth place accuracy. The field strength of the magnet used was approximately 12,000 gauss.

The apparatus was standardized against a nickel chloride solution that had a susceptibility value of  $5.332 \times 10^{-6}$  units per unit volume. This was a 1.3660 ml. solution of specific gravity 1.201. For the purposes here it was practically identical with the solution used by Freed. A second standard nickel solution that would give a magnetic force approximately the same as the average force on the materials studied was prepared. This solution was 0.707 M. and containing 0.04143 g. of nickel per ml. The specific

gravity was 1.097 and the susceptibility of this solution was determined to be  $2.74 \times 10^{-6}$  units per unit volume.

Procedure used to measure paramagnetism. The standard nickel solution was placed in the Gouy tube up to a designated mark and weighed once with the current actuating the magnet off and once with it on. The effect of the magnet was simply the difference. The same procedure was followed for the sample being tested and a redetermination using the standard nickel solution was made as a check. If the measurements on the nickel solution checked then it was assumed that the position of the Gouy tube and the current through the magnet were constant.

Calculations and results. The force  $F$  exerted by a magnetic field on such a tube is

$$(1) \quad F = 1/2 AK (H^2 - H_0^2)$$

where  $A$  is the net cross section of the substance and  $K$  is the susceptibility per unit volume.  $H$  is the magnetic field at the center of the pole gap and  $H_0$  is the field intensity at the ends of the tube.

All the measurements were made at  $25^\circ$ . No effort was made to reduce the temperature to obtain Curie's constant.

Since the upper end of the material is well out of the field,  $H_0$  was considered to be zero. Equation (1) reduces therefore to

$$(2) \quad F = 1/2 AK (H^2)$$

and

$$(3) F_c = 1/2 A_c K_c (H_s)$$

where c refers to the magnetic attraction of the material being tested and

$$(4) F_n = 1/2 A_n K_n (H_s)$$

where n refers to the standard nickel solution.

$$(5) \frac{F_c}{F_n} = \frac{A_c K_c}{A_n K_n}$$

$$(6) A_c K_c = A_n K_n \frac{F_c}{F_n}$$

$$(7) K_n = d_n x_n$$

The factor  $K_n d_n$  is the specific susceptibility of the tube filled with NiCl<sub>2</sub>,  $d_n$  is the specific volume of the tube and  $x$  = susceptibility per gram.

$$(8) A_c = \frac{W_c}{dl}$$

$d$  = density,  $l$  = length of tube and  $W_c$  = weight of sample.

Substituting 7 and 8 in 6:

$$(9) \frac{W_c}{dl} \cdot d_c x_c = A_n d_n x_n \frac{F_c}{F_n}$$

All values are of known magnitude except  $x_c$ , hence, it can be calculated.

The quantity  $x_c$  times the molecular weight is the molar susceptibility  $X_c$ .

The calculations for deoxygenated Co-Ox from the values given in Table III are:

$$x_c = \frac{F_c}{F_n} \frac{K_n d_n}{W_c}$$

$$x_c = \frac{83}{46} \frac{2.74 \times 10^{-6}}{.1914} \quad 1462 = 1.19 \times 10^{-6}$$

$$X_{omolar} = 1.19 (328) = .00394$$



$$U_0 = 2.839 \sqrt{.00394 (293)} = 2.94 \text{ Bohr magnetons}$$

This is probably a free electron spin number of 1. The compound thus has a large orbital contribution.

Following the work on magnetism it was learned that the group at the University of California working under the direction of the National Defense Research Committee on this problem had at their disposal excellent facilities for measuring magnetic properties and further work was abandoned. The results of the California group agreed well with the values given in Table III.

Table III

Description	Sample Weight	Paramagnetic Attraction for Sample	Paramagnetic Attraction for Nickel Chloride Solution	Nickel Chloride in Longitudinal Area	Susceptibility of Nickel Solution	Molar Magnetic Susceptibility	Bohr Magneton Per Cobalt Atom	Probable Free Electron Spin
	$W_0$ g.	$F_0$ mg.	$F_N$ mg.	$D_N$ g./cm. <sup>2</sup>	$K_N \cdot 10^4$	$X_0 \cdot 10^3$	$U_0$	
Co-Ox	.1914	8.3	4.6	.462	2.74	385	2.94	1
Oxygenated Co-Ox	.2009	0.4	4.6	.462	2.74	---	---	---
Disalicylal-ethylenediimine	.2093	-0.7	10.1	.437	5.332	-20.8	---	---
Inactive Red Form of Co-Ox	.2638	7.7	4.6	.462	2.74	266	2.52	1
Disalicylal-propylenediimine Cobalt	.2407	6.1	4.5	.460	2.74	241	2.42	1
Disalicylal-phenylenediimine Cobalt	.1663	13.2	4.6	.462	2.74	618	4.42	2

Interpretation of the results on magnetic susceptibility. The value of one free electron spin for deoxygenated Co-Ox and the diamagnetism of oxygenated Co-Ox does not hinder or support the theory that there is a molecule of water between two cobalt atoms. The cobalt atom in non-coordinating compounds like cobalt chloride has three free electron spins. In a combination like Co-Ox two of these are associated with the coordination bonds with the two nitrogen atoms while the third remains free for oxygenation. If a water of hydration is present it should not be expected to affect the magnetic behavior since many salts have the same magnetic behavior in the form of anhydrous powders, hydrated salts, or in water solution. The similarity of Co-Ox to hemoglobin in magnetic behavior is, however, striking.

The rate of oxygenation of Co-Ox.

Considerable interest attaches to the rate at which oxygen is taken up by Co-Ox under various temperatures and pressures.

Hach and Diehl in the period before the author entered this work performed a number of isolated experiments that provided important information in designing a method for determining the rate of oxygenation accurately. By exposing a sample of Co-Ox carried on a convenient weighing boat to

air, they demonstrated that Co-Ox would absorb oxygen at such a rate that it was completely saturated in a day. When the air was replaced by oxygen the time was reduced to about ten minutes. They also demonstrated that at slightly higher temperatures the absorption did not proceed as rapidly and that at lower temperatures it was somewhat accelerated. As quite separate experiments they demonstrated that the temperature at the center of a large bed of Co-Ox changed as much as 15° due to the heat of oxygenation and that provisions to remove the heat apparently increased the rate.

Several apparatus were designed to measure the rate of oxygenation accurately. These will now be described in detail.

The water manometer rate apparatus. The first rate apparatus was called the water manometer rate apparatus after the 32 foot water manometer constructed as a part of the apparatus. The apparatus (see Fig. 1) consisted of a gas holder, a reaction chamber and a water manometer. Water was used as the retaining liquid in the gas holder and the oxygen was, therefore, delivered saturated with moisture. The gas holder was equipped with a modification of the Mariotte bottle so that it delivered the oxygen at constant pressure, either greater or less than atmospheric pressure. The gas holder held about 2.5 l. and was

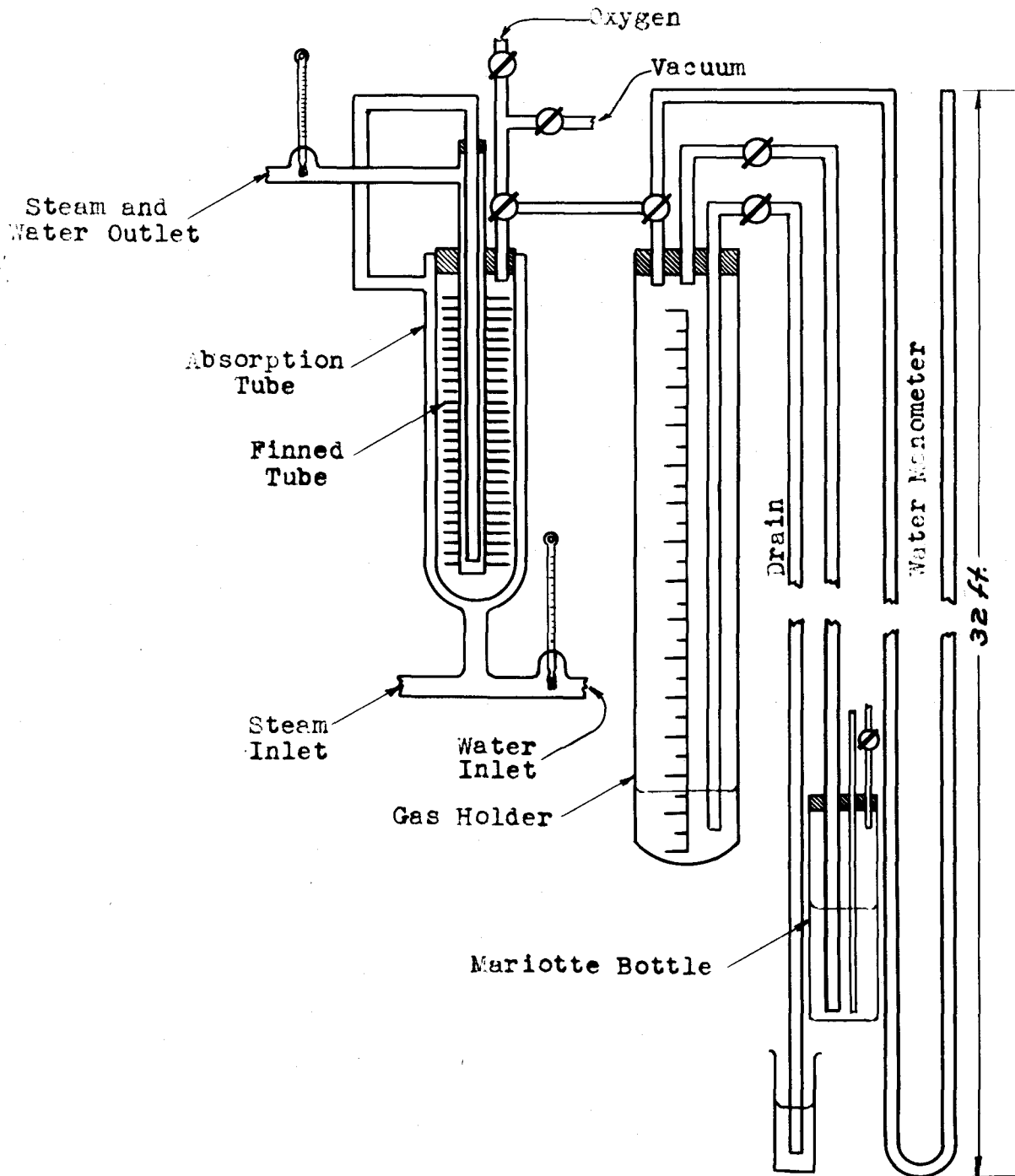


Fig. 1. The Water Manometer Rate Apparatus

calibrated with water delivered from a Morse-Blalock bulb.

The reaction vessel was jacketed and the compound was carried on a metal tube with circular fins spaced about 0.25 inches apart along the tube (part of a commercial refrigerating unit). This tube slipped snugly into the reaction vessel, and provided ample heat contact between the compound and the circulating liquid. Water from a large, well insulated carboy was passed successively through the jacket and the central metal tube bearing the fins; thermometers were placed in the inflow and outflow water and the flow of water was adjusted so that these temperatures were the same throughout a run, thus insuring that the compound remained at a constant temperature. At the conclusion of a run steam was passed through the jacket for 40 minutes to deoxygenate the compound.

A 32 foot water manometer was used to measure the pressure at which the gas was delivered, as a travelling cathetometer for use with a mercury manometer was not available. Time was measured with a stop watch and in general readings of time and gas volume were made every 30 seconds.

Using a constant temperature of 25 to 27°, runs were made at various pressures from 200 to 870 mm. of mercury. As will be seen from Fig. 2, the rate of oxygenation decreased rapidly with pressure, and the per cent of oxygen

taken up at infinite time, taken as four hours, also decreased. The point of inflection of the curves about corresponds to half saturation, and the time of half saturation values were taken as a typical point for the comparison of the rates of different pressures. A plot of the time of half saturation against pressure is shown in Fig. 3.

Holding the pressure constant at 510 mm. of mercury, runs were made varying the temperature from  $-7$  to  $+41^{\circ}$ . As will be seen from Fig. 4 and from Fig. 5, the rate of oxygenation fell off at higher temperatures and again at lower temperatures. The experimental error in this series of runs was rather high and the runs were not always quite reproducible owing to an unknown factor having to do with the activation of the compound. It is evident, however, that a maximum rate of oxygenation occurred between  $17$  and  $23^{\circ}$ .

From the above results it was apparent that the optimum temperature for oxygenation was between  $17$  and  $23^{\circ}$ , and that increasing the pressure of oxygen beyond 900 mm. of mercury does not significantly decrease the time required to oxygenate the compound.

It was expected that the oxygen pressure-oxygenation rate relationship would hold when air was used as the oxygenating agent if the air was circulated freely. Using

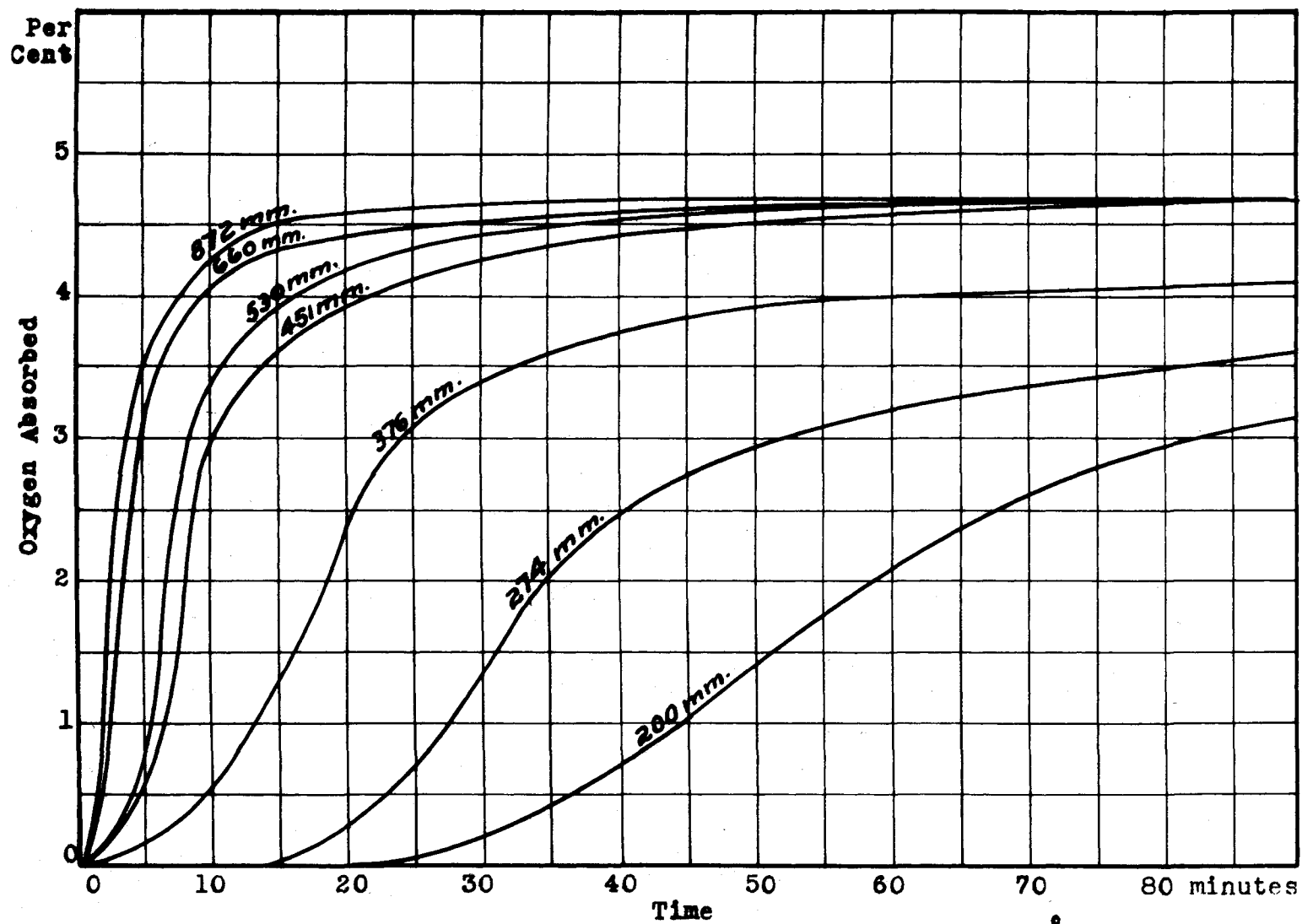


Fig. 2. Effect of Pressure on the Oxygenation of Co-Ox at 25°



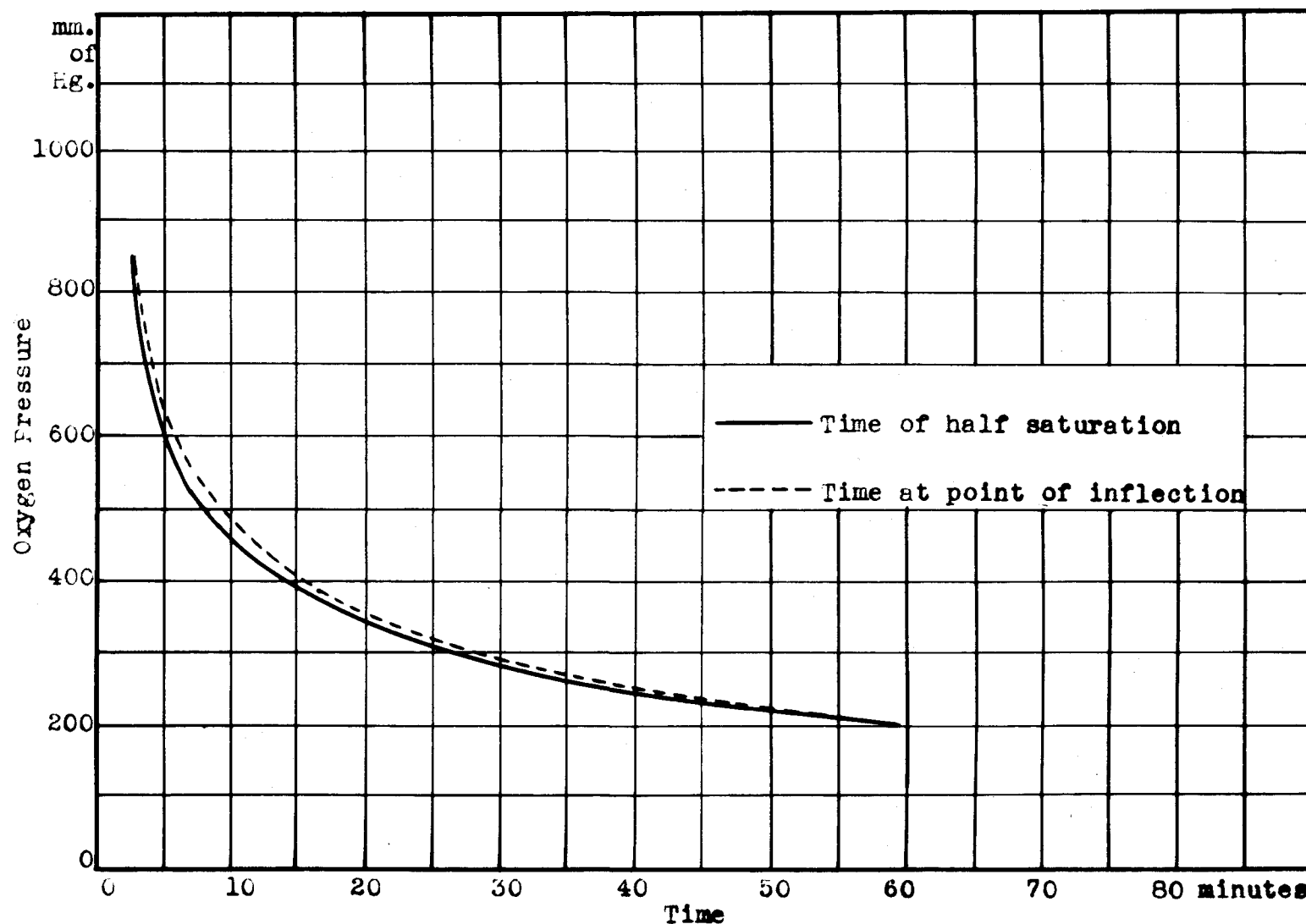


Fig. 3. Time of Half Saturation as Affected by Pressure at Constant Temperature

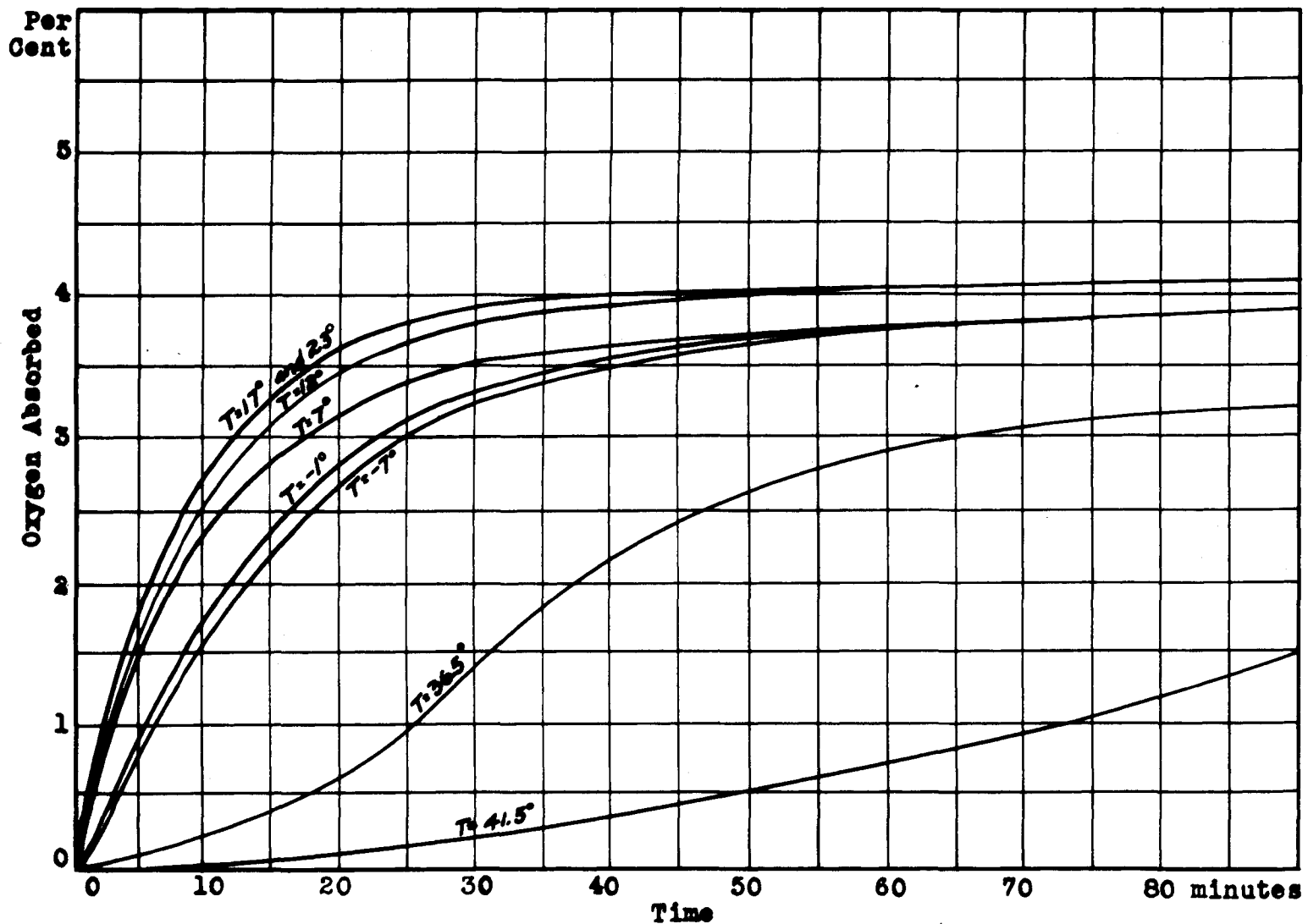


Fig. 4. Effect of Temperature on the Oxygenation of Co-Ox at 510 mm. of Hg.

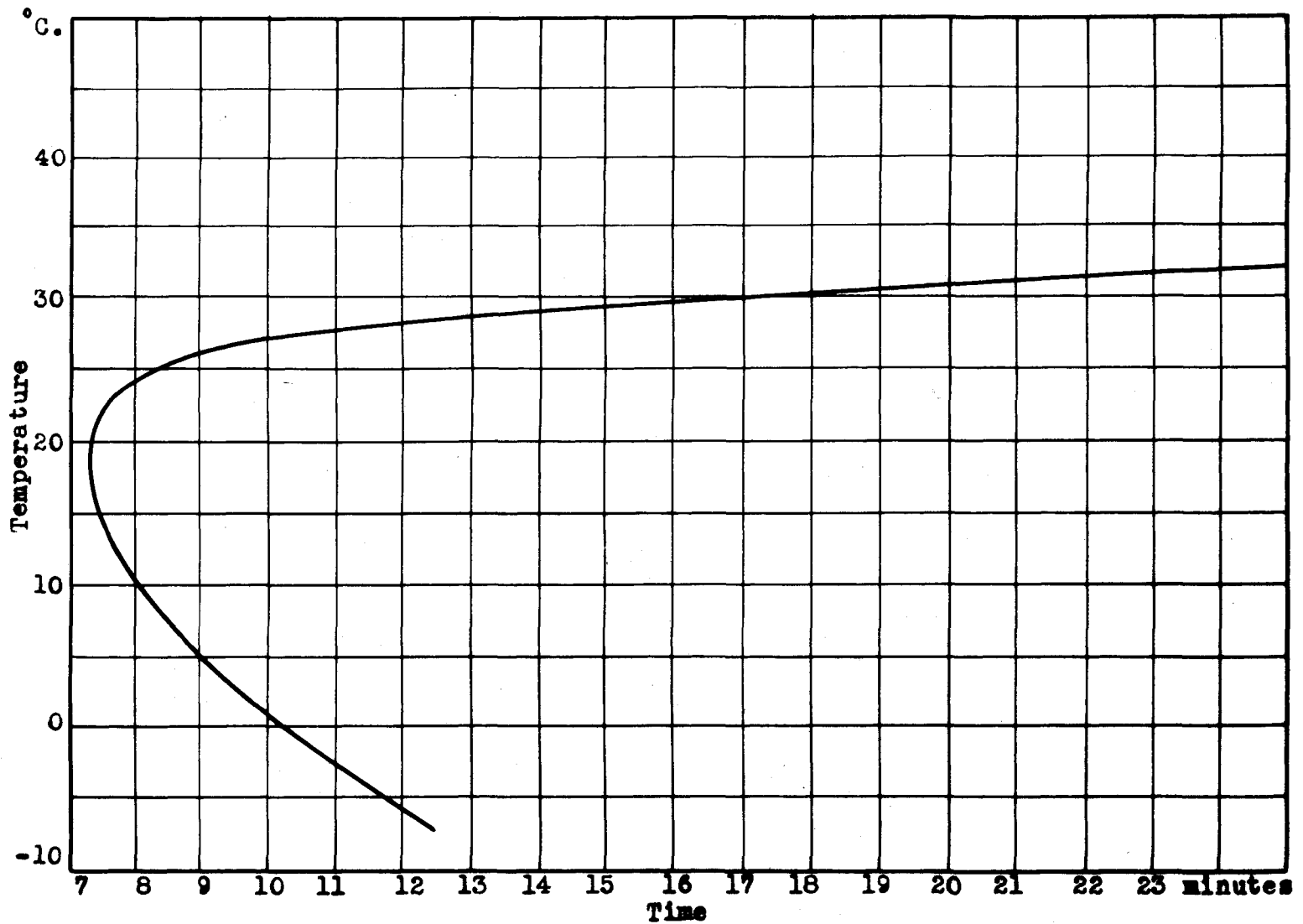


Fig. 5. Time of Half Saturation as Affected by Temperature at Constant Pressure

0.2 as the partial pressure of the oxygen in air and 1000 mm. as a suitable oxygen pressure, an air pressure of 100 pounds should oxygenate the compound in a time of eight to ten minutes.

The time of oxygenation was much greater if the heat of oxygenation was allowed to remain in the material. The temperature of the material rose about 15° under such conditions, and as would be expected, the shape of the oxygenation curve was considerably altered, the upper curved portion being considerably flattened.

The differential manometric capacity and rate apparatus.

This apparatus was constructed for the purpose of measuring oxygen capacity at high pressures but once built a more important use was found in the measurement of the rate of oxygenation in oxygen at relatively high pressures, that is, from 5 to 200 p.s.i.g. This was indeed fortunate as oxygen-carrying compounds other than Co-Ox prepared later in the investigation could not be tested for their rate of oxygenation in the water manometer apparatus since they were highly hygroscopic. Quite as unfortunate was the fact that many of the highly desired features of the water manometer apparatus, principally that of adequate heat transfer, could not be incorporated in the new apparatus.

Construction of the differential manometric capacity and rate apparatus: The differential manometric capacity

and rate apparatus (see Fig. 6) consisted of four pressure chambers A, B, C, and D. They were made from hexagonal brass block. The chambers A and D were approximately the same size while the chambers B and C were about three times as large as A and about the same size. Difficulties of construction made it quite impossible to make these chambers of definite, known volumes or of exactly the same volume.

Chamber A was constructed so that a sample could be inserted for testing. B, C, and D were closed chambers. Valve (1) leading to chamber B and valve (2) leading to chamber C were connected to the oxygen tank. With both valves open, an equal pressure of oxygen was obtained in chambers B and C. When valves (1) and (2) were closed, chambers B and C contained two isolated portions of oxygen of approximately equal size at the same pressure. Valves (5) and (6) connected chambers A and D to the vacuum line. When opened the pressure in chambers A and D dropped to the pressure of the vacuum line, 0.1 mm. Valve (3) connected chamber B to chamber A. Valve (4) in a similar manner connected chamber C to chamber D. With the opening of valves (3) and (4), the manometer registered the pressure changes and came to a final value characteristic of the apparatus when empty. When an oxygen-carrying material was placed in chamber A and the apparatus was made to function in a similar manner, the manometer came to a final value

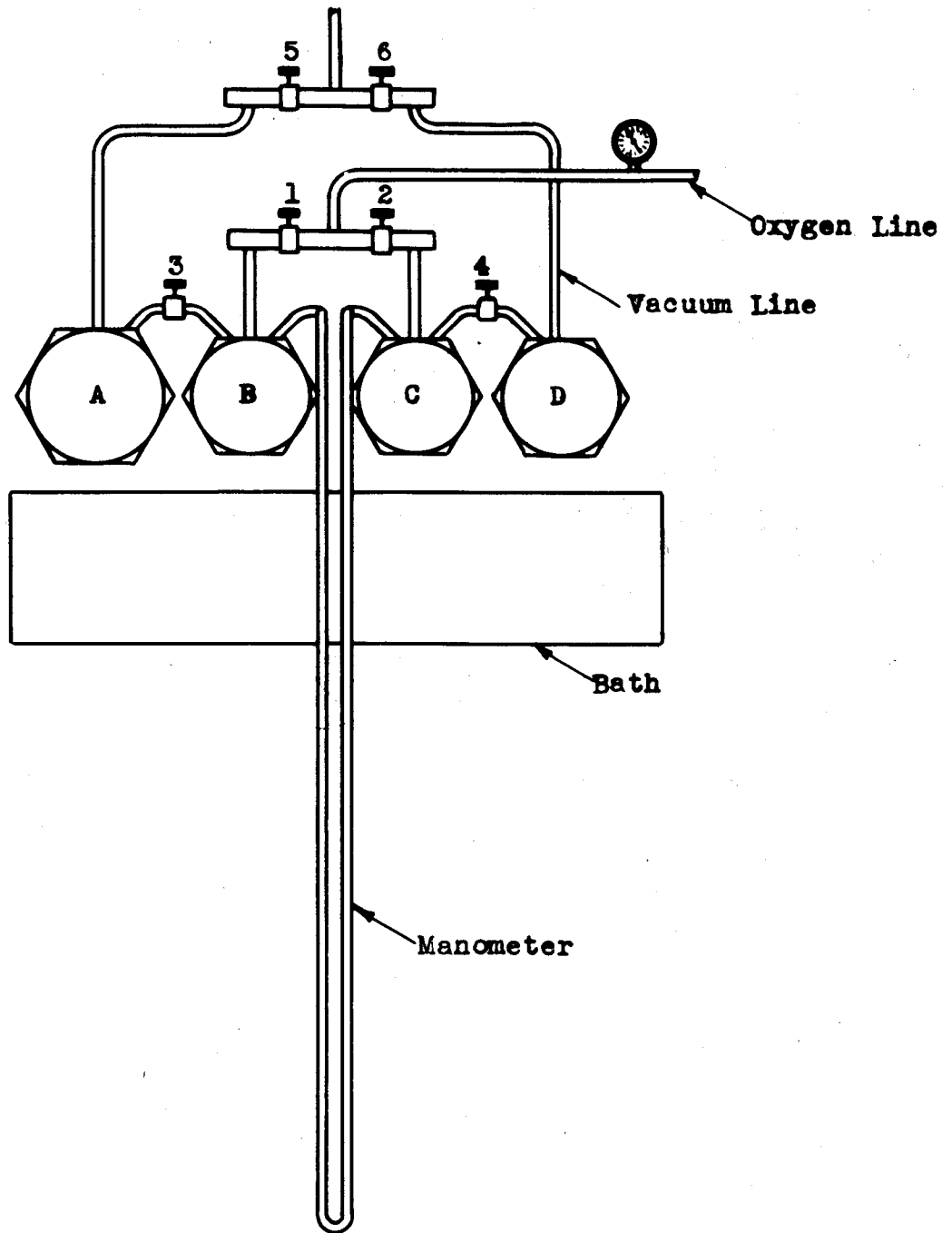


Fig. 6. The Differential Manometric Capacity and Rate Apparatus

characteristic of the chamber when empty, plus the oxygen-carrying capacity of the sample.

Temperature control was provided by raising a water bath up around the chambers by means of a hydraulic jack. The liquid bath (water-alcohol brine) was cooled by a refrigerator, the coils of which were immersed in the bath and heated by a flexible steam line immersed in the bath.

Theory and calibration: It was necessary to find the relation between the change in the manometer reading and the oxygen-carrying capacity of the sample. Operating the apparatus as described, chambers B and C were filled with oxygen to some elevated pressure P and isolated first from one another by closing valves (1) and (2). At the same time chambers A and D were evacuated by opening valves (5) and (6).

Let  $V_A$  equal the volume of chamber A

$V_B$  equal the volume of chamber B

$V_C$  equal the volume of chamber C

$V_D$  equal the volume of chamber D

Then from the simple gas law

$$(1) \quad PV_B = n_B RT$$

$$(2) \quad PV_C = n_C RT$$

Opening the valves (3) and (4) allowed the oxygen from chamber B to enter chamber A and the oxygen from chamber C

to enter chamber D. Then the pressure in chambers A and B differed from that in chambers C and D. The difference registered on the manometer M.

Then:

$$(3) \quad P_{A+B} (V_A + V_B) = n_B RT$$

$$(4) \quad P_{C+D} (V_C + V_D) = n_C RT$$

And:

$$(5) \quad P_{A+B} - P_{C+D} = \text{the change in the manometer reading or the blank correction } \Delta P_b$$

And:

$$(6) \quad \Delta P_b = \frac{n_B RT}{V_A + V_B} - \frac{n_C RT}{V_C + V_D}$$

With a sample present  $n_x$  moles of oxygen are absorbed from the chambers containing  $n_B$  moles of oxygen.

Let  $\Delta P_s$  be the change in pressure with a sample present.

Then:

$$(7) \quad \Delta P_s = \frac{(n_B - n_x) RT}{V_A + V_B} - \frac{n_C RT}{V_C + V_D}$$

Then the increment of pressure change due to the sample alone is  $\Delta P_s - \Delta P_b = \Delta P$  for oxygenation alone.

$$(8) \quad \Delta P = \Delta P_s - \Delta P_b = \frac{n_B - n_x RT}{V_A + V_B} - \frac{n_C RT}{V_C + V_D} - \frac{n_B RT}{V_A + V_B} + \frac{n_C RT}{V_C + V_D}$$

$$(9) \quad \Delta P = \frac{n_B RT}{V_A + V_B} - \frac{n_x RT}{V_A + V_B} - \frac{n_C RT}{V_C + V_D} - \frac{n_B RT}{V_A + V_B} + \frac{n_C RT}{V_C + V_D}$$



Or:

$$(10) \quad \Delta P = \frac{n_x RT}{V_A + V_B}$$

This value of  $\Delta P$  is not the correct one as the volume  $V_A + V_B$  contains a sample occupying considerable space apparently decreasing the volume by an amount  $V_s$ , the volume of the sample.

Then more accurately:

$$(11) \quad \Delta P = \frac{n_x RT}{V_A + V_B - V_s}$$

$V_s$  is easily evaluated being the weight of the sample divided by the density of the sample

$$(12) \quad \Delta P = \frac{n_x RT}{\left( V_A + V_B - \frac{\text{wt. of sample}}{\text{density of sample}} \right)}$$

Converting to per cent oxygen capacity:

$$(13) \quad \% = \frac{\Delta P (V_A + V_B - \frac{\text{wt. of sample}}{\text{density of sample}})}{RT (\text{wt. of sample})} (32) (100)$$

Most of these materials have been found to have a density of approximately 1.5 g./ml.

Therefore, all values are now known or can be measured except the combined volume  $V_A + V_B$ . This was easily determined using equation (10). Oxygen was withdrawn from the apparatus and measured in a Morse-Blalock bulb. The corresponding change in  $\Delta P$  was observed. Changing the volume to moles of oxygen  $n_x$  and substituting to find  $V_A + V_B$ . A volume of 781 cc.

was obtained.

The equation used for the apparatus reduces then to:

$$(14) \quad \frac{\text{The per cent of oxygen capacity}}{\text{oxygen capacity}} = \frac{(\Delta P)(781 - \text{sample wt.})}{(62370)(T) \text{ sample wt.}} \quad (32)(100)$$

Capacity of Co-Ox at high pressure: The first oxygen capacity determined with the differential manometric capacity and rate apparatus was of Co-Ox at 8 p.s.i.g. as a check on the calibration. A sample having a capacity of 4.79 per cent determined by the method given earlier was placed in the apparatus and its capacity determined. The value found was 4.80 per cent using oxygen at 8 p.s.i.g. The next determination was made at 146 p.s.i.g. and the capacity measured 5.14 per cent. This value was discredited until a capacity measurement was made on an oxygen-carrying material developed later called Co-Ox M; its capacity was found to be 4.10 per cent at both 8 and 150 p.s.i.g. Several more oxygen-carrying materials developed later, Co-Ox BT, Co-Ox Pr and Co-Ox SS, were found to have the same value at 8 and 150 p.s.i.g. Co-Ox was then checked and gave a value of 5.14 per cent at 150 p.s.i.g. Evidently Co-Ox is the only material studied capable of absorbing more than one-half mole of oxygen per cobalt atom. The excess oxygen above the theoretical value of 4.79 per cent is probably due to absorption of oxygen on the surface of the oxygenated material.

A very unique oxygen-carrier from a theoretical standpoint was found by Calvin at the University of California and submitted to this laboratory for study. It was di-(3-chlorosalicylal)dipropylenetriimine cobalt which absorbed one molecule of oxygen per cobalt atom slowly and at a very high pressure. Once oxygenated it retained its oxygen long enough for an approximate check by the gravimetric method given earlier. Using the apparatus just described this material was found to have absorbed 6.5 per cent oxygen after 7 hours at 113 p.s.i.g. of oxygen at 5°.

Rates of oxygenation at high pressures: While using this apparatus to measure capacity it was noticed that rates of oxygenation could be obtained from the manometer readings by plotting the change in the readings converted to capacity against time. The apparatus became very useful for this purpose.

With a little effort the time between opening the valves in the operation that allowed oxygen into the chamber containing the sample and the first steady reading on the manometer was cut to about ten seconds. This provided readings more accurate and nearer to zero time than was possible with the water manometer apparatus. Unfortunately the sample was carried in a boat from which the heat transfer was very poor. As may be seen in Fig. 7 the rate curve is

slightly flattened by the accumulation of the heat of oxygenation. Fig. 8 shows some typical rate curves for Co-Ox and a number of related oxygen-carrying materials obtained using the differential manometric capacity and rate apparatus.

This apparatus was found to be of little value at low pressures as the drop in pressure due to oxygenation affected the rate of oxygenation. This feature was largely overcome in the succeeding apparatus, the large volume manometric rate apparatus.

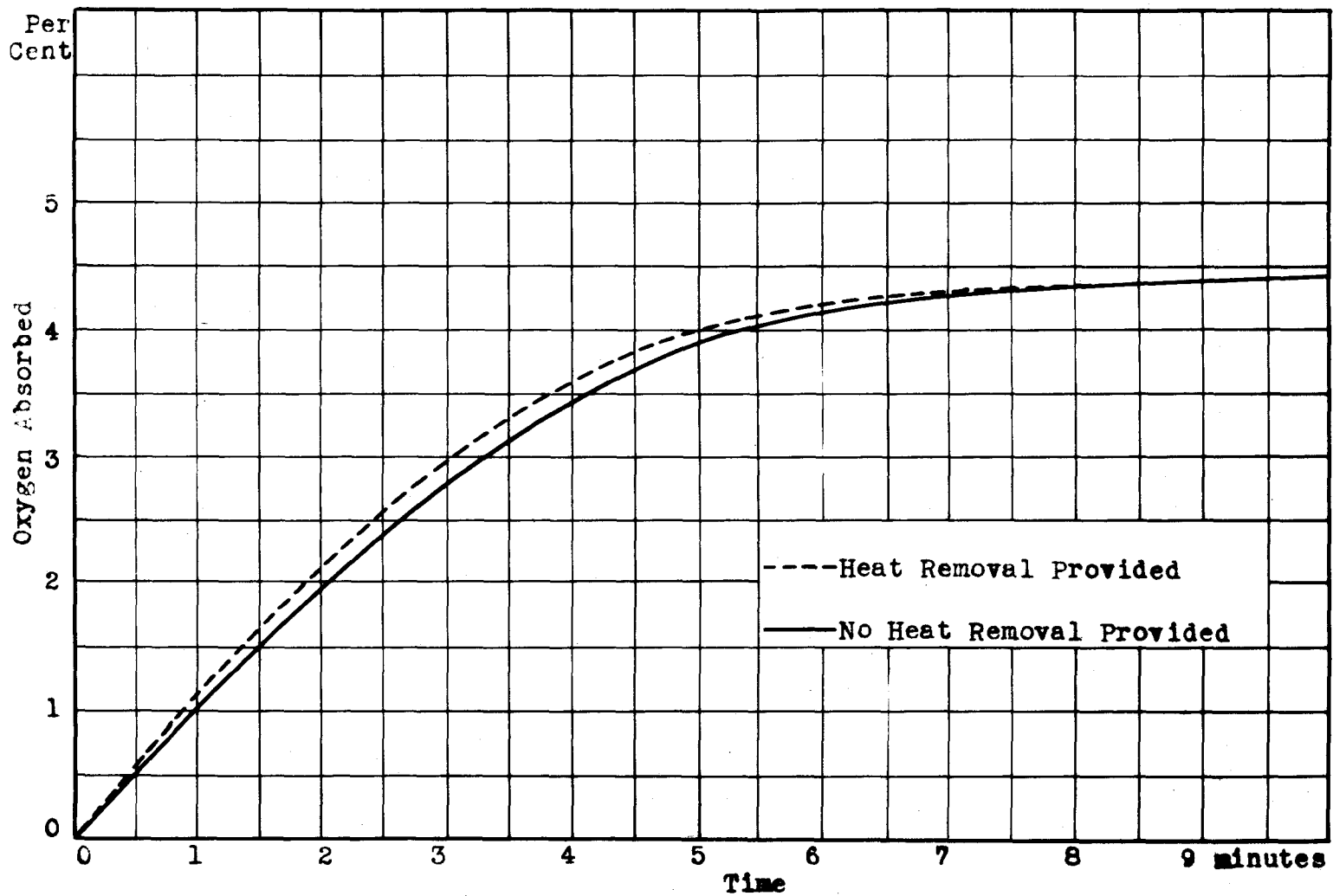


Fig. 7. Rate Curves for the Water Manometer Rate Apparatus and the Differential Manometric Capacity and Rate Apparatus Compared

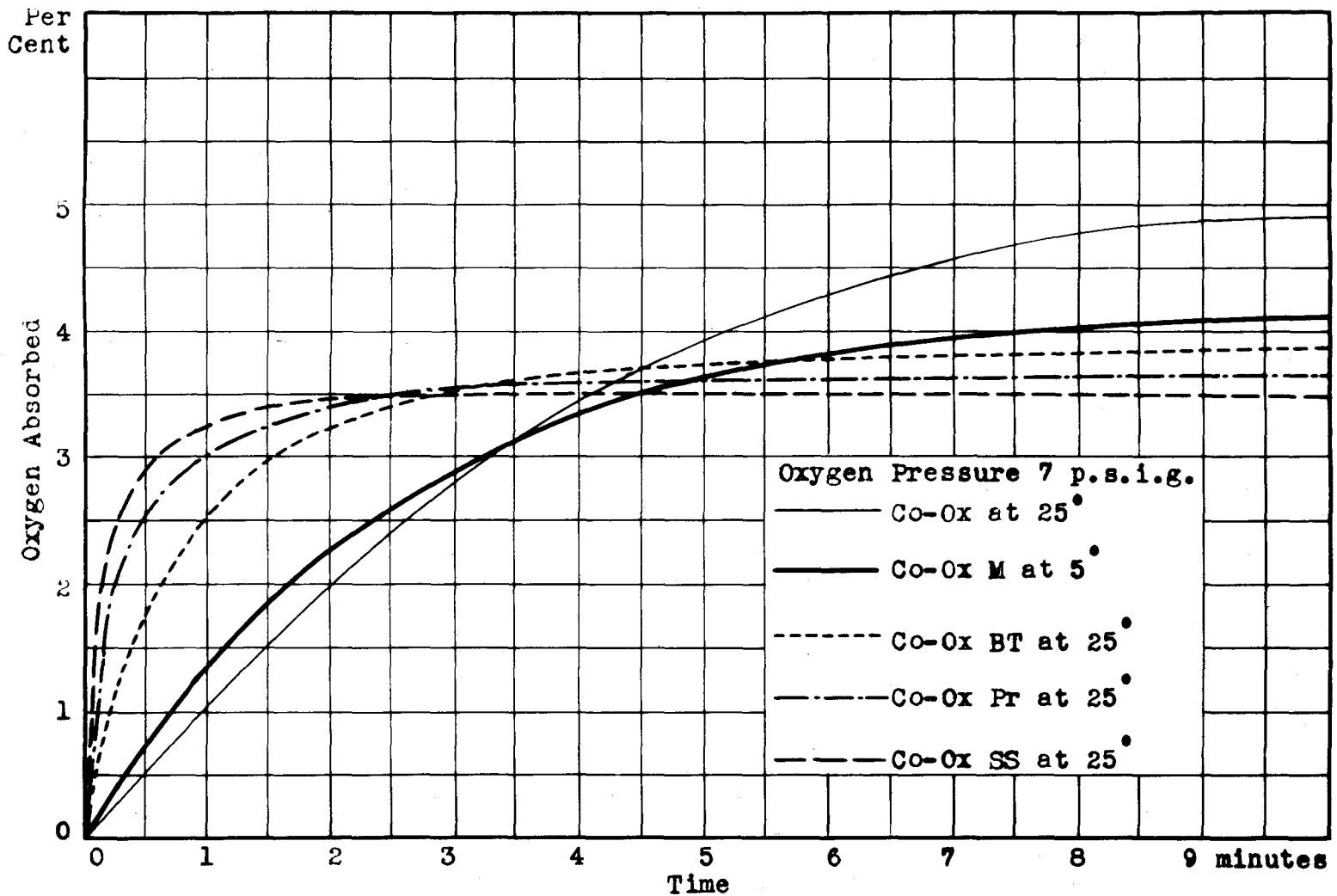


Fig. 8. Typical Rate Curves for Co-Ox and a Number of Related Oxygen-Carrying Materials

The large volume manometric rate apparatus. The large volume manometric rate apparatus was developed to operate at a lower pressure than the differential manometric capacity and rate apparatus and to employ dry oxygen.

The volume of oxygen and the size of the sample were chosen so that the pressure drop due to oxygenation would not measurably affect the rate of oxygenation. The pressure drop was then measured by any of the number of delicate means available such as an inclined oil manometer. The pressure drop was calibrated in per cent oxygenation just as in the case of the differential manometric capacity and rate apparatus.

The apparatus (see Fig. 9) as used in its final form consisted of a 5 l. balloon flask, an upright mercury manometer and an absorption chamber fitted with a 3-way stopcock; one tube of the stopcock connected to the oxygen in the balloon flask while the other was used to admit oxygen to the balloon flask or to evacuate the absorption chamber during deoxygenation. Temperature control was provided by means of a bath raised about the absorption chamber.

Absorption chambers of three different constructions were used. The first was simply a pyrex test tube 22 x 175 mm. The second, principally used by Brouns and Diehl, consisted of a copper tube with crossed fins to assist in

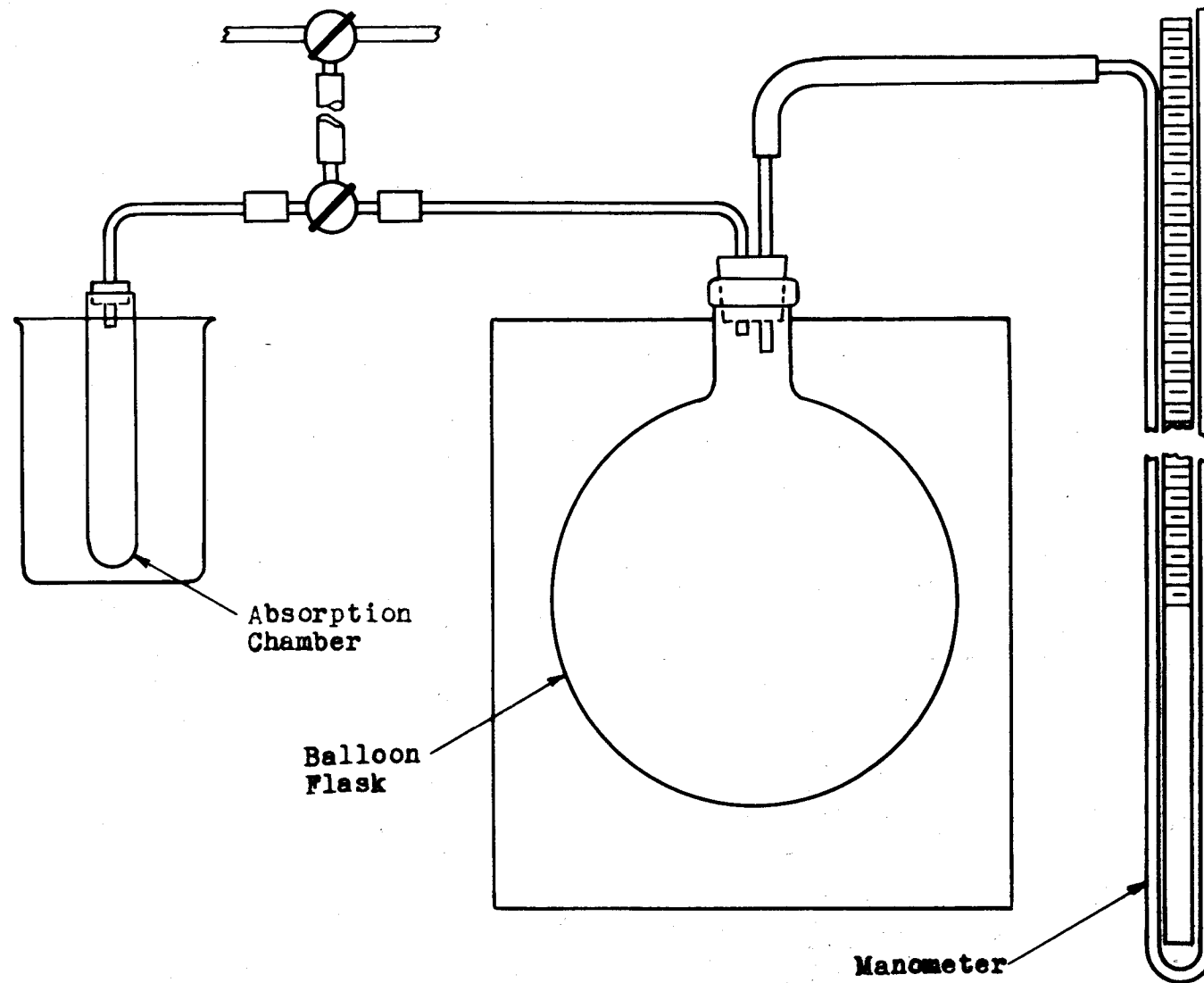


Fig. 9. The Large Volume Manometric Rate Apparatus



carrying away the heat of oxygenation.

The third and most useful was made of pyrex glass, the oxygen-carrying material occupied the annular space between two tubes while water at the temperature of the experiment was circulated through the inner tube and about the outer tube. The principal advantage of this absorption chamber lies in the fact that the maximum distance an oxygen-carrying particle could be from a constant temperature surface was 2 mm. This form of the apparatus gave the same rate of oxygenation of Co-Ox as was found in the water manometer apparatus, as shown in Fig. 3. It has been used for the study of the mixed oxygen-carrying materials described later.

This form of rate apparatus was found to be convenient for the study of the deoxygenation of these materials at a constant oxygen pressure. The oxygen pressure in the balloon flask and the temperature of the water circulating about the absorption tube were adjusted to the conditions desired for the experiment. The stopcock was turned to join the balloon flask and the absorption tube causing the material to start deoxygenating at a rate registered on the manometer. In this manner, the apparatus was used to study the deoxygenation process and the effect of moisture on deoxygenation.

Deoxygenation studies on Co-Ox.

The deoxygenation of Co-Ox depends on the conditions of temperature and pressure. These conditions were determined and it was found that at a given pressure removal of the last increment of oxygen required a somewhat higher temperature than the first. Conversely, if the temperature was constant, the pressure had to be reduced to remove all the oxygen. The deoxygenation temperature and pressure varied also with the various treatment of the sample. Typical data on the deoxygenation of Co-Ox are included in Table IV.

Table IV

Deoxygenation Temperatures and the Corresponding Pressures for Co-Ox

Run No.	Starting Temperature	Final Temperature	Oxygen Pressure
1	45°	50°	3 mm.
2	60°	65°	150 mm.
3	65°	80°	746 mm.

From a practical standpoint in manufacturing oxygen the most appropriate conditions for deoxygenation are 100° and one atmosphere pressure of oxygen, since steam is convenient for heating and gives in addition a large

thermal gradient for the rapid heating of the oxygenated material.

#### Hygroscopic Property of Co-Ox.

The hygroscopic properties of Co-Ox were appreciated only after work had progressed on the material for some time. On one occasion a bed of Co-Ox was allowed to remain in contact with oxygen saturated with water vapor for about a week. The oxygen-carrying capacity dropped nearly one per cent. On another occasion a preparation was found to be damp after it had been stored in contact with air for about 12 hours. This material had lost approximately 2 per cent of its capacity. In each case heating in a vacuum did not restore an appreciable amount of the lost capacity as was found to be the case for some of the materials developed later.

#### The Development of New Oxygen-Carrying Materials

Four principal alterations in the chemical constitution of Co-Ox were made in an effort to find new oxygen-carrying materials. The first was to replace the cobalt atom by other metals having a coordination number of six. Iron and manganese were tried using the same methods for preparing the compounds as were found best for the cobalt compound.

No oxygen-carrying materials were obtained.

The second alteration consisted of replacing the ethylenediamine in the preparation with other diamines, with monoamines, and, with ammonia. Again, the products did not carry oxygen. The third alteration was to substitute materials like pyruvic acid and acetylacetone for the salicylaldehyde portion of the oxygen-carrying molecule. This effort also was unrewarded with active compounds. The fourth alteration, the replacement of salicylaldehyde by substituted salicylaldehyde molecules, produced a number of nonoxygen-carrying materials, and some oxygen-carrying materials of considerable interest.

The first of these oxygen-carrying materials was prepared by Hach and Diehl from 3-nitrosalicylaldehyde, ethylenediamine and cobalt acetate by the method described by Chao and Diehl. This material was prepared again in the present work using the methods described earlier for the preparation of Co-Ox. The product was then subjected to a detailed study in the differential manometric capacity and rate apparatus. The oxygen-carrying properties of this material will be given in a later section covering the experimental work of this thesis.

A corresponding study of 5-nitrosalicylaldehyde, 5-bromosalicylaldehyde and 3-hydroxysalicylaldehyde showed that preparations from these materials did not function as

oxygen-carrying materials.

The most interesting of the oxygen-carrying materials prepared was that of Liggett and Diehl (16), a material prepared from o-vanillin (3-methoxysalicylaldehyde or more accurately 2-hydroxy-3-methoxybenzaldehyde), ethylenediamine and cobalt chloride. The di-(2-hydroxy-3-methoxybenzal)ethylenediamine cobalt, shortened to Co-Ox M for convenience, was found to absorb oxygen from air at a very rapid rate providing the air was dry and the temperature was maintained at about 5°. By the methods of preparation given in this paper the material obtained was inactive unless heated to 170° in a good vacuum. This process, first called activation, was later found to be a dehydration process in which one molecule of water was removed. Contact of this material with atmospheric moisture resulted in an inactive material. Co-Ox M was then studied in the differential manometric capacity and rate apparatus. A consideration of its oxygen-carrying properties will be taken up again in later sections covering the experimental work of this thesis.

The success with Co-Ox M stimulated research on other 3-alkoxy derivatives. Liggett and Diehl immediately prepared di-(2-hydroxy-3-ethoxybenzal)ethylenediamine cobalt which was given the name Co-Ox BT. Brouns and Diehl (17) following a method obtained by Liggett for the successful preparation of the aldehydes needed for the preparation of

3-alkoxy oxygen-carrying materials obtained di-(2-hydroxy-3-n-propoxybenzal)ethylenediimine cobalt. This latter name has been shortened to Co-Ox Pr for convenient reference. A study of these materials showed that the affinity for oxygen increased with the length of the alkoxy chain while the affinity for water decreased. In preparation they retained a water of hydration which was removed readily at 100° in a good vacuum. They were found to absorb oxygen from dry air at room temperature at a rapid rate. Using the method developed by Liggett for the preparation of 2-hydroxy-3-alkoxybenzaldehyde, the preparation of higher members of the 3-alkoxy series was attempted.

Procedure for the preparation of o-alkoxyphenols.

An amount of 110 g. of pyrocatechol is dissolved in 300 ml. of boiling distilled water in a 2 l. round bottom flask fitted with a reflux condenser. While boiling gently 40 g. of sodium hydroxide dissolved in 200 ml. of water is added drop wise. This technique provides a sufficient safeguard against excessive oxidation of the alkaline pyrocatechol by air. Following the complete addition of the alkali a mole of the desired alkyl bromide or alkyl iodide is added in the same manner as the alkali. The mixture is then refluxed gently for 24 hours. In this period all the alkyl bromide or alkyl iodide is consumed

with the attending formation of the o-alkoxyphenol. The o-alkoxyphenol forms an upper layer which is conveniently separated from the water layer in a separatory funnel. It is washed with water and vacuum distilled. The large constant boiling fraction is usually the product desired.

The materials prepared in this manner were converted by the Duff (18) method as modified by Liggett to the corresponding 2-hydroxy-3-alkoxybenzaldehyde.

Procedure for the preparation of 2-hydroxy-3-alkoxybenzaldehyde by the Duff reaction.

An amount of 35 g. of boric acid and 150 g. of glycerol are heated together until the mixture becomes anhydrous, usually 170° for 30 minutes. This mixture is then treated with 25 g. of hexamethylenetetramine mixed with 25 g. of the o-alkoxyphenol prepared above. The temperature is maintained at 150 to 160° by heating or cooling as necessary during the next 15 minutes. It is then allowed to cool to 105° and acidified with a solution of 35 ml. of concentrated sulfuric acid in 100 ml. of distilled water. It is then steam distilled producing up to 20 per cent yields of the 2-hydroxy-3-alkoxybenzaldehyde. There is no unchanged product and no other aldehyde produced.

The preparation of oxygen-carrying materials from the 2-hydroxy-3-alkoxybenzaldehydes.

Using the synthesis described in the previous section, sufficient 2-hydroxy-3-n-butoxybenzaldehyde was obtained for the preparation of di-(2-hydroxy-3-n-butoxybenzal)ethylenediimine cobalt, Co-Ox SS, by the alcohol method given earlier in this thesis. The oxygen-carrying capacity of this material was found to be 3.34 per cent. The properties of this material are given in the section covering the experimental work of this thesis.

A small amount of 2-hydroxy-3-n-amyloxybenzaldehyde was obtained for the preparation of a small sample of di-(2-hydroxy-3-n-amyloxybenzal)ethylenediimine cobalt, Co-Ox Am, by the alcohol method; however, only in sufficient quantities for a study of a few of the oxygen-carrying properties. The capacity of the only sample made was 3.10 per cent. The other data on this material estimated from a few rate of oxygenation determinations and other experimental work are given in the section covering the experimental work of this thesis.

Attempts to prepare 2-hydroxy-3-iso-propoxybenzaldehyde, 2-hydroxy-3-iso-butoxybenzaldehyde, 2-hydroxy-3-allyloxybenzaldehyde, 2-hydroxy-3- $\beta$ -ethoxyethoxybenzaldehyde, 2-hydroxy-3-sec-butoxybenzaldehyde and 2-hydroxy-3-cetoxy-



benzaldehyde were unsuccessful. The Duff reaction on branched o-alkoxyphenols was found to give very low yields while o-cetoxyphenol could not be obtained by the method described above.

Mixed oxygen-carrying materials.

Considerable interest was attached to the possibility of obtaining a material having two aldehyde groups in the molecule instead of two molecules of the same aldehyde. It was believed that some idea of the properties of such compounds could be obtained by simply making a preparation using equimolar mixtures of two aldehydes with ethylenediamine. This would produce, it was believed, one-fourth mole of material containing but one aldehyde and one-fourth mole of material containing the other aldehyde. The remaining one-half mole of material would contain one of each of the aldehydes. The material obtained, however, did not have the properties expected of a mixture of the three materials. The oxygen-carrying capacity was the average of the two values as expected but the oxygenation and deoxygenation temperatures were much lower, much like the melting point of mixtures of similar solid materials is lower than the melting point of either when pure. From this it was seen that the properties of the oxygen-carrying materials could be varied progressively by changing the ratio of the

amounts of the two aldehydes used.

Procedure for the preparation of mixed oxygen-carrying materials. Following the directions given above for the preparation of disalicylalethylenediimine, sufficient quantities of the two Schiff's bases were prepared. These were then mixed in the molecular ratio desired. The mixed Schiff's bases were converted to a cobalt compound just as with a pure Schiff's base, that is by either the alcohol or the water method given earlier for the preparation of Co-Ox. As is quite evident the number of mixtures that may be studied in this manner is almost without limit. A sufficient number have been studied, however, to formulate simple rules relating the ratio of aldehyde used and the effect on the properties of the product.

For these materials a short notation that describes each of the preparations has been adopted. Co-Ox is general for oxygen-carrying materials. Co-Ox P (P for parent) is the oxygen-carrying material from salicylaldehyde. Co-Ox PM represents a mixture of Co-Ox P and Co-Ox M. To indicate the ratio of each in the mixture, the per cent of the first constituent indicated follows the symbol representing a mixture. Thus, Co-Ox MBT 40 would be a mixture containing by analysis 40 mole per cent di-(2-hydroxy-3-methoxybenzal) ethylenediimine cobalt and 60 mole per cent di-(2-hydroxy-3-ethoxybenzal) ethylenediimine cobalt without any reference

to the possible chemical combinations in such a conglomerate. The mixed materials studied for this paper were mixtures of Co-Ox P and Co-Ox BT.<sup>1</sup> Data from the consideration of rates as obtained in the large volume manometric rate apparatus along with tables of other data are given in the section covering the experimental work of this paper.

### The Comparison of Oxygen-Carrying Materials

As new oxygen-carrying materials were obtained they were subjected to experimental studies paralleling those made on Co-Ox. In these studies oxygen-carrying capacity, the time required for oxygenation, the oxygen pressure above which the time for oxygenation does not appear to decrease, the optimum temperature of oxygenation, the minimum deoxygenation temperature at various pressures, and the hygroscopicity became yardsticks for the comparison and evaluation of the oxygen-carrying materials. Each of these properties will be discussed separately and the values for the various compounds studied tabulated.

#### Oxygen-carrying capacity.

The preferred method of measuring the oxygen-carrying capacity was the gravimetric method described earlier. This

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<sup>1</sup>Other mixtures have been studied by Brouns and Diehl, and Liggett and Diehl. Similar results were found.

method, however, was found to be inconvenient and inaccurate for the 3-alkoxy materials and many of the mixed oxygen-carrying materials since these materials were hygroscopic and absorbed moisture from the air during the determination. The other methods used, indicated in Table V, were also described earlier.

Table V  
Oxygen-Carrying Capacity of Co-Ox and Related  
Oxygen-Carrying Materials

Oxygen-Carrying Material	Method of Measurement	Per Cent Oxygen Capacity Found	Per Cent Oxygen Capacity Theoretical
Co-Ox P	Weight	4.80	4.94
Co-Ox M	Rate Apparatus	4.10	4.16
Co-Ox BT	Rate Apparatus	3.82	3.87
Co-Ox Pr	Rate Apparatus	3.44	3.64
Co-Ox SS	Rate Apparatus	3.34	3.41
Co-Ox Am	Rate Apparatus	3.10	3.25
Co-Ox N3	Weight	3.25	3.86
Co-Ox PBT 10	Weight	3.80	3.96
Co-Ox PBT 20	Rate Apparatus	-----	4.05
Co-Ox PBT 40	Rate Apparatus	-----	4.24
Co-Ox PBT 50	Rate Apparatus	4.35	4.35
Co-Ox PBT 60	Rate Apparatus	-----	4.43
Co-Ox PBT 80	Rate Apparatus	-----	4.51
Co-Ox PBT 95	Rate Apparatus	4.50	4.76

Time required for oxygenation.

The large volume manometric rate apparatus was found to be the most useful of the various apparatus used for determining the time required for oxygenation at low pressures. The differential manometric capacity and rate apparatus served best at higher pressures. Rates were measured at several pressures from 100 mm. of mercury up to 150 p.s.i.g. for most of the oxygen-carrying materials. The time required for apparently complete saturation at a moderately high pressure was an important factor in the practical utilization of these materials. The rate curves shown in Fig. 8 are typical of the many rate curves used to obtain the data in the following tables.

Table VI

Time Required for Apparently Complete Oxygenation  
of Co-Ox and Related Oxygen-Carrying Materials

Oxygen-Carrying Material	Time Required for Oxygenation	Experimental Pressure	Conditions Temperature
Co-Ox P	8 minutes	7 p.s.i.g.	18°
Co-Ox M	7 minutes	7 p.s.i.g.	5°
Co-Ox BT	5 minutes	7 p.s.i.g.	18°
Co-Ox Pr	3 minutes	7 p.s.i.g.	18°
Co-Ox SS	2 minutes	7 p.s.i.g.	18°
Co-Ox Am	2 minutes	7 p.s.i.g.	18°
Co-Ox N3	4 hours	150 p.s.i.g.	18°
Co-Ox PBT 10	4 hours	15 p.s.i.g.	18°
Co-Ox PBT 20	4 hours	15 p.s.i.g.	18°
Co-Ox PBT 40	4 hours	15 p.s.i.g.	18°
Co-Ox PBT 50	4 hours	15 p.s.i.g.	18°
Co-Ox PBT 60	4 hours	15 p.s.i.g.	18°
Co-Ox PBT 80	4 hours	15 p.s.i.g.	18°
Co-Ox PBT 95	4 hours	15 p.s.i.g.	18°

The oxygen pressure above which the time for oxygenation does not appear to decrease.

There is a pressure characteristic of each oxygen-carrying material above which the time required for oxygenation does not appear to decrease. This pressure was found for each of the new oxygen-carrying materials prepared for this work by considering the change in the rates of oxygenation with pressure as was done for Co-Ox (see Fig. 3). For these determinations a constant temperature was maintained by providing the best possible conditions for removing the heat of oxygenation from the bed of material being studied.

Table VII

The Oxygen Pressure Above which the Time of Oxygenation does not Appear to Decrease for Co-Ox and Related Oxygen-Carrying Materials

Oxygen-Carrying Material	Pressure Above which the Time of Oxygenation did not Appear to Decrease	Temperature of Experiment
Co-Ox P	950 mm. of Mercury	18°
Co-Ox M	150 mm. of Mercury	5°
Co-Ox BT	<100 mm. of Mercury	15°
Co-Ox Pr	<100 mm. of Mercury	15°
Co-Ox SS	<100 mm. of Mercury	15°
Co-Ox N3	>150 p.s.i.g.	15°

The optimum temperature of oxygenation.

The ideal optimum temperature of oxygenation would, with other things being equal, be as near as possible to the temperature of deoxygenation in order that the amount of cooling necessary to effect oxygenation be a minimum. The rate apparatus were used to estimate this value. The oxygen pressure was held constant and the rates of oxygenation determined at several temperatures. The range of temperatures that could be tried was limited by the experimental conditions to from  $-20^{\circ}$  to  $50^{\circ}$ . As was found for Co-Ox (see Fig. 5) there is a temperature for which oxygenation proceeds at the greatest rate. Above or below this temperature oxygenation proceeds more slowly. The optimum temperature is important in that it determines the extent to which a bed of oxygen-carrying material must be cooled to obtain oxygenation in the shortest possible time. The values for the optimum temperature range of oxygenation for the materials prepared are given in Table VIII.



Table VIII

Optimum Temperature Range of Oxygenation for Co-Ox and  
Related Oxygen-Carrying Materials

Oxygen-Carrying Materials	Optimum Temperature of Oxygenation
Co-Ox P	18-23°
Co-Ox M	0-5°
Co-Ox BT	25-40°
Co-Ox SS	Less than 0°
Co-Ox PBT 10	Less than 0°
Co-Ox PBT 20	Less than 0°
Co-Ox PBT 40	Less than 0°
Co-Ox PBT 50	Less than 0°
Co-Ox PBT 60	Less than 0°
Co-Ox PBT 80	Less than 0°
Co-Ox PBT 95	Less than 0°

Minimum deoxygenation temperature.

The minimum deoxygenation temperature was determined for each new oxygen-carrying material by slowly raising the temperature of a bed of the oxygenated material and observing the temperature at which oxygen was removed against constant pressure. Three pressures were chosen: The first was about 3 mm. of mercury to find the lowest temperature possible for

deoxygenation. The second was against the atmosphere, a convenient determination, made by observing the color change from black to red-brown on a melting point block. The third was made against an atmosphere of oxygen. The latter value was found to be the most practical as it was the temperature to which a bed of oxygen-carrying material must be raised to produce pure oxygen at one atmosphere in an apparatus for large scale production. The values are given in Table IX.

Table IX

Deoxygenation Temperatures for Co-Ox and Related Oxygen-Carrying Materials in a High Vacuum, in Air and Against an Atmosphere of Oxygen

Oxygen-Carrying Material	Deoxygenation Temperature in		
	High Vacuum	Air	Atmos. of Oxygen
Co-Ox P	45-50°	60-65°	65-80°
Co-Ox M	42-50°	no data	80-90°
Co-Ox BT	60-65°	no data	90-95°
Co-Ox Pr	no data	no data	90-95°
Co-Ox SS	no data	no data	85-90°
Co-Ox PBT 10	15°	no data	25-28°
Co-Ox PBT 20	15°	20-25°	25-28°
Co-Ox PBT 40	15°	20-25°	25-28°
Co-Ox PBT 60	15°	20-25°	25-28°
Co-Ox PBT 80	15°	20-25°	25-28°
Co-Ox PBT 95	25°	30-35°	45-50°

Hygroscopicity.

An ideal oxygen-carrying material would not be affected by water. It could then be brought in contact with undried air for oxygenation or even be suspended in water rather than used in powdered form. It might even be possible to effect deoxygenation by the direct application of steam. However, all of the oxygen-carrying materials prepared for this work were markedly changed by water. Co-Ox P, the oxygen-carrying material that absorbed water most slowly, became inactive gradually on exposure to moist air. Other oxygen-carrying materials were rapidly rendered inactive, Co-Ox M being the most hygroscopic of all those studied. Heating for the most part failed to restore the oxygen-carrying ability.

It has been discovered also that water vapor in the oxygen-containing gaseous mixture used to oxygenate an oxygen-carrying material appeared to facilitate the absorption of oxygen. Thus, the optimum oxygenation temperature appeared higher toward moist oxygen than toward dry oxygen. These materials once oxygenated were more difficult to deoxygenate, requiring a higher temperature and lower pressure to complete the process. The degree of hygroscopicity found for each of the materials studied is given in Table X.

Table X

A Comparison of the Hygroscopicity of Co-Ox and Related Oxygen-Carrying Materials

Oxygen-Carrying Material	Hygroscopicity
Co-Ox P	Slight
Co-Ox M	Extreme
Co-Ox BT	Moderate
Co-Ox Pr	Moderate, less than Co-Ox BT
Co-Ox SS	Moderate, less than Co-Ox Pr
Co-Ox AM	Moderate, probably less than Co-Ox SS
Co-Ox N3	Moderate
Co-Ox PBT 10	(
Co-Ox PBT 20	)
Co-Ox PBT 40	(
Co-Ox PBT 50	-) Moderate, decreasing to slight
Co-Ox PBT 60	(
Co-Ox PBT 80	)
Co-Ox PBT 95	(

SUMMARY

1. Two new methods for the preparation of the oxygen-carrying material, disalicylaethylenedilimine cobalt (Co-Ox) have been devised. Both are characterized by the preliminary preparation of disalicylaethylenedilimine, the Schiff's base of salicylaldehyde and ethylenediamine. This material was then reacted with a cobalt salt to give the oxygen-carrying material in a form having a high oxygen-carrying capacity. The methods of carrying out the final step differ in the solvent used. In the alcohol method the solvent used consisted of a 60 per cent ethyl alcohol-water mixture in which the Schiff's base and slightly less than two equivalents of sodium hydroxide were dissolved. The oxygen-carrying material was subsequently precipitated by the addition of a solution of a cobalt salt. Relatively low yields were obtained by this method. In the second method water was used as the solvent, the solution of the Schiff's base being effected because of the two equivalents of sodium hydroxide present. The reaction with the cobalt salt proceeded in two distinct steps: The instantaneous formation of an orange precipitate and the rapid transformation of it into the red-brown oxygen-carrying material. In the method using water as a solvent, the yields were almost quantitative.

Quite unlike the method used by earlier workers for the preparation of Co-Ox, these methods were found to be affected by only three factors: If all the alcohol was not removed from the preparation in the alcohol method then the oxygen-carrying material deteriorated during drying. If two equivalents or more of sodium hydroxide are used in either method then a brick-red isomer of Co-Ox was obtained which did not absorb oxygen. If the oxygen-carrying material was not dried rapidly and out of contact with oxygen the product was found to be low in oxygen-carrying capacity.

Both methods were found to be general and applicable to the preparation of oxygen-carrying compounds from other Schiff's bases.

2. The method for the determination of oxygen-carrying capacity for Co-Ox as used by Chao and Diehl, and by Hach and Diehl was investigated for possible sources of error. It was found that weighing deoxygenated Co-Ox in air, oxygenating in a suitable bomb at 300 p.s.i.g. for ten minutes at room temperature, and weighing again in air, which gave the gain in weight due to oxygenation, was satisfactory providing the oxygenated material was allowed to stand for at least 15 minutes in dry air at the temperature of the balance before making the weighings.

3. Considerable effort was devoted to establishing or disproving the theory first proposed by Diehl that Co-Ox

contained one-half molecule of water per cobalt atom. Co-Ox made from carefully purified reagents was analyzed for nitrogen, cobalt, carbon and hydrogen. The molecular weight calculated from these analyses was approximately eight units too large, the equivalent of one-half molecule of water per cobalt atom.

An effort was made to prepare Co-Ox under anhydrous conditions in absolute alcohol but a new product, orange in color, was obtained by omitting the sodium hydroxide. This orange material was found to contain nitrogen, cobalt and chlorine in the ratio of four to three to two. A structure for this material has been proposed. The orange material reacted with water to produce Co-Ox. It is believed to be the same as the orange precipitate which appears momentarily in the preparation of Co-Ox when water alone is used as a solvent.

4. The magnetic susceptibilities of Co-Ox and a few related materials were measured. The apparatus used was essentially that first proposed by Freed. By measuring the magnetic attraction on Co-Ox and on a nickel solution of known magnetic susceptibility the magnetic susceptibility of Co-Ox was found to be 2.94 Bohr units corresponding to one free electron spin per cobalt atom. The magnetic susceptibility of oxygenated Co-Ox was measured in a similar manner but it was found to be diamagnetic. The change in

magnetic properties for hemoglobin per iron atom during the formation of oxyhemoglobin is two free electron spins. However, this is for the absorption of twice as much oxygen. It appears therefore, Co-Ox and hemoglobin in this respect are quite similar.

5. Three apparatus were developed to measure the rate of oxygenation of Co-Ox and the related compounds studied. In the first of these, called the water manometer apparatus, the rate was determined by the volume of water required to replace the oxygen absorbed. In the second and third apparatus, called the differential manometric capacity and rate apparatus, and the large volume manometric apparatus, the rate was determined by the change in the pressure of the system as measured by mercury manometers. Auxiliary data such as the time, the temperature, the size of the sample and the characteristics of the apparatus were determined in suitable manners. The rate of oxygenation of Co-Ox was measured under various conditions: at temperatures from  $-7^{\circ}$  to  $45^{\circ}$ , and at pressures from 0.2 to 10 atmospheres. The rates of oxygenation of several other materials related to Co-Ox were also determined.

6. The conditions of temperature and pressure for the deoxygenation of Co-Ox were determined. Co-Ox was found to deoxygenate at  $45-50^{\circ}$  in a high vacuum, at  $60-65^{\circ}$  in air and at  $65-80^{\circ}$  in an atmosphere of oxygen.



7. The hygroscopicity of Co-Ox was studied. It was found that Co-Ox must be used in the dry state and that the oxygen-containing gas for oxygenation must be thoroughly dried.

8. Five new oxygen-carrying materials related to Co-Ox were developed using in place of salicylaldehyde the ortho-hydroxyaldehydes: 2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-3-ethoxy-benzaldehyde, 2-hydroxy-3-n-propoxybenzaldehyde, 2-hydroxy-3-n-butoxybenzaldehyde and 2-hydroxy-3-n-amoxybenzaldehyde. These preparations were made by the alcohol method mentioned earlier. The various properties of these materials of importance in their use as oxygen-carrying materials were determined.

9. Oxygen-carrying materials containing two different ortho-hydroxyaldehyde groups were prepared by mixing solutions of two Schiff's bases and converting the mixtures to a cobalt derivative. Several preparations of this character were made using various molecular proportions of disalicylaethylenediimine and di-(2-hydroxy-3-ethoxybenzal)ethylenediimine. The products obtained carried oxygen in the expected amounts but their pressure-temperature oxygenation characteristics varied markedly from those of the pure materials, the temperature of oxygenation at atmospheric pressure being invariably considerably lower.

10. The five properties: oxygen-carrying capacity,

time required for oxygenation, oxygen pressure above which the time for oxygenation does not appear to decrease, minimum deoxygenation temperature, and hygroscopicity were determined for all the various oxygen-carrying materials developed.

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