

STUDIES ON THE OXIDATION OF SODIUM, LITHIUM,  
AND THE ALKALINE EARTH METALS IN LIQUID AMMONIA

by

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## INTRODUCTION

For many years interest in the higher oxides of the alkali and alkaline earth metals was limited chiefly to the peroxides of sodium and potassium. However, since the beginning of the second world war, potassium superoxide has been used extensively as an air purifying agent in oxygen-generating breathing apparatus. The new-found usefulness of this oxide and our inadequate knowledge of this type of compound has led to an extensive study of the higher oxides of the metals of the first two groups in the periodic classification.

These metals are all soluble in liquid ammonia, yielding solutions in which the metals retain many of their metallic characteristics. In this strongly basic solvent the reducing power of the various metals can be studied without appreciable interference from solvation effects. Therefore the study of the oxidation of solutions of these metals in liquid ammonia has constituted one important phase of the general problem of the higher oxides.

Information from the literature concerning the products of oxidation of the various metals in liquid ammonia (previous to January 1, 1949) has been summarized in a review by Watt. The information as compiled by Watt is given in Table I on the following page (1). Later work by Schechter gives more information for sodium, confirming that given in the table (16, 17).

TABLE I

Summary of the Products of Reaction of Oxygen with Solutions of Metals in Liquid Ammonia.

<u>Metal</u>	<u>Oxidation Product</u>	<u>Notes</u>	<u>Reference</u>
Li	$\text{Li}_2\text{O}$ , $\text{Li}_2\text{O}_2$		2
Na	$\text{NaOH}$ , $\text{NaNH}_2$ , $\text{NaNO}_2$	Slow reaction	3,4,5
	$\text{Na}_2\text{O}_2$	Rapid reaction	5
	$\text{Na}_2\text{O}_3$	Not confirmed, later modified	3,4,5
	$\text{NaO}_2$	-77° C.	6
K	$\text{KOH}$ , $\text{KNH}_2$ , $\text{KNO}_2$	Slow reaction	5
	$\text{K}_2\text{O}_2$ , $\text{K}_2\text{O}_4$ ( $\text{KO}_2$ )	Rapid reaction	3,4,5,7,8
	$\text{K}_2\text{O}_3$	Not confirmed	3,4,5
	$\text{KO}_2$		9
Rb	$\text{Rb}_2\text{O}$		10
	$\text{Rb}_2\text{O}_2$ , $\text{Rb}_2\text{O}_4$ ( $\text{RbO}_2$ )	-60° C. (?)	11
	$\text{RbO}_2$		9
Cs	$\text{Cs}_2\text{O}$		10
	$\text{Cs}_2\text{O}_2$ , $\text{CsNH}_2$ , $\text{CsOH}$ , $\text{CsNO}_2$ , $\text{CsNO}_3$	Slow reaction at -60° C.	12, 13
	$\text{Cs}_2\text{O}_2$ , $\text{Cs}_2\text{O}_3$ , $\text{Cs}_2\text{O}_4$ ( $\text{CsO}_2$ )	Rapid reaction at -60° C.	12, 13
	$\text{CsO}_2$		9
Ba	$\text{BaO}$ , $\text{BaO}_2$	Gelatinous ppt.	14, 15

It can be said in general that the rate of reaction and the temperature are important factors in determining the nature of the products. Sodium, potassium, rubidium, and cesium all yield superoxide upon rapid oxidation. The tendency to give superoxide increases in the order in which metals are listed. In slow oxidation the metal oxides first formed react to give lower oxides, hydroxide, and amide (which in turn is oxidized to nitrite). Information for lithium and the metals of Group II of the periodic classification is quite incomplete in the literature.

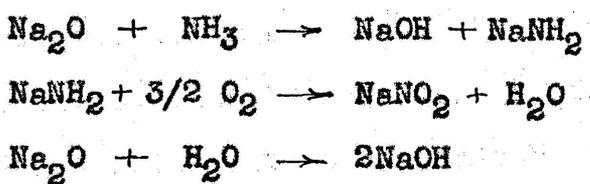
The work to be described in this report is divided into four parts: (I) Magnetic and X-ray studies on the product of rapid oxidation of sodium in liquid ammonia, (II) Studies of the oxidation of lithium and the alkaline earth metals in liquid ammonia, (III) Preliminary studies of the solution and oxidation of magnesium in liquid ammonia, (IV) Spectroscopic studies of the products of oxidation of the alkali metals and the evidence for the formation of lithium superoxide in liquid ammonia. This work represents the completion of the phase of the higher oxide problem dealing with the oxidation of liquid ammonia solutions of the metals as it has been carried out at the University of Kansas.

PART ONE: MAGNETIC AND X-RAY STUDIES ON THE OXIDATION PRODUCT OF SODIUM IN LIQUID AMMONIA

Historical Discussion

An early worker, Joannis, in 1893 reported the formation of an oxide of sodium having the ultimate composition  $Na_2O_3$  (3, 4) when a slow stream of oxygen was bubbled through a solution of sodium in liquid ammonia at a temperature of  $-50^{\circ} C$ . He proposed a two-step process in which a monoxide ammoniate,  $Na_2O \cdot NH_3$ , was first formed and then oxidized further to form the oxide  $Na_2O_3$ . Joannis' analysis consisted of determining the amount of sodium in the product, and calculating the oxygen by difference in weights.

Kraus and Whyte (5) in 1926 studied the slow oxidation of sodium in liquid ammonia more thoroughly and showed that the monoxide, which was first formed, reacted with ammonia to form amide and hydroxide. The amide was then oxidized to form a nitrite. The stoichiometry of the reaction shows that the mixture of hydroxide and nitrite has nearly the same sodium content as a compound having the formula  $Na_2O_3$ .



Kraus and Whyte stated therefore that Joannis' conclusions concerning the product of slow oxidation must have been wrong.

Kraus and Whyte studied the rapid oxidation of sodium in liquid ammonia (oxidation by a faster stream of oxygen than Joannis used) and concluded that the highest oxidation product obtainable was the peroxide. Their conclusion was based upon the volume of oxygen absorbed by a given quantity of sodium in solution.

Schechter (16, 17) showed that sodium dissolved in liquid ammonia could be made to absorb oxygen in greater amounts than would be required for peroxide formation, a fact which indicated the formation of some superoxide. Using an improved technique of rapid oxidation in solution (to be described in Part Two of this report), Schechter was able to get consistently high yields of superoxide. He showed that under the best conditions of rapid oxidation a nitrite-free product was formed which had a consistent composition corresponding to the formula  $\text{Na}_3\text{O}_5$ . Under poor conditions of oxidation the oxygen content of the product was found to be less than that indicated by the formula  $\text{Na}_3\text{O}_5$ , and the product always contained nitrite. Analysis of the product consisted of measuring the volume of oxygen liberated by catalytic decomposition and determining the total alkali content by titration of the residue with standard acid. Schechter's results were confirmed in preliminary experiments by this author.

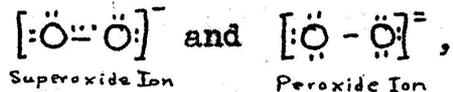
The empirical formula  $\text{Na}_3\text{O}_5$  corresponds to a possible molecular ratio of four superoxide molecules to one peroxide molecule, as represented by the formula  $4\text{NaO}_2 \cdot \text{Na}_2\text{O}_2$ .

Such a product could be either a definite crystalline compound or a constant ratio precipitate of mixed crystals. The validity of such an assumed formula could be tested by two different types of experiments, namely, magnetic susceptibility measurements and X-ray diffraction measurements. Results of such tests will be described below.

## Experimental

### 1. Magnetic Studies

Examination of the structures of the superoxide and peroxide ions,



shows one that the superoxide ion has one unpaired electron and is paramagnetic, while the peroxide ion has no unpaired electrons and is diamagnetic. The product of oxidation of sodium dissolved in liquid ammonia apparently consists of these two oxides. Hence according to the Wiedemann additivity law (19) for magnetic susceptibilities we should expect a resultant susceptibility equal to the sum of the component susceptibilities multiplied by their respective weight fractions. Knowing the susceptibilities of the components and measuring the susceptibility of the mixture, one can readily calculate the composition. The composition so calculated should be the same as that calculated from chemical analysis if the assumed ratio of superoxide to peroxide is correct.

The magnetic susceptibility of the sodium oxidation product was determined by the Gouy method. The apparatus for this purpose was constructed around an electromagnet having a field strength of 8000 gauss and an analytical balance having a sensitivity of ten divisions per milligram. Calculation of the magnetic field strength was based upon the magnetic susceptibility of water. Data and calculations are shown in Table II on the following page. A more complete discussion of the theory and practice of magnetic measurements is to be found in the author's master's thesis (18).

The material was found to be highly paramagnetic, the value obtained for the specific susceptibility,  $\chi_g$ , at 20° C. being  $21.6 \times 10^{-6}$  c.g.s. units. This corresponds to 67 weight per cent of sodium superoxide, based upon the value of  $33.0 \times 10^{-6}$  c.g.s. units recently found for the magnetic susceptibility of pure sodium superoxide (20).

The possible error in this measurement ( $\pm 5\%$ ) is necessarily large since only small quantities of the yellow material could be produced in a single oxidation run. It was necessary to use samples accumulated from several runs, and undoubtedly some decomposition of the product occurred even though all sampling operations were carried out in a dry-box. All attempts to design an apparatus suitable for making large-scale runs were unsuccessful.

TABLE II

Data and Calculations for Determining the Composition of the Product of Rapid Oxidation of Sodium in Liquid Ammonia.

Cell empty

$$w_1 = \frac{8.5610 \text{ (current off)}}{8.5582 \text{ (current = 4.52 amp.)}} - 0.0028$$

$$w_{10} = -0.0028 \text{ (at standard current of 4.5 amp.)}$$

Cell with water

$$w_2 = \frac{9.0882 \text{ (current off)}}{9.0835 \text{ (current = 4.6 amp.)}} - 0.0047$$

$$w_{20} = -0.0045 \text{ (standard current)}$$

Cell with oxide mixture

$$w_3 = \frac{8.7624 \text{ (current off)}}{9.0835 \text{ (current = 4.55 amp.)}} - 0.0153$$

$$w_{30} = 0.0150 \text{ (standard current)}$$

Calculation of magnetic field strength

$$\frac{2 \times 980 \times (w_{20} - w_{10})}{\text{Cell area} \times (\kappa_{\text{water}} - \kappa_{\text{air}})} = H^2$$

$$\frac{2 \times 980 \times (-0.0017)}{0.107 \times (-0.72 \times 10^{-6} - 0.29 \times 10^{-6})} = H^2; H^2 = 41.6 \times 10^6 \text{ (gauss)}^2$$

Calculation of volume susceptibility of oxide

$$\frac{2 \times 980 \times (w_{30} - w_{10})}{0.107 \times (41.6 \times 10^6)} \times 0.029 \times 10^{-6} = \kappa$$

$$\kappa = 7.88 \times 10^{-6} \text{ c.g.s.u.}$$

The apparent density of the oxide was found to be 0.366 grams per cc. Hence the gram susceptibility is  $21.6 \times 10^{-6}$  c.g.s. units. The fraction of superoxide, X, is calculated by the Wiedemann mixture law.

$$21.6 \times 10^{-6} = 33.0 \times 10^{-6} \cdot X - 0.23 \times 10^{-6} (1-X)$$

$$X = \underline{67 \text{ weight per cent.}}$$

The magnetic data obtained in these tests support, but do not prove, the assumption that the sodium oxidation product has the mole ratio of four superoxide molecules to one peroxide molecule.

## 2. X-ray Studies

To obtain further information regarding the composition of the sodium oxidation product some samples were prepared for X-ray diffraction measurements. For this purpose the sodium was oxidized in the usual way and then transferred in a dry-box into the small capillary tubes used in the diffraction camera. Suitable capillary tubes were about one-half millimeter in inside diameter, and were about one inch long. The walls were as thin as was compatible with mechanical strength. The tubes were filled to a depth of about five millimeters.

The X-ray diffraction measurements were made by Professor David H. Templeton at the Radiation Laboratory of the University of California at Berkeley, California. According to Professor Templeton (21) the liquid ammonia oxidation samples showed strong patterns for cubic  $\text{NaO}_2$ , indistinguishable from patterns cast by superoxide samples prepared by high pressure oxidation (22). In addition there was evidence for the presence of two other phases, identified as phase "A" and phase "B". These phases were definitely neither peroxide nor hydroxide, and they were the same phases that were present in lesser amounts in the

samples prepared by high pressure oxidation. It was suggested that these phases A and B must have been hydration products, formed either by moisture in the oxidation process or by moisture picked up during handling. It was also suggested that if any peroxide had been present at any time it might have reacted with water, faster than superoxide, to form the hydrate phases A and B.

It can be concluded from these results that there is no evidence for the existence of a sodium oxide intermediate between peroxide and superoxide. The evidence does not support the assumption of a constant mole ratio corresponding to the formula  $4\text{NaO}_2 \cdot \text{Na}_2\text{O}_2$ , but neither does it conclusively disprove such an assumption. It remains to be shown whether the hydration products found in the samples were formed during the oxidation process or during subsequent handling.

PART TWO: STUDIES ON THE OXIDATION OF LITHIUM AND THE  
ALKALINE EARTH METALS IN LIQUID AMMONIA

Historical Discussion

1. Oxides of the Metals

The literature on the oxides of the metals of Group II of the periodic system is not so complete as that for the alkali metal oxides. The work to be described in this section may add something to our knowledge of these metals and their oxides. Because lithium in many ways resembles the Group II metals, it will be discussed also in this section.

There are three classes of oxides of the Group II metals: monoxides, peroxides, and superoxides. Of these oxides, the monoxides are the most common. They can be formed by the thermal decomposition of the hydroxides, carbonates, or nitrates, the ease of formation decreasing with increasing basic strength of the oxide. Because of their refractory nature and their inertness to many reagents, these oxides are useful for such applications as furnace linings and crucibles.

The peroxides of this group of metals are not so common as the monoxides. These peroxides are more difficult to prepare than those of the alkali metals. The more electropositive alkaline earth metals can be made to form peroxides by high temperature treatment. Barium monoxide, when heated in air to 400° C., is converted to barium

peroxide. The peroxide in turn can be made to dissociate again at low pressures or at temperatures above 400° C. (23). Strontium monoxide has been made to yield 15 per cent peroxide upon heating in oxygen at a temperature of 400° C. and a pressure of 98 atmospheres (24). Calcium monoxide has never been converted to peroxide by such treatment.

Some peroxides have been prepared by wet processes in which the metal salt solutions are treated with sodium peroxide or hydrogen peroxide. Thus lithium has been made to form a peroxide hydrate of composition  $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$  (25), and the alkaline earth metal peroxides have been precipitated as octahydrates of the type  $\text{MO}_2 \cdot 8\text{H}_2\text{O}$  (26). These hydrated peroxides have been dried in vacuo to form the anhydrous products.

Some attempts have been made in the past to form peroxides by the action of oxygen on solutions of these metals in liquid ammonia, as reference to Table I will indicate. Guntz and Mentrel (14) reported formation of gelatinous mixed oxide precipitates containing 7 to 9 per cent peroxide when oxygen was bubbled through solutions of barium in liquid ammonia. Pierron (2) reported a 23 per cent yield of peroxide when lithium solutions in liquid ammonia were treated similarly.

Peroxide stability has been correlated with the size of the metal ion. Barium, the largest ion of the group, forms the most stable peroxide. The radius of the barium ion (1.3 - 1.4 Å) is about the same as the radius of the potassium ion (1.33 Å). The radius of the superoxide ion

(1.28 Å) is about the same as that of the peroxide ion (1.31 Å). Barium peroxide and potassium superoxide both have the calcium carbide type of crystal lattice; hence one would expect these two oxides to be comparable in stability. As the radius of the cation decreases, the stability of the peroxide decreases relative to the stability of the monoxide (26).

Superoxides have been reported for calcium and barium. The alkaline earth peroxides form a series of complexes of the type  $MO_2 \cdot xH_2O_2$  when the hydroxides are treated with 30 per cent hydrogen peroxide. Some of these compounds upon standing deepen in color and acquire the ability to liberate oxygen on treatment with water. This is attributed to superoxide formation. Traube and Schulze (27) reported the preparation of mixtures containing 8.7 per cent calcium superoxide and 8 per cent barium superoxide, respectively, using the above process. Their results with respect to calcium have confirmed by magnetic susceptibility measurements (28).

## 2. Ammoniates of the Metals in Liquid Ammonia

The first study of solutions of metals (sodium and potassium) in liquid ammonia was made by Weyl (29) about 1864. In keeping with the "radical theory" of his time he believed that the metal atom replaced a hydrogen atom in the ammonium radical, thus forming a "metal ammonium." A later worker, Seely, made numerous qualitative tests which indicated that the metals were merely dissolved and not chemically combined with the solvent (30).

Joannis (31) about 1889 made extensive studies on solutions of sodium and potassium in liquid ammonia using techniques which were much copied by later workers. By studying the isothermal variation of ammonia vapor pressure with concentration in solution Joannis found a pressure flat corresponding to the separation of a solid phase. This constant pressure continued until all the ammonia had disappeared from the cell, leaving pure metal. Joannis gave the formula  $MNH_3$  to both the saturated solution and the solid precipitate, since both apparently had the same vapor pressure.

Using Joannis' technique, Moissan (32) found ammoniates of lithium ( $LiNH_3$ ) and of calcium  $[Ca(NH_3)_4]$ . Mentrel (33) and Roederer (34) found ammoniates of the form  $M(NH_3)_6$  for barium and strontium, respectively.

Kraus (35) took issue with Joannis' findings for the alkali metals, saying that the phase rule did not allow the formation of a solid compound. Kraus contended that since only one pressure flat existed in the ammonia pressure-concentration isotherm, only one solid phase could be precipitated from solution. Since the pressure flat continued until all the ammonia was removed from the cell, the solid phase initially precipitated and that finally left had to be identical--that is, pure metal. That the apparent blue color of this solid precipitate was due only to a film of saturated solution covering the metal was shown by the manner in which the blue material could be made to "creep" around over the cell walls.

Benoit (36) in 1923, studying lithium solutions by Joannis' method, thought he found two phases in solution and stated that  $\text{Li}(\text{NH}_3)_4$  was a definite compound.

Jaffe (37), in 1935, made tests on lithium solutions which showed that lithium does form a tetrammine compound, contrary to Kraus' statements. This complex compound was found to exist only in solution. Ammonia pressure-concentration isotherms showed that at  $-181^\circ \text{C}$ . a solid tetrammine compound formed which had the same composition as the saturated solution. Previous workers, Ruff and Zedner (38), had had doubtful results because of uncertainties in temperature control.

From measurements of the Hall effect (a galvanomagnetic effect, which is used to determine the ratio of "free" electrons to metal atoms) Jaffe found that this solid lithium tetrammine compound had the same metallic conduction characteristics as the saturated solution at  $-181^\circ \text{C}$ .

Kraus (7) ran pressure-concentration isotherms on systems of calcium and ammonia. He found definite evidence that a hexammine compound,  $\text{Ca}(\text{NH}_3)_6$ , existed. He found no evidence for the existence of the tetrammine compound reported by Moissan, but he did admit the possibility that the hexammine compound might decompose by steps, giving small amounts of a tetrammine compound.

When ammonia vapor was pumped from a cell containing calcium dissolved in liquid ammonia, the pressure fell until it reached a constant value corresponding to the separation

of a blue solid phase from the solution. This pressure remained constant until all the liquid phase had disappeared, leaving only the solid blue compound. When the last trace of liquid phase disappeared, the pressure dropped abruptly to a lower value. This lower value of the pressure was maintained constant until all ammonia had been removed from the cell, leaving only the pure metal.

The first pressure flat corresponded to a composition  $\text{Ca}(\text{NH}_3)_6$  for the solid compound. The second flat corresponded to the dissociation of this compound into gaseous ammonia and calcium. The composition of the solid compound was determined by weighing the cell and contents when all liquid had just disappeared. It was assumed that the excess in weight over that of the cell plus the metal was due to combined ammonia, proper <sup>allowance</sup> having been made for error due to slight amide formation. Kraus showed that his experimental results agreed with thermodynamic calculations. He also showed that the solid compound had the same optical and electrical properties as the saturated solution--that is, the deep blue metallic color and metallic conduction, both due to the same characteristic molecular state.

Biltz and Huttig (39,40,41), using methods similar to those of Kraus, found corresponding hexamine compounds for strontium and barium. They noted that the tendency to form ammoniates decreases as the atomic number increases.

The heats of solution in calories per gram-atom for the various metals in liquid ammonia are shown on the following page in Table III.

TABLE III

Heats of Solution for Metals in Liquid Ammonia (42).

<u>Metal</u>	<u><math>-\Delta H</math>, cal./gm.at.</u>	<u>Metal</u>	<u><math>-\Delta H</math>, cal./gm.at.</u>
Li	8000	Ca	10000
Na	-1385	Sr	18000
K	$\sim 0$	Ba	14000
Rb	$\sim 0$		
Cs	$\sim 0$		

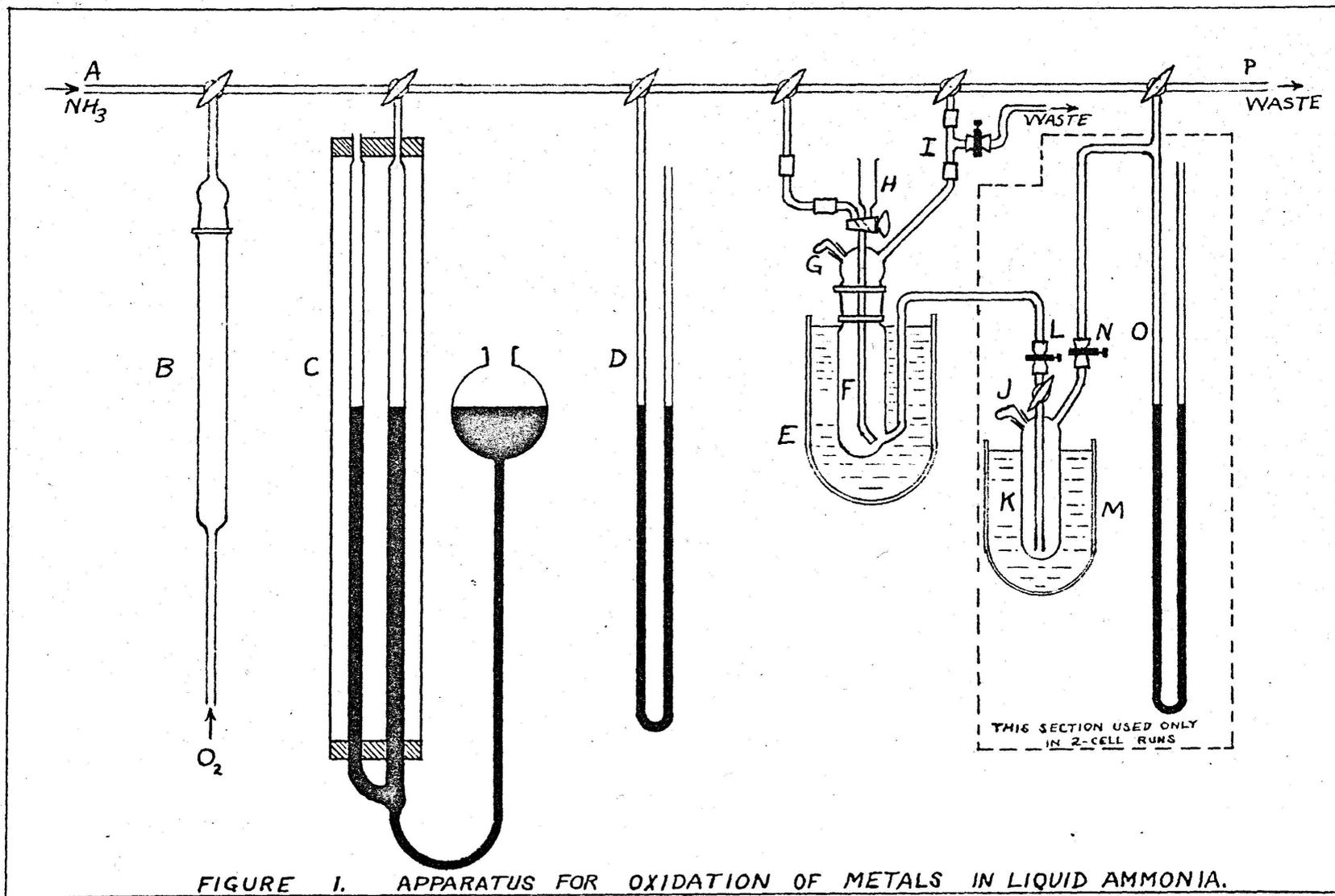
It is to be noted that of the alkali metals, lithium is the only one suspected of forming an ammoniate, and it is the one that has a heat of solution of the same order of magnitude as that of the alkaline earth metals, which do form stable ammoniates. The order of these heats of solution in liquid ammonia parallels the order of corresponding heats of solution in water.

### Experimental

#### 1. Method of Oxidation

In the experiments to be described in this section solutions of the metals in liquid ammonia were oxidized with gaseous oxygen. It was desired to see what products would be formed when these Group II metals were given the same treatment by which superoxides were formed from the alkali metals.

Solutions of the metals in liquid ammonia were rapidly oxidized by two methods, which we shall designate as the one-cell method and the two-cell method. A diagram of the apparatus, which is essentially that designed and used by Schechter in his study of the oxidation of sodium, is shown in Figure 1 (16).



Anhydrous ammonia (refrigeration grade) from a cylinder was admitted to the system at A. It could be condensed in cells F and K by means of Dry Ice-Cellosolve cooling baths E and M. Pressures in the system, measured by manometers D and O, were usually kept below six inches of mercury. For oxidation, the ammonia source was closed off and oxygen was admitted to the system through drying tube B, which was filled with anhydrous magnesium perchlorate. The system was vented during oxidation by opening the pinch-clamp I. Gas evolved during analysis of the product was collected and measured in the burette C. The section of the apparatus which is enclosed in dotted lines in the diagram was used only in runs made by the two-cell process.

For a run made by the one-cell process approximately 75 cc. of liquid ammonia were condensed in cell F after the system had been thoroughly dried by several hours sweeping with a slow stream of gaseous ammonia. After the ammonia was condensed, a stream (40 cc. per minute) of dried oxygen was started bubbling through the cell. A sample of metal, a few milliequivalents in weight, was cut in a dry-box and placed in a small glass sampling capsule for transfer to the reaction cell. The sampling capsule was fitted to the reaction cell by the ground glass joint at G, and the metal sample was dropped into the oxygen-saturated ammonia. The metal dissolved to form a deep blue solution. After several minutes the blue color disappeared, leaving a milky-white suspension. The oxygen stream continued to sweep the system

as the ammonia evaporated to dryness. When the ammonia had been thoroughly swept out of the system, the product was ready for analysis.

For a run made by the two-cell process ammonia was condensed in both cells--about 75 cc. in cell F and about 40 cc. in cell K. The dried oxygen stream was started bubbling through cell F at a rate of about 40 cc. per minute. The metal sample, prepared as described above, was dropped into cell K by means of the sampling capsule fitted to the cell by a ground glass joint at J. Cell K was then closed off by tightening the pinch-clamp N so that, when the freezing bath was removed, the vapor pressure of the ammonia would force the solution up through the center tube into cell F. The flow of this solution was carefully controlled by means of the pinch-clamp L so that no blue color was allowed to persist in cell F. In other words the metal was oxidized instantaneously as the solution entered the oxidation cell. No free metal was allowed to be present to reduce any oxides already formed. After the metal solution had been entirely oxidized, the oxygen stream continued to sweep the system as the ammonia evaporated to dryness. When the ammonia had been thoroughly swept out, the sample was ready for analysis.

## 21. Method of Analysis

Analysis in runs made by either method consisted of catalytic decomposition of the oxide product and measurement of the volume of active oxygen evolved, followed by titration of the solution residue with standard acid to

determine the total base content. Subsequent tests were made for hydrogen in the evolved gas and for nitrite in the solution.

The oxides were decomposed by means of a catalyst consisting of a very dilute suspension of manganese dioxide in water, a neutral catalyst being necessary to avoid interference with the subsequent base determination. The catalyst suspension was added to the cell through the funnel H. The evolved gas was collected and measured in the burette C, a correction being made for the volume of catalyst liquid added to the system. All gas volume measurements were made with the reaction cell immersed in an ice bath at 0° C. and the burette enclosed in a water jacket at room temperature. The use of capillary tubing for all connections minimized the indeterminate volume variations due to momentary temperature changes in the room. After the gas volumes were measured, the solution residue was transferred from the reaction cell to a flask for titration with a standard hydrochloric acid. All titrations were made with methyl orange as an indicator. Calculations were made on the basis of the peroxide decomposition equation:



Nitrite, formed by oxidation of amide, was determined by means of a semi-quantitative spot test (43). This test involved a diazotization and coupling reaction between  $\alpha$ -naphthylamine and sulfanilic acid with formation of a red dye. The amount of diazotization and subsequent dye

formation depended upon the amount of nitrite present in the sample. Stock solutions were prepared of sulfanilic acid in 30 per cent acetic acid and  $\alpha$ -naphthylamine in 30 per cent acetic acid. In carrying out a test one drop of each solution was placed on a porcelain spot plate, and a drop of the unknown solution was then added. By comparing the intensity of the color so formed with color formed by a similar test with a standard nitrite solution, one could estimate the concentration of nitrite in the sample.

In the course of the tests on this group of metals it appeared that occasionally some unoxidized metal was remaining in the oxidation product, and it became necessary to test for hydrogen in the gas evolved on decomposition of the product. The first attempt at such a determination consisted of transferring the evolved gas to an absorption bulb containing alkaline pyrogallol. The pyrogallol was supposed to absorb all the oxygen, leaving any hydrogen or other gases which could not be absorbed. This method was not satisfactory, because the errors inherent in the apparatus were large and the volumes of gas concerned were small.

A more reliable test for hydrogen was accomplished by an ignition process. The evolved gas was transferred to a burette which was connected to a 500 cc. bulb fitted with an electrically-heated platinum filament. The gas was passed into the bulb, and the filament was lighted for about five minutes. The gas was then passed back into the burette, and any decrease in volume was noted. The loss

in volume represented ~~two-thirds~~<sup>three halves</sup> of the volume of hydrogen which had been present, according to the equation



It had to be determined whether there was any gas present other than hydrogen which would be ignited in this test. Since ammonia might have been present in the oxide product either by mechanical entrapment or by possible ammoniate formation, its presence or absence had to be established. That there was no ammonia present in the gas was shown by bubbling gas samples from several runs through solutions of 4 per cent boric acid and then titrating the boric acid solutions with standard hydrochloric acid.

The data and calculations for the analysis of the product of a typical run are shown in Table IV on the following page.

TABLE IV

Data and Calculations for the Analysis of a Typical Oxidation Product (Barium One-cell Oxidation)

Gas evolved in decomposition

Measured volume:	16.95 cc.	Room Temp. = 30° C.
S. T. P. volume:	14.70 cc.	Pressure = 732 mm.
Catalyst volume		
correction:	<u>9.50 cc.</u>	
Net volume gas:	5.20 cc.	
Volume hydrogen:	<u>2.20 cc.</u>	
Net volume oxygen:	3.00 cc.	

Base determination

Volume HCl (0.095N): 15.00 ml.  
 $15.00 \times 0.095 = 1.42$  milliequivalents base.

1 m. e. corresponds to 5.6 cc. evolved oxygen.  
 1.42 m. e. corresponds to 8.1 cc. evolved oxygen.

Hydrogen ignition test

Loss of volume of gas: 3.8 cc., or 3.3 cc. S. T. P.  
 Volume hydrogen:  $\frac{2}{3} \times 3.3$  cc. or 2.2 cc.  
 Corresponds to 0.2 m. e. of metal.

Nitrite test

Volume of solution residue: 100 ml.  
 Color test: 1 drop equivalent to 5 drops 0.0001 N  $\text{KNO}_2$ .  
 Corresponds to 0.05 m.e. nitrite in 100 ml.

Calculations

Percentage peroxide in product:

$$\frac{3.0}{8.1} \times 100\% = \underline{37\% \text{ peroxide.}}$$

Percentage nitrite:

$$\frac{0.05}{1.42} \times 100\% = \underline{3.5\% \text{ nitrite.}}$$

### 3. Results

The results of the oxidation studies on lithium and the alkaline earth metals are summarized in Table V below.

TABLE V

Oxidation of Lithium and the Alkaline Earth Metals in Liquid Ammonia at  $-33^{\circ}\text{C}$ .

Metal tested	One-cell oxidation			Two-cell oxidation		
	Per cent peroxide	Per cent nitrite	Per cent unreacted metal	Per cent peroxide	Per cent nitrite	Per cent unreacted metal
Lithium	$26 \pm 6$ 17 runs	5	0.5	$26 \pm 6$ 23 runs	5	0.5
Calcium	$12 \pm 2$ 8 runs	3 to 10	1	$12 \pm 2$ 6 runs	3 to 10	1
Strontium	$20 \pm 2$ 5 runs	4	2	$25 \pm 3$ 6 runs	4	2
Barium	$37 \pm 6$ 9 runs	4	8	$25 \pm 5$ 7 runs	2	1

#### (a) Lithium

Lithium dissolved readily at temperatures near the boiling point of liquid ammonia to form a deep<sup>blue</sup> solution. There was no evidence that an insoluble phase was formed at such temperatures. Oxidation of the blue solution at this temperature by either the one-cell process or the two-cell process gave a milky-white suspension, which subsequently turned light yellow in color. As the ammonia evaporated, a white residue was left.

Lithium did not dissolve readily in liquid ammonia at  $-78^{\circ}\text{C}$ ., but the metal could be oxidized at this temperature

by dropping the sample into liquid ammonia through which oxygen was bubbling. The metal gradually dissolved, becoming oxidized immediately as it dissolved. No intermediate blue solution of metal was formed. The color of the solution after oxidation at this temperature was a bright lemon yellow. When the solution was allowed to warm up to a temperature near the boiling point of liquid ammonia, the yellow color faded, giving way to a white suspension. The color could not be brought back by cooling the cell again. Whether the metal was oxidized at  $-33^{\circ}$  C. or  $-78^{\circ}$  C. the product after evaporation of ammonia was the same white flaky substance.

The yellow solutions formed by the low temperature oxidation of lithium will be discussed in greater detail in Part Four of this report.

The following results were obtained from the oxidation of lithium.

Seventeen runs made by the one-cell process gave peroxide yields from 20 to 40 per cent and averaged  $26\% \pm 6\%$ .

Twenty-three runs made by the two-cell process gave peroxide yields from 20 to 50 per cent and averaged  $26\% \pm 6\%$ .

The ignition test for hydrogen from unoxidized metal (performed on five of the later runs) showed that less than 0.02 milliequivalent or about 0.5 per cent of the total metal was left unoxidized in any lithium run. This fact agreed with the consistent white appearance of the product.

Nitrite equivalent to about five per cent of the total metal was found in every case.

(b) Calcium

Calcium dissolved in liquid ammonia to form a blue solution in which there was suspended some solid or semi-solid blue material. The metal did not dissolve appreciably when placed in liquid ammonia at temperatures much below  $-33^{\circ}$  C. As the temperature was gradually raised from the initial low value, the metal first formed a dark blue phase, presumably an ammoniate; as the temperature was raised still further, this substance began to dissolve in the bulk of the ammonia to form a blue solution.

Upon oxidation the blue solution was decolorized, leaving a white suspension in which there were a few dark particles. The final product upon evaporation of the ammonia was always a white or light gray powder containing a few dark particles.

In runs made by the two-cell process there was always a large amount of the blue solid matter left behind in the solution cell (K in Figure 1). As the ammonia evaporated from this residue, there was a gray film of metal left on the cell walls.

Oxidation of calcium by either the one-cell or the two-cell process gave products ranging from 8 to 14 per cent and averaging  $12\% \pm 2\%$  peroxide (average of eight one-cell runs and six two-cell runs).

The ignition test for hydrogen showed that 0.03 milli-equivalent or less than one per cent of the total metal was left unoxidized.

The nitrite test gave inconsistent values varying from three to ten per cent of the metal used.

(c) Strontium

Strontium dissolved in the same manner as calcium to form a blue solution with a second dark blue phase in suspension. The same general temperature effect on solubility existed for strontium as for calcium. In the case of strontium, however, the second phase appeared to be definitely liquid. No solid particles were noticed in the strontium solutions as were found in the calcium solutions. As with calcium, though to a lesser extent, some of the metal-rich phase was left behind in the solution cell during oxidation by the two-cell method. Upon oxidation the blue color of the solution gave way to the milky white of the oxide suspension. The product after evaporation of the ammonia was always a mixture of gray and white powder.

Oxidation of strontium by the one-cell process gave an average peroxide yield for five runs of  $20\% \pm 2\%$ . Oxidation by the two-cell process gave slightly higher peroxide yields with an average for six runs of  $25\% \pm 3\%$ .

The ignition test for hydrogen showed an average of two per cent unoxidized metal for all runs.

An average of four per cent of the metal used was found as nitrite.

#### (d) Barium

Barium dissolved the most readily of the three alkaline earth metals, forming the usual deep blue solution. When the metal was added to ammonia at temperatures very much below  $-33^{\circ}\text{C}$ ., there appeared to be two liquid phases; but as the temperature was raised, the solution became homogeneous. Upon oxidation the blue color of the solution gave way to the usual white suspension. The product after evaporation of the ammonia was always a gray powder.

Oxidation of barium in nine runs made by the one-cell method gave peroxide yields averaging  $37\% \pm 6\%$ . Oxidation in seven runs made by the two-cell process gave peroxide yields of  $25\% \pm 5\%$ . A number of early barium runs not reported were made without correction for hydrogen from unoxidized metal. The apparent "oxygen liberation" in analysis gave abnormally high values for peroxide yield in these runs. It was the gray, metallic appearance of the oxidation products from these unreported runs which suggested the need for a test for hydrogen in the analytical procedure.

The ignition test for hydrogen showed that in runs made by the one-cell process an average of eight per cent of the metal was unoxidized, and that in runs made by the two-cell process an average of only one per cent was unoxidized.

The nitrite test showed that about four per cent of the metal was converted to nitrite in one-cell runs and that two per cent was converted in two-cell runs.

#### 4. Discussion of Results

Lithium and the alkaline earth metals behaved nearly alike when oxidized in liquid ammonia. The product of oxidation in every case contained a relatively low percentage of peroxide. This behaviour is to be contrasted with that of the other alkali metals, all of which give high percentages of superoxide when oxidized under these conditions.

The tendency to form peroxide in the alkaline earth metal group increased in the order of increasing ionic size. This order is only qualitative; it should not be inferred that a direct proportionality exists. Lithium, which is smaller than any of the alkaline earth metals, does not fall into such an order on the bases of ionic size alone.

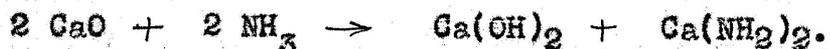
The tendency for unreacted metal to appear in the product of oxidation increased with increasing ionic size. This was true especially in runs made by the one-cell process. There was little unreacted metal in the products of the two-cell runs.

Oxidation by either the one-cell or the two-cell process gave about the same yield of peroxide for lithium and calcium. For the strontium the two-cell process gave slightly higher amounts than the one-cell process. For barium, on the other hand, the one-cell method gave greater yields than the two-cell method. No explanation can be offered for these variations.

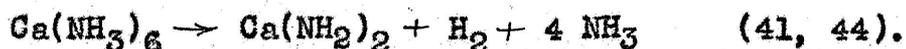
In every case the oxidation product contained nitrite equivalent to a few per cent of the total metal used. This

fact indicates that there was a strong tendency for amide formation to occur.

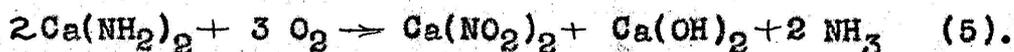
One source of amide formation is the ammonolysis of monoxides, as described in the first section of this report (page 7). The ammonolysis of monoxide proceeds according to the equation



The tendency to form amides can be associated also with the tendency to form ammoniates. It was mentioned in the preliminary discussion in this report that lithium and the alkaline earth metals all are known to form ammoniates in liquid ammonia. An ammoniate can decompose to form an amide as follows:



The amide then can be oxidized to nitrite as shown by the equation



It seems proper to conclude, therefore, that the strong tendency of these metals to form ammoniates constitutes at least one factor which prevents their forming higher oxides to any great extent in liquid ammonia.

PART THREE: STUDIES ON THE SOLUBILITY AND OXIDATION OF  
MAGNESIUM IN LIQUID AMMONIA

Theoretical Discussion

Magnesium is next to the smallest metal in Group II of the periodic classification. Its chemical properties relate it to both the alkaline earth metal group and the zinc subgroup (45). Magnesium is found in deposits with the alkaline earth group and not with the metals of the zinc subgroup. Due to its small ionic size magnesium has a strong tendency to form complex compounds, as do the metals of the zinc subgroup.

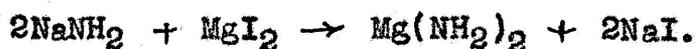
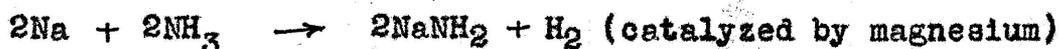
Magnesium monoxide is less basic than the monoxides of the alkaline earth metals; hence it is easily formed by calcining of oxygen-containing magnesium salts such as carbonate or nitrate. Hydrated magnesium salts cannot be dehydrated by heating. Under such treatment they are partially converted to the monoxide.

Magnesium peroxide cannot be formed by oxidation of the monoxide, as was possible with strontium and barium monoxides. Magnesium peroxide has been prepared in impure form by "wet" methods. A variable mixture of magnesium hydroxide and magnesium peroxide hydrate is precipitated when sodium peroxide is added to magnesium salt solutions. The product of this type containing the greatest amount of peroxide that has been reported was one having the composition  $MgO \cdot MgO_2(aq.)$ , which was precipitated when hydrogen

peroxide was added to an alkaline solution of magnesium sulfate (46). This product readily lost oxygen, and after three weeks drying it had the composition  $MgO_2 \cdot 3MgO(aq.)$ . Such magnesium peroxide products are convenient neutral sources of peroxide and are used as such for medicinal purposes.

Magnesium differs markedly from the alkaline earth metals in its behaviour in liquid ammonia. It is reported to be very slightly soluble as a metal in liquid ammonia. Cottrell (47) found that magnesium dissolved directly in liquid ammonia to form pale blue solutions that retained their color for as long as seven years when stored in sealed tubes. Gibson and Argo (48) studied the absorption spectra of magnesium solutions in liquid ammonia and reported that the blue color was the same as the color of sodium solutions of comparable concentrations. This characteristic color was attributed to the formation of ammoniated electron anions in the solutions.

Magnesium reacts slowly with liquid ammonia to liberate hydrogen and form magnesium amide. The reaction of magnesium with liquid ammonia solutions of alkali metal salts also gives amide and hydrogen as end products (49). For example, the reaction with sodium iodide goes as follows:



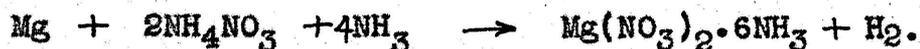
Magnesium reacts with liquid ammonia solutions of alkali metal amides to liberate hydrogen and form alkali metal ammonomagnesiates (49). In the first step magnesium amide is formed as shown by the equation



The magnesium amide so formed then reacts with the alkali metal amide to form an ammonomagnesiate as shown by the following equation:



Magnesium reacts by displacement with ammonium salts (which are acids in liquid ammonia) to liberate hydrogen and form the corresponding magnesium salts.



This behaviour is different from that of the alkali metals, which dissolve in such solutions without hydrogen evolution.



Magnesium forms no solid ammoniates by direct action of the metal and ammonia, but it has formed such compounds under other circumstances. Loomis (50), in 1922, found evidence for the formation of a magnesium hexamine compound when magnesium amalgam (0.3% magnesium in mercury) was treated with liquid ammonia. The ammoniate was not isolated, but it was identified by means of pressure-concentration isotherms and appropriate chemical analyses.

## Experimental

### 1. Direct Solubility Experiments

A few preliminary attempts were made to dissolve magnesium directly in liquid ammonia, as had been done by previous workers.

In one experiment strips of magnesium ribbon, cut and scraped bright in a dry-box, were placed in the ammonia reaction cell (F in Figure 1, page 21). The cell had been dried previously by several hours sweeping with ammonia gas. A quantity of ammonia was condensed in the cell. No visible solution occurred in three hours standing with occasional shaking.

Similar experiments were tried in which ammonium nitrate (an oxidizing acid in liquid ammonia) and ammonium chloride (a non-oxidizing acid in liquid ammonia) were added to the liquid ammonia. No visible reaction occurred with either type of solution.

Experiments in which powdered magnesium was used gave the same negative results as those in which magnesium ribbon was used.

After completion of each of the solubility tests described above the ammonia was evaporated, and the residues were tested for the presence of magnesium. The test used was the qualitative test using alkaline p-nitrobenzeneazoresorcinol ("S. & O. Reagent"), in which the formation of a blue lake indicates the presence of magnesium (51). This

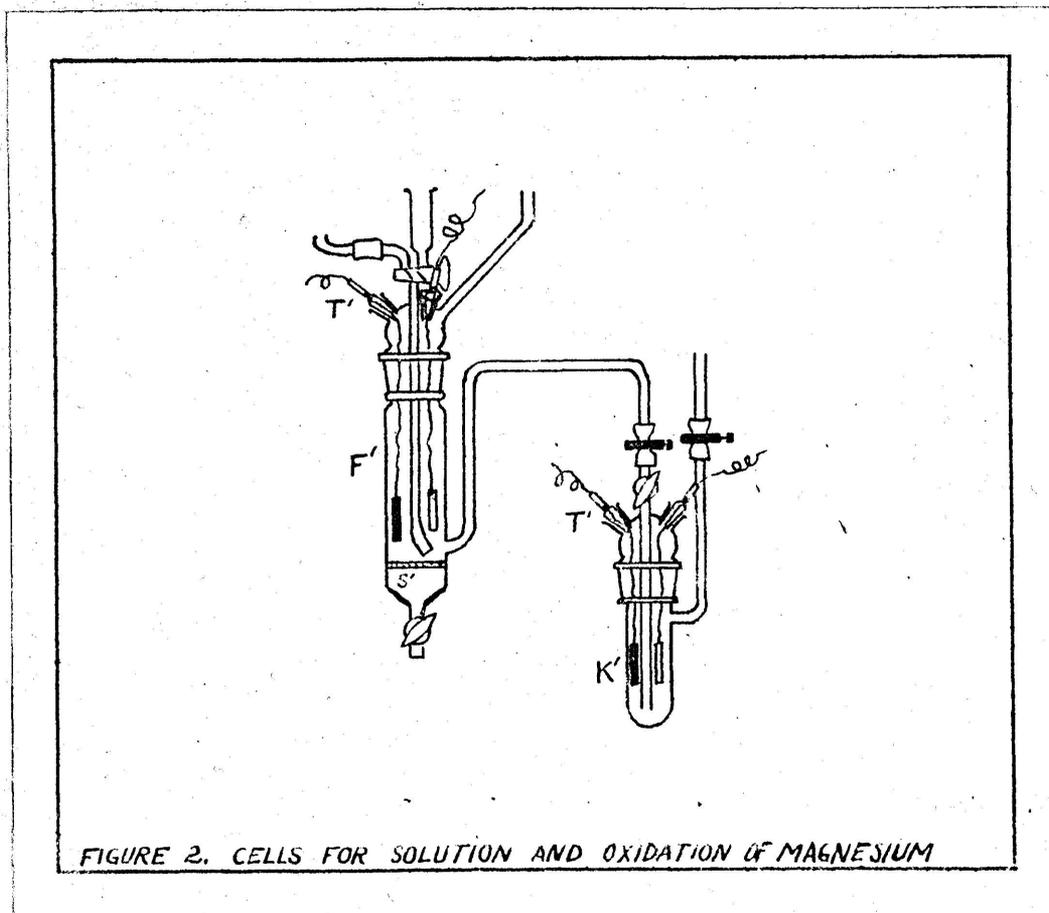
test is sensitive enough to detect quantities as small as  $2 \times 10^{-6}$  grams of magnesium. The test was negative in every case.

## 2. Electrolysis Experiments

The possibility that magnesium might be dissolved in liquid ammonia by an electrolytic method was suggested by the behaviour of aluminum under similar treatment. Magnesium has many properties similar to those of aluminum, and it seems reasonable to compare their behaviour in liquid ammonia. In the course of other investigations at this Laboratory (52) it was shown that in electrolyses in liquid ammonia using aluminum as anode and aluminum iodide as electrolyte a blue color appears around the cathode. The color fades at first, with the concurrent formation of a white precipitate. On prolonged electrolysis the colored substance is regenerated fast enough that the blue color pervades the entire solution. The blue color was attributed to the formation of ammoniated electron anions, which are able to exist in the presence of aluminum cations. The white precipitate was an amide derivative, which was formed as the ionized metallic aluminum reacted with the ammonia.

A few preliminary electrolysis experiments were run which showed that magnesium could dissolve at the anode and form a solution of ionized metal at the cathode. Then more elaborate experiments were conducted to study the products of the electrolysis in some detail.

The apparatus used was essentially the same as that described in Part Two of this report for use in the alkaline earth metal oxidation studies. The only change from the former apparatus lay in the use of ammonia cells suitable for electrolysis. A drawing of the cells is shown in Figure 2 below.



Cells F' and K' in Figure 2 replaced cells F and K in the apparatus of Figure 1 (page 21). The oxidation cell F' was provided with a sintered glass filter plate (S') to permit rapid removal of excess liquid ammonia. Electrical connections into the cells were made by means of platinum wires

sealed through standard-taper ground glass stoppers (T') fitted into the cell-head. Electric current was drawn from the 110 volt D. C. line. The voltage was controlled by means of two 46 ohm rheostats.

It was necessary to have an anhydrous magnesium salt as an electrolyte for electrolysis to take place since pure liquid ammonia is virtually a non-conductor. For this purpose a quantity of ammoniated magnesium bromide was prepared. Magnesium bromide hexahydrate (Merck & Company, Inc.) was placed in the ammonia cell (F' in Figure 2), and ammonia gas was passed through the cell for a few hours. The ammonia displaced the water of hydration, forming an ammoniate. The displacement was completed in three hours, as evidenced by a decrease in heat evolution. The product was washed twice by condensing liquid ammonia in the cell and then drawing the liquid off through the filter. Excess ammonia was then baked out by placing a hot-plate under the cell for a few hours. The final product had a strong odor of ammonia, but it was quite dry and powdery in appearance.

When a solution of magnesium bromide in liquid ammonia was electrolyzed between a platinum cathode and a magnesium anode under an atmosphere of ammonia, the following effects were noted. Magnesium bromide being only slightly soluble in liquid ammonia, electrolytic conduction was quite small at first. The initial current was about one milliampere at a potential of 110 volts. However, as the electrolysis

proceeded at a temperature near  $-33^{\circ}$  C., a blue color began to appear around the cathode, and simultaneously the current began to increase. By the time the blue color had pervaded the entire solution and the system had reached a steady state, the current had increased to one tenth of an ampere. At the same time there began to be considerable gas formation at the anode. The gas evolved at the anode was probably ammonia boiled off due to local heating by the current. The process could be carried on in a closed system; that would not have been possible had the gas been a non-condensable gas such as hydrogen.

Electrolysis was very slow whenever the solution was kept at temperatures much below  $-33^{\circ}$  C. No blue color ever began to form during an electrolysis until the solution was allowed to warm up toward  $-33^{\circ}$  C. Conversely, the high conduction and intense blue color of a solution being electrolyzed at  $-33^{\circ}$  C. could be removed by chilling the cell in a Dry Ice bath.

The fading of the blue color upon cooling was always accompanied by the formation of a flocculent white precipitate which tended to adsorb the blue substance remaining in the solution. This white precipitate also tended to cover the face of the cathode, forming an effective insulator. Except for the hindrance to conduction caused by this film formation, the solution could be made highly conducting, and the blue color could be brought back by again allowing the chilled solution to warm up to  $-33^{\circ}$  C.

In one experiment a quantity of the white precipitate was collected by filtering the solution off through the filter plate in the cell. The precipitate had a glassy appearance when examined under a microscope. It was insoluble in water and dilute sodium hydroxide, but it dissolved readily with gas evolution when treated with dilute hydrochloric acid. It was not determined whether this evolved gas was due to the action of the white material or of bits of metal which may have been present in the precipitate. The precipitate also released iodine when treated with acidified potassium iodide solution.

After the simple electrolysis experiments the next step was to make some oxidation tests on the blue solutions of magnesium. Except for the method of getting the metal into solution, the processes for one-cell and two-cell runs were the same as those described in Part Two in connection with the alkaline earth metal oxidation studies.

For a one-cell run the cell F' was set up with the electrodes in place, and a small quantity of dry magnesium bromide was dropped in. The system was swept out with ammonia gas for a few hours, and then ammonia was condensed in the cell. The electrolysis was started and allowed to proceed until the solution in the cell was quite blue. Then the current was stopped and the oxygen stream was started through the cell at a rate of about 40 cc. per minute. This caused the blue color to fade rapidly, leaving a cloudy

solution. The product after evaporation of the ammonia was a glassy white material similar to that obtained from the simple electrolysis experiments described before.

For a two-cell run both cells F' and K' were set up, electrodes being placed only in cell K'. After a few hours sweeping with ammonia gas, liquid ammonia was condensed in both cells. Electrolysis was started in cell K' and the current was run long enough for the solution to become intensely colored. Then the oxygen stream was started bubbling through cell F', and the solution from cell K' was passed over into cell F'. When one quantity of solution from cell K' was all oxidized, the cell was refilled with liquid ammonia and the electrolysis was started again. This second quantity of blue solution was then passed into the oxidation cell. In most two-cell runs a total of three or four 40 ml. quantities of metal solution was prepared and passed into the oxidation cell. The product of two-cell runs was identical in appearance with the product of one-cell runs.

Attempts were made to analyze the products of oxidation by the gasometric method described in connection with the alkaline earth metal oxidation studies in Part Two of this report. However there was never enough product to give a measurable amount of evolved gas. The products did give positive qualitative evidence for peroxide by two different tests. The products released iodine from acidified potassium iodide in one test. This test is positive but not specific

for peroxide. Another test used was the formation of peroxy-chromic acid. The product was treated with sulfuric acid and a few drops of 5% potassium chromate solution. The peroxychromic acid thus formed made a blue layer when it was extracted with ether.

The products of several runs were tested for nitrite. The spot test described in Part Two of this report gave very faint but positive evidence for nitrite in the samples tested.

### 3. Summary of Results

No quantitative results were obtained from the magnesium studies. It can be said only that magnesium can be dissolved in liquid ammonia as an ionized metal by means of electrolysis. It was not possible to dissolve the metal directly.

The solutions so formed are fairly stable when undisturbed by the effects of chilling or oxidation. Magnesium in liquid ammonia slowly forms a flocculent white precipitate, which is presumed to be an amide derivative. This precipitate formation occurs rapidly under the influence of the disturbing factors mentioned above. Treatment of the blue solution with gaseous oxygen forms a product which gives positive qualitative tests for peroxide and for nitrite.

PART FOUR: ABSORPTION SPECTRA STUDIES ON ALKALI METAL OXIDES  
IN LIQUID AMMONIA: EVIDENCE FOR FORMATION OF  
LITHIUM SUPEROXIDE IN LIQUID AMMONIA SOLUTIONS

Introduction

When a solution of sodium, potassium, or lithium in liquid ammonia is rapidly oxidized at  $-33^{\circ}$  C. by a stream of oxygen, a heterogeneous yellow mixture is formed. The mixture consists of a solution in which some solid matter is suspended. The solid matter is largely yellow superoxide in the case of sodium or potassium, and it is responsible for most of the color shown by the mixture. The solution phase in such a case has only a slight yellow color. In the case of lithium the solid matter is white; all the color of the mixture comes from the solution phase. Evaporation of the ammonia leaves a solid substance which is yellow in the case of sodium or potassium and white in the case of lithium.

Lithium could be simultaneously dissolved and oxidized by dropping a sample of metal into oxygen-saturated liquid ammonia kept at a temperature of  $-78^{\circ}$  C. The resulting solution was colored a bright lemon-yellow. A small amount of white solid matter was carried in suspension. The color of the solution was quite stable at such a low temperature, but it tended to fade with the simultaneous formation of a white precipitate when the temperature was raised toward  $-33^{\circ}$  C. The color could not be restored by again cooling the solution. Evaporation of the ammonia left a white product which was indistinguishable from that produced by oxidation of solutions of lithium at  $-33^{\circ}$  C.

Low-temperature oxidation of sodium or potassium did not produce solutions appreciably different from those produced by oxidation at  $-33^{\circ}$  C. because of the very slight solubility of the oxides. In every case the solution was only slightly yellow-colored; the yellow solid matter carried in suspension provided most of the color of the mixture.

The possibility that the yellow color of the solutions is characteristic of superoxide is suggested by the fact that both potassium and sodium, upon rapid oxidation in liquid ammonia, form yellow solutions or suspensions of superoxide in this medium. Lithium, although it does not form a solid superoxide, does form a yellow solution when rapidly oxidized in liquid ammonia. That the yellow color of such mixtures is due to the presence of the metals or their oxidation products is demonstrated by the absence of any color in mixtures of ammonia and oxygen alone.

Colors are caused by absorption of light in the visible range of the spectrum. Molecular structures capable of such absorption have odd, loosely-bound electrons, which can be excited at relatively low energies. Common examples are the colored ions formed by metals of a transition series. If the yellow color of the solutions with which we are concerned is characteristic of the superoxide structure, then we may expect the wave-length of the absorption band to be related to the energy of the three-electron bond in the superoxide ion.

Little data is available for the bond energy in the superoxide ion, but one can draw an analogy with the helium molecule-ion, for which data are available (53). Calculations and experimental values agree that the bond energy of the three-electron bond in the helium molecule-ion ( $\text{He} \cdots \text{He}^+$ ) is about 58 kilogram calories or 2.52 electron volts per mole. This corresponds to absorption of light at a wave-length of 4900 Å.

Weiss (54), in studies of alkali metal ozonates, found that the ultra-violet absorption band of ozone gas or ozone in acid solution is replaced by a band in the blue region when ozone is dissolved in water or in solutions of potassium hydroxide of concentrations up to 40 per cent. Weiss attributed the appearance of this new absorption band to the formation of potassium superoxide and superoxide ion in the neutral and alkaline solutions. In addition he made some assumptions as to necessary thermochemical data and calculated a value for the electron affinity of the oxygen molecule. The value of the electron affinity as calculated for the reaction



was 2.7 electron volts. This corresponds to absorption of light at a wave-length of 4540 Å.

Other reports on the electron affinity of the oxygen molecule give values of approximately 1 electron volt. Such values would correspond to absorption of light in the far infra-red region of the spectrum.

In order to test the hypothesis that the yellow color of the oxidized metal solutions in liquid ammonia was indicative of the presence of superoxide it was necessary to measure the absorption spectra of the solutions. Experiments to this end and their results are described in the following section.

### Experimental

#### 1. Apparatus

The chief problem in studying the absorption spectra of liquid ammonia solutions lay in obtaining apparatus capable of handling such solutions at temperatures low enough to prevent boiling. Early workers in the field of liquid ammonia spectrophotometry had used visual type instruments, which were readily adaptable to low-temperature techniques. However the susceptibility of these instruments to human errors made it desirable to use a photo-electric type instrument if possible. Since no commercial photo-electric spectrophotometer has been made for use at such low temperatures as are required for liquid ammonia work, it was necessary to improvise a suitable instrument.

For the experiments to be described in this report a Coleman Model 11 Universal Spectrophotometer was modified for use with liquid ammonia solutions. The instrument was changed so that a liquid ammonia cell inside a Dewar flask replaced the conventional absorption cells. No changes were made in the optical or electrical system of the meter.

The sketch in Figure 3 shows schematically the arrangement of the modified assembly.

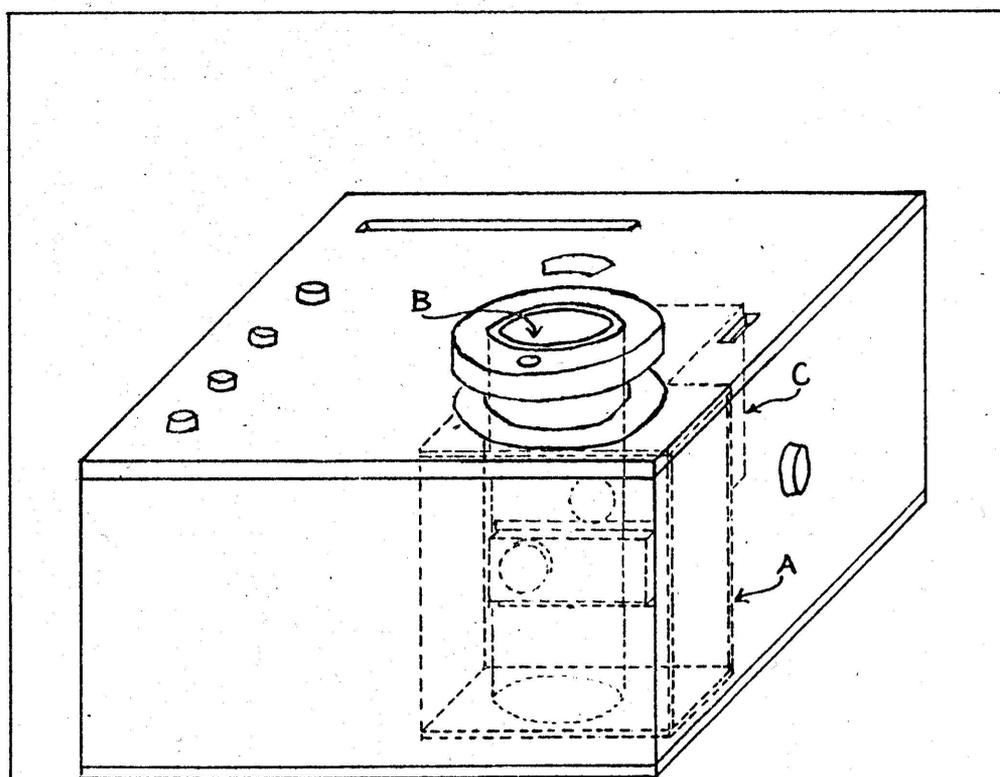
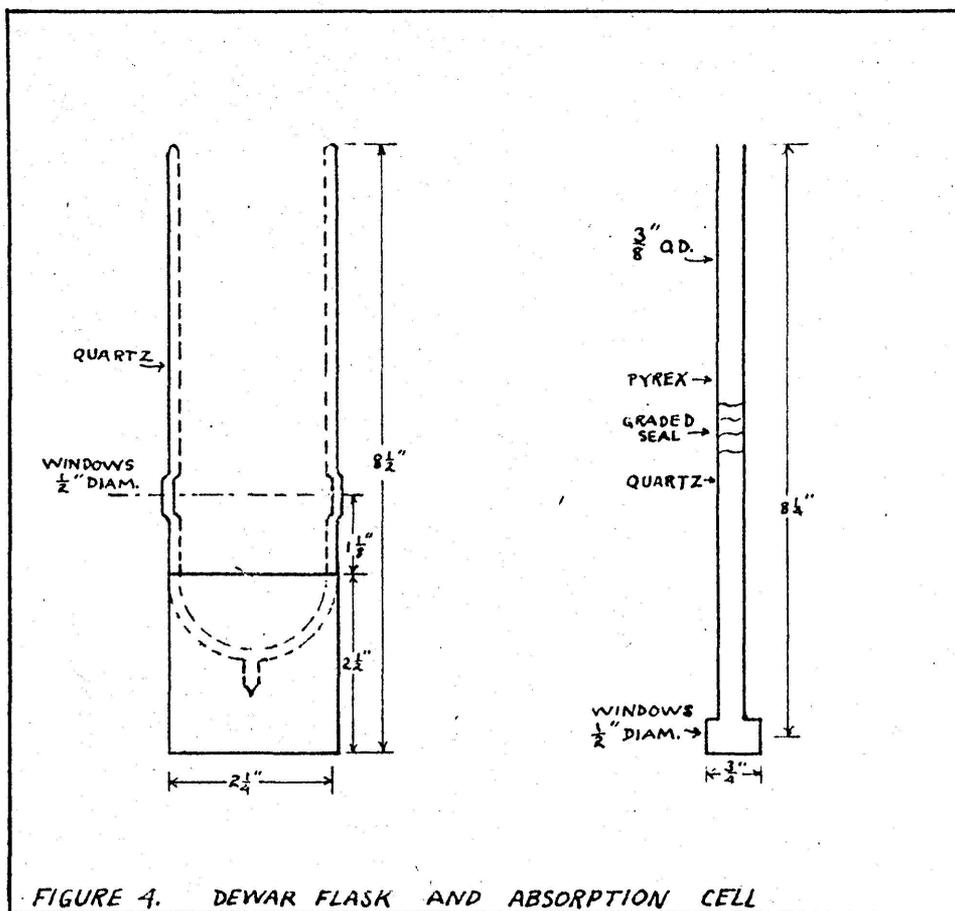


FIGURE 3. SKETCH OF MODIFIED SPECTROPHOTOMETER

It is to be seen that an enlarged cell chamber (A) capable of holding the small Dewar flask (B) is bolted to the monochromator assembly (C) in place of the former cell holder.

The quartz absorption cell and Dewar flask, which were borrowed from the U. S. Naval Research Laboratory, were patterned after the design of Gibson and Argo (55). A sketch of the cell and Dewar flask appears in Figure 4 on the following page.



The absorption cell and Dewar flask were mounted in the instrument case as shown in the sketch in Figure 5 on the following page. The Dewar flask was keyed to the bottom of the cell chamber, and the support arm for the absorption cell was keyed to the instrument case so that the flask and cell could easily be removed and replaced without altering the optical alignment of the system.

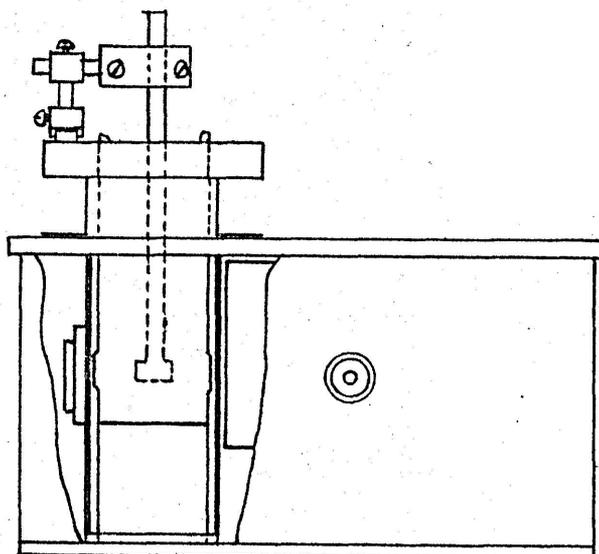


FIGURE 5. CUTAWAY VIEW SHOWING CELL AND DEWAR MOUNTED IN INSTRUMENT CASE

The absorption cell was cooled by means of Dry Ice in a small half-round brass can which was made to fit into the Dewar flask along with the absorption cell. A mixture of alcohol and ether provided thermal contact and also served to prevent frost formation on the cell windows.

## 2. Technique of Measurement

The technique for using the modified Coleman instrument differed from that for using the original instrument. It was not feasible to design the meter for use with two matched absorption cells; therefore it was necessary to measure the apparent transmittance versus wave-length over the entire

wave-length range first for the cell filled with solvent and then for the cell filled with unknown solution. This was accomplished by keeping the slide-wire drum of the meter fixed in one position and letting the galvanometer swing represent the apparent transmittance. The relative difference between the apparent transmittances of solvent and solution at any wave-length then represented the amount of absorption due to the solute at that wave-length.

The type of photo-cell used in the Coleman meter does not have a flat response--that is, it does not give the same response for all wave-lengths of light. Hence it was necessary to adjust the scale potentiometer of the instrument so that the maximum deflection fell at some arbitrary standard place on the galvanometer scale--100 divisions in this case. In addition, for comparison of transmittance of a solution against that of a solvent, one had to adjust the scale potentiometer so that the deflections for solution and solvent at wave-lengths unaffected by absorption would coincide on the galvanometer scale. With these necessary adjustments made, one could plot galvanometer deflection as apparent transmittance against wave-length for both solution and solvent on the same set of coordinates. The difference between the curves divided by the transmittance of pure solvent at any wave-length would represent the fractional absorption of the solution. The calculation formula is shown below.

$$\text{Fractional Absorption} = \frac{\text{Trans. Solvent} - \text{Trans. Solution}}{\text{Trans. Solvent}}$$

Multiplication of the fractional absorption by 100% gives the per cent absorption.

### 3. Preparation of Solutions

Solutions of metals in liquid ammonia were prepared and oxidized in the manner described in Part Two of this report. The solutions were oxidized in a cell equipped with a sintered glass filter so that samples of clear solution could be drawn off. When oxidation of a sample of metal was complete, a small quantity of solution was drawn off into the quartz absorption cell, which was immersed in a freezing bath. The cell was then stoppered and quickly transferred to the quartz Dewar flask in the spectrophotometer so that transmittance measurements could be made.

### 4. Results

The results of absorption spectra measurements on oxidized solutions of lithium, sodium, and potassium are shown in the graphs in Figures 6 to 14 on the following pages. In each graph the lower section shows the apparent transmittance, or galvanometer deflection, plotted against wavelength for solvent and solution. The upper section of each graph shows the per cent absorption plotted against wavelength.

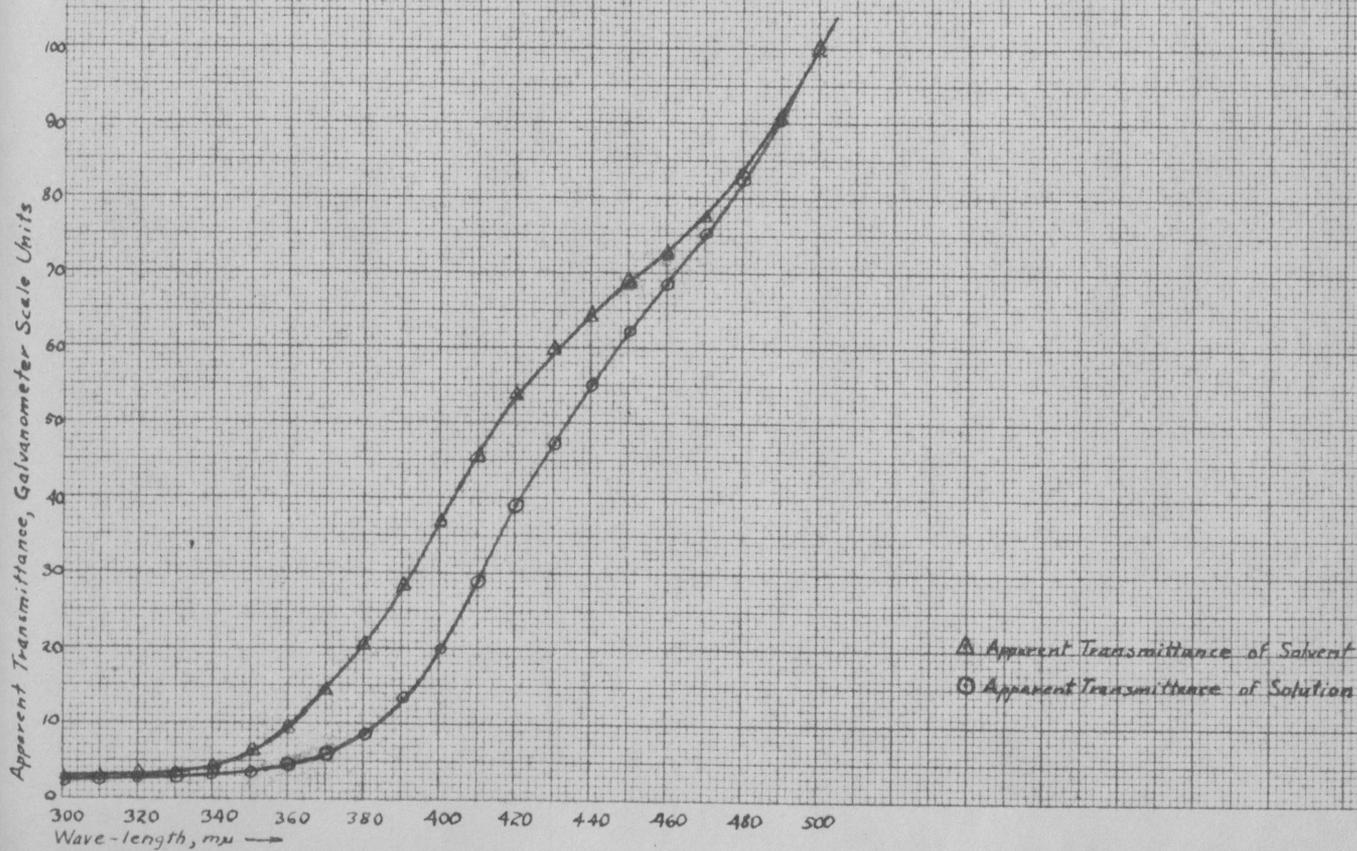
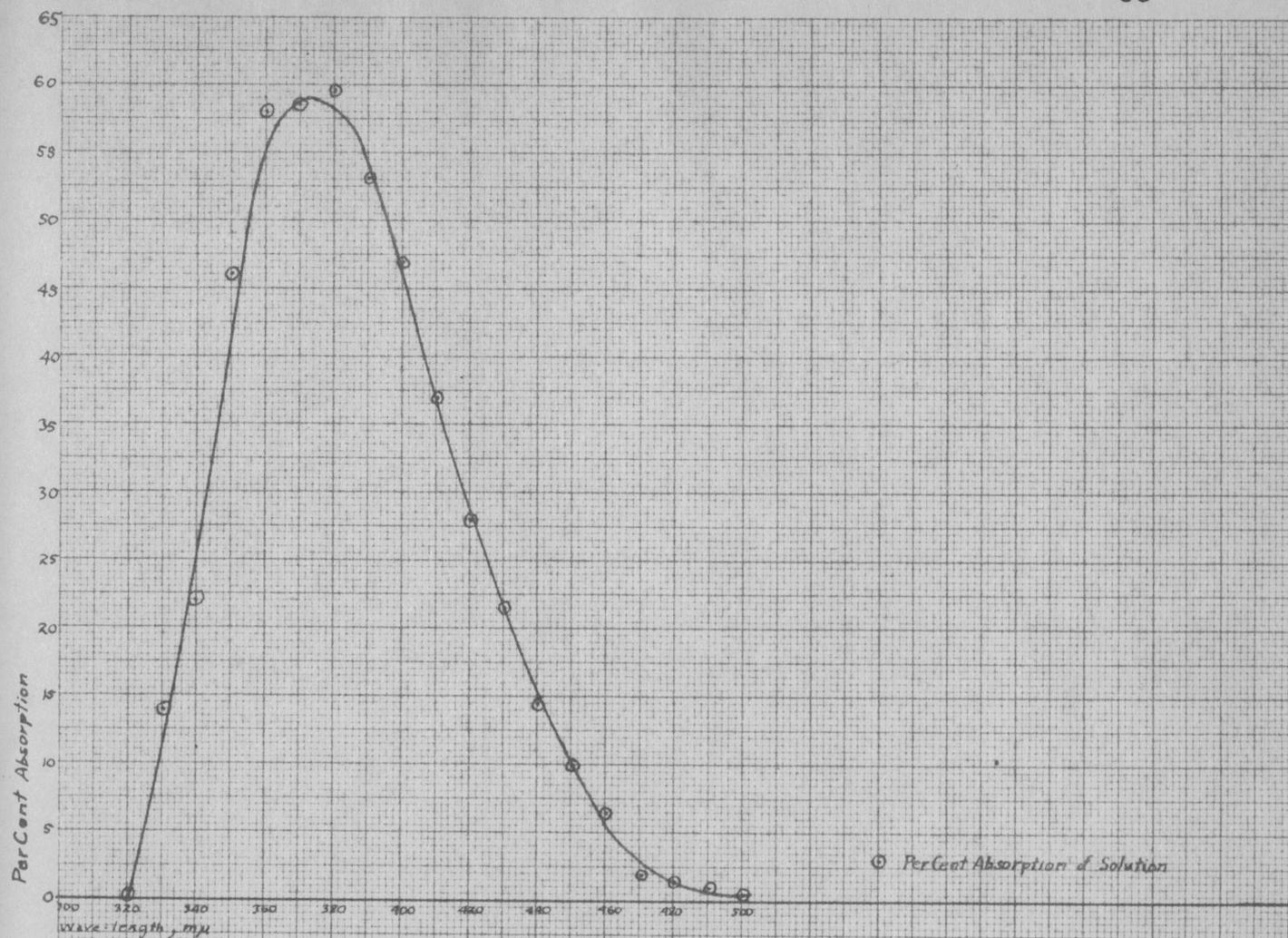


FIGURE 6. LITHIUM OXIDIZED IN LIQUID AMMONIA : ABSORPTION AND TRANSMITTANCE (1)

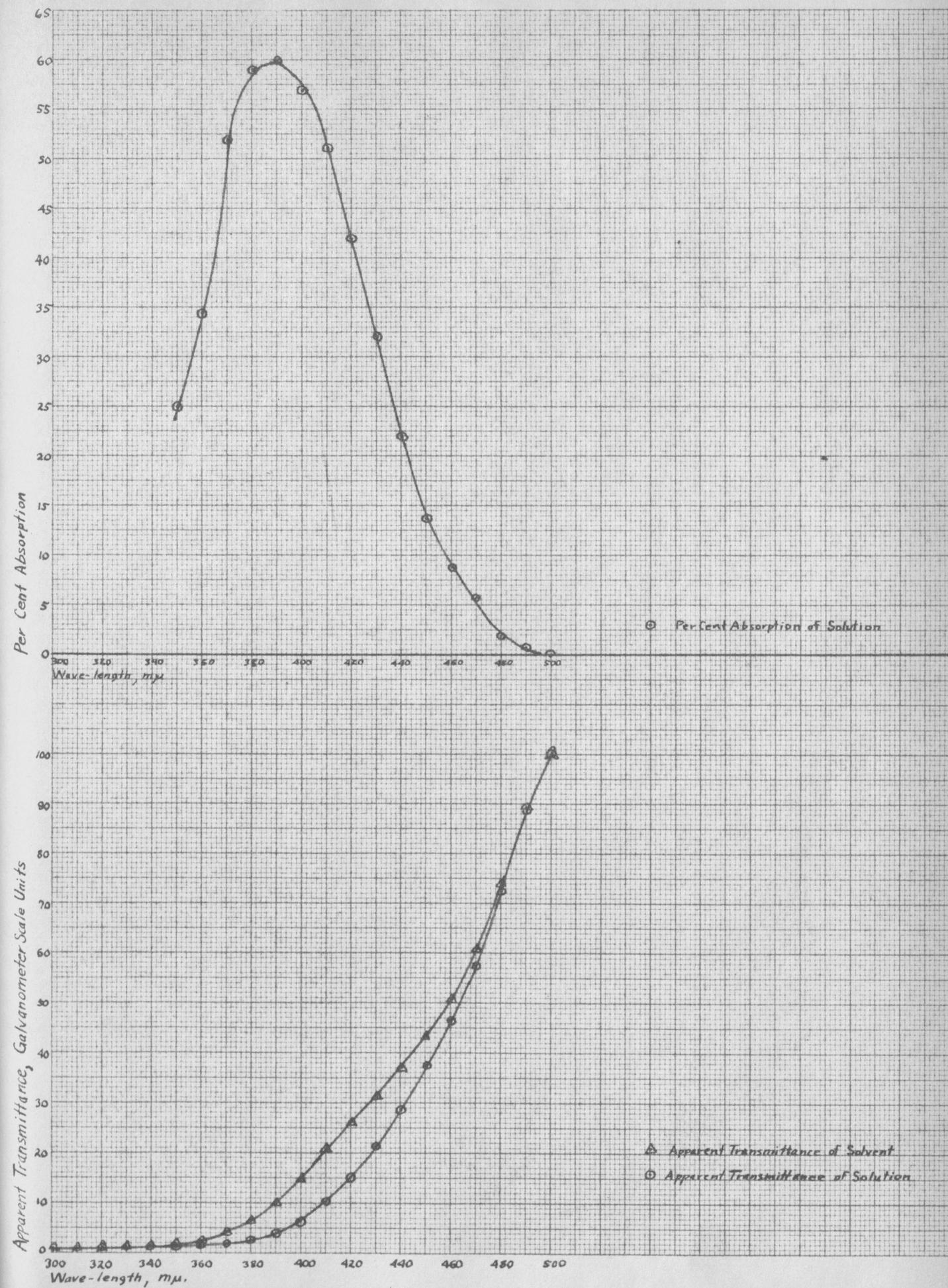


FIGURE 7. LITHIUM OXIDIZED IN LIQUID AMMONIA; ABSORPTION AND TRANSMITTANCE (2)

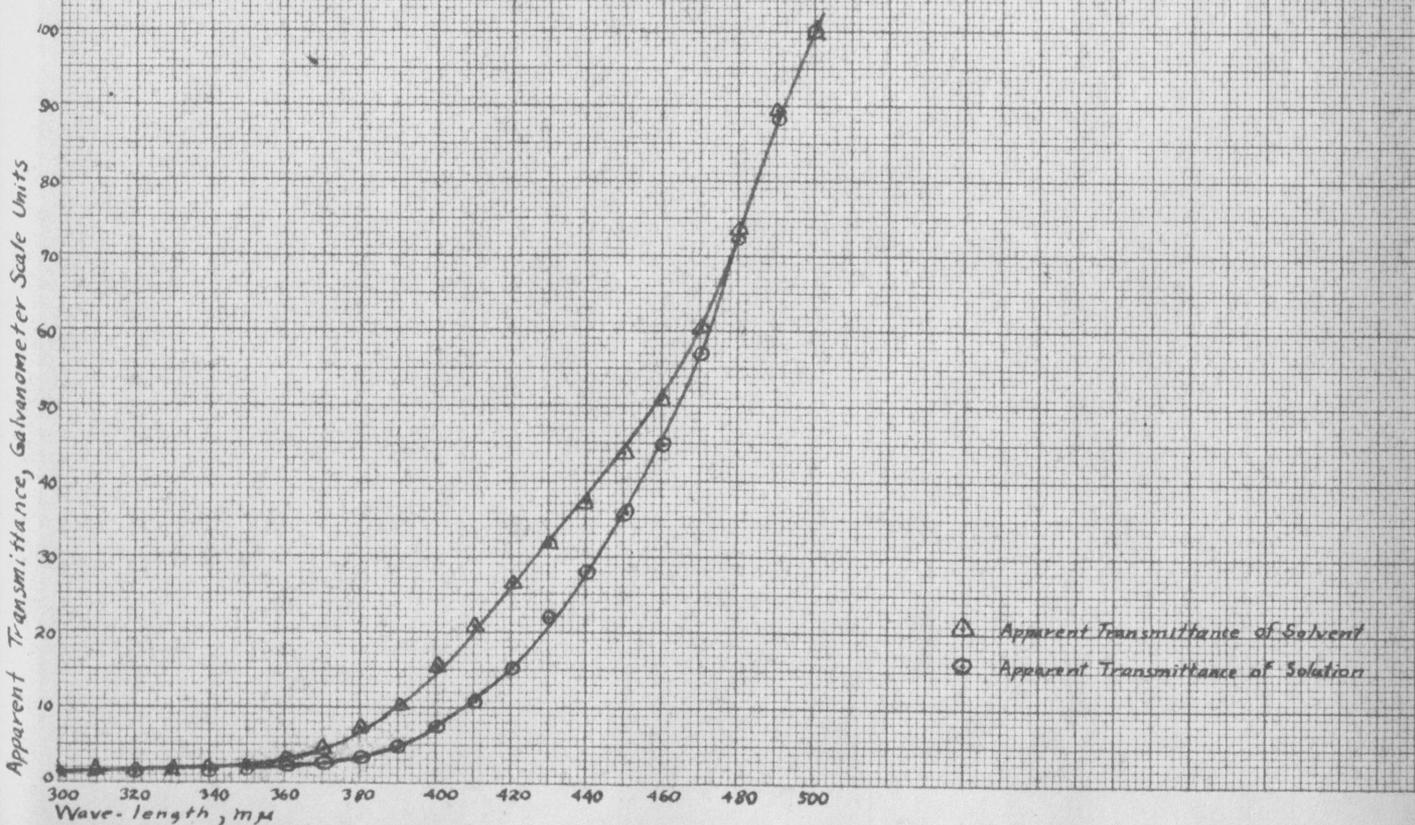
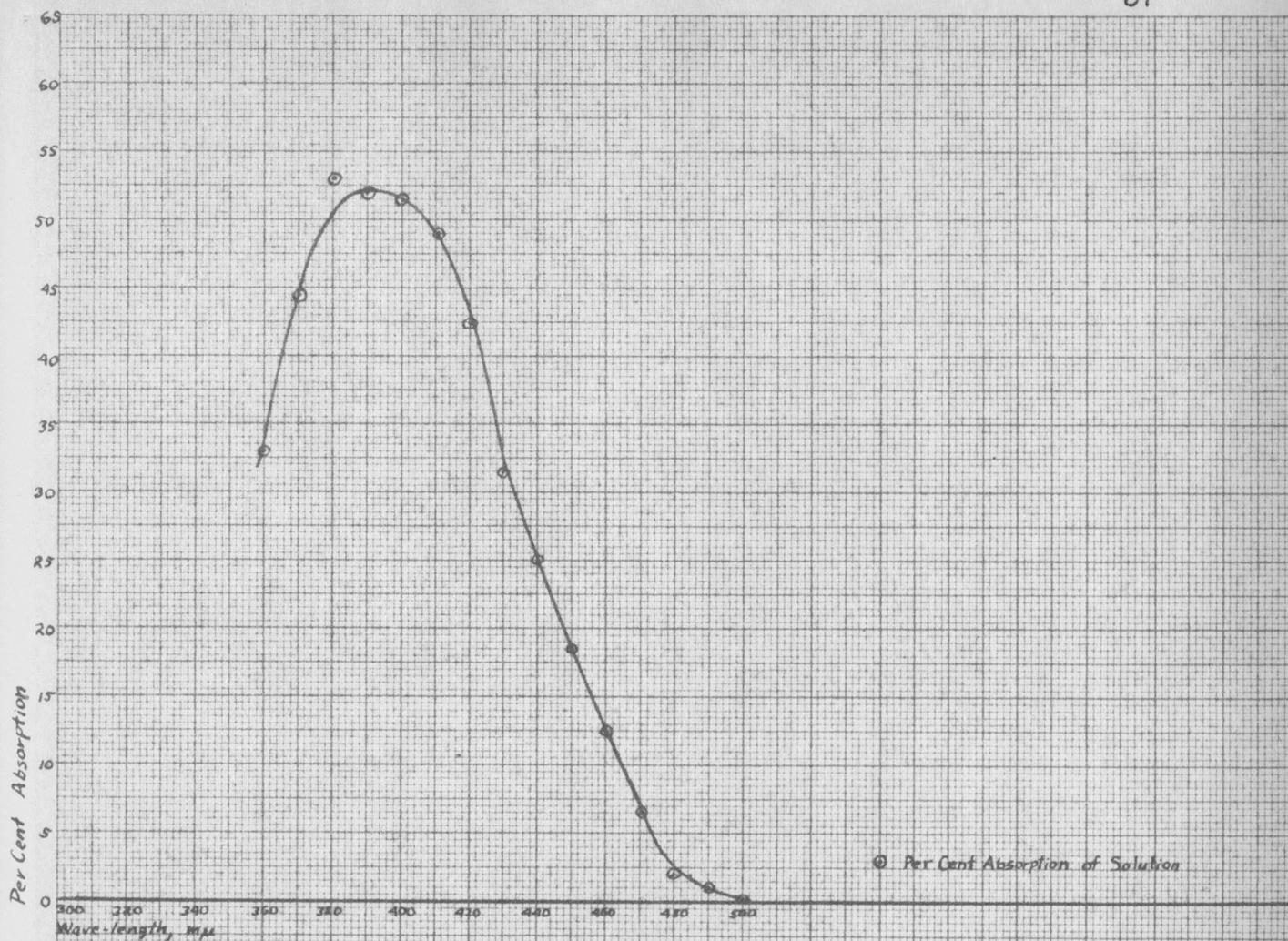


FIGURE 8. LITHIUM OXIDIZED IN LIQUID AMMONIA: ABSORPTION AND TRANSMITTANCE (3)

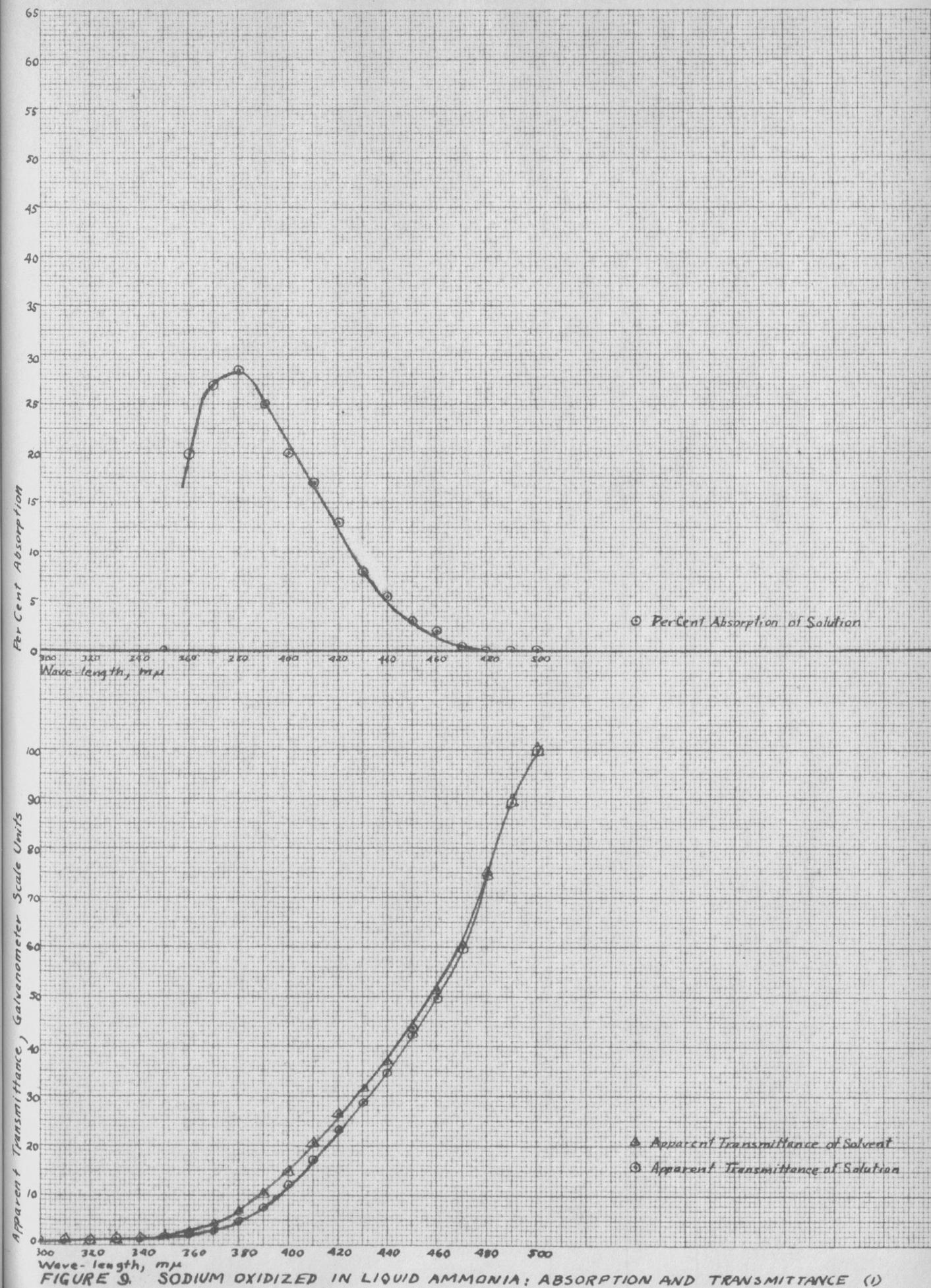


FIGURE 9. SODIUM OXIDIZED IN LIQUID AMMONIA; ABSORPTION AND TRANSMITTANCE (1)

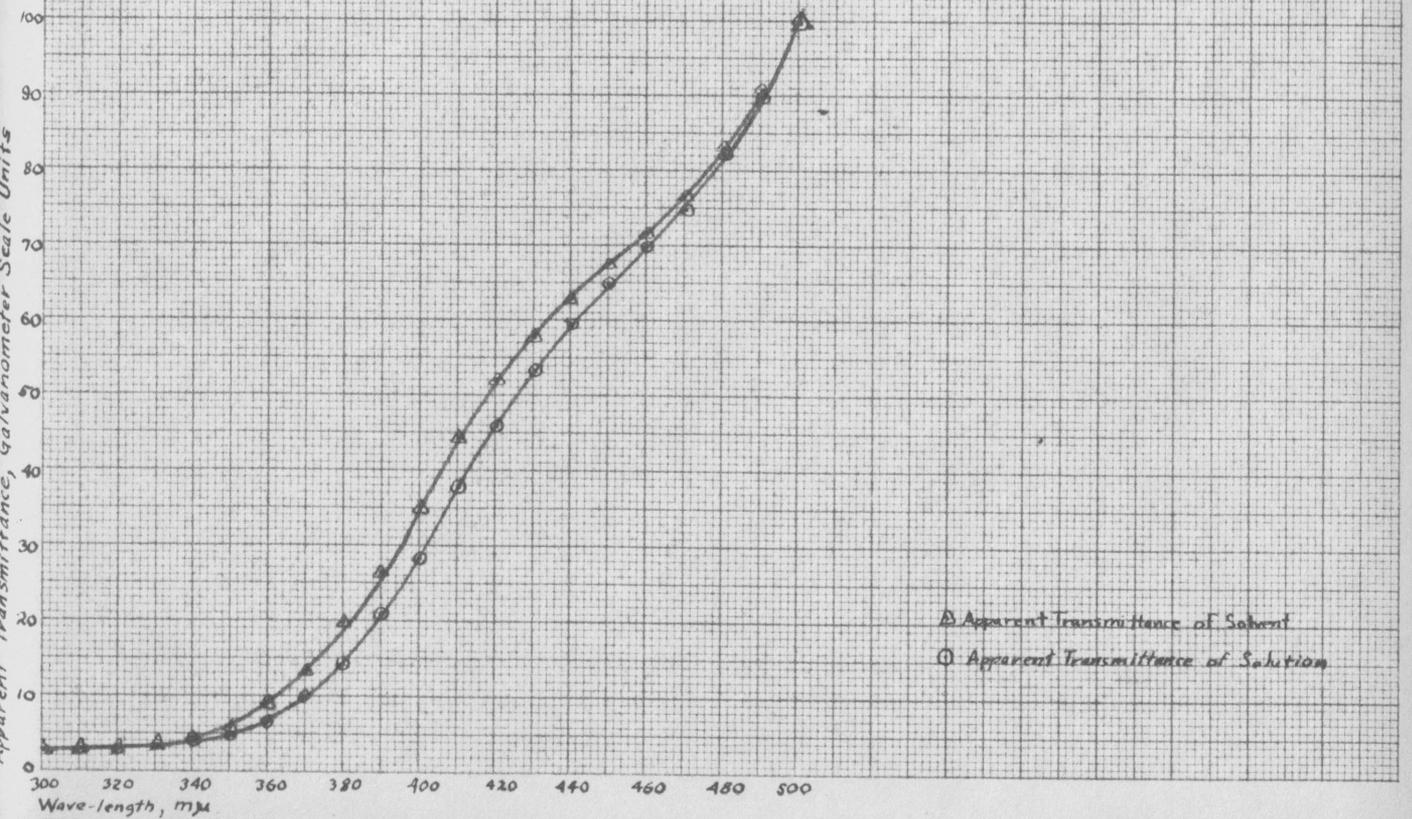
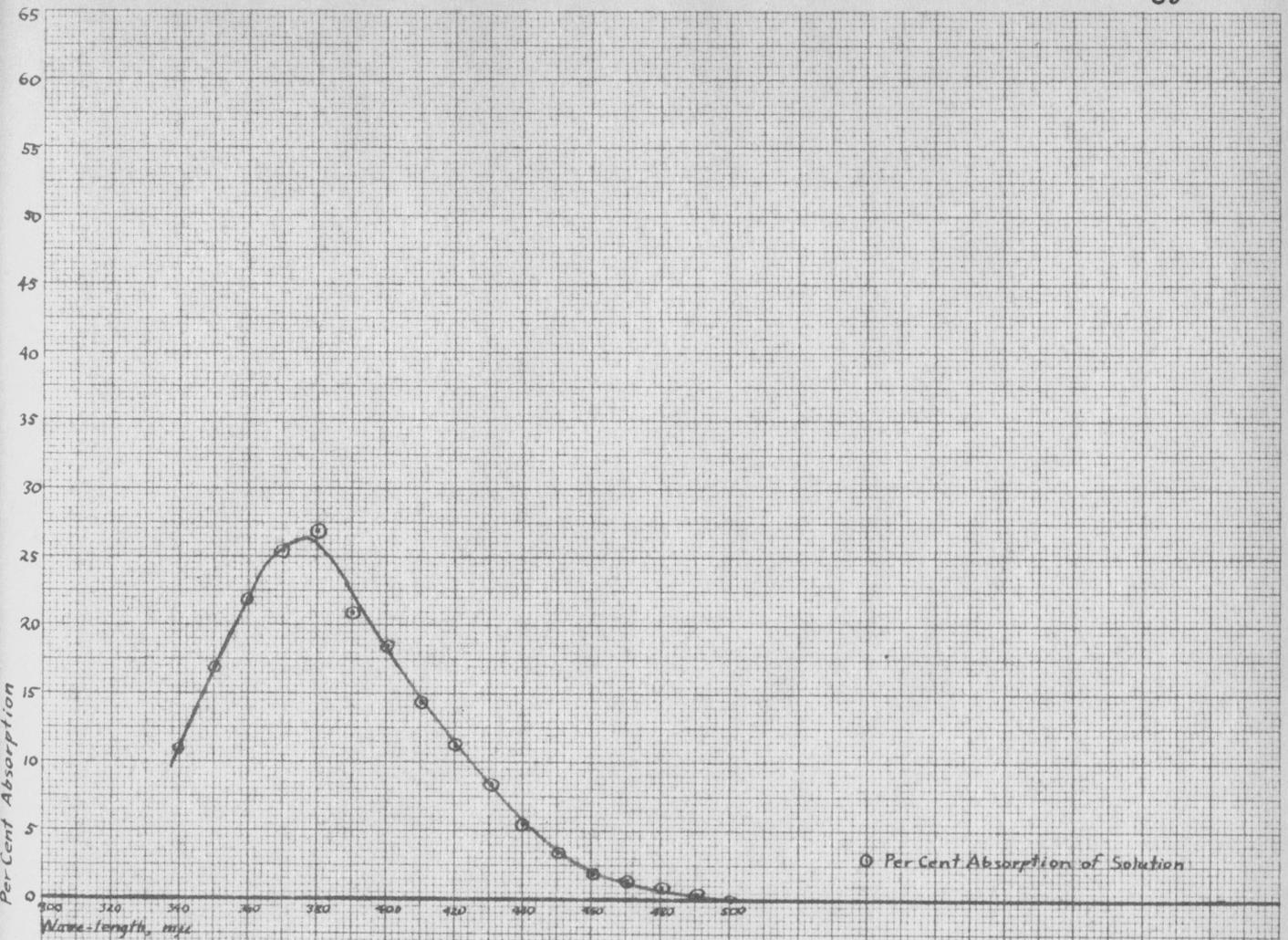


FIGURE 10. SODIUM OXIDIZED IN LIQUID AMMONIA: ABSORPTION AND TRANSMITTANCE (2)

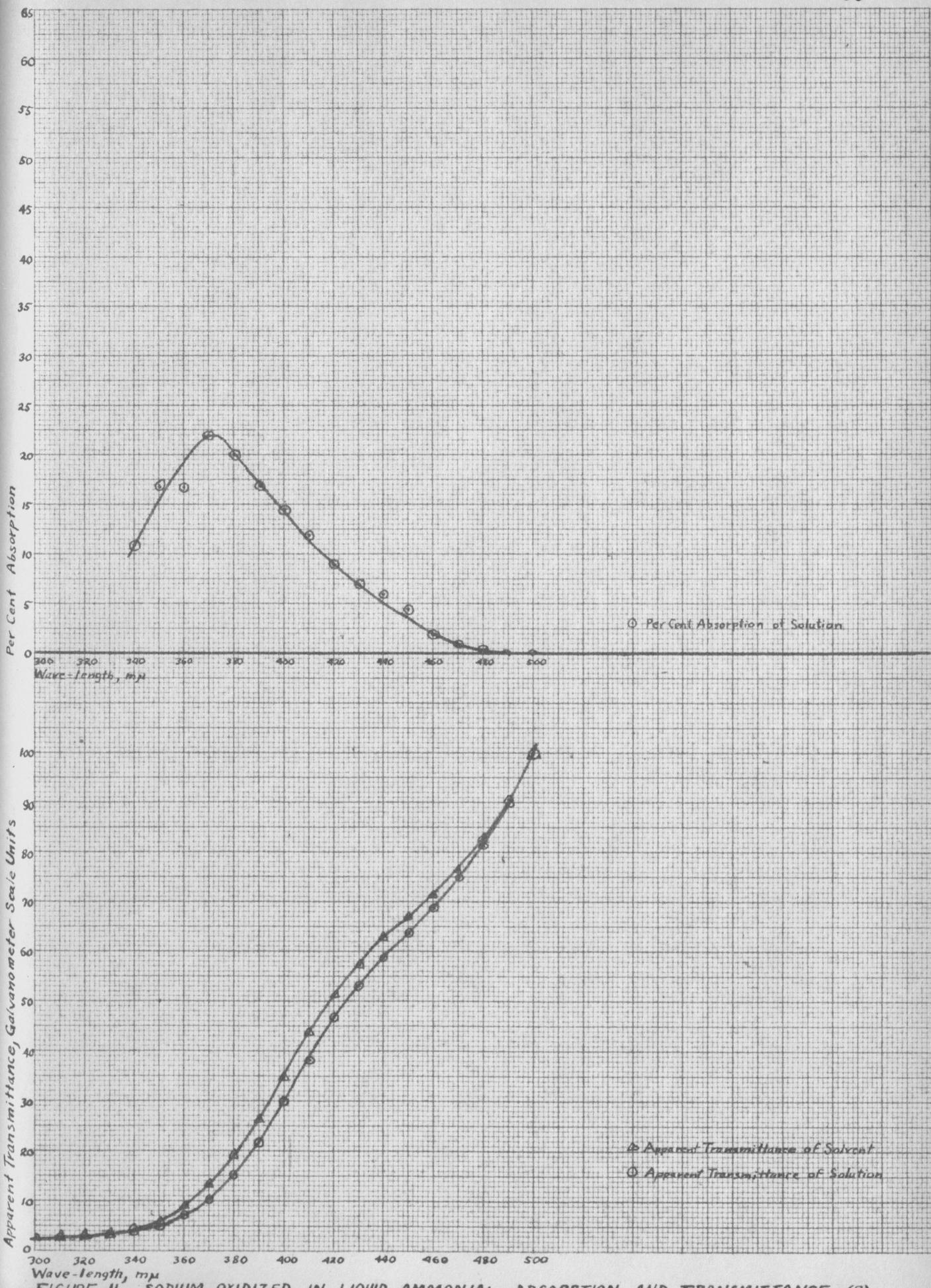


FIGURE II. SODIUM OXIDIZED IN LIQUID AMMONIA: ABSORPTION AND TRANSMITTANCE (3)

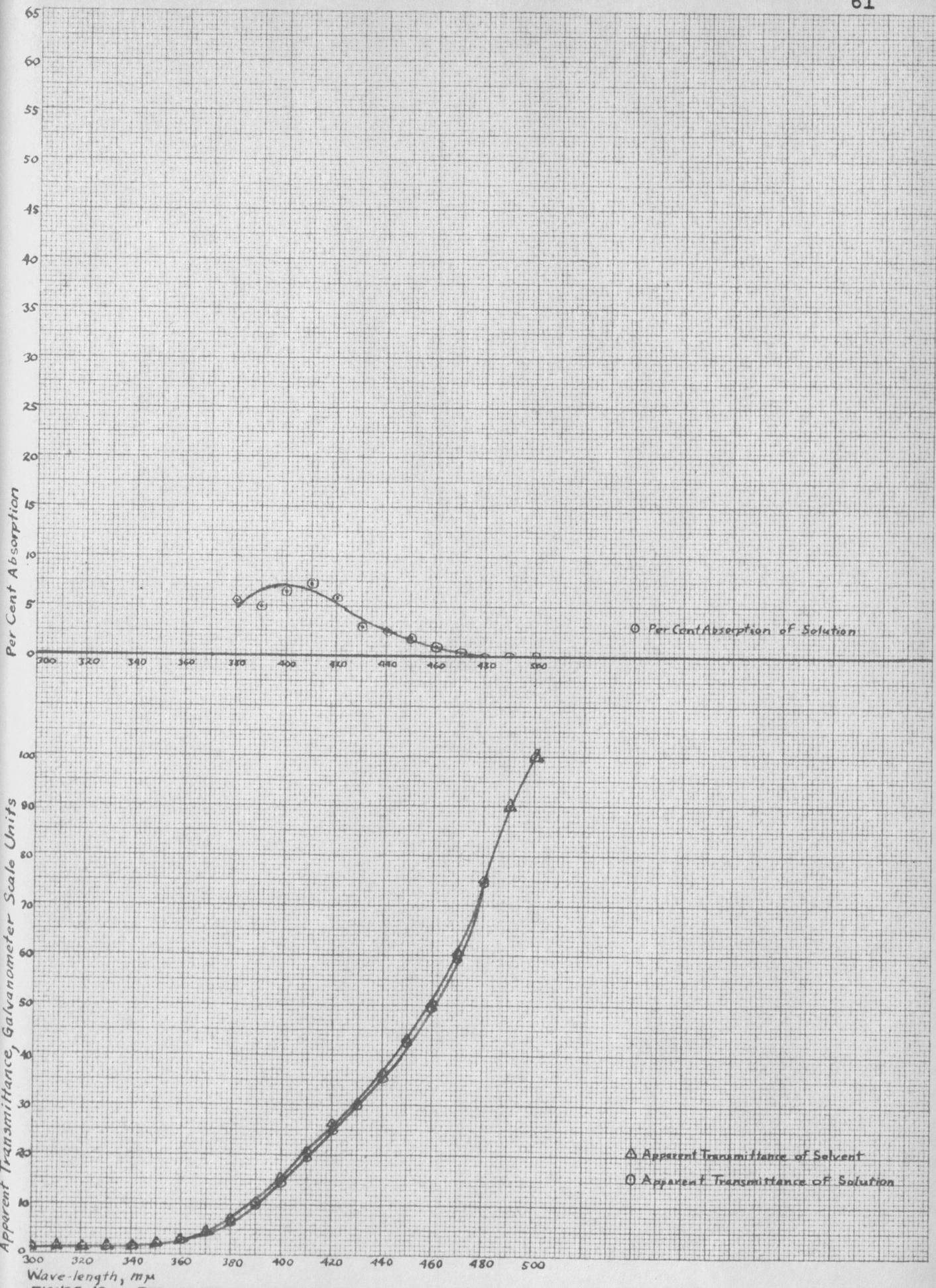


FIGURE 12. POTASSIUM OXIDIZED IN LIQUID AMMONIA: ABSORPTION AND TRANSMITTANCE (1)

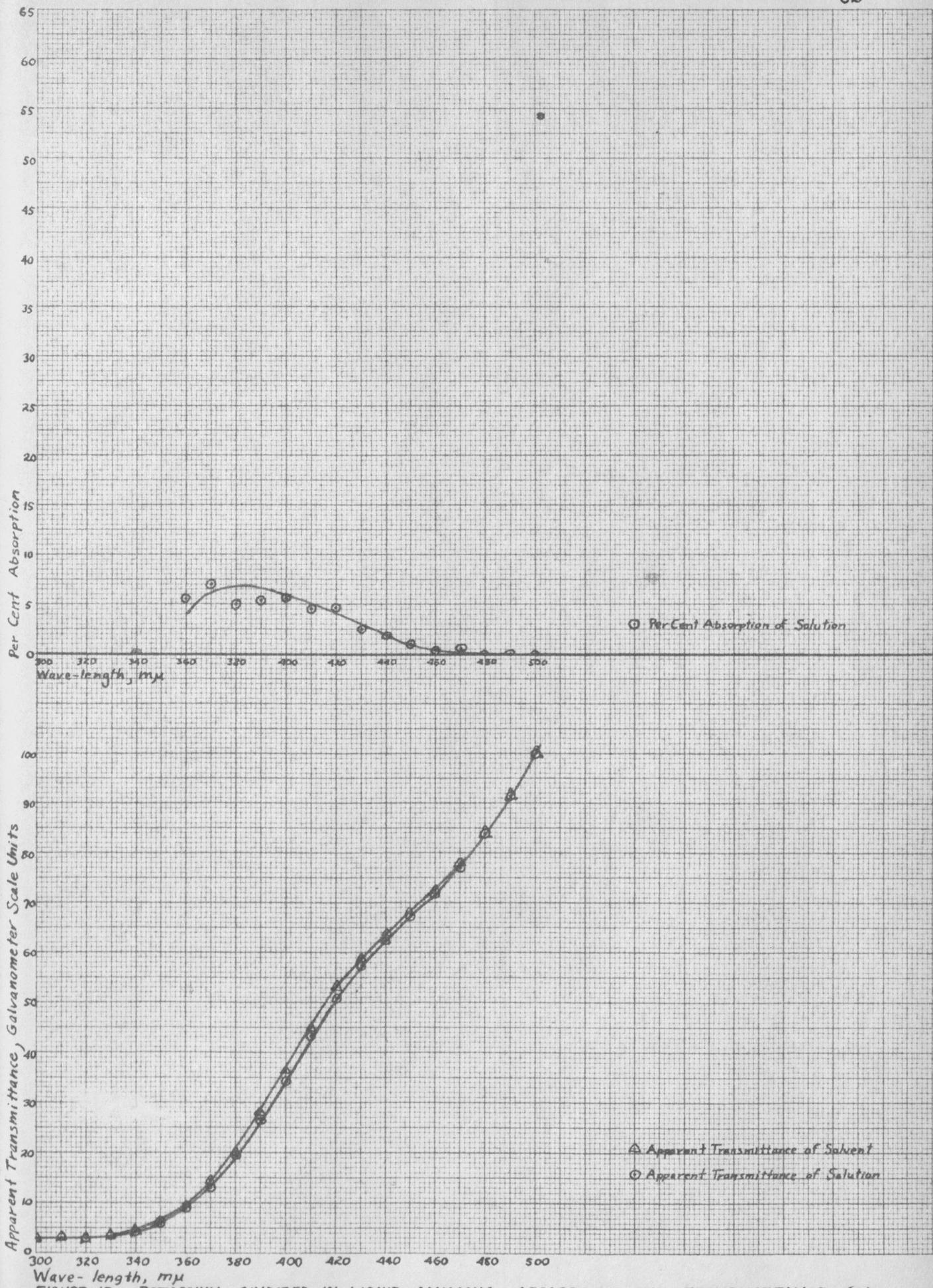


FIGURE 13. POTASSIUM OXIDIZED IN LIQUID AMMONIA; ABSORPTION AND TRANSMITTANCE (2)

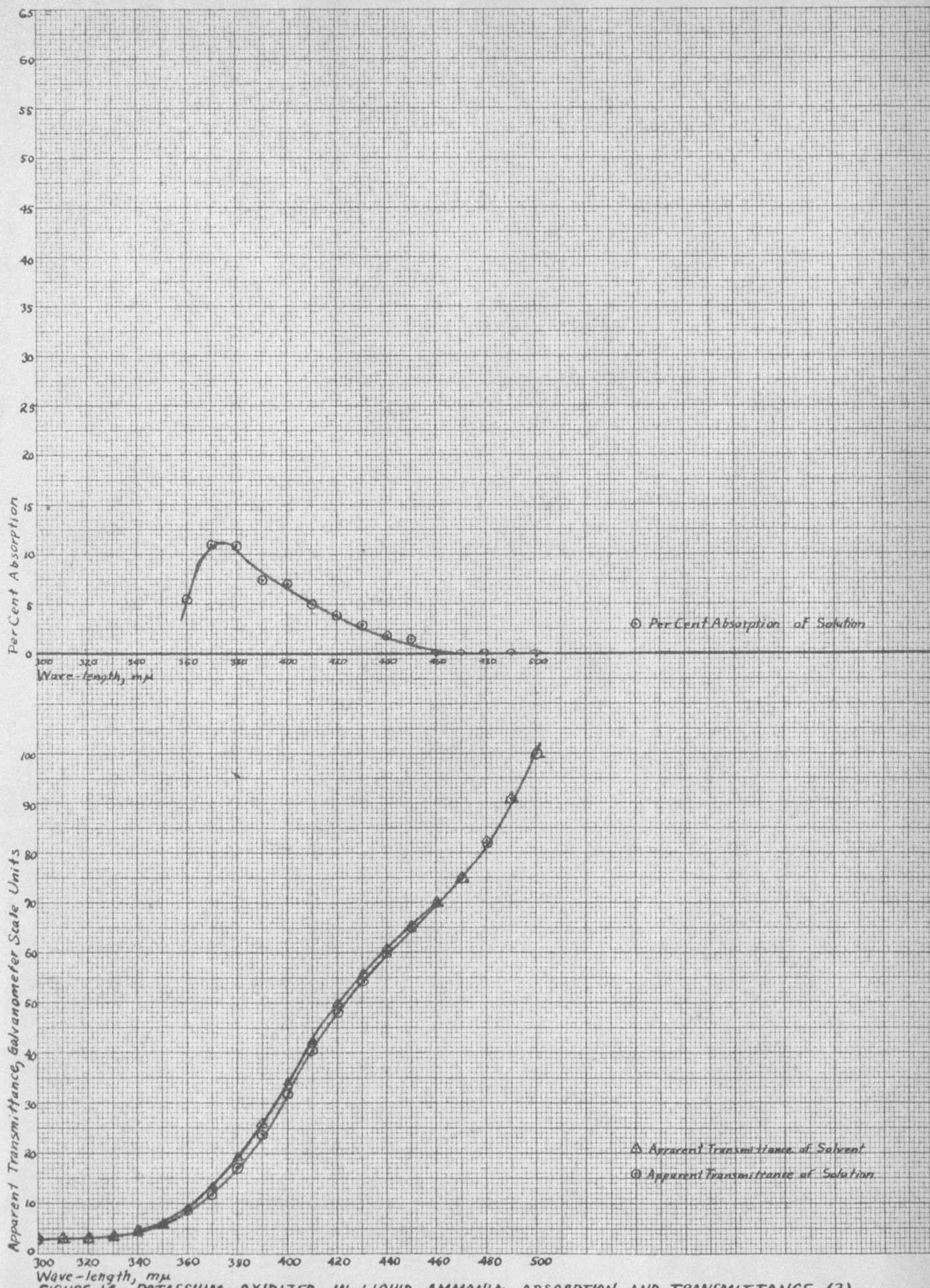


FIGURE 14. POTASSIUM OXIDIZED IN LIQUID AMMONIA: ABSORPTION AND TRANSMITTANCE (3)

The solutions studied in these experiments absorbed only in the blue region; hence the wave-length range covered was only from 300  $\mu$  to 500  $\mu$ . The use of such a short range of wave-lengths permitted the use of a greatly amplified galvanometer response. This was advantageous because the sensitivity of the photo-cell was quite low in the blue region of the spectrum.

Comparison of the upper sections of the graphs shows that in every case the per cent absorption reached a maximum in the blue region of the spectrum. Sample curves for each metal are reproduced together in the graph in Figure 15 on the following page. Because of the lack of sensitivity of the photo-cell in the blue region the absorption peaks are one-sided. That is, they are well-defined only on the side of longer wave-length. When allowance is made for the 35  $\mu$  band width of the Coleman instrument, the maxima in the absorption curves appear to occur reasonably close to the same wave-length, about 380  $\mu$ .

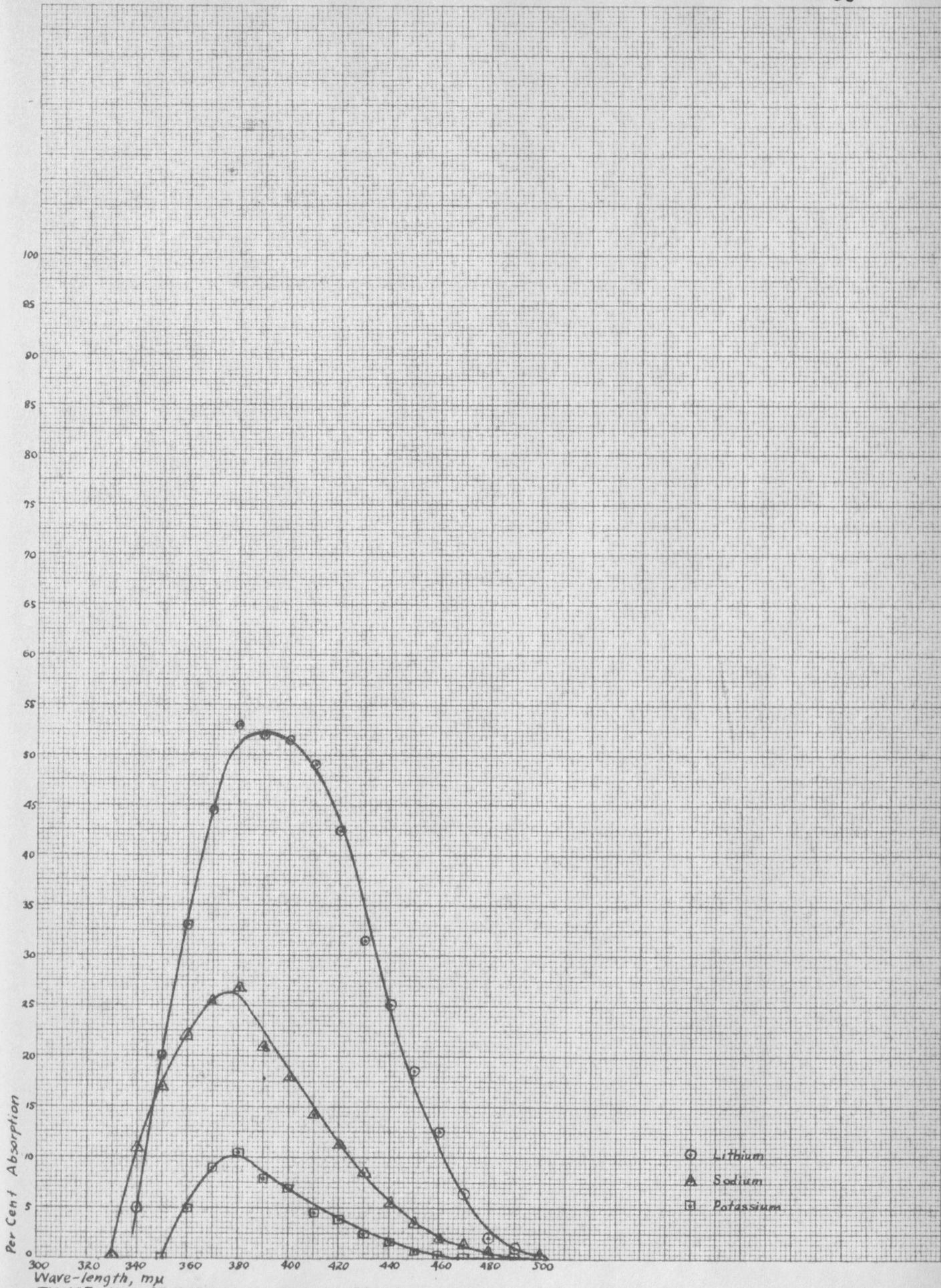


FIGURE 15. ABSORPTION SPECTRA OF PRODUCTS OF OXIDATION OF ALKALI METALS IN LIQUID AMMONIA

The relative heights of the absorption maxima decrease in the order lithium, sodium, and potassium. Though no quantitative measurement of solubility was made, this order might be taken as the order of decreasing solubility of the substance responsible for the absorption.

It seems reasonable to conclude from the results of the absorption experiments that the same substance is responsible for absorption of light in every case and that this substance may be superoxide. If such a conclusion is correct, then lithium has been shown to form a superoxide which is stable in solution at  $-78^{\circ}$  C. even though it does not form the stable solid compound.

The conclusions drawn from these experiments could be checked best by measurement of the absorption spectra with a spectrophotometer with a sensitivity in the blue and violet regions of the spectrum greater than that of the Coleman instrument.

## SUMMARY

The work described in this report completes the study of the oxidation of the alkali and alkaline earth metals in liquid ammonia as it has been carried on at the University of Kansas.

Magnetic susceptibility measurements were made on the product of rapid oxidation of sodium in liquid ammonia. The value of the magnetic susceptibility lends credence to the postulate that the product may be either a definite crystalline compound or a constant-ratio precipitate having the composition  $4\text{NaO}_2 \cdot \text{Na}_2\text{O}_2$ .

This postulate was not supported by the results of X-ray diffraction measurements. X-ray measurements indicate that the product is chiefly  $\text{NaO}_2$  and that there are additional hydrated phases which may have been formed by moisture in the product. It will be necessary to have absolutely anhydrous samples in order to definitely prove or disprove the validity of the formula  $4\text{NaO}_2 \cdot \text{Na}_2\text{O}_2$ .

Complete studies have been made on the oxidation of lithium and the alkaline earth metals in liquid ammonia. All the metals reacted to yield small percentages of peroxide. No higher oxides were found in the products. All the metals formed small amounts of amide as indicated by the presence of nitrite in the oxidation products.

Tests have been described which show that when solutions of anhydrous magnesium bromide in liquid ammonia are electro-

lyzed between a magnesium anode and a platinum cathode solutions of ionized metal are formed. It was shown qualitatively that such solutions can be oxidized by a stream of oxygen to form small amounts of peroxide.

Absorption spectra studies were made on the yellow solutions formed by rapid oxidation of the alkali metals in liquid ammonia. Oxidized solutions of lithium, sodium, and potassium all have an absorption band reasonably close to the same wave-length, 380 m $\mu$ . The intensity of absorption of the solutions decreases in the order named. This evidence supports the postulate that lithium forms a superoxide which is stable in solution in liquid ammonia at  $-78^{\circ}$  C.

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