STUDIES OF THE REACTION OF SODIUM-POTASSIUM ALLOY

WITH 1,2-DIMETHOXYETHANE

By

LARRY A. GRUNDY

Bachelor of Science

Baylor University

Waco, Texas

1949

Submitted to the Faculty of the Graduate School of

the Oklahoma Agricultural and Mechanical College

in Partial Fulfillment of the Requirements

for the Degree of

MASTER OF SCIENCE

1951

STUDIES OF THE REACTION OF SODIUM-POTASSIUM ALLOY
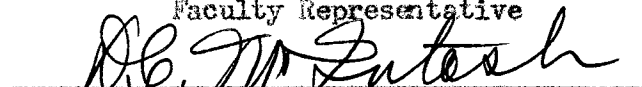
WITH 1,2-DIMETHOXYETHANE

LARRY A. GRUNDY

MASTER OF SCIENCE

1951

THESIS AND ABSTRACT APPROVED:

_____
Thesis Adviser

_____
Faculty Representative

_____
Dean of the Graduate School

<u>ACKNOWLEDGEMENT</u>

The author wishes to express his deep
appreciation of the advice, aid, and direction
accorded him by his adviser in this investiga-
tion, Dr. Irving Johnson.

TABLE OF CONTENTS

I. INTRODUCTION

It has been common experience among chemists working with active metals in anhydrous solvents to observe blue colors of varying intensities and stabilities. In 1891, Beckmann and Paul[1] found that metallic sodium dissolved without evolution of hydrogen in air free solutions of aromatic ketones in dry ether giving dark blue products. Schlenk and Weickel[2] proposed a mechanism for this reaction.

Williamson[3] observed a blue color when sodium-potassium alloy was stirred with 1,2-dimethoxyethane in a creased flask. Qualitative observations showed that under the same conditions 1-methoxy-2-ethoxyethane and dimethoxymethane did not produce the blue color. Sodium metal alone did not produce a blue color in 1,2-dimethoxyethane. Potassium metal alone did produce a slight blue color.

Williamson also made conductance measurements by immersing electrodes in the solution while stirring. It was found that the conductance increased with an increased stirring rate to a maximum value beyond which increasing the stirring rate did not increase the conductance. Under these conditions the conductance was found to increase with decreasing temperature.

II. THE PROBLEM

The purpose of this study was (1) to determine the conditions necessary for the formation of the blue solution resulting from the reaction of sodium-potassium alloy with 1,2-dimethoxyethane and the factors related to its stability and (2) to ascertain the general nature of the reaction producing the blue color.

III. EXPERIMENTAL

In an effort to determine the conditions necessary for the formation of the reported blue color produced by the system of sodium, potassium and 1,2-dimethoxyethane the components were stirred in an open flask with a high speed stirrer. No blue color was produced. When the experiment was repeated with somewhat purer chemicals and a nitrogen atmosphere the color was formed. Further experiments in which solvent of higher purity was used showed that high purity and low temperature were more important in producing a stable blue color than rapid stirring. When a method of preparing the blue solution had been established an apparatus was devised to measure the conductivity of the blue solution as a function of temperature and concentration. The apparatus proved unsatisfactory as constructed because of the difficulty in transfering the blue solution into the conductivity cell. Simplification of the apparatus made possible the transfer of the blue solution into a cell. The conductance of the blue solution was too low to be measured by this cell. Further modification resulted in an apparatus with a low surface area in which the conductance of the blue solution in contact with the alloy could be measured as a function of temperature.

Apparatus and Materials.-- The 1,2-dimethoxyethane used in this study was obtained from the Arapahoe Chemical Company. The commercial product was further purified by distillation from an all glass apparatus to remove nonvolatile impurities. The distilled product was stored over freshly cut sodium metal for at least one hour before use. Nitrogen pressure was used to force the solvent through a sintered glass filter tube from the storage flask into the apparatus. This filtration was necessary to remove the sodium and sodium hydroxide from the solvent.

A eutectic mixture of sodium and potassium, which is approximately 75% potassium by weight (melting point -12°), was used in this study. The alloy was prepared by stirring the metals cut in small pieces under 1,2-dimethoxyethane. The alloy thus prepared was transferred by means of a pipette or medicine dropper.

Capsules of sodium-potassium alloy were prepared in the apparatus shown in Fig. 1. The capsules were made from 6 mm. o.d. tubing with a thin bulb blown at (E). The tube was drawn to a capillary at (D) to aid in sealing off. The technique of drying this apparatus, as well as the other closed systems used in this study, was to alternately evacuate and refill the system with dry nitrogen. After each evacuation the apparatus was heated with a gas flame where possible. When the apparatus was dry it was filled with dry nitrogen. Tube (C) was removed and filled with the proper proportions of sodium and potassium metal. Tube (C) was then replaced and evacuated. A vacuum was maintained by continuous pumping until any volatile material clinging to the metal was distilled into the cold trap (B). The metals were warmed to the melting point of potassium at which temperature they fused together to form an alloy. The alloy formed a large globule which forced the solid impurities to the top or bottom of the liquid. Dry nitrogen was then allowed to enter the tube suddenly. This forced the alloy through a small opening (F) into the capsules. The system was again evacuated. The application of heat at (D) vaporized some of the alloy at that point making the sealing off of the capsule possible.

The nitrogen used was obtained from the Linde Air Products Company. It was dried by passing it through a 30 cm. tube of calcium chloride and a 25 cm. tube of magnesium perchlorate. In studies made using the apparatus

FIGURE 1

N₂   VACUUM

A   B   C   D   E   F
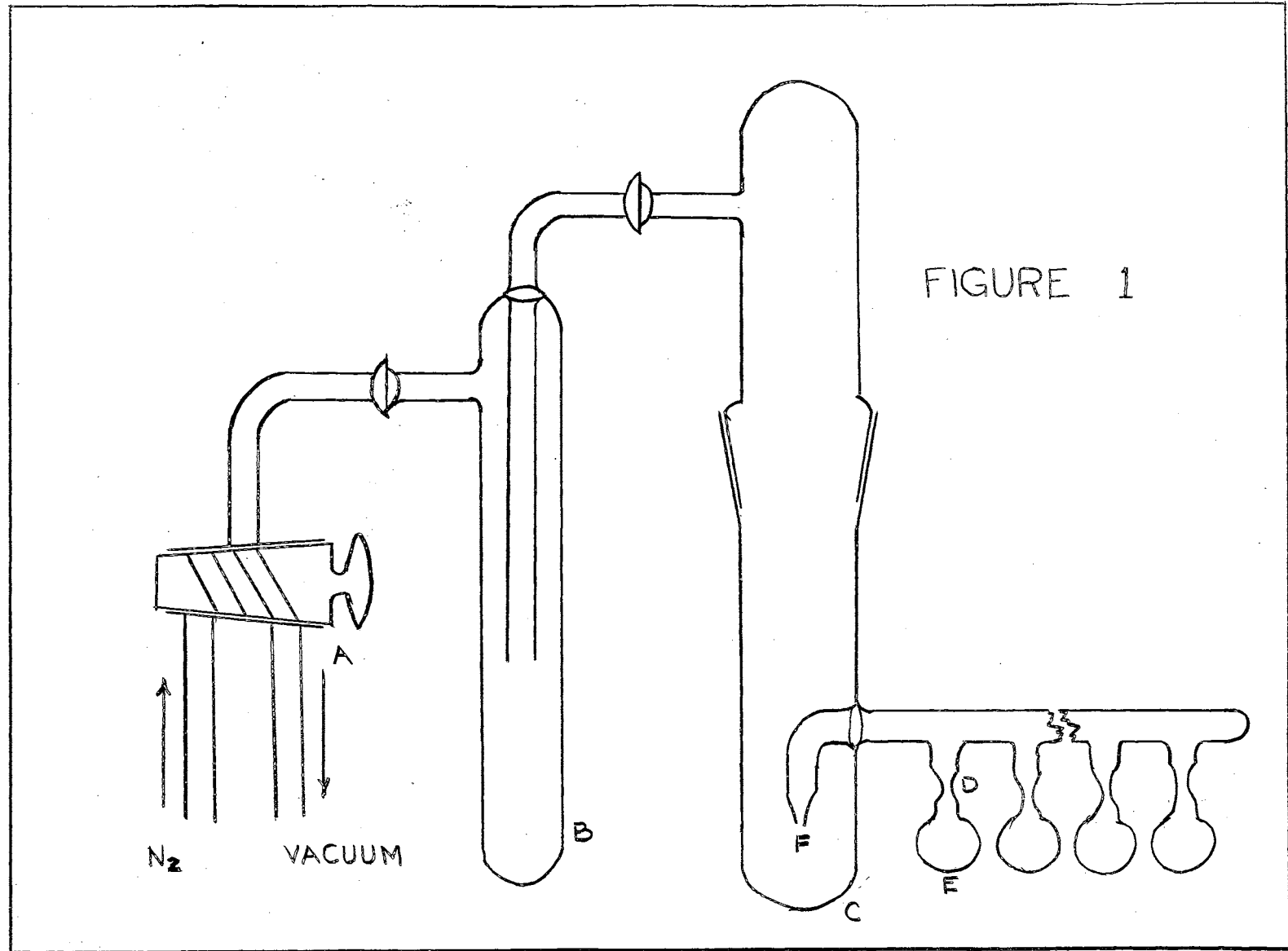
shown in Fig. 3a the nitrogen was freed of traces of oxygen by passing it through a 30 cm. tube of fresh copper turnings heated to above 200° by an electric heating coil. This tube was placed between the drying tubes.

A mixture of carbon tetrachloride, chloroform and solid carbon dioxide was used as a cooling bath. A temperature of -75° could be reached with this mixture.

The vacuum pump used in the study was a Cenco Hyvac pump rated to produce a vacuum of 0.3 microns with a suitable system.

All pieces of glass apparatus were constructed from Pyrex (Corning 774) glass.

Stopcocks and joints were lubricated with Apiezon grease formula M. This lubricant was found to be more resistant to the solvent powers of 1,2-dimethoxyethane than several other common lubricants.

The experiments involving high speed stirring utilized an apparatus similar to that described by Morton[4]. The apparatus is shown in Fig. 2. Both air driven and electrically driven stirrers were used which operated from 2000 to 5000 rpm.

Fig. 3a shows an apparatus built to purify 1,2-dimethoxyethane and prepare the solution under a flow of dry nitrogen. Flasks (W) and (K) have a capacity of 300 ml. Flask (Y) is a 250 ml. creased flask. The tube extending down into flask(Y) is fitted with a fine sintered glass filter on the lower end. Four manometers, one of which is shown in Fig. 3b, were attached to the points marked (A). The manometers served not only to indicate the relative pressures in the system, but also to relieve excessive pressures. Traps were placed at the top of each manometer to prevent mercury from being drawn into the system when sudden pressure

FIGURE 2

FIGURE 3
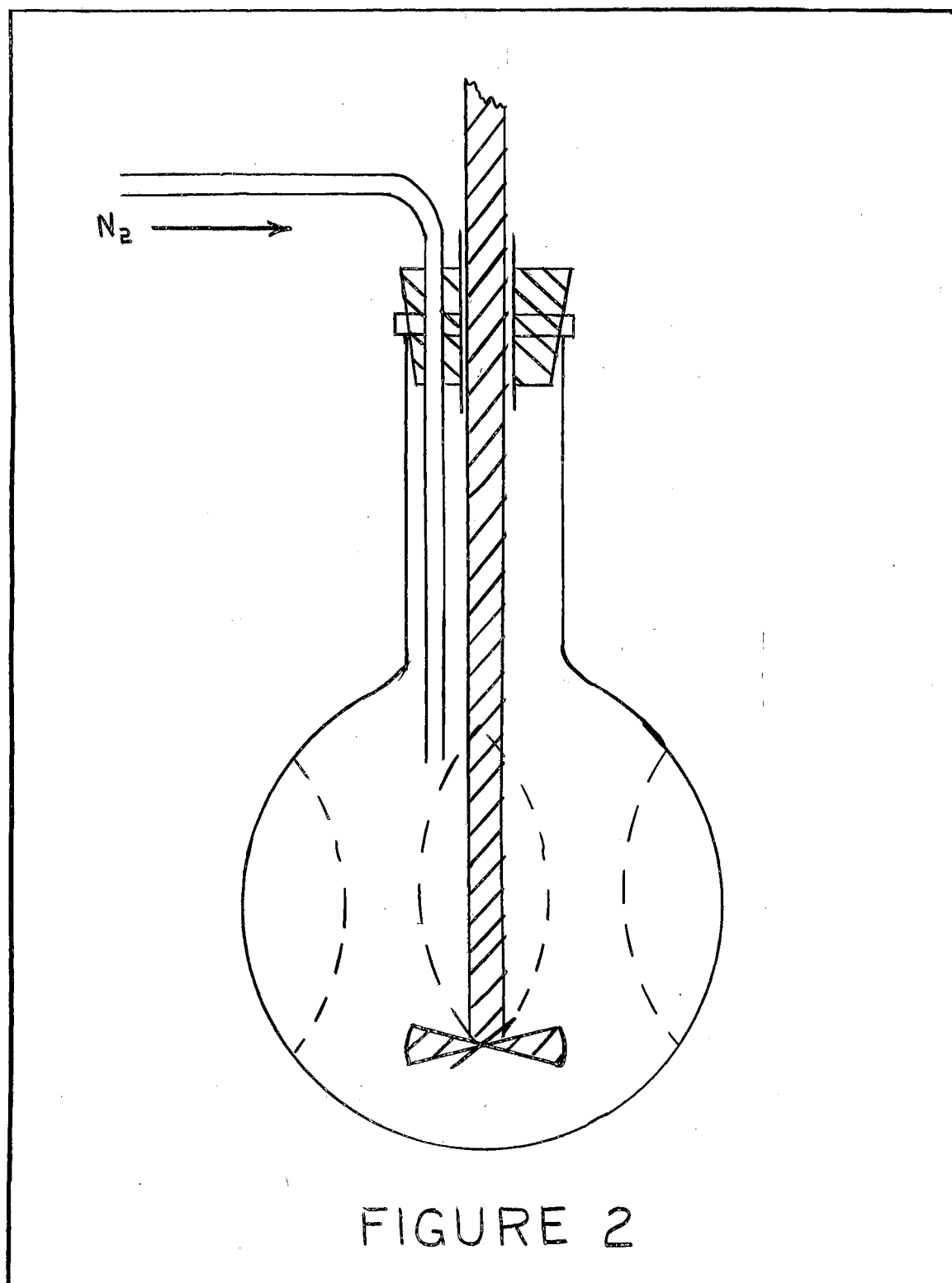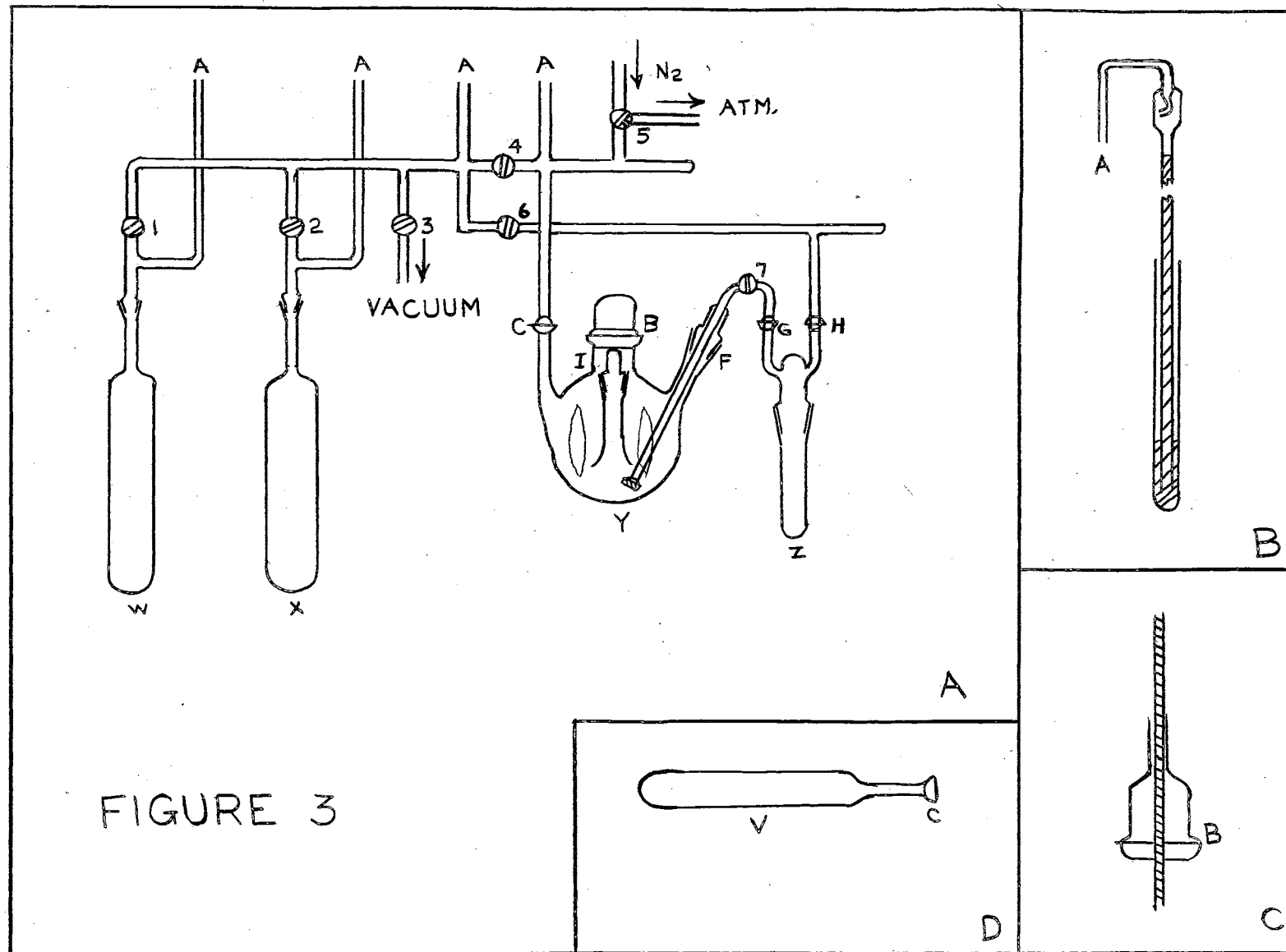
changes occurred. A high speed stirrer could be placed in the creased flask by removing the cap at (B) and putting the sleeve assembly shown in Fig. 3c in its place. The small clearance between the glass sleeve and the stirrer shaft allowed only a small gas leak. A 25 mm. x 130 mm. thick wall test tube was fitted with a spherical joint as shown in Fig. 3d. This could be attached to the apparatus at (C) in place of flask (Y).

An apparatus designed to prepare sealed tubes containing purified 1,2-dimethoxyethane and sodium-potassium alloy is shown in Fig. 4. Side (A) and the upper portion of (B) were constructed from 25 mm. o.d. tubing. The lower portion of (B) was a 25 mm. x 130 mm. thick wall test tube. The sides were connected by a piece of 20 mm. o.d. tubing slanted to prevent the liquid in side (A) from being splashed into side (B) during distillation. The apparatus was opened and closed by blowing out and sealing the top of tube (A). A short piece of iron rod ($\frac{1}{4}$" x 1") was placed in the apparatus. This could be maneuvered with an Alnico magnet to break the capsule.

The apparatus shown in Fig. 5 was built to measure the conductivity of solutions of varying concentration and temperature. Sections (AB) and (EF) were made to function the same as the apparatus in Fig. 4. Tubes (B), (E), and the cell were equipped with reciprocating stirrers operated by passing an intermittent current through solenoids placed just above iron rods sealed in the stirrer shafts. A cooling bath which would automatically maintain a temperature constant within two degrees from room temperature to -50° was built to contain all the apparatus shown inside the dashed line. The cell and diluting mechanism, similar to that of Gibson and Phipps[5], is shown in detail in Fig. 6a. The valve was made from a 7/25 standard taper

FIGURE 4

FIGURE 5

FIGURE 6

A

B
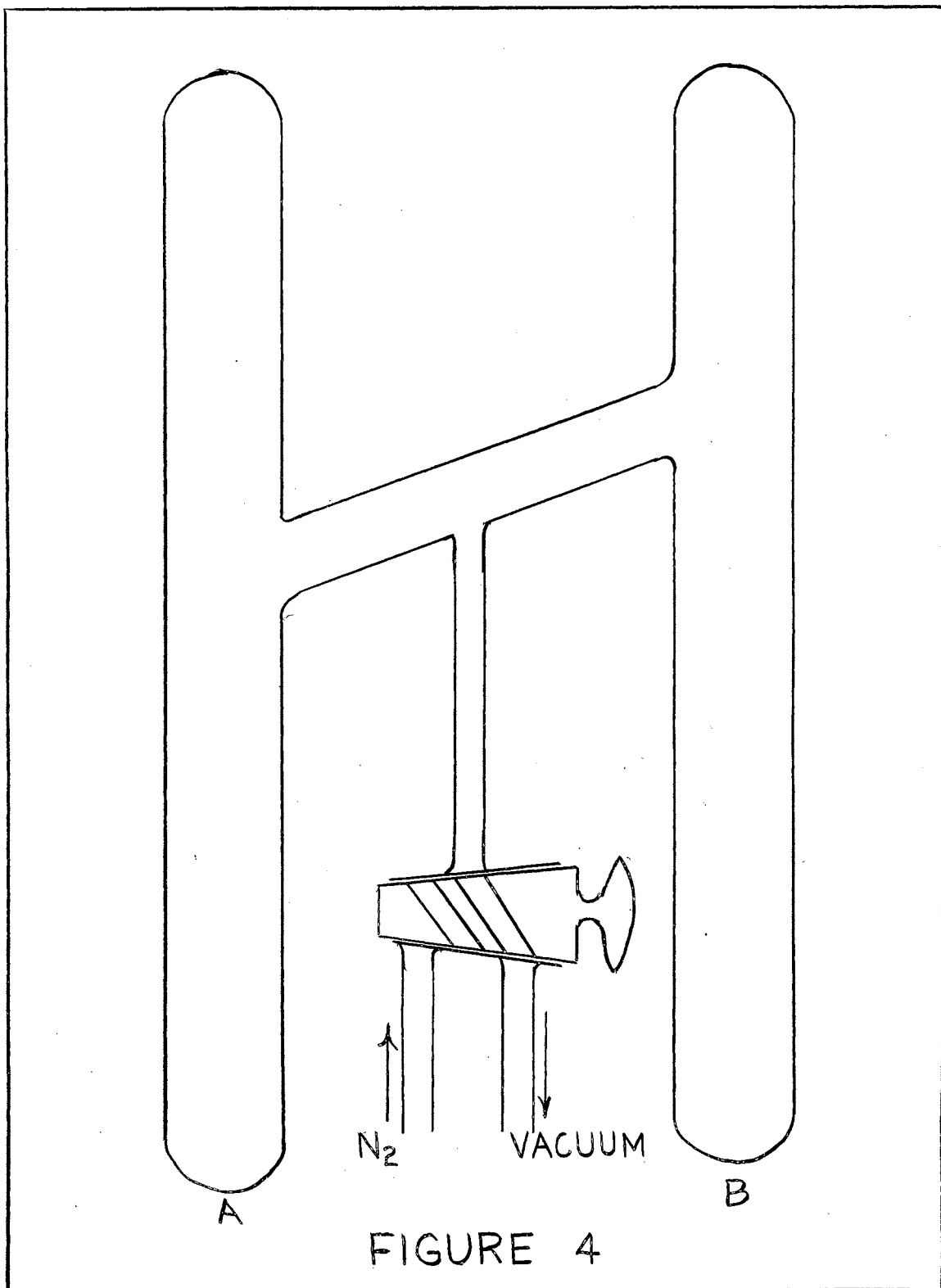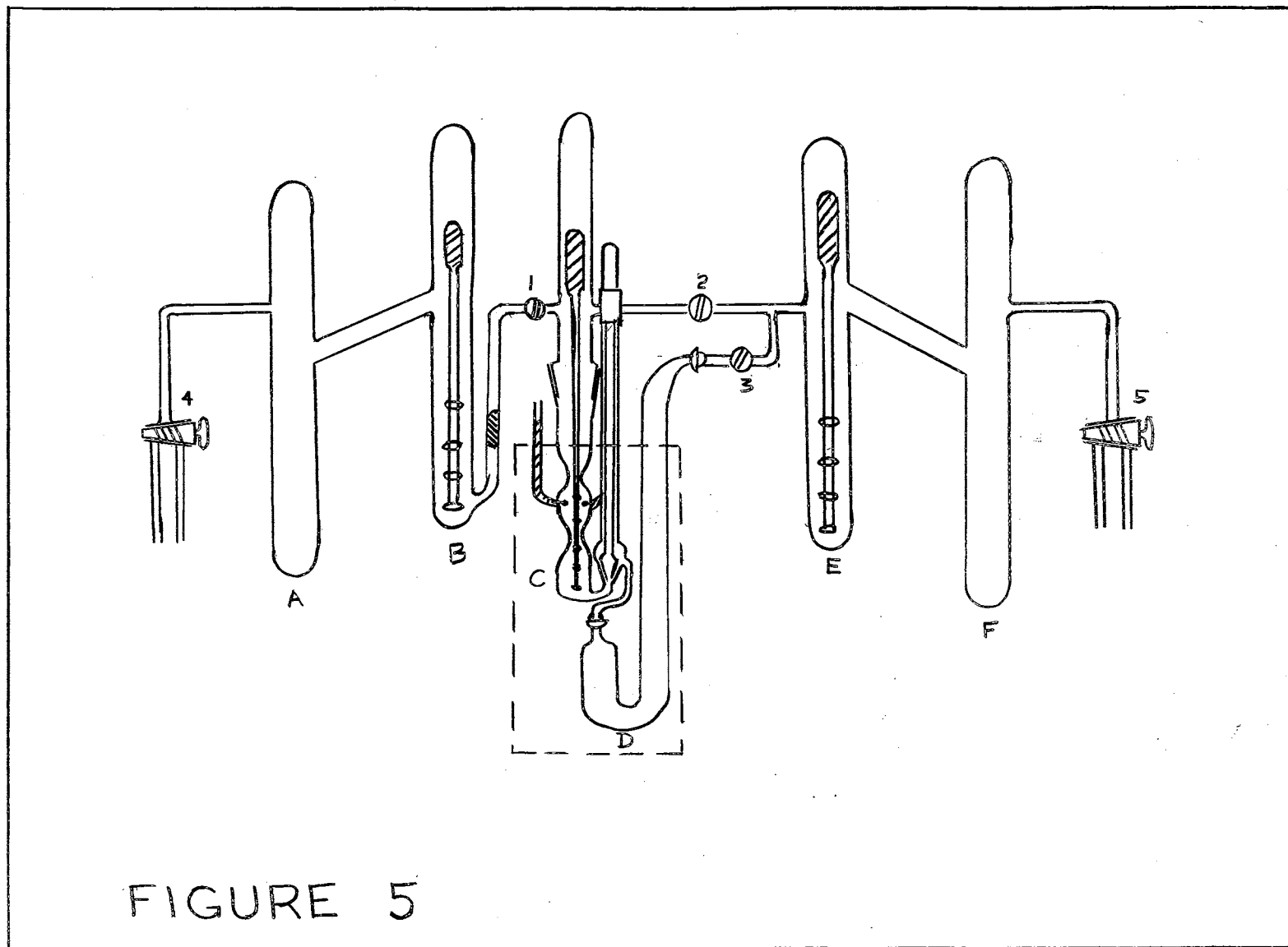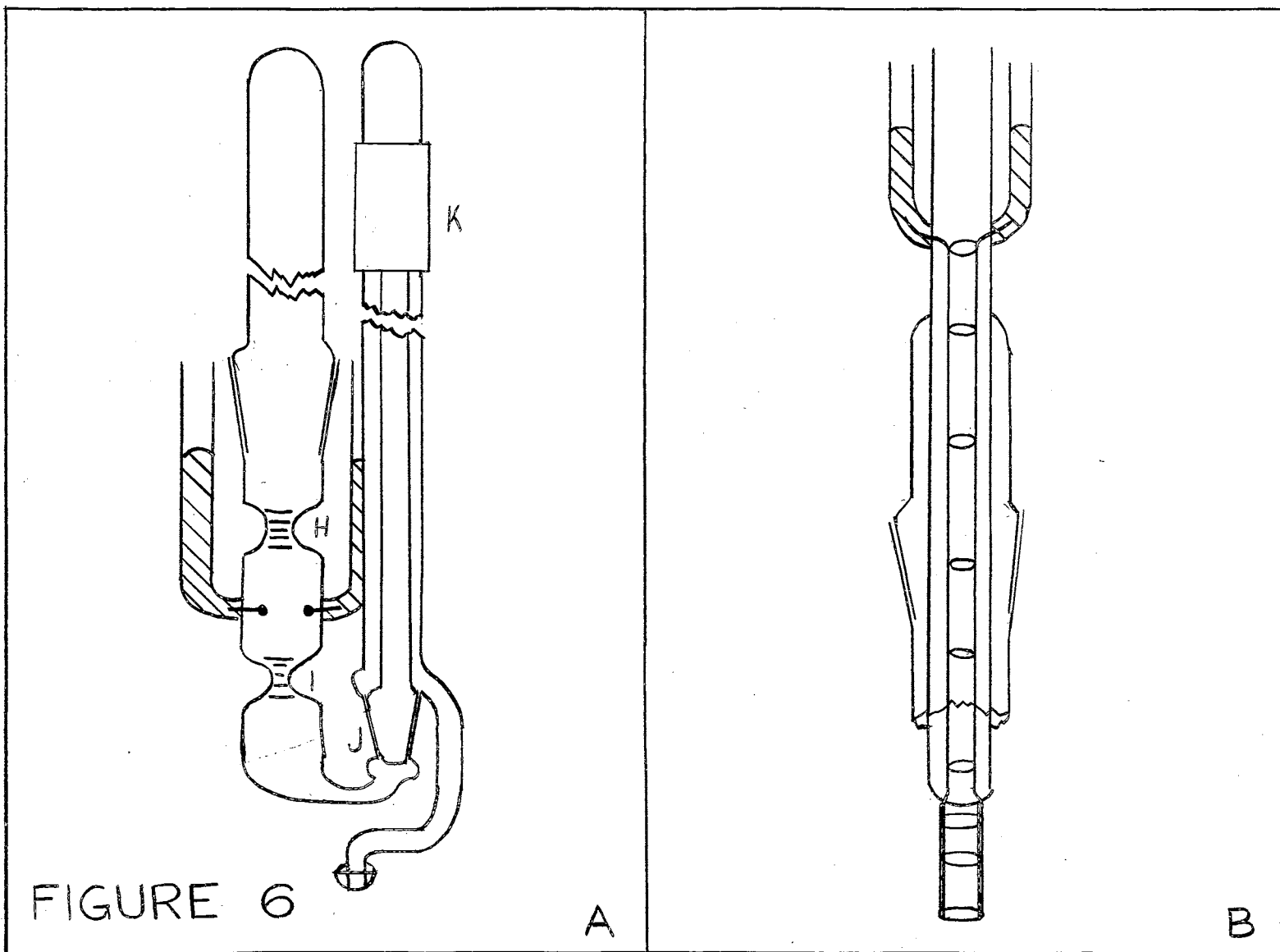
joint and was opened and closed manually through a short piece of _Tygon_ tubing.

The apparatus which was found to be successful in the measurement of the conductivity of 1,2-dimethoxyethane with sodium potassium alloy is shown in Fig. 7. Tube (C) could be removed and replaced with a vacuum line at (L). Vacuum and nitrogen lines were connected to the system at (I) through a three way solid stopper stopcock. A manometer similar to that shown in Fig. 3b was connected to (J). A low temperature toluene thermometer was attached at (D) so that the bulb reached into the solution at (P). The lower portion of (B) was made from a 50 ml. erlenmeyer flask. Plungers were placed in (A) and (B) with capsules of alloy sealed to the lower end. These plungers could be raised and dropped by means of pieces of iron sealed into the tops of the plungers and moved with an _Alnico_ magnet. The cell fitted in (Q) is shown in detail in Fig. 6b. A loose glass wool plug was placed in the apparatus at (K) to prevent splattering from (A) to (B).

The cells used in this study are shown in Fig. 6. The electrodes of the cell shown in Fig. 6a consist of two platinum spheres about 3 mm. in diameter. The electrodes were placed 20 mm. apart. The cell constant for this cell was 3.8 cm.$^{-1}$. The electrodes of the cell shown in Fig. 6b were constructed from platinum strips 10 mm. x 30 mm. separated about 3 mm. by soft glass spacers. The leads from the electrodes were fine platinum wires sealed through _Pyrex_ glass and separated by soft glass spacers. The leads were connected to the bridge through mercury wells in the upper portion of the cell. The tube containing the leads was filled with beeswax to prevent the condensation of water on the leads

FIGURE 7
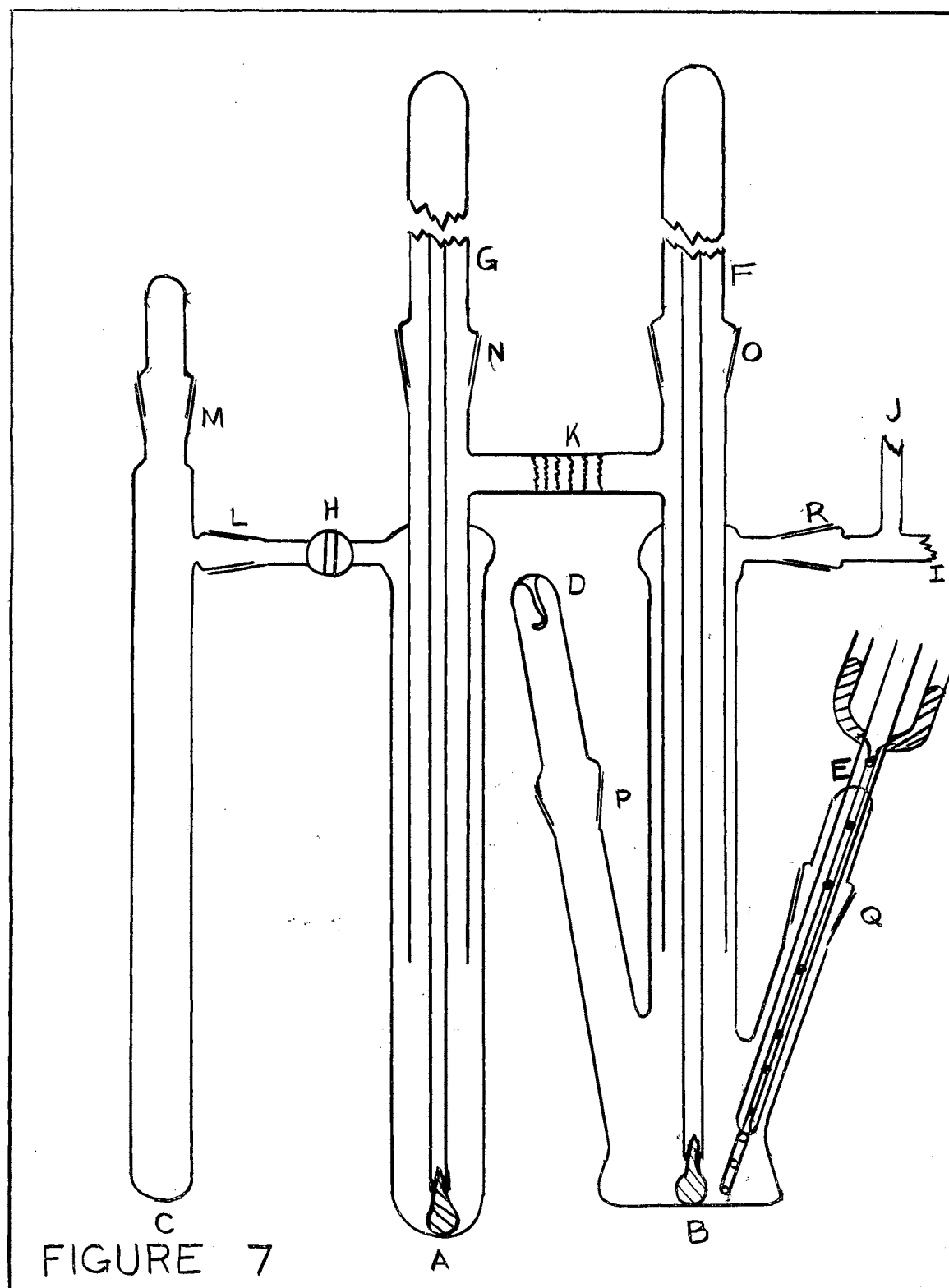
and in the tube at low temperatures. The cell constant of this cell was 0.07 cm.$^{-1}$. The electrodes were plated with platinum black before use in the usual manner. The cell constant was determined by measuring the conductivity of standard potassium chloride solutions at room temperature.

The conductance bridge was a conventional Wheatstone bridge constructed from decade resistance boxes. The resistance of the boxes ranged from 0.1 ohm to 100,000 ohms. The A.C. source for the bridge was a Hewlett-Packard audio oscillator model 200A adjusted to produce a 1000 cycle signal. The signal was amplified by a 1000 cycle audio amplifier described by Luder[6].

Experiments and Observations.-- An attempt to prepare the blue solution under simple conditions consisted of stirring 250 ml. of freshly distilled 1,2-dimethoxyethane with 4 g. of sodium metal and 12 g. of potassium metal in a creased flask with an air driven stirrer at 2000 rpm. Soon after stirring was begun the metals formed a liquid alloy which closely resembled mercury in appearance but had a density of only slightly more than the 1,2-dimethoxyethane. Stirring was continued for two hours. During this time no blue color was observed. A reaction occurred in the flask leaving a dense grey precipitate.

The same experiment was repeated using 1,2-dimethoxyethane purified as described in the previous section. An inert atmosphere of nitrogen dried by calcium chloride was maintained by using the apparatus shown in Fig. 2. The nitrogen flow around the stirrer shaft prevented the diffusion of air into the flask. An electric stirrer operating at 5000 rpm. was used. After a few minutes of stirring a blue color appeared. The intensity of the color varied with the rate of stirring. A higher rate of stirring gave a deeper color unless splashing occurred. If splashing occurred the blue

color was destroyed immediately. When the rate of stirring was adjusted for the deepest color and the flow of nitrogen increased to such a rate as to cause the liquid to splash the color was destroyed. When stirring was stopped the blue color persisted for several minutes. Fading began at the top of the solution. The color in the lower regions of the solution was stable for several hours without stirring. Several unsuccessful attempts were made to siphon or pipette the solution from the reaction flask. Even when the apparatus used was very carefully dried in an oven the solution could not be transferred without destroying the color.

The apparatus shown in Fig. 3a was devised to further purify the solvent and conduct stirring experiments under a more inert atmosphere. After the system was dried and filled with nitrogen stopcocks (1) and (2) were closed and flasks (W) and (X) removed. Three grams of freshly cut chips of sodium metal was placed in each flask. Two hundred milliliters of 1,2-dimethoxyethane was transferred to flask (W). The flasks were replaced, (W) was cooled to $-75°$, stopcocks (1) and (2) were opened and the system cleaned and dried again. The system was evacuated and stopcocks (3), (4), and (6) closed. The cold bath was moved from flask (W) to flask (X). As (W) warmed the 1,2-dimethoxyethane slowly distilled from (W) to (X). Gases evolved by the reaction between the sodium metal and impurities in the solvent were removed by pumping on the system at intervals. When the distillation was complete flask (X) was allowed to warm to room temperature to permit the sodium to react with impurities. The 1,2-dimethoxyethane was then distilled in the same manner into flask (Y). The system was then filled with nitrogen to a pressure slightly greater than atmospheric pressure. The nitrogen pressure prevented the

influx of air when the system was opened as was necessary for the stirring experiments. Three milliliters of sodium-potassium alloy was pipetted into the system through joint (I). Cap (B) was removed and the stirrer placed in position and started. The cold bath was then removed. No color developed until the alloy melted at -12°. At that temperature a beautiful deep blue color formed. This solution had the same characteristics with relation to stirring as the previously prepared solutions. The color however was more intense and the precipitate formed in the earlier experiments did not develop until the lapse of a greater time. When stirring was stopped the color did not fade as rapidly. It was found that high speed stirring was not required for the formation of the blue color. All attempts to transfer the solution were unsuccessful. The solvent could be forced through the filter and into tube (Z). However, regardless of the steps taken to dry the transfer tube by flaming and subjecting the tube to infrared rays for several hours, the blue color always faded before it moved more than a few centimeters up the tube.

A sealed tube containing sodium-potassium alloy and purified 1,2-dimethoxyethane was prepared by attaching tube (V) shown in Fig. 3d, which contained 2 ml. of alloy, to (C) in place of flask (Y). Purified 1,2-dimethoxyethane was distilled into the tube, which was then sealed off under a vacuum. Fifteen minutes of vigorous shaking at room temperature caused the formation of a blue solution in this tube. The color could be retained indefinitely by slight agitation of the tube. When the color faded it could be made to return by a few seconds of shaking. Cooling the tube at -50° after the color had been formed at room temperature caused the blue solution to be stable indefinitely. The tube retained

these characteristics for more than thirty days after its preparation. After several months the alloy became solid. The melting point of the metal was found to be 97°, which indicated that it was practically pure sodium (m.p. 97.5^{o}).

Tubes in which the components were of high purity were prepared by using the apparatus shown in Fig. 4. Thirty-five milliliters of 1,2-dimethoxyethane and 2 g. of sodium were placed in side (A). A capsule of alloy and a clean iron rod were placed in side (B). The solvent in (A) was cooled to -75°. The apparatus was sealed and dried. The solvent was then distilled to (B) and back to (A). 1,2-Dimethoxyethane forms a binary azeotrope containing about 10% water by weight. Any water in (B) would be carried back into (A) with the solvent to react with the sodium. The solvent was distilled back to (B). A small portion was then distilled back into (A). The capsule was broken and the iron rod moved out of (B). The tube was then sealed off. The tube was allowed to reach room temperature and was vigorously shaken. After only a few seconds of shaking a deep blue color was formed. The colored solution was cooled to -75° and held at that temperature for several hours. No change in the appearance was observed. The tube was then warmed to room temperature and held without shaking for 12 hours. The color faded slightly during this period. Only slight agitation was required to revive the original color. As the tube aged the grey precipitate, which was not evident for the first few hours, became more dense and the color more difficult to revive.

This series of experiments initiated the belief that since the stability of the blue color depended largely on high purity and low temperature an apparatus which could maintain these conditions would make

possible the transfer and dilution of the solution. The apparatus shown in Fig. 5 was designed to meet these requirements. Sections (AB) and (EF) were built to function in approximately the same manner as the apparatus shown in Fig. 4. The solution was prepared in (B) and forced through a glass wool filter, (G), and into the conductivity cell. The volume of the original solution could be measured by the calibrations at (H). (See Fig. 6a.) The concentration could be varied by draining the cell through valve (J) to the calibrations at (I) and refilled to (H) by distilling pure solvent from the blue solution in (E). After the desired measurements had been made the contents of the cell could be washed into tube (D). The solvent was then distilled back into (E). The solid residue was to be dissolved in water and analyzed for sodium and potassium. This experiment failed because of the difficulty in retaining the blue color when the solution was transferred from (B) into the cell. The blue color always faded before it reached stopcock (1).

The apparatus was modified so that the solution could be drawn directly into the cell which was connected very close to the tube in which the blue solution was prepared. The cell had characteristics similar to the cell shown in Fig. 6a. The conductance was found to be far too low to be measured with a conductivity cell of this type. Further modification of the apparatus did not improve the measurements. In most cases the large surface of the cell required to house large electrodes also harbored impurities which made the preparation of a stable blue color impossible. Qualitative observations made during these experiments showed that iron oxide or a trace of air inhibits the formation of the blue solution.

The apparatus in which successful conductance measurements were made is shown in Fig. 7. The solvent was purified by distillation from sodium-potassium alloy in flask (C) through the trap in (A), which was held at -10°, into (B), which was held at -75°, with (J) connected to the vacuum line. The liquid trapped in (A) was distilled into a vacuum line attached to (L) after (C) had been removed. The conductance of the pure solvent was measured. The solvent was then distilled back to (A) and the capsule of alloy in that tube broken. The solvent was distilled back and forth from (A) to (B) until the conductance measurements indicated high purity. The conductance of the solvent was then measured as a function of temperature. The capsule in side (B) was broken and the blue solution prepared by stirring with the plunger at a temperature just above the melting point of the alloy. Three types of experiments were performed using the blue solution prepared in this manner.

The conductance was first measured as a function of temperature. The blue solution was cooled to -75° and allowed to stand for several minutes to insure an even temperature throughout the cell before a conductance measurement was made. Other readings were made with the cell in progressively warmer baths. Time was allowed for temperature equilibrium to be reached before measuring the conductivity. The results of these measurements are plotted in Fig. 8. The conductivity of the solvent is somewhat higher than the best values for the pure solvent. This caused the conductivity of the blue solution to be higher than the values obtained in other experiments. The conductivity of the conductor associated with the blue color was obtained by subtracting the conductivity of the solvent from the conductivity of the blue solution. In this and other conductance experiments

Figure 8

○ Solvent

◐ Blue Solution

● Blue Solution
Corrected for
Solvent

Conductance in ohm.$^{-1}$ cm.$^{-1}$ x 10^7

Temperature in Degrees Centigrade
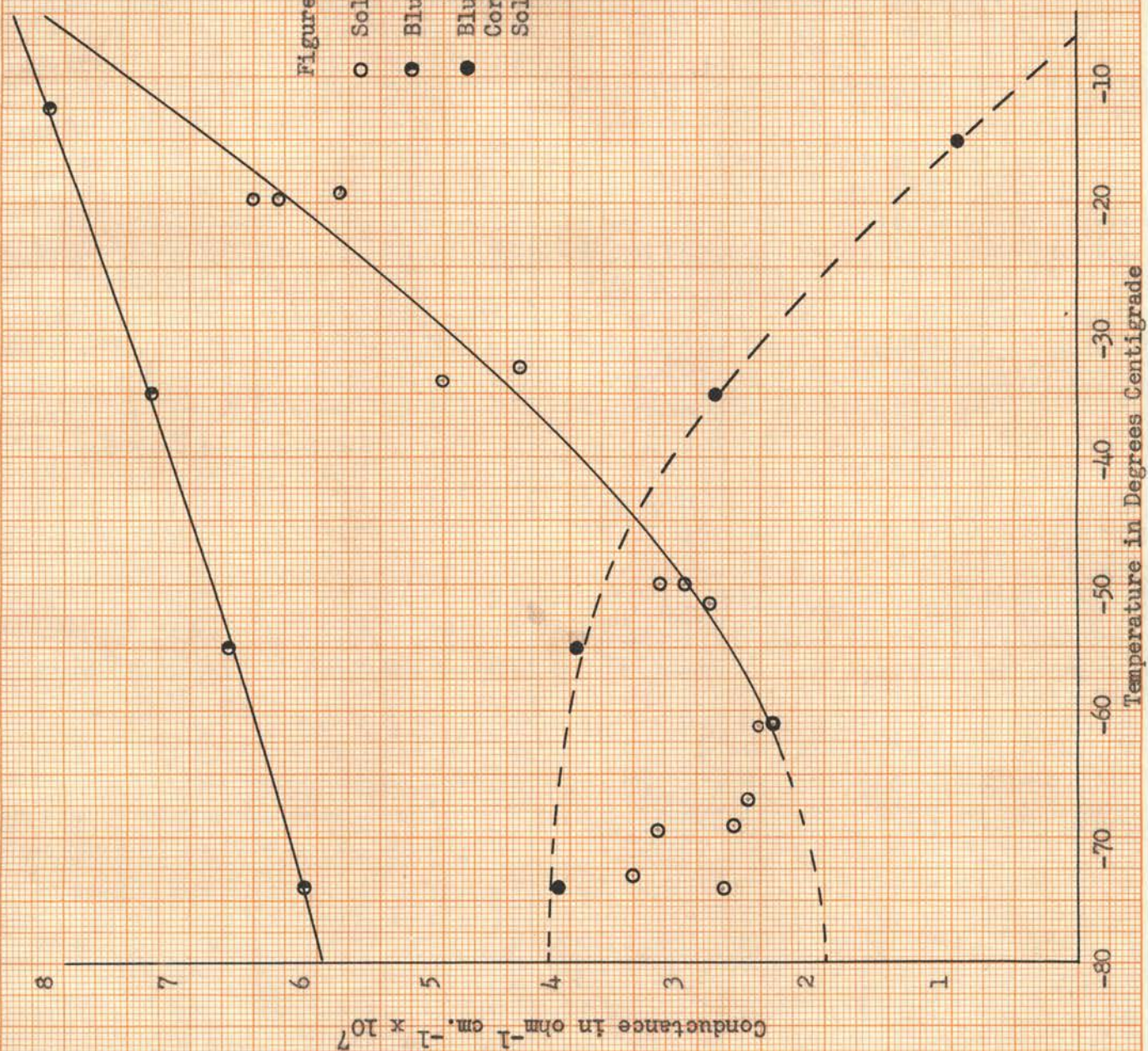
the fact that the conductance of the solution is not dependent on the blue color alone was observed.

While making the measurements described in the preceeding paragraph it was noted that the conductance apparently passed through a maximum value as the cell was warmed. Studies were made in which the blue solution, prepared at the melting point of the alloy, was quickly cooled to -75°, then allowed to warm slowly. The conductance was measured as a function of the time elapsing after removal of the cold bath. In these experiments the cell was warmed from -75° with a bath at -10°. The equilibrium temperature reached by the bath was about -35°. The data obtained from this experiment are plotted in Fig. 9. The data plotted have been corrected for the contribution to the conductance made by the pure solvent. This correction amounted at most to 0.8×10^{-7} ohm $^{-1}$ cm.$^{-1}$

In the last experiment performed using this apparatus the blue solution was formed in the usual manner at about -10°. The temperature was allowed to increase to about 10° and the conductivity measured. The temperature was then quickly lowered to -75° and the conductivity measured. The solution was then allowed to warm to about 10° and the conductivity measured. The solution was then cooled to about -10°, the blue color reformed by stirring, and allowed to quickly cool to -75° where the conductivity was again measured. This last sequence of operations was repeated several times as shown by the tabulation of data given in Table I.

Figure 9
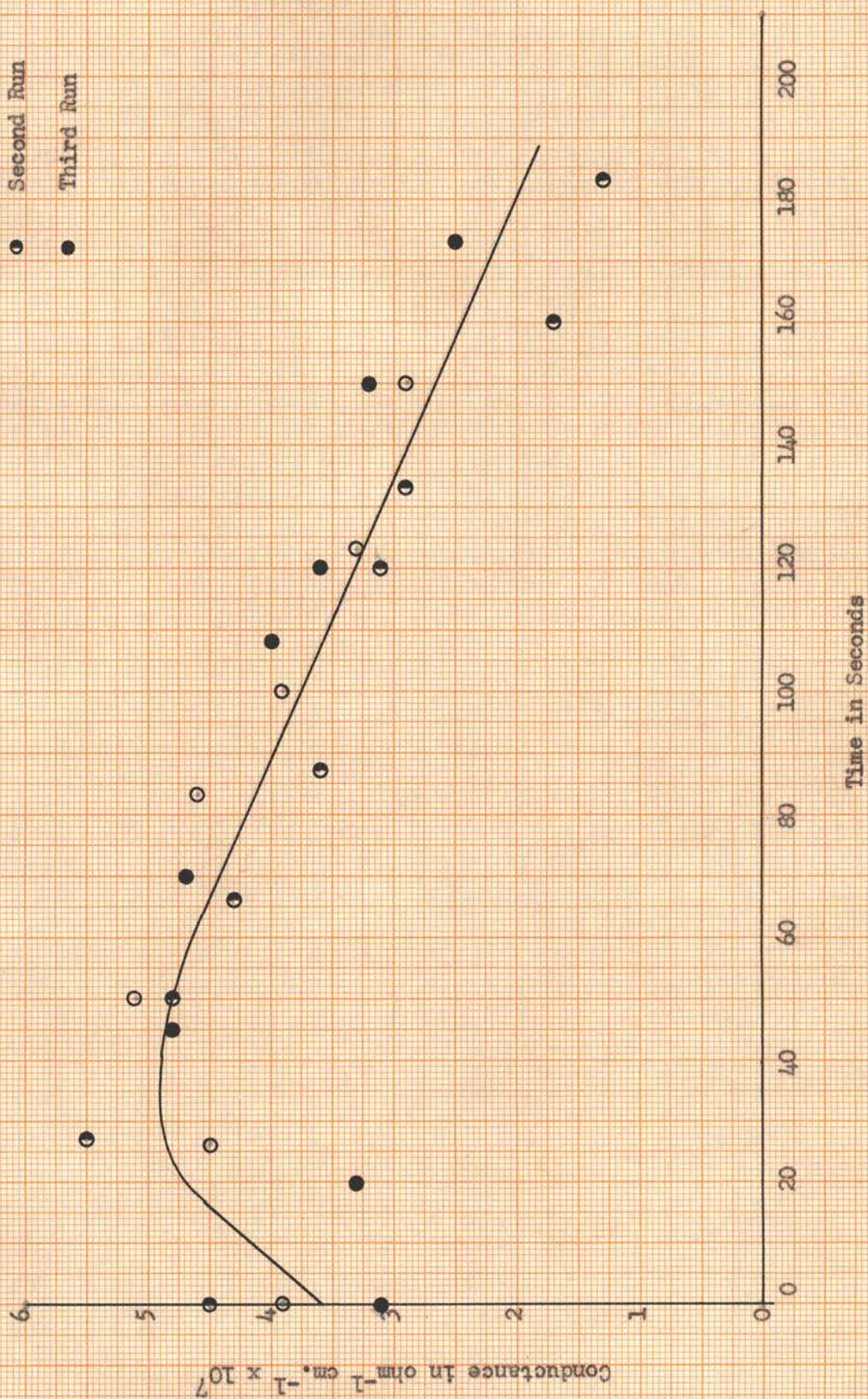
○ First Run
◐ Second Run
● Third Run

Conductance in ohm.⁻¹ cm.⁻¹ x 10⁷

Time in Seconds

22

TABLE I

CONDUCTIVITIES OF THE BLUE SOLUTION

Time,[a] min.	Temp., $^{\circ}$C.	Cond. $\times 10^7$, $ohm^{-1}cm.^{-1}$
0	-23	1.9[b]
2	-23	2.7[b]
5	-23	2.9[b]
20	18	7.1
20[c]	-75.5	12.3
40	15	7.5
40	-75	18.0
80	10.6	8.8
80	-75	21.0
90	10	8.8
90	-75	25.0
100	11	8.4
100	-75	22.0
110	-76	23.0
120	-50	16.6
130	11	9.3
130	-74	19.2
145	-50	17.0
600[d]	-76.5	13.6, 14.7
600	19	6.4
600	-75	16.0

[a] Time was measured from the time the capsule of alloy was broken.

[b] Blue color was not present. The conductivity of the pure solvent at 0° was 0.8×10^{-7} $ohm^{-1}cm.^{-1}$

[c] One to two minutes was required in each case to cool the cell to -75° from the high temperature.

[d] The blue solution was left over night in the -75° bath.

A small amount of air free water vapor was allowed to enter the blue solution at -75° after these data were obtained. The blue color disappeared but the conductivity did not change appreciably. It was no longer possible to reform the blue color in this solution. The conductivity of this solution when heated and cooled closely paralleled that found for the solution in which the blue could be reformed.

IV. THEORETICAL DISCUSSION

Any mechanism proposed to explain the formation and destruction of the blue color and the conducting characteristics of the system of sodium, potassium, and 1,2-dimethoxyethane must be in agreement with the eleven observations listed below.

1. The metal involved in the reaction is potassium.

2. One of the products of the reaction is a white insoluble material.

3. The reacting quantities are very small. The color producing product must be capable of forming an intense blue color at low concentration.

4. The color is formed at the surface of the alloy and seems to diffuse slowly away from the surface when there is no stirring.

5. The intensity of the color is increased by rapid stirring, however, stirring is not necessary to produce the blue color.

6. The blue color is not formed below the melting point of the alloy.

7. The blue color is stable at low temperatures.

8. The conductance of the solution, which is very low, is not dependent on the color.

9. The conductance of the solution after the blue color has been formed never returns to that of the pure solvent.

10. Slight impurities tend to make the blue color far less stable, but do not appreciably effect the conducting characteristics of the solution.

11. The conductance of the solution is greater at -75° than at 0°. As the solution is warmed from -75° the conductance rises to a maximum at about -50°, then drops.

<u>Mechanism of the Reaction</u>. --- The experimental evidence obtained in the present study is not sufficient to unambigously establish a mechanism for the reaction between sodium-potassium alloy and 1,2-dimethoxyethane but is adequate to make the following mechanism highly probably:

$$K + R:R' \longrightarrow K^+ + R:^- + \cdot R' \qquad (1)$$

$$\cdot R' + CH_3OCH_2CH_2OCH_3 \longrightarrow HR' + \cdot CH_2OCH_2CH_2OCH_3 \qquad (2)$$

where R:R' represents a molecule of the 1,2-dimethoxyethane.

The first step (1) in the reaction is a splitting of the ether into an alkoxide ion, either $CH_3OCH_2CH_2O^-$ or CH_3O^-, and a free radical, either $\cdot CH_3$ or $\cdot CH_2CH_2OCH_3$.

The second step (2) in the proposed mechanism is the dehydrogenation of a molecule of the solvent by the free radical produced in the first step. The resulting solvent free radical is postulated to be the molecular species which gives the solution the blue color.

The electrical conductance of the resulting solution is due to the potassium and alkoxide ions produced in the first step of the mechanism.

The potassium alkoxide is only very sparingly soluble in the solvent and consequently will precipitate from the solution. Thus the solution will become saturated almost immediately after the reaction begins.

The molecule HR' produced in the second step will be either methane or methyl ethyl ether. Methane would be expected to be slightly soluble in the solvent and at sufficiently high temperatures and concentrations might be evolved. The methyl ethyl ether would most likely be completely miscible with the solvent.

<u>The Initial Reaction</u>. --- The first step of the proposed mechanism involves the oxidation of the potassium atom and consequently the reduction of the solvent molecule. Thus the solvent molecule must, if the potassium

is to be oxidized, be made to accommodate an extra electron. It seems reasonable to suppose that a solvent molecule with an extra electron will be unstable and decompose into parts which are more stable. It is postulated that the parts are either $(CH_3OCH_2CH_2O:)^-$ and $\cdot CH_3$ or $CH_3OCH_2CH_2\cdot$ and $(:OCH_3)^-$. The possibility of a split into $CH_3OCH_2\cdot$ and $(:CH_2OCH_3)^-$ appears unlikely in view of the instability of both parts. The known reactions of ethers support the proposed split into an alkoxide ion and a free radical. In addition it would be expected that the potassium atom would be most strongly attracted by the most electrophylic part of the molecule-- i.e. the oxygen.

The stability of the potassium-solvent complex, which must be considered to have at least a transient existence in this reaction, can not be decided from the experimental data of this study, but is not critical to the discussion. It is suggested that the known usefulness of this solvent in the metallation of such compounds as napthalene may be evidence that this complex is relatively stable.

The Blue Color.--- The blue color producing molecular species is postulated as being a free radical produced by the reaction of the free radical formed in the first step with a solvent molecule. The color of this free radical may be due to the possibility of a "resonance" of an electron between the following positions:
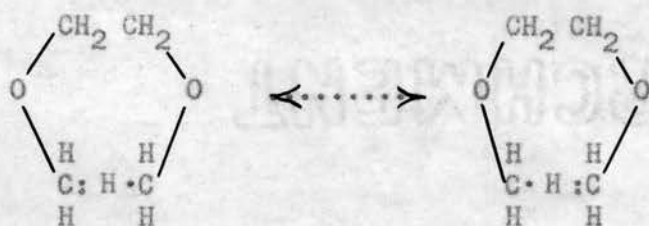
The energy of these two structures is equal. There are three exactly equi-
valent hydrogen atoms on the methyl group which might participate in this
resonance. The known ease by which free radicals remove hydrogen atoms
from other molecules (activation energy about 10 Kcal.) and the proximity
of the other end of the moelcule in this compound makes such a reaction
likely. The fact that the blue color is not found for either the dimethoxy-
methane or the 1-methoxy-2-ethoxyethane, where this particular structure is
impossible, is significant.

The resonance possible in this molecule would suggest that it may be
reasonably stable even though it is a free radical. In a highly purified
solvent the most likely molecules which such a free radical would contact
would be other solvent molecules in which case reaction would result in the
reformation of the solvent free radical.

The need for high purity in the solvent for the stability of the blue
color is obvious in view of the nature of the blue color producing free
radical. Oxygen, water, carbon dioxide, etc. are well known as free
radical destroyers.

Since the rate of formation of the solvent free radical depends upon
the rate of formation of the intermediate (unstable) free radical, which in
turn depends upon the rate of the initial reaction, anything which will
increase the rate of the initial step will tend to increase the concentration
of the solvent free radical, and therefore the intensity of the blue color.
Since this initial step is a heterogenous reaction the rate will be propor-
tional to the extent of the alloy-solution interface. High speed stirring
will therefore cause the blue color to become more intense, unless such
stirring increases the rate of destruction of the solvent free radical by
increasing the contamination of the solvent.

The difficulty of forming the blue color when the alloy is frozen may be explained by the slow rate which potassium will diffuse to the surface of the crystalline solid alloy. Once the surface concentration is exhausted additional potassium must be moved up by the slow process of diffusion in the solid. It may also be that the energy required to remove an atom of potassium from the solid lattice is excessive for the reaction.

The stability of the blue color at low temperatures is understandable in view of the general slowing down of all chemical reactions when the temperature is lowered-- which is especially marked when the activation energy is low-- as is obviously true in reactions involving free radicals.

The Conductance of the Solution. --- A discussion of the conductance of this solution is simply a description of the behavior expected of a very dilute solution of a "strong" electrolyte in a medium of low dielectric constant.

It is well known that the alkali metal alkoxides are salt like substances, which when dissolved in a medium of high dielectric constant are strong electrolytes, i.e. may be considered as completely dissociated into ions. Thus a solution of sodium methoxide in methanol has properties exactly analogous to a solution of sodium hydroxide in water. The ions $CH_3OCH_2CH_2O^-$ or CH_3O^- would be expected to form similar substances with potassium ions.

In a medium of low dielectric constant such salts associate to form ion pairs, which have many of the properties of a weak electrolyte. As the dielectric constant of the medium is decreased the "association constant" for the association of the ions into neutral ion pairs increases. The relation between dielectric constant and this "association constant" has been calculated by Fuoss and Kraus[7]. It is found that as the dielectric constant is decreased a critical value is reached below which association

increases very rapidly at first. This rapid in-

crease in association fall off, but increases

rapidly as the dielectric constant reaches very

low values. The curve in Fig. 10[8] shows the

logarithm of the <u>dissociation</u> constant as a

function of the logarithm of the dielectric

constant for tetraisoamylammonium nitrate in

dioxane-water mixtures. This figure shows

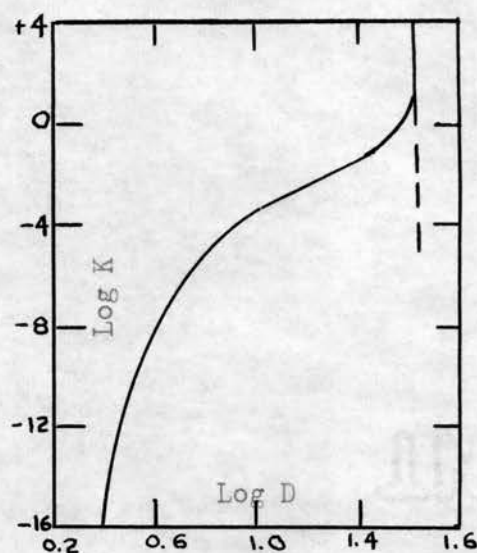that a 1% increase in the dielectric constant

Figure 10

in the region of about 2.4*causes about a 600% increase in the dissociation

constant.

Since both the dielectric constant and the viscosity are important in

determining the actual conductance of a solution, it is necessary to recall

the manner in which the equivalent ionic conductance varies with the

viscosity. It is well known that the product of the conductance and the

viscosity is approximately equal to a constant. For example, for the

potassium ion this product is equal to about 0.2 in a variety of solvents

(methanol, ethanol, acetone, etc.) This is known as Walden's rule. Thus

lowering the temperature (i.e. increasing the viscosity) results in a

decrease in the equivalent ionic conductance.

Since lowering the temperature increases the dielectric constant for

most solvents and also increases the viscosity there are two opposing

factors operating in determining the conductance of the solution with a

change in temperature. The increase in the dielectric constant tends to

increase the number of ions. The increase in the viscosity tends to decrease

the equivalent conductance. It is thus possible in a solution, in which

* Log 2.4 = 0.38

association into ion pairs occurs, for the conductance to actually increase as the temperature is lowered. It is also possible for the conductance to pass through a maximum. Both of these phenomenon have been found in this study.

Unfortunately this explanation may not be rigorously tested because of the lack of data on the exact magnitude of the dielectric constant and the viscosity. Judging from the dielectric constants of similar compounds, it is probable that the dielectric constant is low. There was neither time nor apparatus available to make these measurements for this study.

There are other factors which may be of secondary significance in determining the conductance data observed. One of these might be the time factor in reaching equilibrium of the ions and ion pairs as the temperature is changed.

V. SUMMARY

The blue solution produced when sodium-potassium alloy and 1,2-dimethoxyethane are mixed has been investigated with reference to the conditions related to its formation and stability.

The electrical conductance of the solution has been measured as a function of temperature and of time. It has been shown that the conductance, which is very low, is not directly related to the blue color. The conductance is greater at low temperatures than at normal temperatures and has a maximum value at about -50°. The conductance at a particular temperature does not vary with time.

A mechanism has been proposed involving the reaction of potassium metal with the solvent to produce potassium ions, alkoxide ions, and free radicals. The free radicals react with solvent molecules to produce free radicals which are stabilized by a resonating ring structure. The blue color is attributed to this solvent free radical.

The conductance data is explained by an hypothesis based on the formation of ion pairs in a solvent of low dielectric constant.

BIBLIOGRAPHY

(1) Beckmann, E., and Paul, T., Ann. 266, 1 (1891)

(2) Schlenk, W., and Weickel, T., Ber. 44, 1182 (1911)

(3) Wiliamson, B., Private communication.

(4) Morton, A. A., and Knott, D. M., Ind. and Eng. Chem. 13,
        649, (1921)

(5) Gibson, G. E., and Phipps, T. E., J. Am. Chem. Soc. 48,
        312 (1926)

(6) Luder, W. F., J. Am. Chem. Soc. 62, 89 (1940)

(7) Fuoss, R. M., and Kraus, C. A., J. Am. Chem. Soc. 55,
        1019 (1933)

(8) Harned, H. S., and Owen, B. B., The Physical Chemistry of
        Electrolytic Solutions, Reinhold Publishing Co., New
        York, 1943, P. 192

BIOGRAPHY

Larry Allen Grundy was born in Memphis, Texas, on May 14, 1926. He lived in Memphis until his graduation from Memphis High School in May, 1943. He entered The North Texas Agricultural College, Arlington, Texas, immediately after graduation from high school. He left this college to join the U. S. Navy in May, 1944. He attended U. S. Naval Electronic Schools at Texas A. and M. College, College Station, Texas, Ward Island, Corpus Christi, Texas, and Tounge Point, Astoria, Oregon. He successfully completed the last of these courses in September, 1946. He entered Baylor University, Waco, Texas, in September, 1946. He received the degree of Bachelor of Science in Chemistry in August, 1949.

On September 18, 1948, he married Mary Alyce Thompson of Palestine, Texas.

While an undergraduate at Baylor University he was a member of the Baylor Chapter of the Student Affiliates of the American Chemical Society. He is now a member of this society.

He entered Oklahoma A. and M. College, Stillwater, Oklahoma in September, 1949 as a Graduate Fellow. On completion of his course work in August, 1950, he was employed by Clarendon Public Schools and Junior College, Clarendon, Texas.

THESIS TITLE: STUDIES OF THE REACTION OF SODIUM-POTASSIUM
                ALLOY WITH 1,2-DIMETHOXYETHANE

NAME OF AUTHOR: LARRY A. GRUNDY

THESIS ADVISER: FRANK JOHNSON

The content and form have been checked and approved by the
author and thesis adviser. "Instructions for Typing and
Arranging the Thesis" are available in the Graduate School
office. Changes or corrections in the thesis are not made
by the Graduate School office or by any committee. The
copies are sent to the bindery just as they are approved
by the author and faculty adviser.

NAME OF TYPIST: MRS. J. O. RICHARDSON