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SOLUTIONS OF METALS IN NON-METALLIC SOLVENTS; IV.[1] MATERIAL EFFECTS ACCOMPANYING THE PASSAGE OF AN ELECTRICAL CURRENT THROUGH SOLUTIONS OF METALS IN LIQUID AMMONIA. MIGRATION EXPERIMENTS.

BY CHARLES A. KRAUS.

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Introduction.

As was pointed out in the first paper, the passage of electricity through metals is accompanied by no material processes, in which respect metallic conductors are distinguished from electrolytic conductors. Nevertheless, the hypothesis that in metals, as well as in electrolytes, the conduction process is essentially an ionic one has rapidly been gaining favor, particularly among physicists. Indeed, this hypothesis is unavoidable so long as we postulate a discrete structure of electricity. Of course, we may assume that conduction consists in the motion of a continuous medium, but this assumption lacks experimental foundation.

The present investigation is concerned with the question as to whether or not a transport of matter accompanies the current through solutions of the elementary metals in ammonia. This question has been touched upon by several observers. Cady[2] made observations indicating that

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[1] Previous papers of this series have appeared as follows: "I. General Properties of Solutions of Metals in Liquid Ammonia," THIS JOURNAL, **29**, 1557–1571 (1907); "II. On the Formation of Compounds between Metals and Ammonia," *Ibid.*, **30**, 653–668 (1908); "III. The Apparent Molecular Weight of Sodium Dissolved in Liquid Ammonia," *Ibid.*, **30**, 1197 (1908).

[2] *J. Phys. Chem.*, **1**, 707 (1897).

in concentrated solutions no material effects are visible even for large currents, while in dilute solutions, which are transparent, the metal seems to concentrate at the cathode. Neither of these experiments is conclusive, inasmuch as the effect in dilute solutions may be ascribed to the presence of metal amide or some other metal salt, while in concentrated solution soluble electrode products are not necessarily excluded. Ascoli,[1] working on the problem of electrical endosmosis, observed that ammonia moves against the current through a plug of alumina but that the direction is reversed if a little sodium be added. This observation is not directly related to the question which we have under consideration.

Migration Experiments in Sodium Solutions.

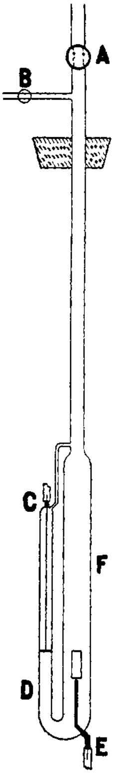

Fig. 1.—Apparatus employed in carrying out electrolyses in sodium solutions.

In order to determine whether the conduction process in metals is an ionic one, it is necessary to determine whether or not the current is accompanied by a transport of matter.

This is best done by observing the migration phenomenon in solutions containing only the metals themselves. Of course, quantitative transference experiments might have been carried out, but the apparatus necessary for such experiments with the solutions in question would have proved very costly, so that it did not seem advisable to adopt this method if the same end could be attained by other means. The phenomena accompanying the current were therefore studied qualitatively. These solutions are peculiarly adapted to a study of this kind. They possess a very characteristic color which makes it possible to observe concentration changes in solutions as dilute as 1/40000 normal. Such a study is interesting in itself, since no other solutions can be observed visually at such great dilutions. Moreover, as we shall see, the electrode products are such as to introduce no disturbing factors.

Experiment 1.—After a number of preliminary experiments a cell was constructed of the form outlined in Fig. 1. The two arms of the cell *D F* were provided with platinum electrodes. The electrode *C*, in the smaller arm *D*, consisted of a circular disk which filled the tube almost completely. The other electrode *E* was cylindrical in form. The electrodes must not be made too small, otherwise the resistance becomes excessive, particularly at the anode, and the solution is heated unnecessarily. Evolution of hydrogen may also result, although this

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[1] *Compt. rend.*, 137 (1903).

disturbing factor may be largely eliminated by reducing the temperature.

After exhausting the tube thoroughly, pure ammonia vapor was introduced under an excess pressure of 25 centimeters. The cock *A* was opened an instant and a bit of metal was dropped into the cell. The metal which was introduced was contained in tubes of different diameters, depending on the amount of metal to be introduced. These tubes were filled by melting the metal *in vacuo* and forcing it into the tubes by a slight pressure of ammonia vapor. Since very dilute solutions were desired in this experiment, the containing tubes consisted of small capillaries. If the solution is under its own vapor pressure, it will boil as soon as a current is sent through the cell. It was necessary, therefore, to increase the pressure on the solution by introducing hydrogen. The hydrogen was generated by the action of ammonia on metallic potassium in ammonia solution, in the presence of platinum sponge.

On applying a potential of 110 volts, with *C* as cathode, the color about the anode at once began to grow less intense while the color of the solution in the smaller tube deepened perceptibly. The solution above the cathode did not change appreciably and served as a standard of reference in determining the color change in the tube below the electrode. At the end of half an hour the smaller tube was quite opaque while the electrode was plainly visible in the larger tube.

On reversing the current, gas was slowly evolved at the electrode *C* and, collecting below it, prevented observations. This difficulty was avoided by reducing the applied electromotive force to 30 volts. Almost immediately on making *C* anode, the liquid both above and below *C* became transparent and colorless, the colorless space being perhaps a few tenths of a millimeter wide. The electrode being a metal and a strong light being placed behind the cell, the electrode surface could be observed very minutely. An appreciable evolution of gas did not take place at the anode, nor did any solids precipitate on its surface. In fact, the only characteristic effect to be observed was the loss of color just mentioned.

Experiment 2.—The cell described above was not entirely adapted to the conditions imposed by the experiments. A second cell was therefore constructed as outlined in Fig. 2. The two arms *I J* were approximately 2 centimeters in diameter and were provided with the electrodes *G H*. At first platinum electrodes were employed, but these were later replaced by gold electrodes, which seemed to catalyze the reaction between ammonia and sodium less than platinum. The electrodes were about 1.5 centimeters square and were placed vertically in the tubes. The connecting tube *K* was made larger in order to reduce the resistance as much as possible. In order to prevent mixing, the tubes *I J* were slightly constricted at the bottom and light glass wool plugs were introduced. The method of introducing the metal was improved so as to exclude the possibility of oxide formation. The tube *J* was connected at the top with a three-way cock *A*. In the two opposite arms *ED*, and passing through the key of the cock, was introduced the capillary *B* containing the metal. The capillary was attached to a larger tube *C*. The tubes *E D* were sealed up and were connected through the third opening of the cock with the apparatus. When desired, the cock was turned through an angle of 90°, a bit of the capillary was broken off, and fell into the tube *J*. On returning the cock to its original position, the capillary could be again introduced into the key by gentle tapping. A potential of 110 volts was applied to the cell and a millanmeter was placed in the circuit. On passing the current through the solution, loss of metal at the anode was plainly observable by the decrease in the intensity of color. The contents of the anode portion were fairly well mixed, since the color intensity was the same throughout. In the immediate neighborhood of the anode, however, a remarkable change occurred. Even when the solution was so concentrated that the electrode could not be distinguished, as soon as the electromotive force was applied, the liquid at the surface of the anode lost its color completely. The anode was therefore surrounded by a space of practically pure ammonia. The colored boundary was everywhere parallel to the electrode surface, apparently coinciding with an equipotential surface. As the solution became more dilute the thickness of the colorless layer increased. Convection currents were present to some extent, but they did not appear to be very strong and could be observed only in rather dilute solutions. Under these conditions it was of course possible to make very minute observations as to any evolution of gas or solid material on the surface of the anode. No evidence was found of an anode product. Apparently the anion disappears altogether when it reaches the anode. We shall discuss this point more in detail after presenting some further experimental data.

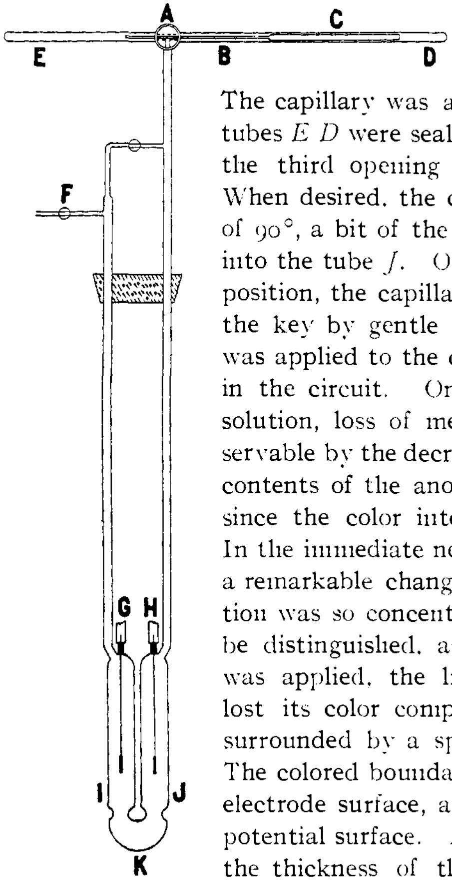

Fig. 2. — Apparatus employed in carrying out electrolyses in sodium solutions.

When the solution about the anode had reached a dilution at which the clear space was plainly visible, the current was reversed, keeping under observation the electrode which up to this moment had been anode.

The clear space at once broadened out in the form of a wedge with the apex at the bottom of the electrode. The blue solution was in contact with the bottom of the electrode which was now cathode. This effect, also, was much more pronounced in dilute than in concentrated solutions.

Experiment 3.—The same cell was employed as in the preceding experiment but a larger amount of sodium was introduced. The following readings were made with the millammeter:

Time	3.50	3.56	4.01	4.15
Current	73.00	70.00	67.00	56.00

The contents were mixed and further readings made as follows:

Time	4.30	4.32	4.35	4.40	4.50	4.55
Current	70.00	81.00	77.00	72.00	60.00	53.00

Toward the end of this experiment the solution in the anode portion had become appreciably more dilute. To a very slight extent the color of the solution in the connecting tube *K* near the anode had also become lighter. The increase in current was due to change in the concentration of the solution about the anode. The initial rise from 70–81 may be due to imperfect mixing or to temperature changes. When the solution about the anode was fairly dilute the current was reversed. The phenomenon described above was repeated. The clear boundary around the anode spread out in wedge form somewhat as indicated by the lines *6 6* in Fig. 5(*b*). Solution could be seen to stream by the cathode at a considerable rate, giving up its metal to the bottom of the electrode. At the same time the color of the remaining solution in the space about the electrode became much lighter and, in fact, disappeared almost entirely. If the current was maintained some time, the color in the space surrounding the electrode again became more intense; but the intensity remained greatest at the electrode as long as the solution was sufficiently dilute to permit of observations. The rapid transfer of metal from the electrode space to the electrode was not observed except when the electrode had previously been acting as anode. In some way the phenomenon is connected with the fact that the anode is surrounded by a space practically free from metal.

It might be suggested that the observed phenomena are due to the formation of sodamide. This assumption, however, is excluded by the fact that the resistance of the solution, as measured approximately by the current, follows the color changes observed at the electrode. It is to be remembered in this connection that the resistance in the cell is confined almost entirely to the electrode under observation, since the solution in the connecting tube and the other electrode space is relatively concentrated. In Fig. 3 are given some examples showing the value of the currents at different times during the observation of an electrode. The same electrode remained under observation in all cases. As abscissae are plotted approximate time intervals. These varied from about one to two minutes. As ordinates are plotted the observed currents in millamperes. The current readings, when the electrode was cathode, are plotted above the zero axis, and below are plotted the currents when the current flowed in the reverse direction. When an ordinate extends across the zero axis it indicates that the current was reversed at this point. As example, we shall consider the first curve in the figure. The solution was already fairly dilute and the electrode was anode. The current read 25. On reversal, the current initially read 25 but fell rapidly to 10, when the electrode was again made anode. The current was now 10 but rose to the original value of 25. The electrode was again made cathode and the current, beginning at 25, fell to a minimum value of 10, after which it rose to 20. On reversal, the current started at 20 and increased to 30, which was higher than the initial value. All these changes in current were accompanied by the corresponding color changes as described above. The second curve illustrates the behavior of the solution somewhat better than the first. At the time interval 7 the electrode was made cathode, the current fell from 15 to a minimum value of 1 at time 9, after which it rose to 5, when the electrode was made anode. The current in this case also rose. It began at an initial value of 5, and reached a maximum of 17 at time 12, after which it fell to 10. At the time interval 10 we have the peculiar condition that the current increases irrespective of its direction.

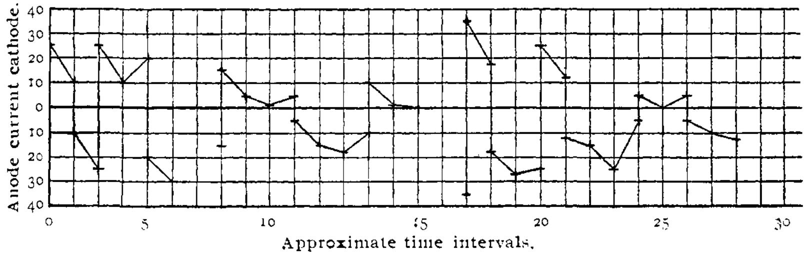

Fig. 3.—Curves showing the dependence of the current on the time and the previous history of the electrodes.

When the electrode is made cathode, the current falls to a minimum. If the current is now reversed the current increases to a maximum which has the same value as the initial cathode current. Thus, at the time 20, the initial cathode value is 25, the minimum cathode value at time 21 is 12, and, on reversal, the maximum anode current is 25 at time 23. If the cathode current is continued beyond the minimum, the anode maximum is greater than the initial cathode value, while if the cathode current is maintained for a short time only, the maximum anode current is less than the initial cathode current. Thus, at time 10, the cathode current has passed through its minimum value. The anode current reaches a maximum of 17, while the initial cathode current is only 15. On the other hand, at time 18, the minimum cathode current has not yet been reached, the maximum anode current reaches only 27, while the initial cathode current at time 17 is 35.

The minimum cathode current is relatively smaller the smaller the initial current. At time 2 the initial value is 25 and the minimum is 10, at time 7 the initial value is 15 and the minimum value is 1, while at time 24 the initial value is 5 and the minimum value is imperceptible with the millammeter. These phenomena are not accidental ones, depending on chance conditions but they are fundamental and readily reproducible. An explanation will be offered below.

After completing the preceding experiment, the tube was allowed to remain in a bath of boiling ammonia for about 15 hours. At the end of that time only a trace of metal was left, it having been converted into sodamide, which remained in solution. On applying an electromotive force of 110 volts the millammeter registered 15, which increased to 25 at the end of 10 minutes. This increase in current was due to the conversion of amide into metal at the cathode. The blue color due to the metal at once appeared at the cathode, on applying the electromotive force, and traveled rapidly toward the anode. The color was most pronounced at the cathode and shaded off gradually to the anode. On reversal, the current continued to increase as before reversal, the increase being from 25 to 40 in 5 minutes. None of the peculiar electrode phenomena observed with solutions of pure sodium could be observed in the amide solution. No matter how the current flows in an amide solution, the net result is a conversion of amide to metal. The contents of the cell were now mixed and electrolyzed for a time until the solution in the anode space finally reached a maximum concentration and began to become more dilute in metal. The time-current readings are given in Fig. 4. On reversal, the color change was reversed and the current increased. After a number of reversals the amide was almost entirely converted into

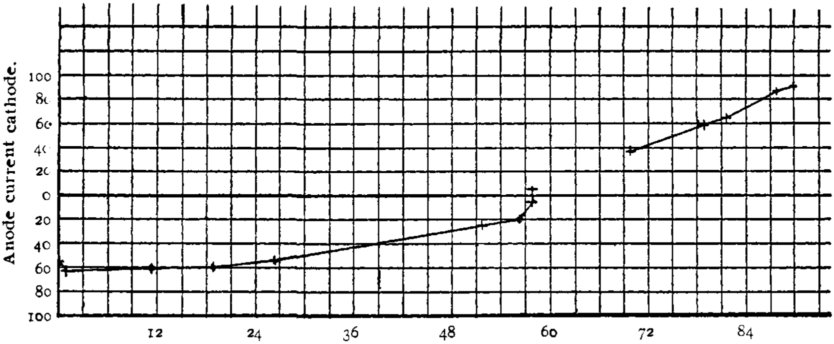

Fig. 4.—Showing the change in the current as electrolysis proceeds.

metal. The phenomena which are characteristic of the metal solutions eventually began to appear, becoming more and more pronounced as the amide was converted into metal.

It is evident from this experiment that the results obtained with solutions of pure sodium are not to be ascribed to the disturbing influence of amide, for the effect of the amide is to obscure the phenomena due to the metal. Only when the amide has largely disappeared do we begin to observe the phenomena due to the free metal itself.

The behavior of metallic sodium in a solution of sodamide is identical with that of potassium in a potassamide solution. Since the experiments with potassamide will be described and discussed in detail in the next section, a further discussion of the results obtained with sodamide need not be undertaken here.

Interpretation of the Results.

Perhaps the most important conclusion to be drawn from the experiments just described is that the conduction process in solutions of sodium in ammonia is an ionic one, for a transfer of matter takes place with the current and this, by definition, constitutes ionic conduction. Just how the conduction process in the metal solutions is related to that process in ordinary electrolytes on the one hand and to that in metallic conductors on the other, remains to be determined.

From the experiments just described, it is evident that sodium is a constituent of the positive ion. We shall designate it by the symbol Na'^{+}, in order to distinguish it from the normal positive ion present in a solution of a sodium salt in ammonia. The negative ion we shall designate, for the time being, by the symbol Y^{-}. In order that the reader may more readily comprehend the arguments which are to follow, it will be well to outline, briefly, the nature of the ions Na'^{+} and Y^{-}. These two ions are in equilibrium in solution with the neutral metal atoms according to the equation

$$Na'^{+} + Y^{-} = Na$$

and both Na'^{+} and Y^{-} are univalent, while the metal atoms Na are monatomic. The ion Na'^{+} is identical with the ion Na^{+}, the normal ion in a solution of sodium salt. The ion Y^{-}, however, constitues a new and remarkable species of anion. This ion is common to all metal solutions in ammonia and gives to these solutions their characteristic properties. It constitutes in fact, the metal anion and we shall identify it with the negative electron.

Aside from the important fact that the conduction process in metal solutions is an ionic one, which follows at once from the preceding experiments, it remains to examine more closely the phenomena taking place in the immediate neighborhood of the electrodes. We will first consider the anode, where the phenomenon is less complex. There can be no question that a gaseous product is not evolved here. The solution being transparent, the formation of minute bubbles of gas would be readily observed. At the same time, the current is by no means inconsiderable, rising to as much as 1/20 ampere. A current of 10 mill-amperes generates a cubic millimeter of hydrogen per second. A gas, therefore, is not evolved. Moreover, no electrolytic product results at the anode by interaction between the negative carrier and the solvent, or the electrode, for in that case we should always have left in the anode space, a certain amount of ionic material. In these solutions, however, the resistance increases to something like a million ohms per centimeter in a comparatively short time. The only remaining possibility, then, is that the negative ion reacts at the anode to form a soluble neutral molecule. As the electrodes are not attacked, such reaction could involve only the solvent itself.

It is difficult to imagine a reaction taking place between ammonia and the anion Y^- to form a soluble, non-electrolytic substance at the anode, unless ammonia itself constitutes the negative ion Y^-. In that case, of course, the ammonia would be discharged at the anode and simply add itself to the remaining solvent. We must not forget that the ion Y^- is formed by dissolving neutral metal atoms in neutral ammonia and that this solution permits of reversible separation of its components. If the metal forms the positive ion Na'^+, as we have shown, then the negative charge only can be associated with the ammonia. According to our present views of matter and electricity, negative electricity consists of discrete charges, called electrons, whose mass is about 1/1000 that of the hydrogen ion. If we assume tentatively that the metal atoms lose electrons when they dissolve in ammonia, then the solvent may of course take up the negative electrons in some way.

Let us examine the nature of the combination between the negative charge, or as we shall now call it, the electron, and ammonia. In general only such atoms or groups of atoms function as anions as have strongly acid properties; that is, they form acids with hydrogen, and with metals they form salts. When a solution of such a substance is evaporated, the salt crystallizes out as a non-conductor. We note at once that ammonia exhibits none of these properties. It has no tendency to combine with hydrogen. Likewise, it shows no tendency to combine with metals to form salts, although it often combines with neutral salt or acid molecules. Ammonia does not combine with the alkali metals to form solid compounds. It does, however, combine with calcium,[1] but in this case six molecules combine with an atom of metal, a number much larger than the valence of calcium would demand if the combination

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[1] THIS JOURNAL, 30, 664 (1908).

were of an electrical nature. It is to be noted in this connection that calcium hexammoniate is a metal and not a salt, indicating that the negative electron which is firmly bound to the anion in salts, is freely movable in this compound. If the negative electron is asscoiated with ammonia at all, the resulting ion is not to be looked upon as an ammonia ion; for the combination between the electron and ammonia is a very loose one, possessing none of the characteristics of actual chemical combination such as we have in ordinary anions.

It is probable that if the negative electron is associated with ammonia, the combination is one resembling that which we have in the case of gaseous ions. It is well known that the negative electron in a gas at ordinary pressures is associated with neutral molecules of gas and that as the pressure is reduced this envelope of neutral molecules is lost. Such combination may well exist between the electron and ammonia in dilute metal solutions. In concentrated solution, however, the electron can not be associated even with ammonia, for, as we shall see, in a concentrated solution no material change can be observed at the anode. If associated with even one atom of ammonia, the solution in the neighborhood of the anode must become diluted and a small change in the concentration of a strong solution is readily observable, owing to the change in its coefficient of reflection.

If the ion Y^- consists of electrons surrounded with an envelope of ammonia, there must exist in solution an equilibrium of the form:

$$Y^- = \varepsilon^- + n\,NH_3 \qquad \text{I}$$

where ε^- represents the negative electron. According to this hypothesis, the negative carrier should move more rapidly in dilute than in concentrated solutions, for the ammoniation of the electrons must increase with increasing dilution. We shall later see that this is actually the case.

On this basis, the phenomena observed at the anode are readily explained. The negative carrier, either free or associated with ammonia, moves to the anode under the potential gradient, and the electron there passes into the metal. The ammonia, if it is associated with the electron, remains behind as solvent. At the same time the positive ion Na'^{+} moves away from the electrode. Right at the surface of the electrode the solution is therefore depleted of metal. If the solution is sufficiently dilute and the impressed electromotive force is sufficiently great, this space may become sufficiently large to be observable, especially as the solution has a very characteristic color and the electrode surface is a bright metallic reflector. The current across this space is maintained by diffusion and convection currents. The more dilute the solution the more pronounced will the above phenomenon appear to be

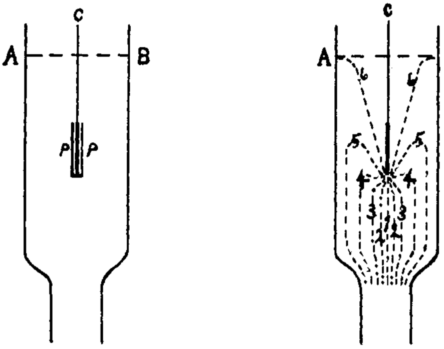
The increase in color at the positive electrode follows at once. Certain peculiarities of the phenomenon at the cathode should, however, be pointed out. The metal can plainly be seen to concentrate at the surface of the cathode, but it may extend over a considerable distance from the electrode, and this effect can scarcely be due to diffusion, which is a very slow process. Convection currents would of course tend to obscure this phenomenon. When one equivalent of current passes through the solution an equivalent of metal does not necessarily reach the electrode, in fact a very small fraction of the metal reaches the electrodes, particularly after the concentration has increased considerably. When a current enters the cathode, in case of an ordinary electrolyte, all the metal must travel to the electrode, or at least up to a point where the medium begins to change, owing to the proximity of the surface of the metal, for the electrons can not exist in ordinary electrolytic solutions except in chemical combination with the negative constituent of the electrolyte, *i. e.*, as negative ion. The negative ions in ordinary electrolytes, however, are constantly moving away from the cathode and there is no source to supply them in the immediate vicinity of the electrode. Therefore the positive carrier must effect the passage of the current between solution and electrode. In the case of the metal solutions, the negative electron is present in the electrolyte at all points, including the surface layer between the electrolyte and the electrode. Under the electromotive force, these electrons move continuously throughout the space from metal to solution. The amount of current carried at any point by the negative carrier is determined by the relative speed of the two carriers. If the speed of the negative carrier increases with concentration, the amount of metal carried will decrease continuously as the electrode is approached.

We have noticed that at the anode surface a space results that contains no electrolyte. This, as we have seen, is due to the fact that the metal moves away from the anode under the potential gradient, and since the positive carrier can not be replaced from the electrode, the solution becomes depleted, and over this space the current is carried entirely by the negative carriers. The remarkable point about this phenomenon is merely the fact that the space over which the negative carriers move becomes visible. It must eventually be considered to exist in all cases where the electrode does not furnish carriers identical with those which are moving away from its surface, for, if the current in metals consists in a motion of negative electrons, as is commonly assumed, it follows from the principle of conservation that these electrons must somewhere pass from the ionic carriers to the metal. If an electrode furnishes an ion which is common with an ion in solution, it constitutes a reversible electrode. Now, although neither electrode in a sodium solution furnishes any material carrier to the solution, both electrodes are reversible. This is simply due to the fact that the negative carriers in the metal are present in solution.

While, at the anode, the movement of the positive carrier Na'^{+} away from the electrode depletes the solution, in the immediate neighborhood of the cathode a corresponding phenomenon does not result, for the reason that the electrode furnishes the negative carrier Y^{-}. If the electrode did not furnish this carrier, a metallic deposit would necessarily have to result on the electrode, or the metal would have to interact with the solvent. So far as dilute solutions of the metals are concerned, we cannot distinguish between the case in which the negative electron passes directly from the cathode into the solution and one in which the negative electron associates itself with the solvent. In concentrated solutions, however, it is possible to obtain evidence showing that the negative carrier is not associated with ammonia.

The phenomena taking place at an electrode when it is reversed from anode to cathode are readily explained. It is evident that although the electrode is now cathode, and metal is on the whole entering the electrode space, it is being collected at the electrode more rapidly than it enters. This seeming paradox finds its explanation when we consider the details of the experiment. In Fig. 5(*a*) is represented the anode. The outline *P P* represents the colored boundary of the solution. The space between the electrode and this boundary is perfectly colorless. The broken line *A B* represents the surface of the solution, *C* is the electrode, and the narrower tube at the bottom connects through a more concentrated solution with the other electrode. If, now, the current is reversed, the current enters chiefly at the bottom of the electrode, for the colored solution is constantly rising, owing to convection. In Fig. 7(*b*) this electrode is represented a few moments after reversal has taken place. As stated, the clear space about the anode expands, on reversal, in the form of a wedge. The volume between the lines *6 6* represents this space, which is entirely free from metal. The lines *6 6* thus form the boundary between solution and pure solvent. Of course, the current can not pass through this pure solvent. The stream lines of the electrical current are therefore somewhat of the form indicated by the dotted lines *1 2 3 4 5*. At the bottom of the electrode these stream lines converge. In this region the potential gradient becomes very great and the ions are moving with high velocity. The solution becomes locally heated and rises. Now, quite near the electrode the liquid is practically at rest, not alone because of the proximity of the electrode surface, but also because the metal which is left there soon reduces the resistance, and consequently the heat generated. On the other hand, at some distance from the electrode, the liquid is again at rest because the current density is small and heating is small. In a very narrow space, then, on each side of the electrode the liquid is rising rapidly while the ions are moving under a high potential gradient.

The result is that the ions are carried to the electrode more rapidly than the solvent carries them upward, owing to convection. The ions are therefore, so to speak, extracted from the solvent which passes by. This motion of the solvent, it may be stated, is very plainly visible. As the solvent moves upward, it is replaced by fresh solution from surrounding points from which, again, the metal is extracted.



(a) (b)

Fig. 5.—Illustrating the phenomena that take place at the electrodes.

This phenomenon may be made more apparent if we consider the boundary *6 6* between pure solvent and solution to be a flexible, non-conducting, impervious membrane. We will suppose that it extends at the bottom to the point at which the convection stream upward begins. As the solvent moves upward and is freed from metal, the boundary is depressed and in this way the metal is swept out of the space surrounding the electrode. In the limit, this membrane coincides successively with the stream lines, but owing to convection and diffusion this does not actually occur. This does not, however, affect the conclusion.

If the electrode is kept cathode long enough, a point will finally be reached where the metal is carried away from the electrode by convection. This is due to the increasing dimensions of the space occupied by metal at the electrode, and to a drop in the potential gradient, which is brought about by both an increase in the area on the electrode in contact with solution and by the great relative increase of the resistance between the electrode and the connecting tube. As metal is gradually carried into the electrode space by the residual current, the concentration of metal in the electrode space increases and the current increases at the same time, owing to a fall in resistance.

The electrode is now cathode and in the immediate vicinity of the electrode surface we have quite a concentrated solution of metal which becomes more concentrated as the electrode is approached. Beyond the immediate electrode region is a comparatively homogeneous dilute solution whose resistance determines the current. If the current is now reversed, the metal is carried away from the electrode under the acting potential gradient, into a space where convection currents reach it and distribute it again throughout the electrode space. The concentration of the solution, as a whole, is therefore greatly increased: the resistance falls, and the current increases. When the metal is thoroughly distributed, the current reaches its maximum value after which it falls, since, on the whole, metal is being carried out of the anode space.

The rate at which the metal is initially collected when the electrode is made cathode and the rate at which it is dispersed when it is again made anode, is very great, much greater in fact than that at which material is carried into or out of the electrode space through the solution in the connecting tube. If the electrode is made cathode only long enough to collect all the metal, so little metal is carried in from without that the anode current, when the metal is again dispersed, will not rise above its original value. If, however, the electrode is maintained cathode for a considerable time, more metal is brought in than will be carried out during the time required for the metal at the electrode to be again distributed through the electrode space. The anode current therefore reaches a maximum value greater than the original one before the electrode was made cathode. The phenomena observed above are thus accounted for.

These phenomena are such as could be observed in the case of ordinary electrolytes, provided that the electrode products were not such as to cause disturbances. In the case of aqueous solutions the concentration of hydrogen ion in water itself may be sufficient to cause difficulties. What makes these phenomena observable in case of the metal solutions, is the simple nature of the electrode products coupled with the fact that visual observations can be made in solutions whose concentrations are far beyond reach in any other known solutions. The only systems that bear a close resemblance in many aspects with the metal solutions in ammonia are ionized gases. It would be profitless to go into this question beyond the mere mention of the analogy.

Experiments with Potassamide.

In the preceding section it was shown that the metal in a sodium solution is a constituent of the positive ion. In the present section we shall identify this ion with the positive ion normally present in an ammonia solution of the salt of the metal. For this purpose migration experiments were carried out with solutions of potassium in potassamide dissolved in ammonia. Potassium was chosen in place of sodium because of the greater solubility of the amide and the greater ease of preparing the base. That the observed phenomena are in no wise altered on changing the metal follows from experiments already described as well as from a large number of facts to be presented later.

The apparatus employed in preparing and studying the amide solutions is outlined in Fig. 6. The tube *P S* is used in preparing the amide solution. The metal is introduced into *S* through *R*, which is afterwards sealed off as shown in the figure. In order to catalyze the rate of production of amide, a quantity of platinum sponge is introduced into *S* along with the metal. In preparing the solutions, the tube *R S* is of course detached from the remaining apparatus at *M*, and is connected with a pump and a source of pure ammonia. After exhausting the apparatus, *S* is placed in a bath of boiling ammonia and pure ammonia is condensed under an excess pressure of about 25 centimeters. When a sufficient quantity of solvent has been condensed, the cock *N* is closed and the tube is detached and removed from the bath. It should be

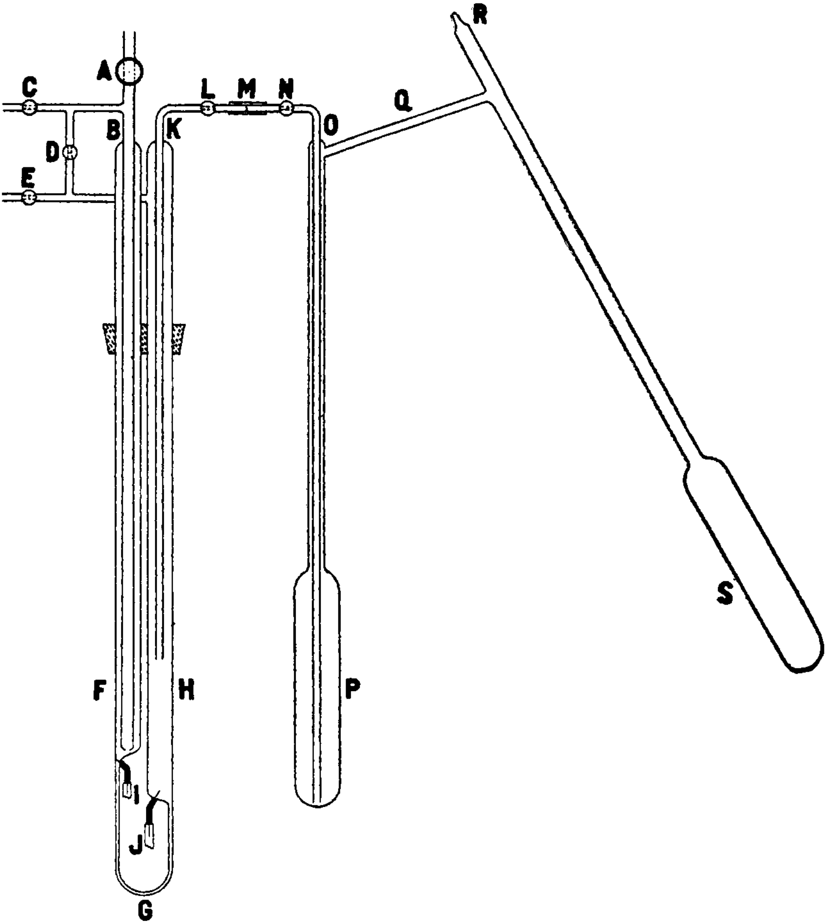


Fig. 6.—Apparatus employed in experiments with solutions of potassamide and potassium.

noted that the apparatus just described should be very carefully made, as, in addition to the normal vapor pressure of ammonia, it has to withstand the pressure due to evolved hydrogen, which may be quite considerable. In case large quantities of metal are employed it is safer to leave the tube in a bath of boiling ammonia until the metal has practically disappeared, the excess of hydrogen being let out from time to time. In any case, the tube must finally be allowed to warm up to room temperature and be left for a considerable time in order to permit any solid materials in the solution to settle to the bottom. The greater portion of the solution is then carefully decanted into *P* through the connecting tube *Q*. The last portion of solvent in *S* is allowed to distil into *P* in order to avoid carrying over impurities.

The apparatus with which observations were made is likewise outlined in Fig. 6. The two tubes *F H* are provided with electrodes *I J* and connected by the tube *G*, about 2 millimeters in diameter. The tube *H* is somewhat longer than *F*, so that, when the electrode *I* is just covered, a considerable quantity of liquid is present in *H*. The purpose of this contrivance will appear presently. The cocks *C* and *E* connect with a source of pure ammonia and a vacuum pump respectively. The use of the tube *B* and cock *A* will be described below. When it is desired to introduce the amide solution, the tube *P S* in which the amide was prepared is attached to the cell *F H* at *M*, as shown in the figure, by means of a bit of pure black rubber tubing, and the amide solution in *P* is surrounded by a bath of boiling ammonia. After exhausting the apparatus, the cell *F H* is surrounded by a bath of ammonia[1] boiling under reduced pressure. The cocks *C E* are closed and *D* is opened. When the temperature of the bath has reached about —45°, the cock *N* is opened and the solution is forced into *H* through *K O* by the pressure of the vapor in *P*. When sufficient solution has been forced over, the cocks *L N* are closed and *P S* is detached at *M*. An electromotive force

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[1] In all cases where a bath of boiling ammonia was employed, the liquid was contained in a vacuum-jacketed tube of cylindrical form. Since the temperatures were not very low, it was unnecessary to silver the tubes, in fact, for purposes of observation it was necessary that they should be unsilvered. To reduce the temperatures below the normal boiling point, the pressure was reduced by means of a glass water-jet pump. The ammonia in this case is of course lost. A brass pump can not be used. A word of caution might be added with regard to the use of vacuum-jacketed tubes. Some manufacturers make these tubes of unnecessarily thin-walled tubing and they occasionally break without apparent cause. Since many experiments require minute observation, this should be borne in mind, as the breaking of a tube under these conditions may entail serious consequences for the observer. For my part I prefer to make the tubes myself, as I feel more confidence in my selection of materials than I do in that of the average glass-blower. Excellent tubes can, however, be purchased on the market. In so doing, it is well to add instructions as to the thickness of wall and careful annealing.

of 110 volts was employed in carrying out the electrolyses, contact being made with the electrodes through tubes containing mercury (only partly shown in figure). As in previous experiments, hydrogen was introduced to prevent the boiling of the solution by the current.

Experiment 1.—On sending a current through the amide solution, gas was evolved at the anode, while metal was discharged, going into solution at the cathode. This was made evident by the fact that the solution about the cathode became blue. As has previously been stated[1] the metal solutions are very strongly absorptive, so that the color change furnishes an extremely delicate means of following up qualitatively the processes that are going on in the solutions. If the electrode *J* was made cathode, the stirring in the cell was sufficient to mix the contents in this arm. Through the narrow tube *G* the color traveled toward the anode at quite a rapid rate. That this was not due to convection or diffusion was shown by the fact that on reversing the current the color at once began to travel in the reverse direction. The solution about *I* now became colored and the color traveled toward *H*. By noting the motion of the color it was shown that the motion was not due to an endosmotic phenomenon, but to the actual motion of charged carriers in the metal solution.

The above cell was altered somewhat by adding a T-branch to the connecting tube at the bottom. After electrolyzing for a time, until a faint color appeared in the bottom of the connecting tube *G*, the branch of the T was filled with this solution. Fresh amide solution was introduced in *H* so as to wash the color out of the connecting tube. By careful manipulation it was possible to obtain a short length of solution which was faintly colored in the middle of the connecting tube *G*. On applying an electromotive force to the cell, this color moved toward the anode at a considerable rate, the length of the colored space remaining practically constant. The direction in which the color moved was reversed on reversing the current.

Experiment 2.—Experiments were now made on the motion of the boundary between potassium and potassamide solutions. The apparatus employed was that outlined in Fig. 6. Since the metal solutions are lighter than the amide solutions, the metal solutions must form the upper layer. Before introducing the amide solution, the cock *L* was closed and cell *F H* was connected through E with the pump and exhausted. When thoroughly exhausted, pure ammonia vapor was introduced through *C* under an excess pressure of 25 centimeters. The cock *A* was opened for an instant and a bit of metal was dropped into the tube *B*, which was provided with a small opening at the bottom. As soon as the metal was introduced into *B*, the ammonia was shut off

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[1] This Journal, 29, 1570 (1907).

and the apparatus was again exhausted. The amide solution was now introduced as has been described above. To prepare the metal solution, the cock *C* was opened and ammonia was condensed on the metal in the bottom of *B*. A solution was formed and forced out into *F* through the opening in *B*. The exact details of manipulation depend somewhat on the concentration of the solution to be prepared. The metal solution displaced the amide in the tube *G* and this process was continued until the boundary was well along the tube *G*.

On passing a current through the cell in such manner that the positive current flowed from metal to amide, it was found that the boundary remained sharp and moved in a direction opposite to that in which the current flowed. The boundary moved more rapidly in dilute than in concentrated solutions and the boundary was more distinct in the more concentrated solutions. As may be seen by referring to the figure, the metal was always prepared in the shorter tube *F*. Under these conditions the electrode *J* was always surrounded by a considerable volume of liquid. This was done in order to avoid disturbances due to the products formed at this electrode. If the electrode *J* was made cathode, metal ions were there discharged and went into solution and the blue color moved toward the anode. When it reached the boundary it soon made observations impossible. With a large volume at the cathode the time required for this disturbing factor to reach the boundary was sufficiently great to permit of the necessary observations. In no case were disturbances introduced by the electrode in the metal solution. This was due to the nature of the process taking place at an electrode dipping in a metal solution. On sending the positive current from amide solution to metal solution, the boundary again moved toward the anode. The boundary, however, was no longer in equilibrium, but became diffuse, the color traveling rapidly toward the anode and in a short time it was impossible to distinguish the position of the boundary.

Experiment 3.—Finally, experiments were carried out in which very concentrated metal solutions were employed. The behavior was much the same as in the preceding experiments with the exception that the motion of the boundary was a very slow one when the current traveled from metal to amide. Another important observation made on the concentrated solutions was the absence of visible concentration changes in the immediate neighborhood of the electrode which connects with the metal solution. The tube here was small and a small change in concentration should be observable, owing to change in the reflecting power of the solution.

Experiments were likewise carried out with solutions saturated with potassamide. On making the metal solution anode, the boundary approached this electrode. In the space left behind by the metal boundary, the tube was observed to be filled with crystals of potassamide. The phenomenon was a very pronounced one, and unusually large crystals were formed.

Nature of the Carriers in a Potassium Solution.

The foregoing experiments enable us to draw a number of important conclusions regarding the nature of the carriers through which conduction is effected in solutions of metallic potassium. The similarity in the properties of solutions of different metals makes it possible to at once extend these conclusions to other metals than potassium.

It follows from the preceding experiments that in dilute solutions of potassium in potassamide, a portion of the current is carried by ionic carriers which are characteristic of these metal solutions. Since the blue color, which characterizes the presence of free metal, travels toward the anode, it might be concluded that the metal in this solution travels in this direction. Such, however, can not be the case, since, as was shown in the first section of this paper, the metal travels in the direction of the positive current. The motion of the color is not, therefore, due to a motion of the metal in the direction of motion of the color. Nevertheless, the color is due to the presence of free metal in solution and under the action of the electromotive force the position of the free metal in the solution approaches the anode. If, then, the metal ion in the solution moves toward the cathode, the shift of the position of the free metal toward the anode must be due to interaction between the negative metal anions Y^- and potassamide, whereby free metal is reversibly produced.

We must not forget that we are dealing here with a comparatively simple system containing only metal and ammonia and their soluble reaction product, potassamide. A large mass of facts shows that potassamide is a basic substance yielding the ions K^+ and NH_2^- in ammonia solution.[1] The amide therefore is in equilibrium according to the equation

$$\frac{(K^+)(NH_2^-)}{(KNH_2)} = A_1, \qquad \text{II}$$

where A is the dissociation constant and the bracketed symbols represent the activities of the corresponding molecular species in solution. At the same time, the metal, as we have seen, is subject to the equilibrium equation

$$\frac{(K'^+)(Y^-)}{(K)} = A_2, \qquad \text{III}$$

where the symbols possess the same significance as in II. We shall now examine what further relations, if any, exist between these quantities.

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[1] Franklin and Kraus, *Am. Chem. J.*, **23**, 302 (1900); Franklin and Stafford, *Ibid.*, **28**, 83 (1902); Franklin, THIS JOURNAL, **27**, 820 (1905).

As an aid in visualizing the observed phenomena, Fig. 7 has been drawn. Here A_1–B_1 represents a migration tube of indefinite length. The molecular species due to the amide are represented by the symbols K^+, KNH_2, and NH_2^-. The metal, which imparts a blue color to the solution, occupies the position 2 as indicated by the broken lines. The molecular species due to the metal are represented by the symbols K'^+, K, and Y^-. After sending the current through the migration tube for a time in the direction indicated by the arrow, the position of the different ions in the tube is shifted as represented in A_2–B_2. The color now appears in the

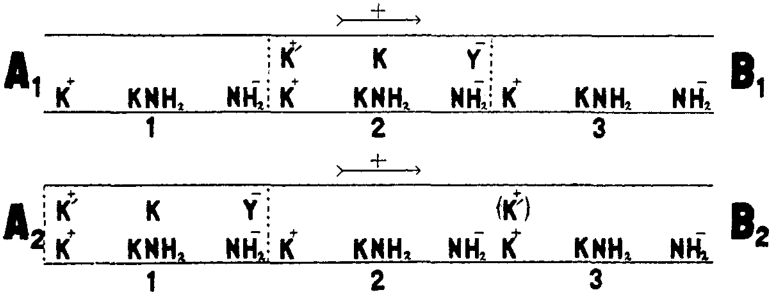

Fig. 7.—Illustrating the motion of potassium in a potassamide solution.

position 1, and, since free metal is there present, the molecular species K'^+, K, and Y^- due to the metal must now be present in this portion of the tube. On the other hand, the positive metal ion K'^+ originally present in 2 must have moved to position 3 as indicated by the symbol (K'^+). There is nothing, however, to indicate in 3 the presence of any molecular species other than that due to the amide. If the ion K'^+ of the metal differs from the ion K^+ of the amide, it must be able to react reversibly with the amide ion to form potassium ion. The simplest assumption is that the ion K'^+ of the metal is identical with the ion K^+ of the amide. Similarly, since free metal is present in 1, as indicated by the color, and since only the ion Y^-, originally present in 2, has moved into 1, it follows that K'^+ and K must be formed by interaction between Y^- and KNH_2, in which reaction ammonia may take part. It is thus clearly shown that the metal anion Y^- reacts reversibly with the potassium ion K^+ of the amide to form free metal, and that the metal cation K'^+, if it is not identical with the potassium ion of potassamide, reacts reversibly with the amide ion NH_2^- to form the normal potassium ion. In view of these and other facts to be presented later, we may safely adopt the simple hypothesis that the positive ion in the solution of a metal is identical with the positive ion of a salt of the metal. The equilibrium in the solution of metal and amide is completely described by equations II and III where K'^+ is to be replaced by K^+.

Experiments 2 and 3 furnish us with some information as to the speed of the carriers in the metal solutions. As stated, the boundary is well defined when the positive current flows from metal to amide solutions and diffuse, if the current is reversed. It is a well-known fact that the boundary between two solutions with a common ion will be permanent if the current flows in such direction that the more slowly moving ion follows the boundary, while it becomes diffuse if the current is reversed. This shows that the ion Y^-, which is present in the metal solution, travels faster than the ion NH_2^- of the amide solution. The constants of the solutions are not sufficiently well known to enable us to make any quantitative calculations. The speed, however, with which the ions Y^- travel through the concentrated amide solution makes it probable that its speed must be considerably greater than that of the NH_2^- ion. In a subsequent paper definite evidence will be adduced as to the relative speeds of the Y^- and Na^+ ions.

The experiments on the saturated amide solutions in which amide is formed at the boundary is very striking, although it adds little to what has already been deduced from preceding experiments. If the motion of the ion NH_2^- is arrested at the boundary, as it is, it follows that amide must be precipitated from solution, provided the metal solution is sufficiently concentrated. In many respects the boundary of the metal solution behaves like a metal electrode. The amount of amide crystallizing out at the boundary depends on transport numbers of the positive and negative ions in amide and metal solution, respectively.

Although experiments have not been carried out for the express purpose of determining if any changes occur at the electrodes in very concentrated solutions, the evidence indicates that material effects are there lacking. No concentration changes could be observed, nor did the solutions give indications of stirring. Certainly no gas was evolved at the electrode, whatever the direction in which the current flowed. In that event it becomes an interesting problem to determine what becomes of the ion Y^- which is present in the metal solution.

Summary.

It is shown that the conduction process in solutions of metals in ammonia is an ionic one. The metal constitutes the positive ion and is identical with the positive ion of a salt of the metal dissolved in ammonia.

The negative ion constitutes a new species of anion. It consists of a negative charge, an electron, surrounded by an envelope of solvent molecules. The electron is thus in equilibrium with ammonia according to the equation:

$$\varepsilon^- . (NH_3)_n = \varepsilon^- + nNH_3.$$

At the same time the electron is in equilibrium with the metal cations and the neutral metal atoms according to the equation

$$M^+ + \varepsilon^- = M\varepsilon,$$

where M^+ signifies the cation and $M\varepsilon$ the neutral atom.

BOSTON, July 14, 1908.

ON THE DISSOCIATION PRESSURES OF CERTAIN OXIDES OF COPPER, COBALT, NICKEL AND ANTIMONY.

H. W. FOOTE AND E. K. SMITH.

Received June 25, 1908.

In this article we wish to give the results obtained in measuring the dissociation pressures of certain oxides of copper, cobalt, nickel and antimony at high temperatures.

When an oxide decomposes reversibly into oxygen and a lower oxide or a metal, the dissociation pressure is a function of the temperature and independent of the relative amounts of the solids. The problem of measuring dissociation pressures consists, then, in determining the temperature of the oxide, and the pressure of the oxygen evolved.

The form of apparatus used in the work is shown in Fig. 1. It is not drawn to scale. The oxide was placed in the boat *a* of platinum or porcelain. The boat was in the center of a porcelain tube about 60 cm. long, and 15 mm. inner diameter, which was heated by an Heraeus platinum resistance furnace *e*. The temperature was measured by a platinum and platinum-rhodium thermo-couple. The junction of the two wires was directly over the center of the boat at *d*. The wires were insulated from each other by a small quartz tube passing through a rubber stopper in one end of the porcelain tube. The latter projected far enough beyond the ends of the furnace so that the rubber stoppers did not become hot. The other end of the porcelain tube was connected with a mercury manometer *f* by a glass tube passing through a rubber stopper. A branch of the glass tube connected with a pump is capable of lowering the pressure to less than a millimeter. The ends of the pyrometer wires

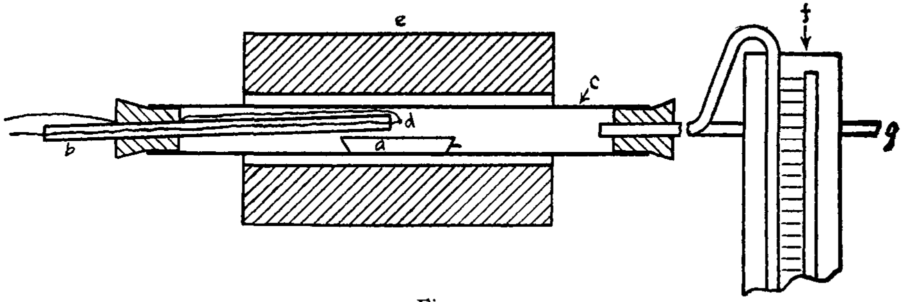

Fig. 1.