

above, hydrogen appears to exert a similar negative catalyzing effect, but not as pronounced, on the reaction between hydrogen and oxygen.

Conclusions.

The ignition temperatures of mixtures of:

Hydrogen and oxygen, carbon monoxide and oxygen, hydrogen, oxygen and nitrogen, carbon monoxide, oxygen and nitrogen, and hydrogen, carbon monoxide and oxygen, were determined by the "adiabatic compression method," and the possible sources of error fully discussed.

It is shown how the ignition temperature of any gaseous mixture containing hydrogen, carbon monoxide, oxygen, and an inert gas, may be calculated.

The reaction between hydrogen and oxygen is shown to be bimolecular and between carbon monoxide and oxygen, trimolecular.

The velocity coefficient per 10° rise in temperature is calculated to be 1.31 at about 800° and 1.13 at about 900° for the reaction between hydrogen and oxygen, and 1.24 at about 900° and 1.14 at about 1000° for the reaction between carbon monoxide and oxygen.

The reactions between hydrogen and oxygen in the presence of an excess of hydrogen and between carbon monoxide and oxygen in the presence of an excess of carbon monoxide do not follow the simple laws of chemical kinetics.

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SOLUTIONS OF METALS IN NON-METALLIC SOLVENTS; I. GENERAL PROPERTIES OF SOLUTIONS OF METALS IN LIQUID AMMONIA.

By CHARLES A. KRAUS.
Received September 11th, 1907.

INTRODUCTION.

The present investigation was undertaken for the purpose of obtaining evidence regarding the nature of the process of electrical conduction in metals. In order to indicate in what respect the solutions of metals in non-metallic solvents are of especial importance in connection with the problem of metallic conduction, it will be necessary to consider, briefly, the experimental aspects of this problem, particularly in relation to the methods to be employed in its attack.

To account for the electromagnetic properties of metals, especially for the relation between electrical and thermal conduction, the electron theory of metallic conduction has been advanced. According to this theory, the passage of electricity through a metallic conductor is effected by the movement of charged carriers, the electrons, whose mass, relative to charge, is many times smaller than that of the hydrogen ion, and whose

state, when present in metallic substances, resembles that of a gaseous system. In the light of this theory, the process of metallic conduction is in many respects similar to that of electrolytic conduction; and it should be possible to obtain direct evidence proving the existence of the carriers as well as determining their nature. With regard to their external manifestations, however, the two processes differ widely; for, while in electrolytic conductors the current is accompanied by a transport of matter, in metallic conductors material effects appear to be altogether wanting. Herein lies an obstacle which has thus far checked all efforts to prove, directly, the existence of charged carriers in metals. That material effects are quite absent, however, has by no means been demonstrated; the order of magnitude of these effects may merely be much smaller than that observed in the case of electrolytic conduction. To give a definite answer to this question, it will not only be found necessary to employ highly refined methods for detecting the changes sought for, but the system to be investigated will have to be selected with a view to obtaining that best adapted to the problem in hand.

Under the most favorable conditions, however, it is doubtful whether the study of the conduction process in solids will lead to results immediately applicable in the solution of the problem of metallic conduction. Our knowledge of the solid state of matter, in general, is far too limited to enable us to determine the nature of the processes which are specifically involved when electricity passes through a metal. The study of the conduction process cannot be successfully carried out until the molecular state of the system has been established; even in the case of electrolytes the progress of investigation is governed by this condition. Only in the case of gaseous systems and certain simple types of liquid systems may the study of this process be undertaken with a measure of success.

It is highly probable that many results obtained in the study of ionized gases are in some degree applicable to the problem of metallic conduction. Their applicability, however, is restricted by the fact that ionized gases are not in a state of equilibrium, while the ionic concentrations are necessarily extremely small. On the other hand, gaseous systems which are normally in a conducting state, such as the vapors of the alkali metals, do not readily lend themselves to investigation.

The most advantageous conditions for the study of the problem of metallic conduction may be expected to exist in solutions of metals in inactive, non-conducting solvents. The solvent would here serve as a basis of reference with respect to which the state of the system might be determined, just as in the case of electrolytic solutions the presence of the solvent has made it possible to determine the nature of the conduction process in them. It may be expected that such solutions of metals will exhibit pronounced metallic properties when concentrated, and that, as

the concentration diminishes, these properties will suffer modification, gradually approaching a limiting condition which is characteristic for solutions of this kind. As a class, the metals possess many striking properties in common whereby they are rather sharply distinguished from non-metallic substances. In solution, this community of properties should reappear, and the characteristic differences between metals and non-metals should manifest themselves in a corresponding divergence in the properties of their solutions. As is well known, the metals conduct the electrical current with remarkable facility, and it may be expected that in their solutions they will retain this property in some degree. If, then, the process of metallic conduction consists in a motion of charged carriers as the electron-theory postulates, in dilute solutions of metals, where complicating auxiliary phenomena are largely eliminated owing to the highly attenuated state of the dissolved substance, any fundamental relationships between the processes of electrolytic and metallic conduction should be clearly brought out.

It is the purpose of this investigation to show that solutions of metals in non-metallic solvents exist, and that such solutions exhibit well defined and characteristic properties. Moreover, the molecular state of the more dilute solutions will be determined, and it will be shown in what respects the process of conduction therein is related to the process of conduction in electrolytic solutions. Finally, an attempt will be made to determine to what extent the process of conduction has undergone modification in consequence of dilution.

That the alkali metals are soluble in liquid ammonia has long been known, and at various times the metallic nature of these solutions has been conjectured. Their significance, however, in relation to the study of the state of metallic substances, particularly to that of the metallic elements, has never been fully realized. It is in this connection that the writer was led to take up the investigation of solutions of metals, and, as will appear in the sequel, the expectation that these solutions would furnish a means of attacking the problem of metallic conduction has been amply justified. At the time that this investigation was undertaken, almost no quantitative data relating to the physico-chemical properties of the metal solutions in liquid ammonia were available, and even some of the more qualitative facts were not established. It was necessary, therefore, to make an exhaustive study of these solutions. The prosecution of this investigation has made great demands on both time and patience, and progress has at times seemed painfully slow. Not only was it necessary to develop an extensive technique, in order to manipulate successfully an extremely reactive solute and a highly volatile solvent, but the number of experiments had to be multiplied many times in order to exclude certain

disturbing factors which have their origin in a slow reaction taking place between the two components.

Although in certain directions, this investigation is as yet incomplete, the accumulation of material makes it desirable to publish the results obtained. Because of the length and comparatively independent nature of the different investigations involved in this problem, it seems best to present them separately. The lack of existing data on which a more precise study of the physical properties of metal solutions in ammonia could be founded, made it necessary to do much preliminary work of a qualitative character. The greater portion of these results will be embodied in the first two papers, of which the first will deal with some of the general properties of the solutions in question, and the second with the question of the formation of compounds between ammonia and metals. The third paper will treat of the molecular weight of sodium dissolved in liquid ammonia; the fourth and fifth papers will embrace a preliminary survey of the electrical properties, while succeeding papers will treat of these more in detail. Although the chief interest centers about the conduction process in these solutions, many of the results obtained have a bearing on other questions. These will be treated incidentally as they appear in this discussion. In view of the nature of the subject, the general discussion of the results will be reserved until a fairly complete presentation of the experimental data has been made.

In the course of this investigation of solutions of metals, the writer has been led to search for other metallic systems possessing properties such that their study might yield results throwing light on those molecular conditions which impose upon a body its metallic properties. Several such systems have been found. One of these is the series of solutions formed between sulphur and tellurium and another is a series of electropositive metallo-organic groups, namely: CH_3Hg , $\text{C}_2\text{H}_5\text{Hg}$, and $\text{C}_6\text{H}_5\text{Hg}$, which have been obtained in a free state and which exhibit distinct metallic properties. Although a detailed study of these systems, particularly the latter, is attended with serious experimental difficulties, it is hoped that an outline of their properties may shortly be given.

The greater portion of this investigation has been carried out in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology during the past three years. It is with much pleasure that the writer avails himself of this opportunity of acknowledging his indebtedness to Professor A. A. Noyes, both for the use of the facilities of the Research Laboratory, and for that interest which has made it possible to carry this investigation to a successful conclusion.

GENERAL PROPERTIES OF SOLUTIONS OF METALS IN LIQUID AMMONIA. Solubility Relations.

According to the literature, the following metals are soluble in liquid

ammonia, namely: Sodium, potassium,¹ lithium,² rubidium, caesium,³ calcium,⁴ barium,⁵ and strontium.⁶ Magnesium is likewise somewhat soluble,⁷ while lithium⁸ and caesium⁹ are soluble in methylamine.

Since different solutions exhibit different degrees of stability, it was found desirable to extend, as far as possible, the number of solutions that may be formed. In determining whether or not a metal is soluble, it is necessary to have a dry solvent and a clean metallic surface. In all doubtful cases the metal was melted in the solvent and while in the act of solidifying, the containing tube was shaken vigorously. In this way the metal was obtained in the form of very small globules. This process was repeated a number of times, after which the tube was allowed to stand undisturbed for some months. Lithium was thus found to be soluble in ethylamine, although less so than in methylamine. In propylamine, lithium is insoluble, as was shown by precipitating the metal electrolytically from a solution of its salt. Potassium dissolves rather slowly in ethylenediamine, giving a solution which does not possess sufficient stability to make it valuable for experimental purposes. Other metals have not been investigated in this solvent. Sodium and potassium are insoluble in ethylamine; and sodium, potassium and, lithium are insoluble in secondary and tertiary amines. According to Moissan, sodium and potassium are insoluble in methylamine¹⁰ which is free from ammonia.

Another series of solutions possessing great interest, has been obtained by Palmaer¹¹ in electrolyzing solutions of tetra-alkylammonium salts in ammonia. The blue solution, which under these circumstances is formed at the cathode, is ascribed to the presence of the free electropositive group. In view of the characteristic nature of the color of the metal solutions in ammonia, it seems highly probable that Palmaer's interpretation is correct. These results of Palmaer I have been able to verify, and in addition, it has been found that tetrapropylammonium salts exhibit a behavior similar to that of the methyl and ethyl derivatives, while with

¹ Weyl, *Ann. Physik.*, 121, 601 (1864).

² Seely, *Chem. News*, 23, 169 (1871).

³ Moissan, *Compt. rend.*, 136, 1177 (1903).

⁴ Moissan, *Ibid.*, 127, 685 (1898).

⁵ Guntz, *Ibid.*, 133, 874 (1901); Mentrel, *Ibid.*, 135, 740 (1902).

⁶ Guntz, *Ibid.*, 133, 1209 (1901).

⁷ Seely states that magnesium is insoluble. However, according to observations made by Dr. F. G. Cottrell, of the University of California, and communicated to the writer by letter, this metal dissolves in ammonia if precautions are taken to have a clean metallic surface in contact with the pure solvent.

⁸ Moissan, *Compt. rend.*, 128, 26 (1899).

⁹ Rengade, *Ibid.*, 140, 246 (1905).

¹⁰ *Ibid.*, 128, 26 (1899).

¹¹ *Z. Elektrochem.*, 8, 729 (1902).

the amyl derivative a blue solution could not be obtained. Because of their lack of stability, these solutions could not be further studied.

The blue colored halide salts of sodium and potassium may likewise be mentioned here. These salts are formed by the action of strong Röntgen rays¹ and by the action of the alkali metal vapors on their halide salts at higher temperatures,² while a blue sodium salt occurs in nature. The color of these salts has been ascribed to the formation of a subhalide salt,³ to the formation of a solid solution of the metal in the salt,⁴ and finally to the presence of ultramicroscopic particles of the free metal.⁵ That the color of these salts is not due to the presence of a subhalide is indicated by the fact that sodium chloride crystallizes from a solution of sodium in ammonia as a colorless salt.⁶ While in some cases, at least, the color is due to the presence of particles of free metal, it is possible that, under certain conditions, solid solutions may be formed. In preparing the amides of the alkali metals by passing ammonia gas over the fused metals, a blue colored solution is formed which loses its color under the action of an excess of ammonia. This color has been ascribed by Titherly to the formation of a solution of the metal in the fused amide.

Solutions of Metallic Compounds.

In addition to the solutions of the elementary metals which have just been described, a few instances are known where metallic compounds dissolve in liquid ammonia. Joannis⁸ has shown that lead dissolves in ammonia solutions of sodium, provided the latter metal is not present in excess; in solution, two atoms of lead are present for one atom of sodium. As with solutions of the elementary metals, at a given vapor pressure of ammonia, metal is precipitated, redissolving on addition of ammonia. Lead, I find, is likewise soluble in solutions of potassium, while tin is soluble in solutions of sodium. The lead solutions have a greenish color while the tin solutions exhibit a red color. Both are very stable, as is shown by the fact that such solutions have remained sealed up for several years without losing their characteristic color. According to Lebeau⁹ the compound Li_3Sb is soluble in ammonia.

From a brief preliminary study which I have carried out, it appears that the ammonia solutions of metallic compounds exhibit properties

¹ Goldstein, *Ann. Physik.*, **59**, 371 (1895).

² Giesel, *Ber.*, **30**, 156 (1897).

³ Wiedemann and Schmidt, *Ann. Physik.*, **54**, 622 (1895).

⁴ Elster and Geitel, *Ibid.*, **59**, 487 (1896).

⁵ Siedentopf, *Physik. Z.*, **6**, 855 (1905); *Z. Elektrochem.*, **12**, 635 (1906).

⁶ Cf. Joannis, *Compt. rend.*, **112**, 392 (1891).

⁷ *J. Chem. Soc.*, **65**, 508 (1894); **71**, 469 (1897).

⁸ *Compt. rend.*, **113**, 795 (1891).

⁹ *Ibid.*, **134** (1902).

very different from those of solutions of the elementary metals. They exhibit polarization, as was shown by the fact that in resistance measurements, in which a telephone was used, a very poor minimum was obtained with bright platinum electrodes, whereas solutions of the elementary metals, whether dilute or concentrated, give an excellent minimum even when extremely small electrodes are employed. The conductivity-temperature curves for these solutions are similar to those of ordinary electrolytes¹, in which respect, again, they differ from solutions of sodium, as will be seen from results appearing in a subsequent paper.

In passing a current between lead electrodes in a solution of the sodium-lead compound, it was found that lead is precipitated on the anode and dissolved at the cathode, as appears from the following results: With a current of 0.106 ampere flowing for 54 minutes there was found a gain of 1.432 g. of lead at the anode and a loss of 1.473 g. at the cathode. Assuming two gram-atoms of lead per equivalent of electricity, the calculated value is 1.473 g. In another experiment with a current of 0.106 ampere flowing for 40 minutes the loss and gain were found to be 1.075 g. and 1.085 g. of lead respectively; calculated 1.091 g. Especial care was not taken to exclude loss of material nor was the current measured with an accuracy of more than 1 per cent. The differences between the observed and calculated values are doubtless due to errors of this character. From these results it appears that for every equivalent of electricity, two gram-atoms of lead are transferred from the cathode to the anode. It is probable, therefore, that in solution the ions, Na^+ and Pb_2^- , act as carriers for the current. That ammonia may be associated with either or both of these ions is by no means excluded.² If such should be the case the part played by the ammonia may be expected to be similar to that which the solvent plays in connection with the ions of ordinary salts.

On electrolyzing a solution of sodium chloride with a lead cathode, and an anode of sodium amalgam, the compound is formed at the cathode, as is shown by the color change. Also, on adding lead iodide to a solution of metallic sodium, the compound is formed, provided the lead salt is not added in excess of that required to just form the compound. Solutions of the compound of lead and sodium are stable in the presence of sodium chloride; with ammonium chloride a metallic precipitate results, along with evolution of gas, doubtless hydrogen. The addition of a lead salt precipitates a spongy metal, presumably metallic lead. In general, the addition of the salt of a metal causes a metallic precipitate which contains both lead and the metal in question. All these facts harmonize with the assumption that the ions Na^+ and Pb_2^- are present in solution.

¹ Franklin and Kraus, *Am. Ch. J.*, 24, 83 (1900).

² Cf. Joannis, *loc. cit.*

Since these solutions are purely electrolytic conductors, they are not of special significance in connection with the main purpose of the present investigation.¹ They are, however, of great interest in showing that under proper conditions there may be present in solution, a kind of ions otherwise unknown, namely: anions composed of metallic elements. Furthermore, if the solutions of the sodium-lead compound in ammonia may be looked upon as a solution of the metallic compound NaPb_2 , it follows that this compound possesses polar properties; in other words, this metallic compound may be looked upon as being of the nature of a salt. Conclusive evidence regarding this point can be obtained only by a detailed study of the properties of these solutions.

The Solubility Diagram for Sodium in Ammonia.

The solubility of the metals in ammonia is, on the whole, very great. According to Ruff and Geisel² one atom of sodium, potassium and lithium dissolves in 5.87, 4.74 and 3.87 molecules of ammonia respectively, at 0° . The solubility of potassium increases slightly with the temperature, that of sodium decreases, while that of lithium remains sensibly constant over a temperature range of 100° .

The complete solubility diagram of the metals in ammonia is not known. The behavior of sodium, however, has been studied sufficiently to make it possible to predict the general form of the curve for the more dilute solutions. This curve is represented in Figure 1, in which the continuous lines represent actual determinations, while the broken lines are conjectured, not being based on actual determinations. The points on the branch AB represent solubilities of sodium in ammonia as determined by Ruff and Geisel.³ The points on the branch DE were determined approximately by the writer from conductivity data, while the point F is the freezing point of pure ammonia.

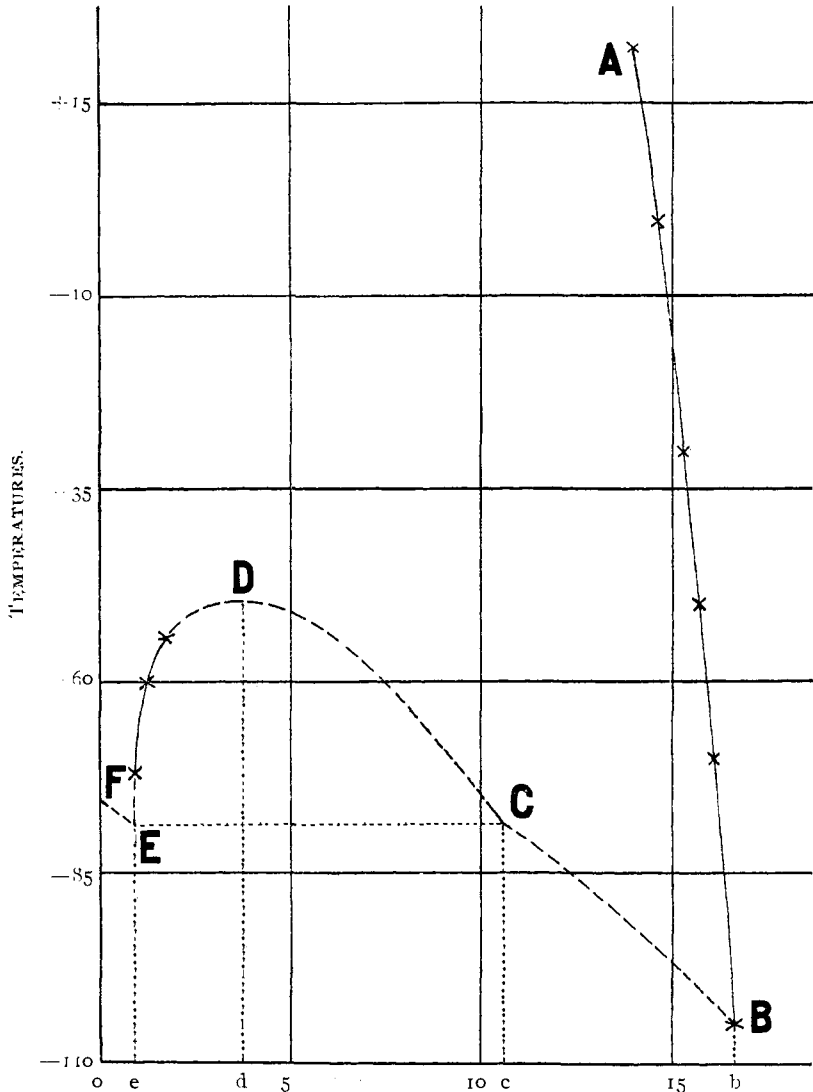
The curve FE represents the composition of solutions in equilibrium with solid ammonia. On the curve CDE two liquid phases are in equilibrium, namely: solutions of concentration $d-c$ with solutions of concentration $d-e$. On BC, again, solutions of concentration $b-c$ are in equilibrium with solid ammonia; and finally, on BA, solutions are in equilibrium with solid sodium. On cooling a solution whose composition lies between c and e , separation takes place into two liquid phases, for which D is the point of complete miscibility. This point has not been determined, but its temperature is known to lie below -33° and and above -56° , probably not far from -50° , while the critical compo-

¹ Since writing the above, I have had occasion to work with more concentrated solutions of the sodium-lead compound. It appears that very concentrated solutions of this compound possess marked metallic properties, although by no means as strong as those of solutions of the elementary metals. It seems likely, therefore, that these solutions of metallic compounds will have to be included in this investigation.

² Ber., 39, 828 (1906).

³ Loc. cit.

sition probably lies considerably below 10 per cent. (by formula weight) of sodium. The point E has not been determined but, since this solu-



COMPOSITION. PERCENTAGES OF SODIUM ACCORDING TO FORMULA WEIGHT.

FIGURE I.—Solubility Diagram for Sodium in Ammonia.

tion is comparatively dilute, its freezing point can not lie much below the normal freezing point of ammonia.

The separation of the sodium solution into two liquid phases is a most striking phenomenon. The more dilute solution, dark blue in color, appears at the bottom ; while above it appears the more concen-

trated solution, presenting a characteristic bronze colored metallic appearance. The fact that both series of solutions contain less than 15 per cent. of sodium is very remarkable; it serves well to illustrate how rapidly the properties of these solutions change with concentration. These changes are of an order of magnitude not met with in the case of any solutions hitherto investigated; the actual magnitude of the changes involved will appear later when the more detailed investigations come up for discussion.

It would be interesting to extend the curve AB to the melting point of sodium. Since this point lies near 96° and the solubility of sodium in ammonia at 22° is decreasing with the temperature, it seems improbable that the curve AB will reach the melting point of sodium without exhibiting a maximum. If such is the case, a second series of partially miscible liquid phases must exist¹, containing larger percentages of metal. Of course, a compound may make its appearance and change the form of the curve. Experiments at higher temperatures should lead to valuable results.

Whether or not other metals exhibit the same properties as sodium can not be predicted with certainty. However, from certain observations recorded by Moissan² and Mentrel³, it is probable that solutions of calcium and barium will be found to behave like those of sodium⁴.

Mixed Solvents.

The first observations on the solubility of metals in mixed solvents are due to Moissan⁵, who showed that lithium is soluble in methylamine which has been diluted with ether. From a qualitative study which I have made of a considerable number of solvents it may be concluded that, in general, the alkali metals are soluble in any inactive solvent containing a considerable quantity of ammonia. If the solvent is miscible with ammonia in all proportions and sufficient metal is added, two liquid phases usually result. One of these consists chiefly of ammonia and, retaining nearly all the metal, possesses a decided metallic appearance, while the other consists chiefly of the inactive solvent and, containing but little metal, appears blue. If the neutral solvent possesses a very limited solubility for ammonia, as for example toluene, the solutions of

¹ This view gains some support from recent investigations which I have carried out with alloys of sodium and potassium. From these it appears that ammonia gas is somewhat soluble in the liquid alloy of the two metals. The details will appear later.

² *Compt. rend.*, 127, 685 (1898).

³ *Ibid.*, 135, 740 (1902).

⁴ It has since been found that calcium behaves in a manner similar to that of sodium. In this case, however, the point of complete miscibility must lie much above room temperatures. The concentration of the more dilute phase is in the neighborhood of 1/10 molal at -33° .

⁵ *Compt. rend.*, 128, 30 (1899).

the metal are very dilute; with other solvents, such as the amines, a very considerable solubility for the metal may result.

The addition of a salt of a metal to a solution of the metal itself in ammonia results in a depression of the solubility of the metal; in fact, it usually results in the production of a second liquid phase if sufficient metal is present to cause saturation of the dilute solution. Thus, on adding sodium chloride, in excess, to a strong solution of sodium, two liquid phases result, one of metallic appearance, containing most of the metal; the other of a blue color, more dilute in metal, and probably containing the greater proportion of salt.

Stability.

The rate of reaction between ammonia and the dissolved metal, whereby the corresponding amide is formed¹ together with hydrogen gas, is of great importance from an experimental standpoint, since the presence of the amide necessarily affects the results of all quantitative measurements. The stability of the solutions increases in the order: potassium, calcium, lithium, sodium. The reaction, however, is one that is catalyzed by many substances². As follows from results to appear later, it is probable that the metallic oxides and hydroxides exert a catalytic action, and for this reason some change may result in the order of stability when pure substances are employed. The necessity for excluding catalytic agents greatly increases the experimental difficulties in studying the metal solutions.

Influence of Pressure on Stability.

According to Joannis,³ the rate at which hydrogen is evolved in a sealed tube containing a solution of sodium decreases with time. This behavior he ascribes to the influence of the increasing hydrogen pressure on the rate of reaction. Such an influence is scarcely credible; nevertheless, its possibility and the fact that it would afford a means of decreasing the rate of reaction at higher temperatures, is of so great a practical importance that it seemed worth while to investigate the question more carefully.

The apparatus employed is outlined in Figure 2. The pressure was measured by means of a Crosby gauge G, graduated in pounds and reading to as high as 400 pounds. This gauge was specially constructed for use with liquified gases and was very reliable. The sodium solution was contained in the tube C about 15 centimeters long and of one centimeter diameter. The apparatus was provided with a mercury injector I, by means of which mercury could be introduced into, or withdrawn from the system. The gauge and connecting tube, as far as A, were

¹ Joannis, *Compt. rend.*, 112, 392 (1891).

² Compare Joannis, *loc. cit.*; Franklin, *this Journal*, 27, 831 (1905).

³ *Loc. cit.*

filled with oil; the connecting tube D and the tube AB were filled with mercury, and by means of the injector the mercury was always main-

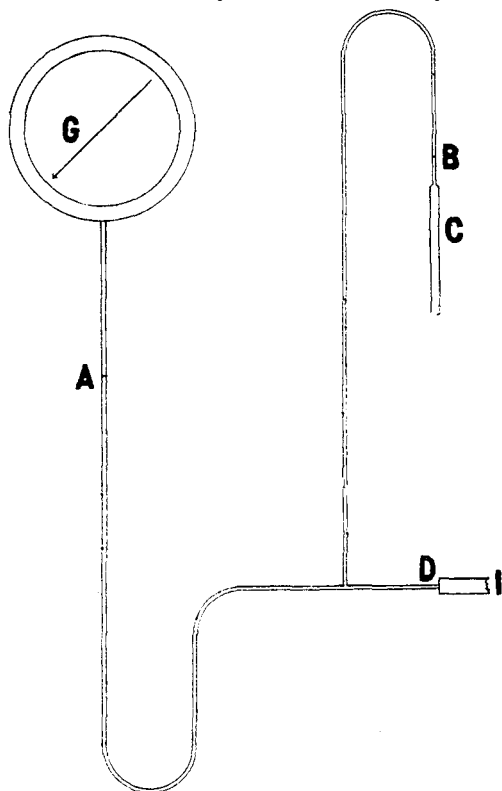


FIGURE 2.—Apparatus Employed in Measuring the Rate of Evolution of Hydrogen from a Sodium Solution. Dimension Reduced in Ratio of 10:1.

tained at the fixed point B in order to keep the vapor volume in the tube C constant.

Approximately 1.5 g. of pure sodium were introduced into the tube C. This was accomplished by exhausting the apparatus and forcing melted sodium through a glass wool filter by means of a small pressure of pure ammonia gas. The tube in which the sodium was melted and filtered was attached to the tube C and sealed off as soon as the metal had been forced over. A sufficient quantity of pure dry ammonia¹ to dissolve all the sodium was distilled into C through a connecting tube (not shown in the figure) which was later sealed off. A portion of this ammonia was again evaporated, leaving 1.5 cubic centimeters in the tube. The purpose of this operation was to leave the metal in a less compact form

¹ In all cases where quantitative results have been obtained, pure ammonia has been employed, the method of purification being that of Franklin and Kraus, in which the solvent is distilled from a solution of sodium or other active metal *Am. Ch. J.*, 23, 284 (1900).

in order to insure equilibrium conditions. Since excess of metal was always present, the vapor pressure of the solution necessarily remained constant. After sealing up the apparatus the tube C was placed in a thermostat and maintained at a temperature of 36° within a few hundredths of a degree. The results are represented graphically in Figure 3. Similar results were obtained in a duplicate experiment.

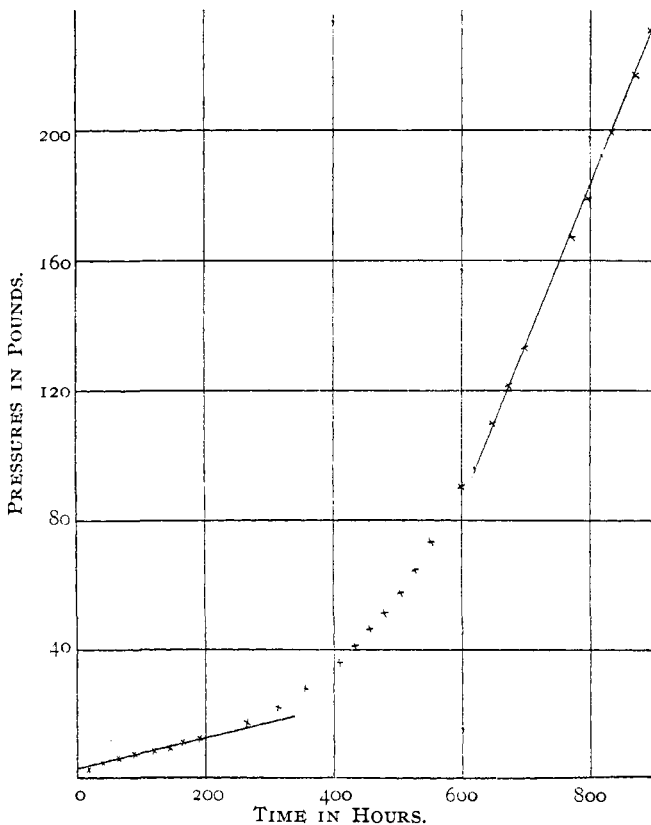


FIGURE 3.—Plot, Showing Rate of Evolution of Hydrogen from a Sodium Solution in Ammonia.

It will be seen from the plot that for the first 250 hours, the pressure increases at a nearly constant rate, but that during the next 400 hours, a great acceleration takes place, after which the rate again becomes nearly constant. Ultimately, of course, the rate of evolution of hydrogen must decrease again owing to diminution in the amount of the reacting constituents. In this experiment the ammonia used up did not exceed 25 per cent. of the initial quantity.

It is probable that this observed acceleration of the rate of the reaction, $\text{Na} + \text{NH}_3 = \text{NaNH}_2 + \frac{1}{2}\text{H}_2$, is due to the catalytic action of the solid product, sodamide, which soon begins to precipitate from the solution

on account of its small solubility. There is no indication, therefore, that an increase in the concentration of hydrogen in contact with a sodium solution causes a decrease in the rate of reaction between sodium and ammonia.

Some Physical Properties.

As is well known, concentrated solutions of the metals possess metallic luster, somewhat of a bronze color. The color in question differs but slightly for different metals although the appearance of yellow tints is noticeable in the case of calcium. More dilute solutions, beginning at about 2 or 3 normal, show no metallic luster, but possess a very characteristic deep blue color. In thin films, the concentrated solutions likewise appear blue in transmitted light; but even for the blue rays the absorption is very great. A solution of sodium in ammonia containing $1/250$ gram-atom of metal per liter, just allows the filament of a 16 candle-power lamp to be distinguished through a thickness of 1 centimeter. The absorptive power of potassium in ammonia is practically identical with that of sodium.

On evaporating a solution of metal in ammonia, the vapor pressure of the solvent decreases with increasing concentration of the solution until a saturated solution is obtained, when the pressure remains constant until all the ammonia has been vaporized and free metal remains behind. The change of this pressure with temperature has been determined by Joannis¹ for solutions of sodium and potassium. The temperatures at which the different metals are attacked by ammonia vapor at atmospheric pressure have been determined by Moissan² as follows: lithium, 70° ; sodium, -20° ; potassium, -2° ; rubidium, -3° ; caesium, 40° ; calcium, 20° .

The heats of formation of saturated solutions of sodium and potassium from solid metal and ammonia vapor have been determined by Joannis¹, who found 5.2 and 6.4 calories per gram-atom of metal, respectively. These values are in good agreement with those deduced thermodynamically from the pressure-temperature curves. The amount of heat evolved in dissolving the metals in liquid ammonia is very small indeed, for the heat of vaporization of ammonia at its boiling point is 5.6 calories,³ thus indicating that the forces coming into play in the process of solution are extremely feeble.

Summary.

The behavior of non-metallic solvents is investigated with respect to

¹ Ann. chim. phys., 7, 49 (1906)

² Compt. rend., 127, 685 (1898); 136, 1177 (1903).

³ It might be inferred from this that at 20° , the equilibrium pressure in the case of calcium is equal to one atmosphere. As will appear from results to be communicated in the next paper, such is not the case. The discrepancy is doubtless due to the slowness with which equilibrium establishes itself.

⁴ Compt. rend., 109, 965 (1889).

⁵ Franklin and Kraus, Am. Ch. J., 21, 12 (1899).

their power of dissolving metals. Lithium is found to be soluble in ethylamine and potassium in ethylenediamine. In the higher members of the primary amines as well as in the secondary and tertiary amines, the alkali metals are insoluble. The behavior of mixed solvents has also been studied. As a rule, the alkali metals are soluble in any inactive solvent containing considerable ammonia, and the solubility is the lower the smaller the amount of ammonia present. If sufficient metal be added to a solvent containing ammonia, the system, in general, separates into two liquid phases which differ markedly in their content of metal as well as in appearance. A similar separation takes place when salt is added to a metal solution in ammonia.

Dilute solutions of the compound NaPb_2 are shown to be electrolytic in nature. An investigation of the products of electrolysis of these solutions indicates that the ions Na^+ and Pb_2^- are present, since two gram-atoms of lead are transferred from the cathode to the anode for one equivalent of electricity. A number of reactions in which this compound takes part have been studied and the results are in accord with this hypothesis. Tin likewise is soluble in an ammonia solution of sodium.

The form of the solubility curve for sodium in ammonia is in part given, in part conjectured from indirect observations. It is shown that over a limited range of concentration two solutions of sodium coexist. Both contain less than 15 per cent. of sodium (according to the formula weight), and their critical point of solution lies in the neighborhood of -50° and 10 per cent. of sodium.

A study is made of the rate of the reaction, $\text{Na} + \text{NH}_3 = \text{NaNH}_2 + \frac{1}{2}\text{H}_2$ as it takes place in a sealed tube at different times. After an initial period of some days, during which the rate of reaction is nearly constant, a great acceleration is observed. This acceleration is probably due to the catalytic action of solid sodamide, which begins to precipitate out after a time. Contrary to the observations of Joannis, there is no indication that the rate of the above reaction is retarded by the presence of hydrogen gas.

Boston, September 7, 1907.

THE CATALYSIS BY ACIDS AND BASES OF THE MUTAROTATION OF GLUCOSE.

By C. S. HUDSON.

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The mutarotation¹ of aqueous solutions of glucose follows the formula of a monomolecular reaction. As is well known its rate is enormously

¹ This term which has been introduced by T. M. Lowry is here adopted in preference to the words "birotation" and "multitrotation," as a name for the slow change in the power of rotating polarized light that is shown by freshly prepared solutions of glucose and other related sugars.