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SOLUTIONS OF METALS IN NON-METALLIC SOLVENTS; III.[1] THE APPARENT MOLECULAR WEIGHT OF SODIUM DISSOLVED IN LIQUID AMMONIA.

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Introduction.

The earliest determinations of the molecular weight of metals in ammonia are due to Joannis,[2] who investigated solutions of both sodium and potassium. His method consisted essentially in determining the change in the vapor pressure of the solvent on addition of a known quantity of metal. From these data he calculated the molecular weight by means of Raoult's law. Of the two determinations made with sodium the pressure change was observed directly in one case, while in the other case the boiling point of the solution under atmospheric pressure was determined, and the pressure of the pure solvent was found by interpolation from its vapor pressure-temperature curve. There is some doubt as to this latter measurement because the boiling point of ammonia was assumed to be —38.2°, whereas the true boiling point of ammonia is —33.46°.[3] Since the results of Joannis are rendered doubtful by the application of Raoult's law to solutions of very high concentration, it is unnecessary to discuss here the experimental errors to which they

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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).

[2] *Compt. rend.*, **115**, 820 (1892); *Ann. chim. phys.*, **7**, 35 (1906).

[3] Gibbs, THIS JOURNAL, **27**, 851 (1905); Franklin, *Ann. Physik*, **24**, 367 (1907).

are subject. The most dilute solutions measured were approximately 3.69 and 3.76 normal with respect to sodium and potassium, respectively, while the composition of one sodium solution was as high as one atom of metal per 5.5 molecules of ammonia. A saturated solution of the metal contains approximately 5 molecules of solvent per atom of metal. In view of the extraordinary properties which these solutions exhibit, the application of Raoult's law is not justified without the support of corroborative evidence.

Franklin and Kraus[1] have determined the molecular weight of sodium and lithium in ammonia by the boiling point method. This method is not capable of a high degree of precision in the case of ammonia solutions, but the results obtained are more trustworthy than those of Joannis, inasmuch as the solutions were less concentrated. The concentration of the sodium solutions varied from 0.3 to 1.3 normal and the apparent molecular weight showed a regular increase from 36 to 59. With lithium similar results were obtained. It should be noted that errors affecting this method, such as loss of solute due to reaction with the solvent or with impurities contained therein, tend to make the observed molecular weight larger than the true one. It is certain that, in general, the molecular weight of metals in ammonia is not double their atomic weight.

The intermediate value obtained by Franklin and Kraus may be due to one of several causes. If both double and single atoms were present in solution in a state of equilibrium, the molecular weight would not be a multiple of atomic weight, and with dilution the apparent molecular weight would decrease owing to increased dissociation. On the other hand, the laws on which the calculation of the molecular weight depend may be inapplicable. This question will be discussed more fully below. In any case, a study of more dilute solutions should yield results that may be interpreted with some degree of certainty.

The present investigation was undertaken with this object in view. It will be shown in what follows that the molecular weight of sodium dissolved in ammonia is certainly as low as 23, while there is evidence indicating that in sufficiently dilute solution the molecular weight falls below this value.

Choice of a Method.

In studying the molecular weight of the metals in ammonia we are somewhat restricted in our choice of a method because of the reactivity of the solute as well as the volatility of the solvent. We are limited, therefore, to the direct determination of the vapor pressure change or to the concomitant changes in the fixed points of the solvent, namely: the freezing and boiling points. The freezing point method was discarded because of lack of facilities for this kind of work. It has since

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[1] *Am. Chem. J.*, 20, 850 (1898).

developed, however, that this method is inapplicable for another reason, to which we shall subsequently refer. As concerns the boiling point method, we are not only confronted with certain difficulties of manipulation, but the constant for the molecular elevation of the boiling point is only 3.4°, even lower than that of water.[1] Moreover, these solutions exhibit a decided tendency to superheat. Owing to the catalytic action of metallic substances,[2] this difficulty can not be avoided by the introduction of platinum tetrahedra or other suitable substances.

Either the vapor pressure change may be measured directly or an inert gas may be bubbled through the solution. The latter method is practically excluded by difficulties inherent in the method. In a 0.1 normal solution the pressure change is only 0.2 per cent. In other words, to obtain a difference of 20 mg. in the amount of solvent evaporated in the pure solvent and in the solution, 10 grams of liquid would have to be evaporated. To evaporate this quantity of solvent would require a long time, relatively large quantities of solvent, and consequently elaborate apparatus to ensure saturation of the inert gas and equilibrium of temperature. If carried out at —33°, where the vapor pressure is one atmosphere, it is evident that saturation could be obtained with great difficulty, if at all.

By a process of exclusion, therefore, we arrive at a direct determination of the vapor pressure change as the only feasible method of determining the molecular weights of the metals in ammonia. It is true that the objections raised to other methods apply in a measure to this method. Thus, the pressure change in a 0.1 normal solution amounts to only 0.2 per cent., which, at the boiling point of liquid ammonia, corresponds to a pressure change of 1.5 mm. While this change is small, it is nevertheless readily measurable with almost any desired degree of accuracy. The chief source of error lies in the difficulty in establishing equilibrium conditions. At the boiling point of liquid ammonia a temperature change of 0.001° affects the total vapor pressure to the extent of 0.004 per cent. As we have seen in a 0.1 normal solution, the total vapor pressure change due to addition of solute is 0.2 per cent. Under these conditions the pressure differences are affected as much as 2 per cent. by a temperature change of 0.001°.

It is plain, then, that we must carry out our vapor pressure determinations with the greatest care as regards temperature equilibrium. The best conditions for accurate temperature regulation prevail at room temperatures. So far as our specific problem is concerned, other advantages in addition to ease of temperature regulation result as we work nearer room temperatures. The total pressure change, which in a 0.1

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[1] Franklin and Kraus: *Loc. cit.*, p. 836.

[2] THIS JOURNAL, **29**, 1567 (1907).

normal solution is only 1.5 mm. at —33°, is increased to 11 mm. at 15°, while the pressure change due to 0.001° is reduced from 4 to 3 per cent The only serious disadvantage that results is a great increase in the pressure which the apparatus must withstand, since at 15° the vapor pressure of ammonia is as much as seven atmospheres. A further source of error is due to the fact that the vapor begins to deviate appreciably from the gas laws. If necessary, however, we may correct for this error.

In determining the vapor pressure change it is of course necessary to measure the pressure change differentially by balancing the pressure of the pure solvent against that of the solution. Any other arrangement is out of question in view of the fact that the differences to be determined are so small a part of the total pressures.

Description of Apparatus.

The apparatus employed in these experiments consists essentially of three parts: First, a thermostat that enables convenient temperature regulation to at least 0.001°; second, a device for measuring quickly and accurately pressures of the order of 1 centimeter; and third, the containing vessels for solution and solvent, together with the means for agitating the liquids and auxiliary apparatus for preparing the solutions.

The Thermostat.—It is obvious that the temperature of the thermostat must be kept below the temperature of the room, otherwise the solvent will distil over into the cooler connecting tubes. Instead of a heating device for regulating the temperature, we require, therefore, a cooling device. Of course, it would be possible to use both a heating and a cooling agent, carrying on the regulation by means of the heating agent, but this is both unnecessary and undesirable. Another point to be considered is the fact that the thermostat must necessarily be a small one; for the containing vessels are fixed, and in preparing the solutions the manipulations require that the containing tubes should be free from the thermostat. The thermostat, therefore, must be a removable one.

A sheet metal tank 14 inches long, 5 inches wide, and 12 inches deep was employed. It was covered with hairfelt insulation and was so arranged that it could be clamped in position or removed in a few moments. A stream of water was employed as cooling agent. The water flowed through a 12 foot length of small copper tubing wound in the form of a spiral and placed centrally in the thermostat. Within this coil, about 4½ inches in diameter, was fixed a screw stirrer driven at any desired speed by a motor and a system of reducing pulleys. Before reaching the copper cooling coil the water passed through a short length of small flexible rubber tubing. This tubing was placed in an adjustable clamping device which was actuated by a relay. When an electric current flowed through the relay the clamp compressed the rubber tubing to any desired extent, so that the water flow could be made as small as desired. On the other hand, when the electric current in the relay was interrupted the clamping device was released and the rubber tube expanded as far as the adjusting screws of the clamp permitted. At all times, therefore, a current of water flowed through the cooling coil of the thermostat. The minimum flow was all but sufficient to compensate the inflow of heat from without, while the maximum flow was just sufficient to over compensate this heat flux to the same extent. This condition is the fundamental one that must be fulfilled by any accurate thermal regulating system. The process of regulation consists in a series of increasing and falling temperatures in the thermostat. Unless these are made sufficiently slow to enable the regulator of the electrical current to follow the temperature of the thermostat, the temperature of the regulator lags behind that of the thermostat and relatively greater temperature fluctuations result than would otherwise be the case. The regulator which was used to control the current in the relay consisted of a series of glass tubes filled with about 200 cubic centimeters of mercury. These tubes were provided with a small capillary and a tube carrying a stopcock, which latter was employed in adjusting the mercury level in the capillary. A platinum wire was sealed in the mercury reservoir for purposes of electrical contact, while another contact was provided in the form of a small pointed adjustable platinum wire which projected into the capillary. The regulator was placed in parallel with the relay and with a fairly high non-inductive resistance in order to avoid sparking. As the temperature of the thermostat rises, the mercury expands until it touches the platinum point in the capillary, when the electrical circuit is completed through the mercury. Its resistance being low, the current passes through this circuit while the current in the relay is decreased to such extent that the clamping device is released and the flow of water is increased in the cooling coil. The temperature of the thermostat at once begins to fall, the mercury contracts until contact is broken and the cooling current is cut down by the relay, which is thrown into action by the current. In a properly compensated system the times elapsing between make and break should be equal and should not be shorter than one minute. This presupposes that the temperature of the cooling water as well as that of the surrounding air remains fairly constant. If this condition is not fulfilled, exact compensation is impossible and greater fluctuations result in the temperature of the thermostat. These conditions were usually fulfilled in the experiments described below. In some cases, however, observations had to be discontinued because of erratic fluctuations in the temperature of the room or of the cooling water. When working properly, no change could be observed in the thread of a Beckmann thermometer and often no readjustment was required in the course of half a day. When the temperature fluctuated, satisfactory readings could not be obtained with the manometer.

The Containers.—As already stated, a differential method was employed in determining the pressure change. The general scheme of the apparatus employed is outlined in Fig. 1. Here *I I'* are the containers. In order that temperature changes should affect both solvent and solution equally, the containing tubes were made as nearly identical as possible and they were always filled with equal quantities of liquid. To obtain equilibrium conditions it is necessary to keep the liquid gently agitated. This was accomplished by means of an electromagnetic device. Two small bucket-shaped vessels of glass, *J J*, open at the bottom, were connected by a length of small glass rod with a length of platinum chain, which in turn was attached to the movable iron cores, *L L*, of the electromagnets. These cores were sealed in glass tubes in order that the containing tubes could at any time be cleaned with strong reagents. The upper portion of the cores were attached to the top of the tubes by means of platinum iridium springs, *N N*. When in equlibrium, the stirrers hung suspended some centimeters from the bottom of the containers, while the iron cores hung near the bottom of the solenoids, *M M*. On passing a current through the solenoids the stirrers

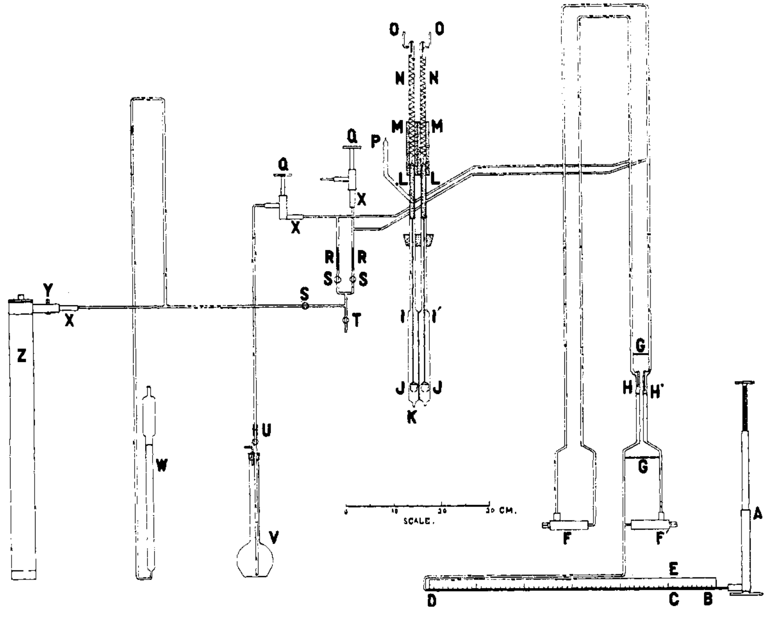

Fig. 1.—Apparatus employed in determining the vapor pressure of solutions of sodium in liquid ammonia.

were raised, to fall again as soon as the current was interrupted. The current in the solenoids was interrupted periodically in a mercury cup by means of a device which was actuated by a metronome. This made it possible to vary the period of the vibrating system in any desired manner. The amplitude of the vibration was controlled by a changeable resistance placed in series with the solenoids. In this manner it was possible to obtain equilibrium without difficulty, provided the temperature regulation was satisfactory.

The Tensimeter.—In measuring pressures of the order of 1 centimeter, it was desirable to employ a method admitting of rapid measurements with an accuracy of not less than 1/25 mm. Because of the solubility of ammonia in various substances and because of the necessity of keeping the solution free from even traces of impurities, it was necessary to use a mercury manometer. It is well known that unless large reservoirs of mercury are employed, surface forces tend to keep the metal from reaching an equilibrium position. If, however, mercury is forced simultaneously into both arms of the manometer, equilibrium establishes itself readily. In the methods commonly in use, the settings are made by adjusting the mercury surfaces to small points by means of a microscope. It seemed much better, however, to adjust the mercury surface to metallic points by noting the point at which contact is made by means of an alternating current and a telephone. This method is very delicate. In a preliminary test of the method, where fairly large mercury surfaces were employed, settings were made which varied not more than 0.0004 mm. This precision could doubtless be improved with a little care. For the measurements of the present experiment it was quite unnecessary to obtain any such degree of accuracy in the settings and a less sensitive apparatus was employed. The tensimeter arrangement is shown in Fig. 1. H H' are the platinum points to which the mercury levels are adjusted. The mercury in the manometer connects through F' D C B with a cylinder, A, filled with mercury and provided with a movable piston. On screwing down the piston, mercury is injected into the manometer. If the pressure on both mercury levels is the same, a certain amount of mercury must be injected into the manometer in order to carry the contact from H' to H. The pressure on the level at H is the vapor pressure of the solution contained in the tube I, while that on the level at H' is the pressure of the pure solvent contained in the tube I'. The point H is about 1 centimeter higher than the point H'. Suppose, now, that the pressure on the level at H is less than on the level at H'. Then, when the mercury level is in contact with the point H', the level in the other arm lies nearer H than it would if the pressures were the same on both surfaces. Therefore, in order to bring the mercury surface in contact with the point H, we need to inject less mercury than in the first case where the pressures on the two surfaces were equal. If we can measure accurately the difference in the amount of mercury injected in the two cases, we have the means for measuring accurately the pressure difference corresponding to these two positions.

To measure the amount of mercury injected, a very simple and convenient device was employed. In the connecting tube *B C D*, whose diameter was about 1 mm., the mercury was interrupted by a short column of air, *C*. The amount of mercury in the manometer up to the point *C* was therefore fixed. On injecting mercury into the manometer, the point *C* of the mercury-air boundary moved along the capillary and the volume of mercury introduced into the manometer is equal to the volume of the capillary over which the boundary moves. A scale was placed alongside the capillary and the position of the end of the mercury thread was read off with a reading glass, which was mounted on a movable carriage.

The capillary tube was calibrated to establish its uniformity of bore. The value of one millimeter difference of mercury level was determined by calibrating directly against a large bore manometer in which the difference in level was measured with a microscope cathetometer. One millimeter of mercury gave a change of 13.80 mm. on the scale of the capillary. When the pressure on the two mercury surfaces was the same, the thread on the scale was deflected 142.2 mm. when contact was carried from the point *H'* to the point *H*. If the pressure of the solution was ΔP mm. less than that of the solvent, the value of ΔP was obtained by the formula

$$\Delta P = \frac{142.2 - \Delta S}{13.8},$$

where ΔS is the scale deflection observed in carrying the contact from the point *H'* to the point *H*. Here ΔS is positive when mercury is withdrawn from the manometer. In other words, when $\Delta S = 0$, contact is made at both points simultaneously and $\Delta P = \frac{142.2}{13.8}$. When ΔP is greater than this value, contact is first made with the point *H* instead of *H'*.

A small induction coil, such as is employed in bridge work, was used to actuate the telephone. The greater portion of the current, however, was shunted through a fairly low resistance. A double throw switch was employed to throw the current from the point *H'* to *H*. A fixed contact was made with the mercury in the manometer through a metal valve, *F'*, whose purpose will be described presently. The air in the capillary was so adjusted that the end of the mercury thread was at the extreme position on the scale when contact was made with the upper point *H*. The scale was about 60 centimeters long and a difference in level of almost 3 centimeters could be measured. Greater pressure differences were measured directly with a cathetometer.

The main object in adjusting to two points instead of to one was to eliminate temperature influences on the mercury in the manometer. If readings were made on one point only, any temperature change would cause the mercury to expand and the zero reading would change. When two points are employed, a difference is obtained which is independent of the temperature except in so far as the density of mercury changes, which change is negligible in these experiments.

In manipulating the apparatus, considerable pressure differences were often obtained. A valve, *F'*, was therefore placed in the manometer, by means of which the connection between the two arms could be shut off. To read the higher pressures, however, a second manometer was connected with the first. This manometer, also, was provided with a valve, *F*, which was closed when ammonia was allowed to escape from one of the containers.

Auxiliary Apparatus.—In carrying out the vapor pressure determinations it is necessary to withdraw ammonia from the tensimeter. For this purpose the two metal valves, *Q Q*, are provided. It is essential that these valves be free from leakage. The most convenient method of securing this condition was to employ a flat aluminum valve seat. The apparatus could be left exhausted for days without visible leakage. In order to attach the metal valve to the glass connections, no kind of cement or wax may be employed. This was a source of difficulty until metal and glass were joined directly by a method of which a description will be given elsewhere.

The ammonia employed in preparing the solution is contained in a small steel cylinder, *Z*, provided with a valve, *Y*. The method of purifying the solvent has already been described. The tube *W* is a contrivance for providing an outlet for the ammonia vapor when preparing the solutions. If the pressure rises above 25 centimeters, the height of the mercury column in *W*, the excess of gas escapes through the mercury. This contrivance should never be omitted in handling ammonia. At the points *R R* the connecting tubes are constricted. When the apparatus has been filled with the desired amount of ammonia, the connecting tubes are sealed off at these points. Before filling the apparatus with ammonia, the air must of course be completely exhausted. This was done by means of an automatic mercury pump which was connected with the apparatus by means of the cock *T*.

Manipulation of the Apparatus.

Great care had to be exercised in setting up the apparatus in order to avoid the disturbing effect of impurities. All connecting tubes, as well as the containers, were carefully washed with alkali and with chromic acid, and finally with water, and dried. The tubes *O O* were used in drying the tubes *I I'*. The stop-cocks were lubricated with a paraffin mixture containing a little rosin. The cocks were much smaller than those commonly employed and they were finally polished with rouge. The polishing eliminates the tendency to "stick" almost completely. A minimum quantity of lubricant was employed. After seating the key properly, any excess lubricant was washed out with ether, then with chromic acid and finally with water.

Introduction of the Metal.—The apparatus as depicted in Fig. 1 is incomplete in that the means for introducing the metal into the tube *I* has not been shown. Since the method employed in the present measurements has been adopted in all succeeding investigations, we shall describe it here in detail. A tube about 40 centimeters long and 4–6 millimeters in diameter is joined to the bottom of the containing tube *H*, as shown in Fig. 2, by means of the capillary *F*. The tube *A* is connected with a second tube, *B*, of about the same diameter and 10 centimeters length, a stop-cock, *C*, being introduced between the two. When the apparatus is in position, the top of the tube *A* is sealed off and the air is exhausted by means of the pump, the cock *C* being open. When completely exhausted, the pump is shut off by means of the cock *T* (Fig. 1), the cocks *S S' V* (Fig. 1) are opened, and ammonia is allowed to enter and fill the apparatus, when the cock *C* is closed. In the meantime a piece of sodium of desired size is freshly cut from a larger piece of clean, dry metal. The top of the tube *A* is cut off, and a steady stream of ammonia gas issues from the opening, as the supply cylinder has not been shut off. The bit of metal, *E*, is dropped into the tube and the glass rod *D*, whose shape and size are evident from the figure, is dropped on the metal. The object of this glass rod will appear below. The tube *A* is now sealed off and the apparatus is at once exhausted, the cock *C* remaining closed, so that the tube *B* remains filled with pure ammonia gas. Ammonia cannot be passed through the phosphorus pentoxide drying tube of the pump. For this reason the pump is equipped with a second drying tube containing metallic sodium in a finely divided state, and this drying tube is employed when ammonia is to be exhausted from the apparatus.

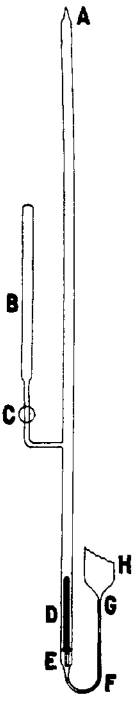

Fig. 2.—Apparatus employed in introducing metallic sodium.

When the apparatus is thoroughly exhausted, the metal is surrounded by a bath of melted paraffin and a small flame is placed under the bath. When the temperature reaches about 100°, the sodium melts. With small quantities of metal, in some cases only 25 milligrams, the coating of oxide prevents the metal from melting down. For this reason the glass weight *D* was placed on the metal. Its weight crushes the metal down as soon as it is melted. The cock *C* is now opened. The pressure of the ammonia on the surface of the liquid metal rapidly forces it through the capillary *F* into the tube *H*, leaving the oxide behind in *A*. The bath is then removed and the capillary sealed off at *G*.

Preparation of the Solution.—Having introduced the metal, the apparatus was thoroughly exhausted, after which the pump was shut off. The tubes *I I'*, Fig. 1, were surrounded with a bath of ammonia boiling under atmospheric pressure, and ammonia was allowed to enter the apparatus from the purifying cylinder *Z* under an excess pressure of 25 centimeters of mercury. The flow of ammonia gas into the tubes *I I'* was controlled by the cocks *S S*. About 20 grams of solvent were introduced into each tube. The supply cylinder was now shut off and the bath was cooled slightly below —33°, which was accomplished by simply dropping the tube containing the condensing liquid slightly below the stopper. This reduced the pressure in the tubes *I I* below that of the atmosphere, whereupon the tubes *R R* were sealed off. The ammonia bath was now removed, and a water bath was substituted to bring the temperature of the apparatus into the neighborhood of that of the thermostat, about 15°. At the same time the cocks *Q Q* were opened and ammonia was allowed to escape into the air. The object of this operation was to remove a small quantity of hydrogen which may, in part, have resulted from interaction of the metal on the solvent in the process of preparing the solution, while another part may have come over from the stock cylinder along with the ammonia vapor. The levels of the liquid in the tubes *I I'* were, of course, kept equal.

The thermostat, which had previously been set into operation and adjusted, was now placed about the tubes, and in case the temperature of the bath was changed on introducing the tubes, a little hot or cold water was added to bring back to temperature at once. The valve *F* was opened, when ammonia was let out of the apparatus, care being taken that the pressure difference in the tubes *I I'* did not exceed the range of the manometer. In all other cases both valves were kept closed. When the auxiliary manometer showed that thermal equilibrium was nearly established, the metronome was set going, which put the stirrers into action. The best results were obtained with a fairly rapid motion of the stirrers over a short path. The valve *F'* of the manometer was now opened and the mercury was adjusted to the lower point *H'* by means of the movable piston *A*. The settings were made with great facility.

The piston was screwed down very slowly, otherwise the rapid displacement of ammonia vapor by the mercury in the manometer disturbed the equilibrium. As soon as a sound was heard in the telephone the motion of the piston was stopped and the scale reading was observed. A resetting was then made. If equilibrium conditions existed in the apparatus, the settings remained constant, otherwise they varied regularly or irregularly according as the disturbing influence was regular or irregular in its nature. If a satisfactory setting could be obtained on the first point, the telephone contact was switched to the second point and the mercury setting was obtained When reproducible settings had been obtained at both points, the manometer valve, *F'*, was closed and the valves *Q Q* were opened to allow ammonia to escape. During this operation the thermostat was dropped below the tubes *I I'* in order that it should not be cooled off by the evaporating ammonia. The solvent that evaporated from the tube *I* containing the solution, was collected in the flask *V* containing a weighed amount of water. When a sufficient change had been effected in the concentration of the solution, the escape of ammonia was interrupted and the flask *V* was replaced by a second, connection being made at *U*. At the end of a series of experiments the flasks were all weighed, from which the amount of ammonia present in the solution at any time was calculated. After bringing the tubes to approximate temperature again, the thermostat was replaced and a new set of pressure measurements was obtained. As a rule, with a single sample of metal, measurements were made on two solutions whose concentrations were approximately in the ratios of 1 : 2. In most cases, however, several independent measurements were made at each concentration, by allowing a smaller quantity of ammonia to escape, usually from 0.3 to 0.6 gram.

Source of Errors.—Initially about 20 grams of ammonia were condensed in each tube. Accurate measurements could not be obtained, however, with this quantity of ammonia in the tube, probably because of imperfect stirring. Beginning with about 12 grams, however, satisfactory results could be obtained. For this reason no results have been incorporated in this paper for solutions containing more than 12 grams of ammonia. All results obtained with solutions containing less than 12 grams are incorporated in the tables which follow below.

When the amount of ammonia reached about 6 grams, the experiment was concluded. The ammonia was allowed to escape and collected in the weighing flask *V*. The tube *I* was then connected with the pump and exhausted to free it completely from ammonia. When completely exhausted, the tube *P* was cut off and absolute alcohol was introduced through the opening in order to dissolve the metal. A rubber tube was attached to *P* and the pressure reduced very slightly, when the tip *K* at the bottom of the container *I* was cut off. The object of the reduced pressure was to prevent the liquid from flowing out at the moment the tip was broken off. An instant later the titrating receptacle was placed under *K* and the liquid was allowed to run out. After washing out the tube *I* a number of times with water, the resulting solution was titrated with hydrochloric acid, methyl orange being used as indicator in order to avoid inconveniences due to carbon dioxide.

One of the disturbing factors that entered in the earlier experiments was the interaction between the metal and the solvent, which is accompanied by an evolution of hydrogen. The interaction of 0.25 mg. of sodium affected the pressure in the apparatus employed by 0.25 millimeter. It is obvious that it was necessary to have a means of getting rid of any evolved hydrogen. This was done by simply allowing a portion of the ammonia in the container *I* to escape. In the earlier experiments the evolution of hydrogen was sufficient to cause a noticeable change in the readings with the time. The rate of change was observed and the true reading was obtained by extrapolation. In later measurements, however, this source of error was completely eliminated. The following corrections were made in connection with this source of error:

Experiment:	I.	II.	III.	IV.	V.	VI.	VIII.
Correction........	5.0	0.0	3.4	0.8	0.0	0.0	0.0 per cent.

The experimental results, together with data necessary in the calculations are given in the following tables. In the first table the Roman numerals indicate the number of the series of experiments. The second column gives the temperatures, the third column the amount of metal in grams. The pressures of the pure solvent in millimeters as given in the fourth column are interpolated from the values of Regnault at 0° and 25° by means of the equation

$$\log P = K - \frac{Q}{46\,T}$$

where $K = 7.9257$ and $Q = 5554$. In the fifth column are given the densities[1] of liquid ammonia at the temperature of the various experiments.

Finally, in the sixth column, is given the weight in grams of 100 cubic centimeters of vapor. These were employed in correcting for the ammonia present in the vapor space. They were determined experimentally and are in agreement with those of Dieterici. No particular effort was made to determine the vapor density with a considerable degree of accuracy, as a large error here would make but a small error in the final results. The total volume of the apparatus was 76 cubic centimeters. The total weight of ammonia was divided by its density to

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[1] Brounn: Verflüssegtes Ammonials Lösungs Mittel, p. 15.

determine the volume of the liquid. Subtracting this from 76 and multiplying the result by the weight of 100 cubic centimeters of vapor, the weight of ammonia in the vapor was obtained.

TABLE I.

Exp. No.	t.	Na.	p.	D.	S.
I.	15.1	0.06480	5425	0.6136	0.57
II.	15.1	0.1511	5425	0.6136	0.57
III.	15.9	0.03270	5581	0.6118	0.59
IV.	15.8	0.2514	5568	0.6120	0.59
V.	15.4	0.1122	5492	0.6129	0.58
VI.	16.0	0.04763	5607	0.6116	0.60
VIII.	19.0	0.02500	6190	0.6090	0.66

In the second table the first two columns explain themselves. All the experiments in a single series were made under identical conditions except that the concentration of the solution was changed. The third column contains the pressure differences in millimeters of mercury. As was stated above, in some of the earlier experiments hydrogen was evolved. In such cases the pressure differences have been corrected as there indicated. The percentage change in pressure is given in the fourth column. The total ammonia and the ammonia present in solution, after correcting for the vapor, appear in the fifth and sixth columns respectively. The logarithms of the dilutions and the dilutions in liters per mol. of metal are found in the seventh and eighth columns. The ninth column contains the molal-composition of the solution in atoms of metal per 100 molecules of the metal and ammonia. Finally the molecular weight is given in the last column as calculated from the equation of Raoult,

TABLE II.

No.	Exp. No.	ΔP.	$\frac{\Delta P.}{P} \cdot 10^2$.	NH_3.	NH_3 corr.	log V.	V.	$\frac{n}{N+n} \cdot 10^2$.	M.
1	I.	20.2	0.3750	11.94	11.71	0.6972	4.979	0.4104	25.36
2	II.	43.0	0.7927	11.48	11.25	0.3108	2.046	0.9910	28.80
3	III.	12.4	0.2222	11.00	10.75	0.9570	9.057	0.2261	25.41
4	IV B. . . .	77.1	1.388	10.25	10.00	0.0395	1.095	1.841	30.70
5	IV C.	96.1	1.726	7.90	7.63	-1.9213	0.834	2.903	32.23
6	V F. . . .	40.2	0.7318	9.44	9.18	0.3516	2.247	0.9038	28.46
7	V G. . . .	53.2	0.9695	7.07	6.80	0.2197	1.659	1.220	29.06
8	VI F. . . .	18.12	0.3231	10.13	9.88	0.7609	5.767	0.3587	25.27
9	VI G. . . .	18.52	0.3303	9.92	9.67	0.7515	5.643	0.3665	25.31
10	VI H. . . .	26.6	0.4743	6.69	6.42	0.5728	3.739	0.5558	26.47
11	VI I	26.8	0.4778	6.66	6.39	0.5716	3.729	0.5614	26.39
12	VIII E. . . .	10.00	0.1615	12.49	12.23	1.1317	13.54	0.1519	21.58
13	VIII F. . . .	10.30	0.1663	12.15	11.87	1.1187	13.14	0.1565	21.62
14	VIII G. . . .	15.26	0.2465	7.72	7.42	0.9118	8.162	0.2516	23.43
15	VIII H. . . .	16.00	0.2584	7.36	7.05	0.8893	7.750	0.2669	23.53

$$\frac{n}{N+n} = \frac{\Delta p}{p},$$

where n is the number of atoms of solute and N the number of molecules of solvent present in the solution. In terms of the numerical quantities employed, this equation reads:

$$M = \frac{17\text{Na}}{\text{NH}_3}\left(1 - \frac{\Delta p}{p}\right)\frac{p}{\Delta p}.$$

Na and NH_3 are the weights of sodium and ammonia, respectively, in grams and 17 is the molecular weight of gaseous ammonia.

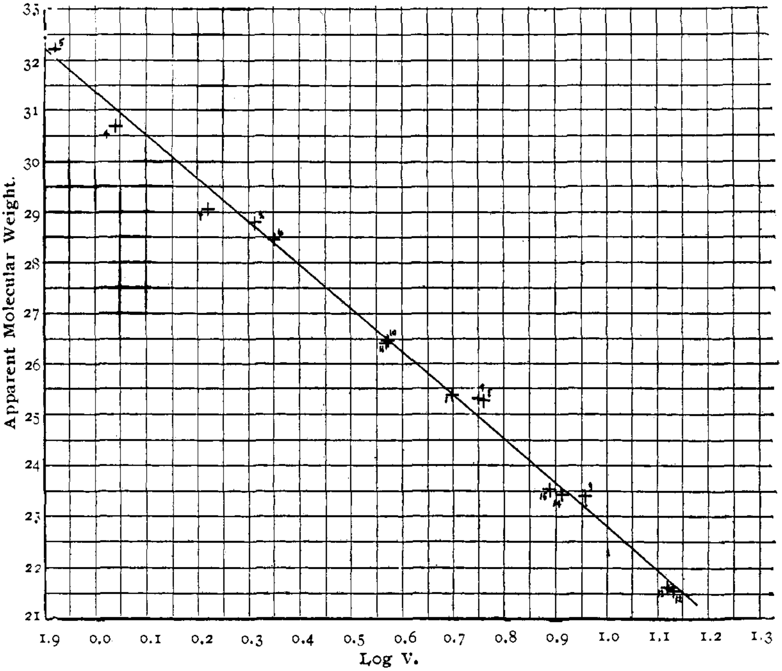

Fig. 3.—Showing the relation between the apparent molecular weight and the concentration of sodium dissolved in ammonia.

The results are shown graphically in Fig. 3, where the logarithms of the dilutions are plotted as abscissae and the apparent molecular weights as ordinates. It is evident that the molecular weight of sodium is near its normal value in 0.1 normal solutions. With increasing concentration the molecular weight seemingly increases, although at slightly more than normal concentration the molecular weight is still much lower than that obtained by Joannis.[1] Curiously enough, the molecular weight in the most dilute solution is slightly less than the normal value. Although the deviation from the normal value is much less than the maximum deviation of the points on the curve, it might be supposed that the low value is due to some constant factor that tends to render all the values too low. This is not the case, however, for in that event the curve

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[1] Loc. cit.

should approach asymptotically, a line drawn parallel to the log V-axis and 23 units above it. The regular slope of the curve indicates that the true molecular weight lies at least as low as indicated in the curve and that at greater dilutions it lies considerably lower. In a later paper it will be shown that sodium dissolved in ammonia undergoes ionic dissociation, each atom breaking up into two univalent ions.

It now remains for us to determine the meaning of the results in more concentrated solution. At first sight, we might conclude that the atoms of sodium are in dynamic equilibrium with diatomic or polyatomic molecules. This is the view adopted by Joannis. On the other hand, we may expect that the laws applied in calculating the molecular weight of the metal are inapplicable. We should bear in mind, in this connection, the exceptional nature of these solutions.

In order to gain a better understanding of this question we must consider the conditions under which Raoult's law may be applied. If Raoult's law holds, the pressure is a linear function of the composition of the solution. Therefore, the vapor pressure-composition curve of the mixture must be a straight line, both for the partial pressures of the components as well as for the total pressure of the mixture. Many cases of this kind are known; in general, any two substances which are nearly related in constitution and properties obey this law. In other cases, however,

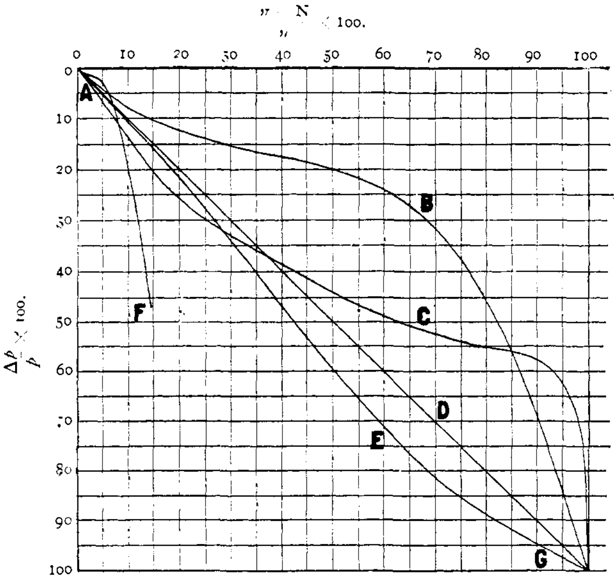

Fig. 4.—Showing the Relation between the Partial Pressure of One Component and the Composition of Completely Miscible two Component Systems.

Raoult's law does not hold. In Fig. 4 are plotted typical examples of partial vapor pressure-composition curves. For the sake of comparison the actual partial pressures have been divided by the pressure of the pure solvent. The form of the curve remains unaltered, the different ordinates merely being reduced in such ratio as to give a common value for the pressure of the pure solvent. The straight line ADG represents the vapor pressure curve for solutions of ideal substances which obey Raoult's law. The curve ABG is that of acetone,[1] in which varying amounts of carbon bisulphide have been dissolved. The deviation here is very pronounced. Even in relatively dilute solutions the law of Raoult is inapplicable. The curve AEG is that of acetone with varying amounts of chloroform. There the deviations from Raoult's law are distinctly less than they are in the case of carbon bisulphide, but the deviation is in the opposite direction. Finally, in the curve ACG, which gives the partial vapor pressure of pyridine in solutions of pyridine and water, we have a combination of the two preceding cases, the curve cutting the theoretical straight line.

So far as Raoult's law is concerned, we see that deviations of many kinds occur. In all cases, however, the law may be applied, if the solutions be made sufficiently dilute. What may be the cause of the deviations in different cases is uncertain. A change in the molecular weight of the solute would of course cause a deviation from Raoult's law in one sense of the term. The deviation, however, manifests itself in extremely dilute solutions and is in the direction of too large a change in pressure. On the other hand, a change in the molecular state of the solvent, or combination between solvent and solute would both cause deviations in concentrated solutions, although in opposite directions.

Finally, another factor may cause a deviation. Raoult's law, namely, is a generalization of Dalton's law for the pressure of gaseous mixtures. According to this law every gas exerts a pressure dependent on its concentration alone, irrespective of what other molecular species may be present. Applied to liquids, this law states that if any fraction of the molecules present in a liquid be replaced by an equal number of molecules of a second liquid, the remaining fraction of the first liquid exerts the same activity, or vapor pressure, as it did before the substitution had taken place. In view of the deviation of gases from the simple laws, it would be surprising if, in the case of liquids, the substitution did not exert an influence on the remaining molecules, particularly when the new molecules are very different from those replaced. The greater the difference in the nature of the two substances, the greater will be the deviations from Raoult's law. Unfortunately, measurements of

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[1] The data for these curves were obtained from a paper by Zavidski, *Z. physik. Chem.*, **35**, 129 (1900).

the partial pressure of liquid mixtures have thus far been confined to cases in which the two components are miscible in all proportions.

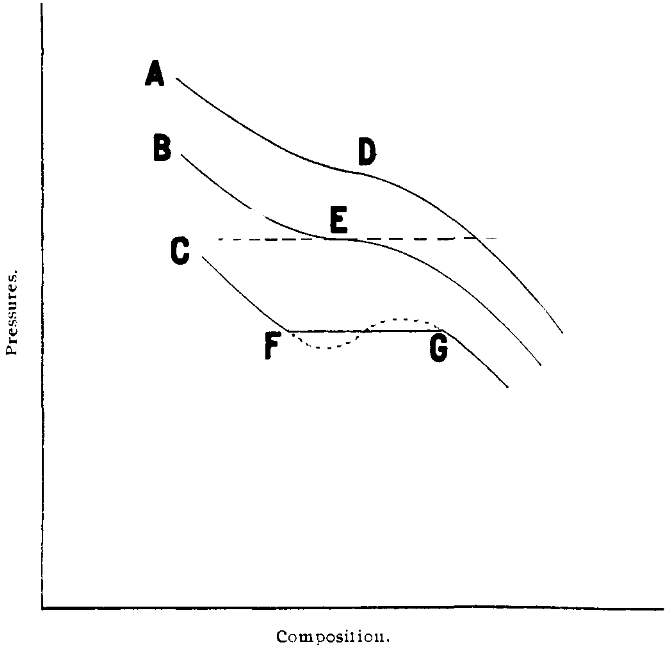

Fig. 5.—Showing the change in the form of the vapor pressure-composition curves with temperature.

By proper temperature change a homogeneous mixture may, in general, be made to separate into two phases. The effect of temperature on the tendency to separate into two phases is illustrated in Fig. 5, where pressures are plotted as ordinates and compositions as abscissae. The curve A is that of the vapor pressure of one component of a liquid mixture, in which the components are miscible in all proportions. With falling temperatures, in general, the tangent to the curve at the point of inflexion D becomes more nearly parallel with the axis of composition. Finally, a temperature is reached where the tangent becomes parallel to the axis as represented in curve B. The liquid mixture is now at the critical temperature and the point E represents the critical composition. On lowering the temperature further, a two phase system will, in general, result. The vapor pressure curve is represented by C. Here compositions between F and G can not be realized. The theoretical vapor pressure curve between F and G resembles that of a one component system below the critical point and is represented by the dotted curve FG. The pressures in this region correspond to unstable states. Pronounced deviations from the theoretical vapor pressure curve of a component in a liquid mixture represents a tendency of the mixture to separate into two phases in this region. Whenever we find liquid mixtures separating into two phases at one temperature we must expect to find deviations from Raoult's law at higher temperatures, even though the components are miscible in all proportions. In general, the critical region lies between the compositions of 25 and 75 per cent. of either component. The curves in Fig. 4 indicate such a behavior. But it is possible that the critical composition may lie in much more dilute solutions, or there may even be two critical regions. Moreover, the second component need not be a volatile component or even a liquid, although such cases have not been studied heretofore.

It has already been mentioned that the solutions of the metals in ammonia exhibit very exceptional properties and that the properties vary very rapidly with concentration. Moreover, as is well known, the metals present certain properties which are entirely wanting in non-metals. In other words, there must exist in metals certain molecular conditions which are characteristic of this state of matter. In dissolving a metal in ammonia we are replacing molecules of solvent by molecules of a substance which present as great a difference from the solvent molecules as we can hope to realize at the present time. The applicability of Raoult's law is therefore to be questioned. Of course, in sufficiently

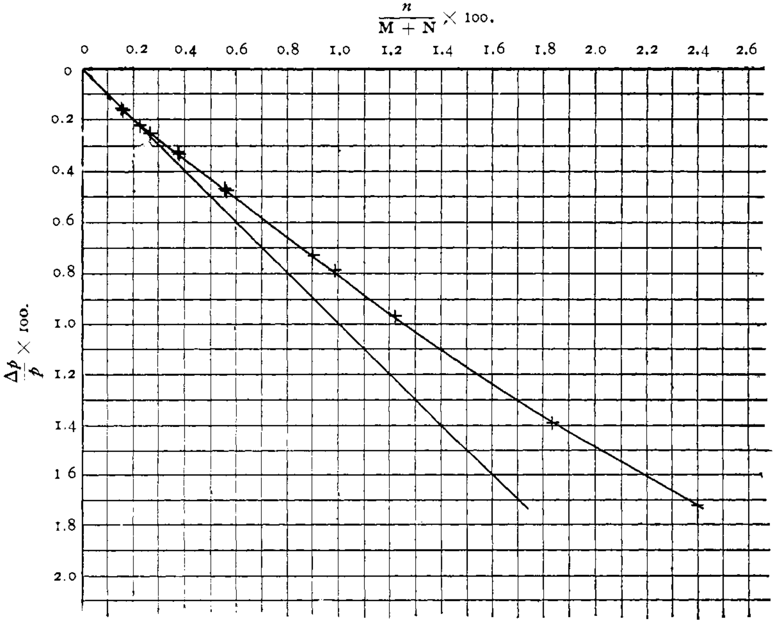

Fig. 6.—Showing the relation between the composition of solutions in ammonia and the percentage change in pressure.

dilute solutions Raoult's law must apply even here, but the point at which appreciable deviations appear may be expected to lie in more dilute solutions than would be the case for a non-metallic solute.

Let us now examine the vapor pressure curve for sodium dissolved in ammonia. In this case we have a peculiarly simple system, inasmuch as we have only one volatile component, and the partial pressure coincides with the total pressure. In Fig. 6 the reduced pressures $\frac{\Delta p}{p}$ are plotted against the molal concentration $\frac{n}{n+N}$. We see that there is a strong deviation from the ideal vapor pressure curve which is represented by the straight line. This deviation is in the direction in which the pressure would be changed by association of the solute, but whether or not this is actually the case cannot be decided without further evidence. To this point we shall return shortly.

It is interesting to note that the deviations observed here begin in very dilute solutions, almost 0.1 normal, and that they increase rapidly. The curve cannot be said to approach the theoretical curve tangentially, but gives signs of crossing it at about 0.1 normal. In dilute solutions, therefore, the observed pressure changes are too great. The curve has not been followed out to sufficiently dilute solutions to preclude the possibility that this deviation may be due to experimental errors, but, as was brought out in connection with Fig. 3, the concordance of the results indicates that the true molecular weight is less than the atomic weight of sodium. Evidence corroborating this point will be adduced in a later paper.

Returning, now, to a discussion of the more concentrated solutions of sodium in ammonia, we may make use of some vapor pressure measurements of Joannis[1]. These measurements, with one exception, were made with sodium solutions at 8.9°. The temperatures varied somewhat about this point and the pressures have been corrected to 8.9° by means of the temperature coefficient of the vapor pressure of pure ammonia. The values of $\frac{\Delta p}{p}$ have been calculated from these data of Joannis and combined with the values obtained in this paper. Since the temperature in the two cases differed by only from 6° to 7°, there can be no objection to combining the results in this way. The results appear plotted in the curve AF of Fig. 4 and in part on a larger scale in Fig. 7. The curve is a very remarkable one. Initially the pressure curve deviates strongly to one side of the theoretical curve in dilute solutions, then it cuts the theoretical curve, and in more concentrated solutions it deviates even more strongly in the other direction. The

[1] *Ann. chim. phys.*, 7, 21 (1906).

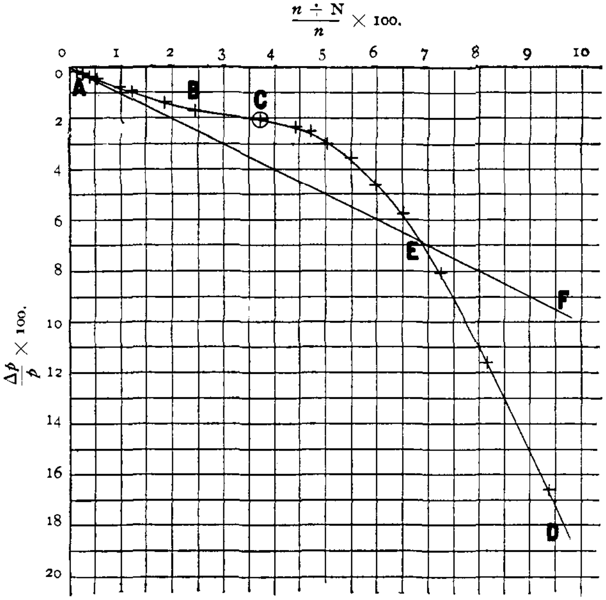

Fig. 7.—Vapor pressure-composition curve for solutions of sodium in ammonia.

curve stops at the point F (Fig. 4) for the reason that at this point the solution is saturated with sodium. If lithium were used, however, in place of sodium, the curve would continue in the direction F and to a point for which the value of $\frac{\Delta p}{p}$ would be only about 1/60 and of $\frac{n}{n + N}$ about 1/4. The vapor pressure-composition curve of the sodium solution resembles that of solutions of water in pyridine, but the deviations occur in reverse order, they are much greater, and the common point with the theoretical curve lies in much more dilute solutions.

The point *C*, which is circumscribed with a circle, represents the point at which Joannis determined the molecular weight of sodium in ammonia at 0°. That the molecular weight calculated at this point by Raoult's law should be much greater than those found in this investigation is evident. It is apparent, also, that at still greater concentrations the molecular weight calculated in this manner will reach a maximum after which it will again diminish passing through the normal value of 23 at the point E and then decreasing below this value. From the results of Franklin and Kraus[1] it is probable that lithium behaves in a similar manner. That a calculation of molecular weights in the more concentrated solutions is meaningless, requires no further demonstration. It remains, however, to determine if the initial deviation may not be due to asso-

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[1] *Loc. cit.*

ciation of the solute. To decide this we must recall that, as was shown above, the point at which the curve becomes parallel to the axis of composition is the critical point of the solution and that at lower temperatures the solutions in this region become unstable, separating into two liquid phases. As may be seen from the figures the pressure curve at room temperatures is only very slightly inclined to the axis of composition. At lower temperatures, therefore, these solutions should separate into two phases. In an earlier paper,[1] the general form of the solubility curve was given and it was shown that below -56° the sodium solutions actually separate into two phases and that the critical point[2] lies near 3 per cent. of metal, a point that corresponds with the abnormality in the vapor pressure curve as determined in the present investigation. The deviations from the theoretical vapor pressure curve are not, therefore, due to association but are due to a change in the nature of the medium which has its seat in the pronounced difference in the nature of the two components. The difference in properties between sodium solutions containing 1 atom and 10 atoms of metal per 100 molecules of solution, respectively, is greater than that between acetone containing ten per cent. of carbon bisulphide, and of carbon bisulphide containing ten per cent. of acetone. What the nature of the changes are that result when a sodium solution is concentrated will be shown in another communication.

Summary.

A method has been devised which has made it possible to determine the pressure changes resulting in ammonia, on addition of sodium, with an accuracy of about 1 per cent., when the total pressure change was as small as 10 millimeters. The measurements were carried out at approximately 15°, and the dilution of the solutions varied from 1 to 13 liters per gram-atom of sodium.

In dilute solutions the molecular weight is certainly as low as 23, and there is evidence for believing that the molecular weight is even lower in solutions beyond 0.1 normal.

In more concentrated solutions the pressure change is smaller than is

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[1] THIS JOURNAL, 29, 1565 (1907).

[2] Since writing the above, a paper has appeared by Ruff and Zedner, *Ber.*, **41**, 1948 (1908), which furnishes the necessary quantitative data for the critical point of sodium solutions. The critical temperature is shown to be —46° and the critical composition 2 molal per cent. of metal. My deductions with regard to this point are thus independently confirmed. These authors have also measured the change in the boiling point for solutions of sodium, potassium and lithium. These results are likewise in agreement with the results of this paper, that is, in fairly dilute solutions, the apparent molecular weight is too great and in concentrated solutions it is too small. This corresponds to the deviation of the vapor pressure first on one and then on the other side of the theoretical curve.

to be expected from Raoult's law. This might be ascribed to association of the atoms of the solute. It is shown, however, that the deviation of the pressures from Raoult's law are due to the abnormal properties of the system under consideration. From the form of the complete vapor pressure curve of sodium solutions, it appears that the deviation is due to the fact that there is a tendency for the solutions to separate into two phases for which the critical point lies near 3 molal per cent. of metal. That separation takes place in this region at lower temperatures has been shown in an earlier paper. The law of Raoult can not, therefore, be applied to solutions more concentrated than 0.1 normal.

BOSTON, June 9, 1908.

THE DETERMINATION OF VAPOR PRESSURES OF SOLUTIONS WITH THE MORLEY GAUGE.

BY O. F. TOWER.

Received June 6, 1908.

Vapor pressures of liquids were first measured by the static method, which consists essentially in introducing the liquid under investigation into the Torricellian vacuum of a barometer and noting the distance the mercury column falls.[1] Many accidental and almost unavoidable circumstances render this method uncertain, so that within recent years it has been but seldom employed. Many other methods have replaced it. In one, an indirect method developed by Ramsay and Young,[2] the vapor pressure of a solution is calculated from observations of its boiling point under different pressures.

The methods, however, used most commonly, recently, divide themselves into two classes, which may be designated as the "differential" and the "dynamic" methods. In the "differential" method the difference between the two vapor pressures, commonly that of a pure solvent and one of its solutions, is measured by means of a suitable gauge. Dieterici[3] employed as a gauge a membrane connected with a pointer; any difference in pressure on the two sides of the membrane would cause a movement of the pointer which could be read off on a scale. Smits[4] employed a so-called "micromanometer" based upon the principle that if a U tube, whose upper portions are considerably widened so that they have a diameter n times that of the lower portion, is filled with a liquid, any movement of the level in the upper portions produces a movement of n times the distance in the lower. It is of course necessary to have a visible meniscus in the lower portion of the tube. This was accom-

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[1] See Magnus: *Pogg. Ann.*, **38**, 93 (1836).

[2] *Phil. Trans.*, A **183**, 107 (1892).

[3] *Wied. Ann.*, **50**, 47 (1893); **62**, 616 (1897); and **67**, 859 (1899).

[4] *Z. physik. Chem.*, **39**, 385 (1902).