

a Meker burner. On dissolving in dil. hydrochloric acid, there was no residue. The solution was made up to 250 cc. Silicon was determined in the customary way—iron and titanium colorimetrically. The determination of zirconium by precipitation as phosphate or otherwise, presents, according to Marden and Rich, so many uncertainties as to be unreliable for a sample of high purity. An attempt was made, therefore, to determine zirconium by volatilization of the fluoride in the absence of sulfuric acid. This volatilization, however, proved to be only partial. By 12 successive treatments with hydrofluoric acid solution, the residue was reduced progressively to 2%. This determination was, therefore, not made. Analysis showed 0.36% of ferric oxide, 0.70% of silica and 1.00% of titania; after purification, the percentages were 0.00, 0.00 and 0.92, respectively.

Summary

Zirconia is best dissolved by fusion with a mixture of borax and soda. The fusion, when taken up in dil. hydrochloric acid, cannot be separated from insoluble residue by direct filtration. It was found that by precipitating the hydroxide, the residue is entangled and can then be filtered and washed. The hydroxide can then be dissolved on the filter and filtered clear by repeatedly pouring the filtrate through the precipitate. A very little sulfuric acid added to this filtrate precipitated very gelatinous, zirconium basic sulfate which, however, could be coagulated by heating nearly to boiling and then filtered and washed free from iron and aluminum. Titanium was also precipitated as basic sulfate and could not be removed to any great extent.

The process, while complicated and slow, seems to be efficient in removing iron, alumina and silica.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 21]

THE MOLECULAR WEIGHT OF THE SODIUM-TELLURIUM COMPLEX IN LIQUID AMMONIA AS DERIVED FROM VAPOR-PRESSURE MEASUREMENTS

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Introduction

As a result of the investigations of Kraus,¹ Posnjak,² Smyth,² and Kraus and Chiu,³ the atomic proportions in which sodium appears combined with lead and with tellurium in liquid ammonia solution have been definitely established.

¹ Kraus, *THIS JOURNAL*, **29**, 1556 (1907).

² Posnjak, see Smyth, *ibid.*, **39**, 1299 (1917).

³ Kraus and Chiu, *ibid.*, **44**, 1999 (1922).

In equilibrium with metallic lead, one atom of sodium appears combined with 2.25 atoms of lead in ammonia solution. Smyth has suggested that in solution several lead compounds containing various amounts of lead exist in equilibrium with each other. Since the ratio of lead to sodium appears to be independent of concentration, the equilibrium among the complexes is not displaced by concentration change.

In the case of solutions containing sodium and tellurium, the ratio of tellurium to sodium, varies as a function of the concentration (of sodium), as was shown by Allison,⁴ Power⁵ and Kraus and Chiu.³ At a concentration in the neighborhood of 2 *N*, the ratio of tellurium to sodium has a value of approximately 2.02, and this ratio remains very nearly constant to concentrations as low as 0.5 *N*, after which it begins to decrease as the concentration decreases.

Kraus and Chiu have investigated the system, sodium-tellurium-ammonia, in some detail and have established the fact that the reaction between sodium and tellurium takes place in several stages. The first product of the reaction is the normal telluride, Na_2Te , which compound further reacts with tellurium to form a solution the composition of which corresponds to the formula Na_2Te_2 . The composition of the solution remains fixed so long as the normal telluride is present.⁶ In the presence of the free metal (tellurium) the telluride Na_2Te_2 reacts further with tellurium to form a telluride or a mixture of tellurides containing larger amounts of this element. As has already been noted, the ratio of tellurium to sodium in a solution in equilibrium with free metallic tellurium varies with the concentration.

The question naturally arises: What is the nature of the solutions of the complex telluride? It has been shown that, in solutions containing the compounds of sodium and lead and sodium and antimony, the less electro-negative element functions as anion, since it may be precipitated in the free state on the anode by electrolysis. In the case of a normal salt, such as the telluride, Na_2Te , there is every reason for believing that in solution the tellurium is present as a normal telluride ion carrying 2 negative charges. When, however, the normal telluride reacts further with tellurium, the question arises: Is a complex anion formed, consisting of the original telluride ion associated with other atoms of tellurium; or, conceivably, does the valence of the tellurium ion change? In the former case the formula of the first complex telluride would be Na_2Te_2 , while in the latter case its

⁴ V. C. Allison, *Thesis*, Clark University, 1916.

⁵ F. W. Power, *ibid.*, Clark University, 1917.

⁶ At low concentrations, the ratio of tellurium to sodium in the solution would, of course, diminish if the solubility of the normal telluride, Na_2Te , were appreciable. The solubility of the normal telluride, however, is extremely low, for which reason, at higher concentrations, this ratio in solutions which are in equilibrium with the normal telluride remains fixed.

formula would be NaTe . That is, we should in one case have the complex telluride ion Te^{--}Te with 2 negative charges, and in the second case the ion Te^- with a single negative charge. It is by no means obvious that the latter process may not occur. So far, we have so little information regarding complex compounds of this type that it would be unsafe to draw any definite conclusion without further data.

If the complex telluride ion carries 2 charges, then obviously the formula of the compound will be $\text{Na}_2\text{Te}^{--}\text{Te}_x$. By means of molecular weight determinations it should be possible to distinguish between the alternative possibilities suggested above. According to Franklin and Kraus,⁷ the molecular weight of salts in ammonia solution at ordinary concentrations is practically normal, which corresponds roughly with their electrical properties, since their ionization at ordinary concentrations is comparatively low. It might be expected, therefore, that the molecular weight of the complex tellurides could be determined in ammonia solution. As Kraus has already pointed out,⁸ the only readily available method for determining molecular weights in ammonia solution is that of determining the vapor-pressure change due to the solute. In the following investigation, therefore, this method has been adopted for the purpose of determining the molecular complexity of the complex tellurides in ammonia solution.

Apparatus and Experimental Method

The experimental method employed in this investigation is essentially the same as that employed by Kraus in determining the molecular weight of sodium in liquid ammonia solution. The apparatus employed consists essentially of 4 parts: first, a thermostat, by means of which the temperature may be maintained constant to 0.001° or better; second, a device for measuring accurately pressure differences of the order of magnitude of 1.0 mm. of mercury; third, the containing vessels for the solutions and the solvent, together with means for agitating the liquids; and fourth, a means of introducing known amounts of the metals and of ammonia into the containing vessel.

The Thermostat.—It is essential that the temperature be kept below that of the surroundings; otherwise the solvent will distil into the cooler parts of the apparatus. Cooling was accomplished by allowing cold tap water to flow continuously through a 3-meter length of copper tubing of 5 mm. internal diameter. This tube was immersed in the thermostat liquid, as will be described more in particular below.

The desired temperature was maintained by means of a steel encased mercury thermo-regulator and an electrically heated coil of heavy resistance wire. The copper cooling tube, in the form of a flat spiral, and the heating element, of bare Nichrome wire wound in spiral form, were placed concentrically around the shaft of the stirrer and just above a cylindrical tube in which the stirrer revolved. It was found necessary to maintain very vigorous stirring. The thermostat contained approximately 110 liters of

⁷ Franklin and Kraus, *Am. Chem. J.*, 20, 837 (1898).

⁸ Kraus, *THIS JOURNAL*, 30, 1197 (1908).

kerosene. Even though the thermostat seemed to be regulating well within 0.001° , it was found impossible to obtain consistent readings of the pressure. Apparently, the tubes containing the pure ammonia and the ammonia solution of the telluride were subject to temperature fluctuations due, in part at least, to incomplete mixing of the liquid in the thermostat. Increasing the stirring through the introduction of additional stirrers did not prove effective.

In order to overcome this difficulty, a square box *C*, of which a section is shown in Fig. 1, 11.5 x 30.5 cm. internal dimensions, constructed of 1cm. asbestos board, and provided with a chimney projecting 6 mm. above the liquid in the thermostat, was then placed around the containers *A* and *B* as shown in the figure. All the joints in this

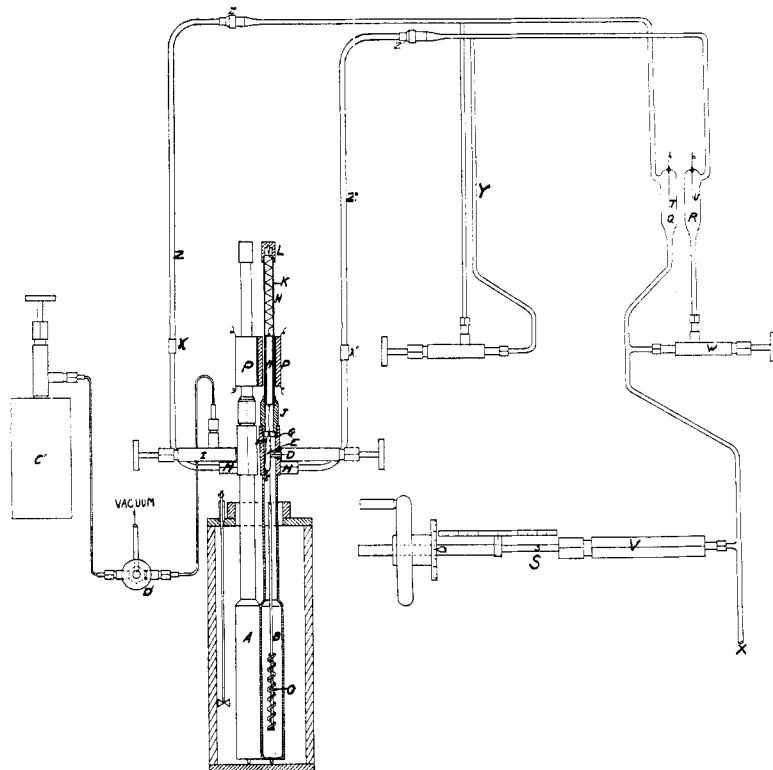


Fig. 1.—Apparatus employed in determining the vapor-pressure lowering due to complex tellurides dissolved in liquid ammonia.

box were made tight so that no liquid passed in or out. The liquid in this box was stirred vigorously by means of a small propeller, driven from the same motor as that which drove the large stirrer in the main thermostat. With this arrangement it was found possible to obtain reasonably consistent readings. The box served to integrate the temperature fluctuations in the main thermostat in the immediate neighborhood of the containers *A* and *B*.

The Containers.—The general scheme of the apparatus is shown in Fig. 1. *A* and *B* are the containers. These are identical in every respect except that *B* is fitted with a means, shown at *D*, for introducing the sodium into the ammonia. The tube *B* is shown in section. The containers are constructed of steel, and are lined with glass

nearly up to the hexagonal connecting piece to which *H* is attached. The steel shell has a thickness of approximately 0.8 mm. and the glass lining is of approximately the same thickness. The upper part of *B*, to which the movable plunger *D* is attached, is constructed of 2.5cm. hexagonal steel stock. This hexagonal portion is provided with 2 outlets. One of these outlets, into which *H* is screwed, leads to the pressure-measuring device; the other is fitted with a valve similar to *I*, shown attached to *A* in the figure. Each container consists of 2 parts which are screwed together, a tight joint being obtained by means of the conical seat shown at *G*. The upper portion of *A*, as of *B*, consists of the short 22mm. hexagonal steel section *J* to which is screwed and soldered the brass tube *K*. This tube has an internal diameter of 1 cm. and a wall thickness of 1.5 mm. At the top, *K* is provided with a conical seat fitting into the brass cap *L*. *M* is a piece of steel rod of 8 mm. diameter and 9 cm. in length. This rod is suspended from the cap *L* by means of a spring of steel piano wire. From the lower end of *M* is suspended the glass stirrer *O* by means of a length of platinum-iridium wire. The stirrer *O* is made by wrapping a glass rod of 3 mm. diameter spirally around another rod of approximately the same size. The stirrer system is actuated by means of the solenoids *PP*, the current in which is interrupted at regular intervals by means of a motor-driven contact device.

The means for adding the sodium is shown at *D*. The sodium is contained in a small glass capsule *E*, into which it is introduced by a method similar to that described by Kraus.⁹ *B* is provided with the lugs *LL*. The capsule rests on the lower lug, while the upper lug with the plunger *D* serves to hold the capsule in position. The capsule *E* is placed in position just before the 2 parts of *B* are screwed together. At any desired time subsequently, it may be broken and allowed to drop to the bottom of the container below by simply forcing the plunger *D* inward against the capsule. The valve *I* on Container *A* and an identical one on *B* are used during the evacuation of the system, and the introduction and the removal of ammonia.

The Tensimeter.—The tensimeter consists essentially of the displacement piston *S* and 2 glass tubes *Q* and *R*, provided with platinum contacts *T* and *U* ground to needle points. By means of the displacement piston *S*, mercury may be transferred from the cylinder *V* into the tubes *Q* and *R*. For differences in pressure of less than 2 cm. of mercury, use is made of the 2 contact points at the lower ends of *T* and *U*, as will be explained below. Tube *B*, containing the solution, is connected to *R* containing the point situated at the higher level. *A* is connected to the tube *Q*. The connecting tubes leading from the containers to *Q* and *R* are arranged as follows. *ZZ* are flexible copper tubes of 5 mm. internal diameter soldered to the fittings *H*. These tubes are connected to the glass tubes attached to *Q* and *R* by means of glass to metal seals⁹ shown at *Z'Z'*. The vertical distance between the ends of the contact points *T* and *U* is accurately determined by means of a cathetometer. The distance through which the displacement piston *S* moves in order to carry the mercury in *Q* and *R* from the level of the lower point to that of the upper point is accurately determined and is indicated on a scale *S* placed alongside the piston. This scale is divided into 32nds of an inch (0.8 mm.). A dial on the nut, which rotates once when the piston moves through a distance equal to one scale division, is divided into 100 divisions, and this serves accordingly to divide each $\frac{1}{32}$ inch into 100 parts. Contact between the platinum points and the mercury in the tubes *Q* and *R* is indicated by means of a telephone receiver placed in a circuit containing a small induction coil. This arrangement makes possible reading pressure differences with a precision of 0.01 mm. of mercury.

In order to read the difference in the level of the mercury surfaces in *Q* and *R*, the following procedure is carried out. Contact is first made with the lower

⁹ Kraus, U. S. pat. 1,046,084, Dec. 3, 1912.

contact point in Q and the reading of the position of the piston S is noted on the adjacent scale. Mercury is now injected or withdrawn from Q , and R , depending upon whether the difference in pressure is less or greater than the distance between the points, until the upper meniscus makes contact with the point in R . For example, to obtain the actual value of the difference in pressure on the 2 surfaces when this is less than the distance between the 2 points, the equivalent height of mercury injected at S is subtracted from the distance between the points. When the difference in pressure is greater than that between the points, the equivalent height of mercury withdrawn is added to the distance between these points.

Pressure differences greater than 2 cm. of mercury are determined by reading directly the position of the menisci in Q and R by means of a cathetometer. A sheet of polished metal placed behind the meniscus, with strong illumination from the front, gives a very sharply defined outline of the meniscus when viewed through a telescope. Readings with the cathetometer under these conditions could readily be reproduced with a difference of less than 0.05 mm. of mercury.

Valve W serves to separate the 2 limbs of the manometer system, Q and R , when desired. An auxiliary mercury displacement piston, not shown in the figure, is connected at X . This piston has a capacity approximately 4 times that of S and is employed to adjust the surfaces in Q and R to any desired initial point. At Y is shown an auxiliary manometer, which serves to indicate the relative pressures in the system when these pressure differences are very large, as they often are when ammonia is withdrawn from the tubes containing the solution or the pure solvent.

The arrangement for introducing ammonia into the containers will be described in connection with the experimental procedure.

Experimental Procedure

The glass-lined portions of the containing tubes A and B are thoroughly cleaned with hot chromic acid cleaning mixture. The exposed metal portions of the containers, the internal portions of the valves, and the metal connections are washed with alcohol and ether and wiped clean with cotton. The tellurium,¹⁰ in stick form, is introduced into the glass-lined tube B immediately after cleaning. The capsule E , containing a known quantity of sodium, is placed in position as shown at D , and B is closed by means of the screw joint G . The tubes A and B are then placed in position, A in its permanent position in the thermostat and B in a convenient position in which it may be surrounded with a bath of liquid ammonia. Connections to the flexible copper tubes ZZ are then made by soldered joints $X'X'$. The ammonia is contained in a light steel cylinder C' . This ammonia is purified by distillation into C' from a tank in which it has previously been purified by the methods described by Franklin and Kraus.¹¹ C' is connected to a valve D' by means of a length of flexible copper tube. The valve D' allows of connections being made with the vacuum system, when desired. A second flexible tube leads from the opposite side of D' to the valve I . This arrangement makes possible the evacuation of the connecting tubes between C' and either container A or B . Such an arrangement was found necessary when it was desired to introduce ammonia into A or B without evacuating the entire system.

In order to introduce ammonia into the container A , the procedure is as follows. C' is accurately weighed and connected to D' by means of a conical compression joint. The valve I is opened and A , together with all its connections, is evacuated. When the pressure has fallen to a few thousandths of a millimeter of mercury, Valve D'

¹⁰ The tellurium employed in this investigation was prepared in connection with an earlier investigation in this Laboratory. See Kraus and Chiu, Ref. 4.

¹¹ Franklin and Kraus, *Am. Chem. J.*, **23**, 284 (1900).

is closed and the valve on C' is opened. The cylinder C' rests on a platform balance and is surrounded by a light electrical heater of tubular form. Approximately the desired quantity of ammonia is now distilled into A from C' . The valve I is then closed, C' is disconnected and weighed, and thus the exact amount of ammonia introduced into A may be obtained.

The expanded portions of A and B have a capacity of approximately 100 cc. About 60 g. of ammonia is introduced into A and B . About $\frac{1}{3}$ of this is blown into water contained in a 1000cc. flask, the exact amount of ammonia thus removed being determined by weighing the flask before and after the absorption of ammonia gas. This removal of ammonia was found necessary in order to insure complete elimination of foreign gases from the system. A trace of foreign gas on either side of the system has an appreciable influence on the pressure difference when this difference reaches a value of a few millimeters of mercury.

The introduction of ammonia into B is carried out in a manner similar to that already described in the case of A . The tube B is outside the thermostat, and with all its connections, including Q , is thoroughly evacuated before the ammonia is introduced. The lower portion of B is then introduced into a bath of boiling ammonia contained in a Dewar flask. About 5 g. of ammonia is now distilled from C' into B . The capsule E containing the sodium is then broken and allowed to drop into the ammonia in the container B . This container is then shaken for a period of 30 minutes in order to facilitate the initial reaction between the sodium and the tellurium. The bath of liquid ammonia in the Dewar flask is then removed and when B has come nearly to room temperatures it is placed in position in the thermostat as near to container A as possible; 55 g. of ammonia is now distilled into B in addition to that already introduced and about $\frac{1}{3}$ of this ammonia is blown off, as has already been described in connection with the procedure in filling A . This then gives the first concentration of the sodium-tellurium complex, for which measurements on the pressure difference are carried out. After having determined the difference in pressure between the solution and the pure solvent at this concentration, further quantities of ammonia are removed, the amounts being accurately determined by absorption in water and weighing. In this way the vapor pressure of the solution, relative to that of the pure solvent, is determined at a series of concentrations. The ammonia present in the container at the last concentration is determined by absorption in water and all concentrations are calculated back from this value.

In the first attempts to carry out the reaction between the sodium and the tellurium in B , the tube B was placed in position in the thermostat and ammonia was condensed in this tube at the temperature of the thermostat, 18° . Under these conditions, it was found that hydrogen is evolved when the sodium is dropped into the ammonia, owing to the formation of sodium amide. As a result it was found impossible to determine the true vapor pressure of the solution. In order to overcome this difficulty, the reaction was carried out at the temperature of boiling liquid ammonia, as has just been described.

It is necessary to correct for the quantity of ammonia present as vapor above the surface of the liquid and in the various connecting tubes. This quantity was determined by filling the apparatus with ammonia vapor under the pressure existing in the cylinder C' . The weight of this ammonia was obtained by weighing C' . Knowing the mass of ammonia present, the temperature and pressure, it was possible to calculate the corrections within the necessary limits of precision. In applying the correction at the various concentrations, the volume of liquid ammonia was subtracted from the total volume of the apparatus as determined. The above method of correction is not entirely accurate; but, in view of the fact that the correction in any case is very small, it was found unnecessary to determine the correction with a greater degree of precision.

After the completion of an experiment at a series of concentrations with a given quantity of sodium, ammonia is again introduced into the container B , which still con-

tains the sodium-tellurium compound, and a new set of readings is made at a series of concentrations.

The amount of ammonia in the container *A*, about 30 g. as a rule, was maintained constant during an experiment.

Experimental Results

The results of all experiments carried out in the manner described are given in the following table. At the head of each sub-table is given the

TABLE I
VAPOR-PRESSURE LOWERING OF SOLUTIONS OF THE COMPLEX SODIUM TELLURIDE AT DIFFERENT CONCENTRATIONS

Liquid ammonia				Ratio
G.	$\frac{n}{n+N} \times 10^4$	$\frac{\Delta P}{\text{Mm. Hg}}$	$\frac{\Delta P}{P} \times 10^4$	$\frac{\Delta P}{P} / \frac{n}{n+N}$
Series 1, 0.1113 g. of Na, 17.9°				
31.386	26.2	8.19	13.6	0.54
21.186	38.8	12.54	20.9	0.54
15.536	52.7	17.27	28.7	0.54
10.261	79.8	26.05	43.2	0.54
6.446	126.0	39.07	65.6	0.52
Series 2, 0.055 g. of Na, 17.9°				
42.198	9.63	2.42	4.1	0.43
13.582	29.9	10.25	17.0	0.56
8.897	45.6	14.56	24.2	0.53
Series 3, 0.055 g. of Na, 17.9°				
25.648	15.8	4.64	7.7	0.49
17.348	23.4	7.35	12.2	0.52
10.916	37.4	12.60	20.9	0.56
Series 4, 0.055 g. of Na, 19°				
37.721	10.8	3.07	4.9	0.46
27.166	15.0	5.16	8.28	0.55
15.876	25.6	8.99	14.4	0.56
10.366	39.1	14.28	22.9	0.58
Series 5, 0.1398 g. of Na, 19°				
40.041	25.8	7.60	12.2	0.47
30.454	33.8	10.9	17.5	0.52
19.384	53.0	17.2	27.7	0.52
14.314	71.7	22.9	36.9	0.50
9.154	112.0	35.9	57.7	0.51
Series 6, 0.1398 g. of Na, 20°				
38.909	26.5	8.2	12.8	0.48
28.767	35.9	12.0	18.7	0.52
20.904	49.3	17.0	26.5	0.54
15.272	67.3	22.8	35.5	0.53
11.362	90.6	32.0	49.8	0.55

number of the series of the experiment, the weight of sodium employed in the series in question, and the temperature at which the experiment was carried out. In the first column is given the weight of liquid ammonia;

in the second column, the value of the molal fraction, $\frac{n}{n+N} \times 10^4$; in the third column, the pressure difference, ΔP , in millimeters of mercury; in the fourth column, the relative pressure difference, $\frac{\Delta P}{P} \times 10^4$; and in the fifth column, the ratio $\frac{\Delta P}{P} / \frac{n}{n+N}$.

Discussion

The purpose of this investigation was to determine the complexity of the telluride in solution. Since even the binary salts are relatively slightly ionized at concentrations in the neighborhood of 0.1 N and since, in general, the ionization of salts of higher type is much lower than that of typical binary salts, it follows that the ionization process of the dissolved telluride might be expected to have little influence on the observed vapor-pressure change. In order to determine the complexity of the telluride, the molecular weight of the dissolved complex must be determined. It is, of course, obvious that in such a determination the true molecular weight of the dissolved compound is not obtained in any case, but merely the number of moles of dissolved substance in the mixture. If the laws governing dilute mixtures hold, then the number of moles of solute for any given composition of the mixture may obviously be determined from the relative vapor-pressure change of the solution, according to Raoult's law. Whether or not the conditions of dilute systems are fulfilled in solutions of electrolytes at a given concentration cannot be predetermined. If, however, the relative lowering of the vapor pressure can be determined at a series of concentrations, some inference may be drawn as to whether the conditions of a dilute system are fulfilled in a given case from the manner in which the vapor pressure varies as a function of the concentration at low concentrations.

If Raoult's law holds, then obviously $\frac{\Delta P}{P} = \frac{n}{n+N}$. In other words,

the ratio $\frac{\Delta P}{P} / \frac{n}{n+N}$ equals unity, and a plot of the observed values of

$\Delta P/P$ against those of $\frac{n}{n+N}$ should yield a straight line, the tangent of

whose slope is unity. If the laws of dilute solutions are not fulfilled, then a plot of the values of $\Delta P/P$ against the fractional composition will lead to a curve which, at sufficiently low concentrations, where the deviations from the laws of dilute solutions become small, approaches the theoretical straight line asymptotically. From vapor-pressure determinations at a series of concentrations, therefore, it is possible to reach a conclusion as to whether or not the laws of dilute solutions are fulfilled within the limits of experimental error.

In the preceding table, n is the number of atoms of sodium and N the

number of moles of ammonia in the mixture. If the complex telluride contained only a single atom of sodium in the molecule, the value of the ratio $\frac{\Delta P}{P} / \frac{n}{n+N}$ should be unity; while, if 2 atoms of sodium were present in the molecule, the ratio should have a value of 0.5.

In Col. 5 of the table are given the values of the ratio $\frac{\Delta P}{P} / \frac{n}{n+N}$ for different concentrations of the solution. An inspection of the table will show that this ratio has a value in the neighborhood of 0.5. In Fig. 2 the values of $\frac{\Delta P}{P} \times 10^4$ are plotted against values of $\frac{n}{n+N} \times 10^4$. While there is considerable variation among the various points due to errors which

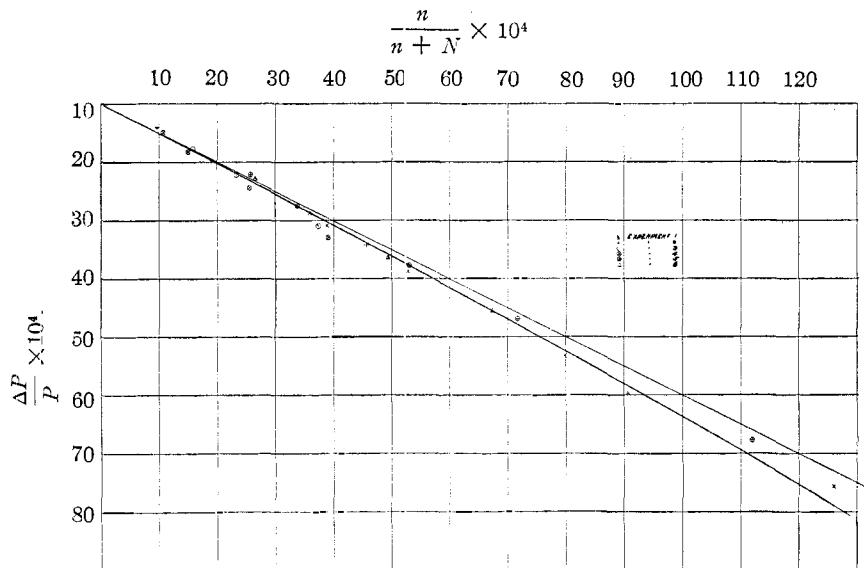


Fig. 2.—The variation of the vapor pressure of the sodium-telluride solution as a function of composition.

could not be eliminated entirely, it is clear that the points determine a curve which approaches an asymptote for which $\frac{\Delta P}{P} / \frac{n}{n+N}$ has a value 0.5. The straight line appearing in the figure represents this asymptote. In the more dilute solutions, the points follow this theoretical curve within the limits of the experimental error, but at higher concentrations the deviations from this curve become appreciable, although the deviations are nowhere large. The mean value of the ratio $\frac{\Delta P}{P} / \frac{n}{n+N}$ is 0.52, with a maximum variation from 0.43 to 0.58. The higher values of the ratio

at the higher concentrations are doubtless in part due to deviations from Raoult's law, while at lower concentrations they are probably in the main due to experimental errors. At the lowest concentrations, the total volume occupied by the solution was approximately 80 cc., under which conditions it is difficult to establish equilibrium between the liquid and the vapor phase. At the same time, at these concentrations, the total pressure change is of the order of magnitude of 3 mm. On the whole, the results are as concordant as might be expected, in view of the conditions under which the experiments were carried out. The lowest concentration is approximately 0.03 *N*. The results show conclusively that 2 atoms of sodium are present per molecule of the complex telluride whose composition, therefore, is represented by the formula Na_2Te_x , where, according to the measurements of Kraus and Chiu, x varies from 3.8 at concentration 0.084 to 4.04 at 2.45.¹²

Since the number of atoms of sodium present in the molecule corresponds with that of the normal telluride, Na_2Te , it may be concluded that the valence of tellurium in the complex does not change, when the complex is formed. The complex tellurium ion, therefore, has the constitution, $\text{Te}^{--}\text{Te}_y$, where $y = x - 1$. The complex telluride ion is formed by the addition of tellurium atoms to the normal telluride ion. Kraus and Chiu have shown that at least 2 complex tellurides exist in ammonia solutions under different conditions. In a solution in equilibrium with the normal telluride, the composition of the solution corresponds with that of the compound Na_2Te_2 . The constitution of the complex anion resulting from this compound, therefore, corresponds with the formula Te^{--}Te . In the first stage of complex formation, a single atom of tellurium attaches itself to the normal telluride ion. In the final solution in equilibrium with metallic tellurium, a number of complexes may be present, although in view of the fact that the value of x under these conditions approaches very close to 4.0 it is not improbable that there is present in the solution the ion $\text{Te}^{--}\text{Te}_3$.

Since the valence of the telluride ion in the complex is the same as that of the normal telluride, the valence of the telluride ion does not change on formation of the complex. This has an important bearing on our conceptions of the constitution of complex ions of this type. As has already been pointed out, other of the less electropositive heavy elements, such as lead, tin and antimony, form complex compounds with the alkali metals which resemble the complex tellurides in many respects. In the case of antimony, the initial compound formed is Na_3Sb and there is evidence indicating that the initial compound formed with lead is Na_4Pb . In the case of the latter element, however, the normal plumbide is not stable with respect to the complex and free metallic sodium in solution, decomposition occurring ac-

¹² The concentration is expressed in atoms of sodium per liter of pure ammonia.

ording to a reaction of the type: $\text{Na}_4\text{Pb} \longrightarrow \text{Na} + \text{NaPb}_x$. In the presence of excess lead the ultimate composition of the solution corresponds with that of the compound $\text{Na}_4\text{Pb}\cdot\text{Pb}_8$. The normal plumbide has a constitution corresponding to the formula Na_4Pb , and, in view of the behavior of the telluride solutions, it may be inferred that the valence of the plumbide ion remains unchanged in the complex. On the other hand, without an actual determination of the molecular weight of the plumbides in solution, it cannot be definitely stated that the negative valence of the plumbide ion may not vary from complex to complex. It is, of course, well known that the positive valence of certain elements, such as lead, for example, varies with conditions; and it is, therefore, conceivable that a similar variation may occur in the case of the negative valence of metallic elements. It appears unlikely, however, that a change of the negative valence occurs on mere addition of the element in question.

As has been pointed out by one of us in an earlier paper,¹³ the results obtained from a study of the various complexes in liquid ammonia, and particularly of the complex tellurides, have an important bearing on our conceptions as to the nature of metallic compounds. In the first place, there is clearly brought to view the important property of elements, in general, of functioning as negative ions. This property is common to the typical elements of the seventh, sixth, fifth and fourth groups, and possibly to certain elements of the third. That is, it has been definitely shown that these elements form complex compounds which are soluble in liquid ammonia and that, in solution, the more electronegative element is associated with a negative charge. In order to account for the properties of metallic compounds, therefore, we must take into account, first, the tendency of the more electronegative elements in their compounds to act as negative ions; and, second, the tendency of the negative ions of these elements to form complex ions in the presence of larger amounts of the same elements. The electrochemical properties of these compounds in ammonia solution clearly show that in solution they possess all the properties characteristic of electrolytes, that is, of salts; and there is apparently nothing to differentiate solutions of these compounds from ordinary salts in the same solvent under similar conditions. These compounds in solution, therefore, are in fact salts. In solution they differ from other salts with which we are familiar only in that the negative ion is complex with its composition dependent upon conditions, while in the case of most salts the negative ion has a fixed composition. Nevertheless, although these compounds are true electrolytes or salts in solution, in the free state, they exhibit, for the most part, characteristic metallic properties. In general, the metallic properties of these compounds are the more pronounced, the less electronegative the negative constituent, and the less electropositive

¹³ KRAUS, THIS JOURNAL, 44, 1216 (1922).

the positive constituent. Thus, the normal telluride is entirely non-metallic, while the normal antimonide is a metal. So, also, the sulfides of the alkali metals are non-metallic while those of heavy metals are metallic. The lower the atomic weight of the electronegative element in a given group of elements, the less pronounced are the metallic properties of its compounds. Thus, the normal phosphides of the alkali metals are non-metallic.

It should be noted, also, that no considerable reaction occurs between the solvent and the metallic compound when the process of solution takes place. The energy effects accompanying solution are apparently of a very low order of magnitude, thus indicating that no fundamental reaction occurs in which the character of the compound in solution is materially altered from that in the solid state. It may be inferred, therefore, that metallic compounds between strongly electropositive elements, such as the alkali metals, and the less electropositive elements such as lead, tin, etc., have a salt-like structure; that is, they possess an ionic constitution. In this way it is possible to account for many of the properties of metallic compounds which otherwise cannot readily be reconciled with present conceptions as to the constitution of elementary substances.

One of the striking features of the interaction between a given pair of metallic elements is the large number of compounds derivable from a single such pair of elements. Such compounds cannot be accounted for on the basis of any of the accepted theories of valence or of atomic structure. Taking into account, however, the tendency of the less electropositive metallic elements to form negative ions and, furthermore, the tendency of these ions to form complexes, compounds of this type are readily accounted for and may be harmonized with present views of atomic structure. Every element, thus, has an electropositive, as well as an electronegative valence. The negative valence is one for the seventh group of elements and increases by one in passing to an adjacent group from left to right, just as the positive valence increases in passing from group to group from right to left in the periodic table. The negative, as also the positive, valence is 4 for the fourth group of elements. Whether or not the negative valences may increase above 4 cannot be stated. The chief distinction between electronegative and electropositive valence, aside from the sign of the charge, is that the ions carrying a negative charge have a great tendency to form definite complexes with other atoms. The nature of the combination, in this case, is, at present, not understood. Nevertheless, we are dealing here with a phenomenon which is in no sense restricted to a small group of elements.

While the only metallic compounds whose constitution can be arrived at are those which are soluble in liquid ammonia, it does not follow that such an ionic constitution is restricted to compounds which are soluble.

It is possible, and indeed probable, that many, if not all, metallic compounds are of this type, the more electropositive constituent being present as a positive ion and the more electronegative constituent as a negative ion. In these compounds the electronegative constituent, at any rate, may be present in the form of a complex ion. Whether the positive constituent may likewise form a complex ion under suitable conditions cannot now be stated.

In the past the term "salt" has been restricted to non-metallic compounds having ionic constitution, namely, compounds exhibiting ionic properties in solution and in the pure state and showing no metallic properties. Metallic compounds, on the other hand, have practically not been classified, and, for the most part, have been sharply differentiated from the salts. According to the views here proposed, there is no sharp line of demarcation between the salts and metallic compounds. The property of metallicity is a more or less accidental one, depending, of course, upon the nature of the elements present in the compound, and particularly upon the relative electropositiveness and electronegativeness of the constituents. In other respects, however, there is nothing to indicate any marked break in the physical and chemical properties of binary compounds between two elements, as we pass from ordinary salts to true metallic compounds. If one constituent is strongly electropositive and the other constituent strongly electronegative, then the resulting compound is a typical salt which shows no metallic properties. As, however, the electropositiveness of one constituent and the electronegativeness of another constituent becomes less pronounced, the metallic characteristics become more accentuated and the resulting compounds exhibit metallic properties, except in the case of elements which are relatively very strongly electronegative and electropositive. Thus, practically all the compounds of the halogens with other elements are either salt-like or neutral substances. It is only seldom that they show metallic properties.¹⁴

In the case of elements of the sulfur group, the normal compounds with the alkali metals appear throughout to be non-metallic. Certain of the complex compounds, however, such as the tellurides, exhibit metallic properties even in the case of the alkali metals, as has already been noted. On the other hand, even the normal tellurides of the less electropositive elements, such as silver and lead, exhibit distinctly metallic properties. Indeed, we are not confined, here, to the tellurides; as is well known, the

¹⁴ It is interesting to note in this connection that cuprous iodide is a typical salt-like substance, exhibiting purely non-metallic properties in the pure state. It absorbs iodine in the solid state, however, yielding a substance exhibiting metallic properties which are a function of the amount of iodine absorbed. The greater the amount of iodine present in this system, the more do the properties resemble those of characteristic metallic substances. [Baedeker, *Ann. Physik*, **22**, 765 (1907); **29**, 566 (1909). Baedeker and Pauli, *Physik, Z.*, **9**, 431 (1908).]

normal sulfides and even the oxides of many elements exhibit metallic properties in certain states as, for example, some of the iron oxides and some of the natural sulfides of lead. There is nothing to indicate that, in their constitution, these metallic compounds differ materially from similar non-metallic compounds which exhibit a salt-like structure. The structure of all such compounds, therefore, is essentially of the same type, corresponding to that of normal salts, while the metallic properties are determined primarily by the relative electropositiveness and electro-negativeness of the elements concerned in the compound. Metallic compounds should, therefore, be classed with the salts.

Summary

1. The vapor pressure lowering due to the complex sodium-tellurium compound in liquid ammonia has been measured at a series of concentrations down to 0.03 N .

2. When the values of $\Delta P/P$ are plotted against values of $\frac{n}{n+N}$, where n is the number of atoms of sodium in the mixture, a curve results which in dilute solution approaches very closely to a straight line, for which the value of $\frac{\Delta P}{P} / \frac{n}{n+N}$ equals 0.5. Apparently Raoult's law is very nearly obeyed by solutions of the complex telluride in liquid ammonia, and from the value of the above ratio it follows that 2 atoms of sodium are present per molecule of the complex telluride present in solution. The complex telluride ion, therefore, carries 2 charges. The formation of the complex telluride consists in the addition of tellurium atoms to the normal telluride ion, the valence of the telluride ion undergoing no change under these conditions.

3. The bearing of this result on our conceptions of the nature of other similar complexes in ammonia solution and of metallic alloys in general is discussed.

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