order to obtain worth-while results. This method of measuring ultraviolet intensity has been in use in this Laboratory for a number of months. The results obtained have been constantly checked by comparison with those obtained by employing copper-constantan thermopile and filters, the agreement frequently being remarkable. While the method does not approach the sensitiveness of the thermopile, it is of sufficient accuracy for most ordinary determinations and has the advantages that it does not require frequent calibration, is not affected by vibration and magnetic disturbances, and requires no corrections for visible and infra-red radiations.

The authors wish to express their appreciation of the assistance rendered by Messrs. Harry Lockwood, Hugh Fraser and Gustave Hunkele in making checks and tests on the data and theories presented in this paper.

Summary

1. The photochemical decomposition of oxalic acid in oxalic acid-uranyl sulfate solution has been studied qualitatively and quantitatively in various regions of the ultraviolet spectrum.

2. The reaction has been shown to follow zero order for a considerable extent of time; the temperature coefficient was found to be 1.035 for an interval of 10°.

3. The absorption spectrum was studied and quantitative measurements of radiations were made employing a quartz spectrograph, a copper-constantan thermopile and special filters.

4. The photo-sensitizer, uranyl sulfate, was shown to be most effective when used in small quantities. A possible inhibitory action due to screening has been discussed.

5. The employment of the decomposition of the oxalic acid solution as an ultraviolet radiometer for the quantitative measurement of ultraviolet energy has been outlined.

NEWARK, NEW JERSEY

THE SO-CALLED "METAL AMMONIUMS." THE VAPOR PRESSURES OF SOLUTIONS OF LITHIUM IN LIQUID AMMONIA

BY CHARLES A. KRAUS AND WARREN C. JOHNSON

RECEIVED OCTOBER 18, 1924 PUBLISHED MARCH 5, 1925

Solutions of the alkali metals in liquid ammonia were first studied by Weyl[1] in 1864. At that time the radical theory was near the height of its popularity and it was only natural that Weyl should have interpreted his observations in terms of the theory then prevailing. According to his views, the metals are joined to nitrogen of ammonia, forming substituted ammonium radicals. Seeley,[2] who studied these solutions at a somewhat

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

[2] Seeley, *Chem. News,* **23,** 169 (1871).

later date, contended that the metals are in solution in ammonia as such and that, therefore, they are not united to nitrogen in the form of an ammonium group. Joannis,[3] working at a still later date, revived the ammonium theory and carried out a great deal of painstaking experimental work in support of this theory. He believed that he showed, by analytical methods, that the metals may be obtained in association with ammonia. He carried out molecular-weight determinations of the metals in solution by the vapor-pressure method, the results of which he interpreted as demonstrating that the molecules in solution contain two atoms of sodium.[4] Among others, Moissan[5] applied the method of Joannis with corresponding results. The term "metal ammonium" thus found its way into the literature quite generally and is still employed by many writers.

Ruff and Geisel[6] and Kraus[7] examined the solution of alkali metals in liquid ammonia from the standpoint of the phase rule and adduced conclusive evidence of the non-existence of a solid phase containing ammonia in combination with an alkali metal. Kraus showed that calcium, indeed, forms a solid phase in which six molecules of ammonia are associated with an atom of the metal.[8] He pointed out that this compound should be looked upon as an ammoniate, analogous to ammoniated salts such as $CaCl_2.6NH_3$, rather than as a metal ammonium. Mentrel[9] and Roederer[10] established the existence of hexammoniates in the case of barium and strontium. Biltz[11] has since corroborated the earlier work of Kraus as well as that of Mentrel and Roederer. Kraus[12] has pointed out that the molecular-weight determinations of Joannis are without significance since Raoult's law is not applicable in the case of these solutions.

In the light of our knowledge of the properties of radicals at the present time, it appears highly improbable that the alkali metals could appear as substituents for hydrogen in the ammonium group, and we should have reason for doubting the correctness of the so-called "metal ammonium" theory even if there were no evidence to the contrary.

Recently Benoit[13] has published the results of an investigation of the phase relations in the system lithium-ammonia. He studied the vapor pressure of lithium solutions as a function of concentration and found three

[3] Joannis, *Compt. rend.*, **112**, 391; **113**, 795 (1891).

[4] Joannis, *ibid.*, **115**, 820 (1892).

[5] Moissan, *Compt. rend.*, **127**, 685 (1898); **128**, 26 (1897).

[6] Ruff and Geisel, *Ber.*, **39**, 831 (1906).

[7] Kraus, THIS JOURNAL, **30**, 653 (1908).

[8] Moissan at an earlier date [*Compt. rend.*, **127**, 685 (1898)], using the method of Joannis, ascribed to the calcium compound the formula $Ca(NH_3)_4$.

[9] Mentrel, *ibid.*, **135**, 790 (1902).

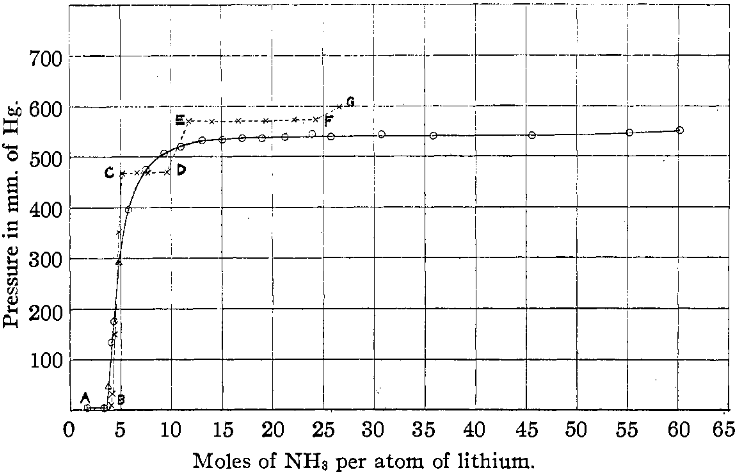
[10] Roederer, *ibid.*, **140**, 1252 (1905).

[11] Biltz, *Z. anorg. Chem.*, **114**, 241 (1920).

[12] Kraus, THIS JOURNAL, **30**, 1197 (1908).

[13] Benoit, *Bull. soc. chim.*, **33**, 908 (1923).

regions within which the pressure is apparently independent of the composition of the system; in which, in other words, two phases in addition to the vapor phase co-exist according to the phase rule. Benoit's curve is shown as a broken line in the accompanying figure. It will be seen that in this curve there appear three horizontal portions, AB, CD and EF, respectively. Benoit assumes that in region EF, two liquid phases, one concentrated and the other dilute in lithium-ammonium are in equilibrium with each other and with the vapor phase. Along CD he assumes that a solution of ammonia in lithium-ammonium is in equilibrium with presumably pure molten lithium-ammonium. Along AB, according to Benoit, the molten lithium-ammonium dissociates with the formation of ammonia vapor and solid metallic lithium. A sharp break occurs at the point B, corresponding to a composition of four molecules of ammonia per atom of lithium. Benoit considers that this indicates the existence of a lithium-ammonium to which he assigns the formula $[Li(NH_3)_4]_2$.



Benoit's interpretation of his results is by no means convincing, and the curve which he obtained presents a form so remarkable that it appeared worth while to examine this system somewhat more particularly. Benoit gives few details regarding the apparatus employed and the procedure followed. It is known that it is very difficult to establish equilibrium between a liquid and a vapor phase and it appeared not improbable that this may have been a source of error in Benoit's investigation.

Experimental Part

The apparatus was so designed that the vapor pressure of solutions of lithium in liquid ammonia could be determined from the saturation point to a concentration so low that only a single liquid phase exists. The solutions were made up in a cylindrical tube having a diameter of 35 mm. and a total capacity of about 300 cc. Within this tube a stirrer was suspended by means of a platinum-iridium spiral. A core of soft iron, encased in glass, was suspended between the stirrer and the spiral. The stirrer was actuated by means of an intermittent current passing through a solenoid surrounding the vapor-pressure tube in the nieghborhood of the core. The stirrer was maintained in continuous motion and thus served to establish equilibrium between the liquid and the vapor phase. This was found to be essential, particularly in the case of the more concentrated solutions, since even with the stirrer in continuous operation an hour or more was required to establish equilibrium. The pressure was measured by means of a mercury manometer, a cathetometer reading to 0.1 mm. being employed in making the observations.

The ammonia introduced was measured according to the method of Kraus,[14] in pipet cells graduated in 0.01 cc. Lithium was freshly cut under dry petroleum ether and rapidly introduced into the vapor-pressure tube from which a stream of ammonia vapor was issuing. The tube was then sealed and immediately exhausted with a high-vacuum pump. A known quantity of ammonia was then introduced from the measuring cells and, the stirrer having been set in operation, the pressure was measured when equilibrium was established. A small quantity of ammonia was then withdrawn and the pressure again read when equilibrium was reëstablished. The equilibrium was thus approached from both sides in every case. In many instances several check determinations were carried out.

For the purpose of withdrawing ammonia, the vapor-pressure tube was connected to a reservoir having a volume of approximately 500 cc. which could be filled at any time either in whole or in part with mercury, a movable reservoir being provided for this purpose. The ammonia withdrawn from the vapor-pressure tube into the reservoir was determined by noting its temperature, pressure and volume. The reservoir also served another purpose. At times, in the case of the more concentrated solutions, a small amount of hydrogen was evolved, owing to the formation of lithium amide. This could be removed at any time, by sweeping the hydrogen into the reservoir.

The vapor-pressure tube was surrounded by a bath of ammonia contained in a cylindrical Dewar tube. Several series of determinations were carried out at the boiling point of liquid ammonia, but difficulty was experienced in securing temperature control. This difficulty was largely overcome by boiling the ammonia bath under reduced pressure at a temperature of —39.4°. This temperature was determined by means of a calibrated toluene thermometer and was checked by determining the vapor pressure of pure ammonia at that temperature and comparing with the value obtained by the Bureau of Standards.[15] The vapor pressure was found to be 555 mm.

At the end of a series of determinations, the ammonia was allowed to

---

[14] Kraus, THIS JOURNAL, **43**, 749 (1921).

[15] Cragoe, Meyers and Taylor, *Bur. of Standards, Sci. Pub.*, **369** (1920).

evaporate and the last traces were removed by means of a high-vacuum pump. The lithium was then dissolved in a mixture of alcohol and ether and finally washed out with water into a platinum dish. The solution was partially evaporated to expel traces of ammonia which might be present and was then neutralized and acidified with sulfuric acid. The lithium was then determined as lithium sulfate. In the first and second series of measurements, the lithium was free from iron but in the third series a few per cent. of iron were present. This was determined and corrected for. The lithium was examined for the presence of sodium and potassium and found to be substantially free from these elements.

Results.—The results of three series of determinations at —39.4° are given in Table I which requires no further explanation. The results are shown graphically in Fig. 1, the points of the first series being represented by a combination of crosses and circles, the second by circles, and the third by triangles. Only the first two points of Series 1, relating to the saturated solution of lithium in ammonia, are shown on the plot. The remaining points of this series are in substantial agreement with those of Series 2 and 3, but are markedly less consistent among themselves than are the later determinations owing to the fact that sufficient precaution was not observed in regulating the temperature.

TABLE I

VAPOR PRESSURE OF SOLUTIONS OF LITHIUM IN AMMONIA AT —39.4° AT DIFFERENT CONCENTRATIONS

SERIES 1, 0.3601 G. OF LITHIUM

Mols. of NH_3/Li...	1.72	3.40	4.88	6.65	8.13	9.94
Mm. of Hg........	3.5	3.7	281.7	443.2	492.8	518.4
Mols. of NH_3/Li...	11.76	13.67	15.53	19.55	23.63	
Mm. of Hg........	533.4	541.3	541.4	544.5	542.5	

SERIES 2, 0.3139 G. OF LITHIUM

Mols. of NH_3/Li...	4.07	4.38	5.79	7.56	9.34	10.97	13.13	15.08	17.13
Mm. of Hg........	134.8	174.8	395.5	474.8	506.7	520.3	532.2	534.1	536.8
Mols. of NH_3/Li...	19.04	21.33	23.48	25.79	30.81	35.88	45.66	55.25	60.13
Mm. of Hg........	536.2	538.7	545.0	538.8	543.6	540.3	539.7	546.8	549.6

SERIES 3, 0.5324 G. OF LITHIUM

Mols. of NH_3/Li...	3.80	3.78	3.77	4.86
Mm. of Hg........	51.8	47.5	45.2	290.6

Discussion.—As may be seen by referring to the figure, the results obtained are remarkably concordant. The most dilute solution measured, containing 60.13 molecules of ammonia per atom of lithium, showed a vapor pressure of 549.6 mm. which is only about 5 mm. below the vapor pressure of pure ammonia. At higher concentrations, the pressure remains substantially constant at a value of 540 mm. At still higher concentrations the curve is concave toward the axis of concentration, the tangent of the curve increasing the less rapidly, the higher the concentration.

In the neighborhood of the saturation point, the curve is amost vertical. The saturated solution has a vapor pressure of 3.6 ± 0.1 mm.

With a view to finding the concentration of the saturated solution, three points (represented as a single point on the plot) were determined very near the saturation point (Series 3) at pressures ranging from 45.2 to 51.8 mm. On extrapolating the vapor-pressure curve until it intersects the horizontal line of the saturated solution, there is obtained a value of 3.61 molecules of ammonia per atom of lithium for the composition of the saturated solution. This value is markedly lower than that obtained by Ruff and Geisel and still lower than that obtained by Benoit.

The form of the curve is similar to that of sodium. The temperature is evidently just a little below the critical point which, according to Ruff and Zedner,[16] is —35°. Such variations of the points as occur are due to temperature fluctuation. The vapor pressure of ammonia at this temperature varies approximately 25 mm. per degree and a variation of 5 mm. would be accounted for by a temperature variation of 0.2°.

A comparison of our curve with that of Benoit shows an entire lack of correspondence. Benoit states that his measurements were carried out at —38.5°, but his temperature must have been somewhat higher than this since, for a solution containing 26.6 molecules of ammonia per atom of lithium, he records a vapor pressure of 598 mm. while the vapor pressure of pure ammonia at —38.5°, according to the Bureau of Standards,[15] is 583 mm. The results obtained at the boiling point of ammonia are not given here, but they agree substantially with those obtained at the lower temperature, although the variations, due to lack of temperature control, were markedly greater. In view of the precautions observed to insure equilibrium and the concordance of independent series of determinations, we can only conclude that Benoit's results are affected by some unknown source of error. It seems not unlikely that he failed to establish equilibrium conditions.

It will be noted that a value of 3.61 molecules of ammonia per atom of lithium has been obtained for the composition of the saturated solution. This is much below the value 4.0 obtained by Benoit. It is scarcely conceivable that our result can be in error by any amount which would lead to an integral value. It seems evident that, so far as the phase relations are concerned, solutions of lithium in ammonia correspond very closely to solutions of sodium in the same solvent. While it is possible and even probable that the lithium atoms (or ions) in ammonia are associated with molecules of the solvent, we have no ground whatsoever for considering that in these solutions there is present a molecular complex bearing a resemblance to the ammonium and other similar groups. The term "metal ammonium" should be stricken from the literature.

---

[16] Ruff and Zedner, *Ber.*, **41**, 1958 (1908).

Summary

The vapor pressures of solutions of lithium in liquid ammonia at —39.4° have been measured from the saturation point to a concentration of 60 molecules of ammonia per atom of lithium.

The saturated solution contains 3.61 molecules of ammonia per atom of lithium. With increasing dilution, the pressure rises rapidly at first and then more slowly until the region of two liquid phases is reached, when the pressure remains constant at approximately 540 mm. This pressure is only about 15 mm. below the vapor pressure of pure ammonia.

The curve is entirely regular and no indication is found of the singularities recorded by Benoit. There is no evidence indicating the existence of compounds of the alkali metals with ammonia of the nature of ammonium groups.

Brown University, Providence, Rhode Island

[Contribution from the Wolcott Gibbs Memorial Laboratory, Harvard University]

INTERNAL PRESSURES PRODUCED BY CHEMICAL AFFINITY

By Theodore W. Richards

Received November 10, 1924 Published March 5, 1925

Recently[1] internal pressures due to cohesion have been discussed and approximately evaluated. The interpretation, which was only a preliminary sketch, was limited to isotropic elements, because they present the simplest problem.

Chemical affinity must also exert pressure in its action, and often the pressures thus produced must exceed those produced by cohesion. The present brief communication endeavors to show that the same principles which apply to cohesion may apply also to chemical affinity, bearing in mind the fact that chemical affinity acts most strongly on the portions of the atoms in immediate juxtaposition and does not envelop each atom equably over its whole surface after the manner of cohesion in an isotropic element. Just as the heat of evaporation may be accounted for by the work involved in separating atoms under the influence of the changing balance of pressures, so the heat of chemical combination may be accounted for chiefly by the work done by the more considerable pressures produced by chemical affinity.

Table I gives the results of the new method (depending upon coefficient of expansion) as applied to compounds. For this purpose, molal volume is substituted for atomic volume in Equation 3 of the previous paper;

---

[1] Richards, This Journal, **46**, 1419 (1924). This paper and other earlier papers are summarized in *J. Franklin Inst.*, **198**, 1 (1924), which is a more comprehensive and less detailed discussion of the general bearings of the problem.