determined by titration against a known thiosulfate solution. The bromide in solution was determined by evaporating 10 cc. of the solution and weighing the residue.

The concentrations vary over almost the whole range up to saturation, and although the results of Worley for potassium bromide have not such a wide range, yet the two curves are similar. In dilute solutions the ratio of bromine to bromide is about 1 mole Br_2 to 1 mole NaBr but for more concentrated solutions the ratio becomes greater. For solutions of sodium bromide near saturation the ratio is about 2.5 moles bromine to 1 mole salt. For iodine[1] the ratio becomes smaller, as the concentration increases; in other words, the solubility curves for bromine and iodine in bromide solutions have opposite curvatures.

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ACTION OF AMMONIA UPON AMMONIUM THIOCYANATE.[2]

BY W. P. BRADLEY AND W. B. ALEXANDER.

Received November 3, 1911.

Deliquescence.—The number of substances which deliquesce in dry ammonia gas is very limited. Those which deliquesce in ammonia at ordinary temperature and at a pressure of approximately one atmosphere are the following:

Salts: NH_4SCN, ammonium thiocyanate,[3] NH_4NO_3, ammonium nitrate,[4] $Hg(CN)_2$, mercuric cyanide,[5] $Ag_2Pt(SCN)_6$, silver platini-thiocyanate.[6]

Non-metallic compounds: ICN, cyanogen iodide,[7] BrCN, cyanogen bromide,[8] $SO_2(NH_2)_2$, sulfamide,[9] BI_3, boron iodide,[10] AsI_3, arsenious iodide.[11]

Elements: Lithium,[12] potassium,[13] caesium,[14] strontium,[14] iodine.[15]

[1] See preceding paper.

[2] Read before the Conn. Valley Section, Am. Chem. Society, Oct. 7, 1911.

[3] We have been unable to find any mention of this case of ammonia deliquescence in the chemical literature. The fact is known, however, in some quarters at least, among those interested in ammonia refrigeration.

[4] Divers, *Chemical News*, 27, 37 (1873); *Z. physik. Chem.*, 26, 430 (1898). Raoult, *Compt. rend.*, 76, 1261–2 (1873). Franklin and Kraus, THIS JOURNAL, 27, 213 (1905).

[5] Franklin and Kraus, *Am. Chem. J.*, 23, 300 (1900).

[6] Peters, *Ber.*, 41, 3185 (1908).

[7] Bineau, *Ann. chim. phys.*, 67, 234 (1838).

[8] Bineau, *Ibid.*, 70, 257–61 (1839).

[9] Franklin and Stafford, *Am. Chem. J.*, 28, 95 (1902).

[10] Besson, *Compt. rend.*, 114, 542–4 (1892).

[11] Besson, *Ibid.*, 110, 1258–61 (1890).

[12] Moissan, *Ibid.*, 127, 687 (1898); *Bull. soc. chim.*, [3] 21, 906 (1899). Ruff and Geisel, *Ber.*, 39, 828–843 (1906). Kraus, THIS JOURNAL, 30, 657 (1908).

[13] Ruff and Geisel, *loc. cit.* Moissan, *loc. cit.*

[14] Ruff and Geisel, *loc. cit.*

[15] Hugot, *Compt. rend.*, 130, 505 (1900). Colin, *Ann. chim. phys.*, 91, 263 (1814).

Compounds of carbon mono-potassium cyanacetamide[1](?), nitroform ammonia.[2]

This list of only sixteen substances deliquescent in ammonia at a pressure of one atmosphere and at temperatures above zero would be increased a little if substances deliquescent at temperatures below zero were to be included. Thus, potassium platino-thiocyanate, $K_2Pt(SCN)_4$, deliquesces below —10°, and the corresponding silver salt, $Ag_2Pt(SCN)_4$, below —20° (Peters); rubidium, below —3° (Ruff and Geisel); and sodium[3] and barium[4] below —20°.

Scarcely any quantitative data appear to exist for pressures higher than one atmosphere.

The meagerness of the list is due of course in part to the fact that ammonia deliquescence has not been studied as thoroughly as deliquescence in water vapor. It is far from likely, however, that ammonia deliquescence will prove to be of as frequent occurrence as the other. A substance deliquesces when the actual pressure of the vapor in contact with it exceeds the vapor tension which is characteristic of its saturated solution at the same temperature. And it must be remembered that in the case of deliquescence in water vapor we are dealing, as a rule, with a very small *partial pressure* of water vapor mixed with air, while, in every case in the foregoing list, the ammonia gas which caused the deliquescence was pure, or nearly so, and exerted therefore a pressure of about one atmosphere. We have found no recorded cases of deliquescence in ammonia under diminished pressure. It may be considered quite certain that under any considerable diminution of pressure the list would be much smaller than it is, and it is quite possible that for pressures corresponding to those of water vapor in air it might be wiped out altogether.

Of all the substances for which we have quantitative data, ammonium sulfocyanate appears to be the most deliquescent in ammonia. We have found that deliquescence ceases only at 88°. The substance which stands nearest to it in this regard is lithium, whose upper limit is 70° (Ruff and Geisel, Moissan). Caesium and strontium cease to deliquesce at 40° (Ruff and Geisel), and ammonium nitrate at 29° (Raoult), or 23° (Divers).

Compounds of Ammonia and Ammonium Thiocyanate.—It is a matter of common knowledge that ammonia unites in definit proportions with a multitude of substances, yielding so-called ammoniates, and that in many of these the ammonia plays a similar role to that of water of crys-

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[1] Franklin and Stafford, *loc. cit.*

[2] Franklin and Kraus, This Journal, 27, 214 (1905).

[3] Moissan, *loc. cit.* Ruff and Geisel, *loc. cit.* Seely, *Chem. News*, 23, 169–70 (1871). Weyl, *Poggendorff's Ann.*, 121, 601–12 (1864).

[4] Mentrel, *Bull. soc. chim.*, [3] 29, 496 (1903); *Compt. rend.*, 135, 740–2 (1902).

tallization in hydrates. Frequently one and the same substance will give two or more such compounds with ammonia. In the majority of cases more or less satisfactory analyses for these compounds are at hand. In cases where analysis is difficult, or where a set of ammoniates of a given substance is to be scouted in a preliminary way, the methods of physical chemistry afford valuable means not only of detecting their existence, but also of determining their ammonia content, as well as certain of their physical constants. In the work which follows, the solidification curve of ammonia solutions of ammonium thiocyanate is used for this purpose. The method has already been applied for the same purpose to solutions of ammonium nitrate and of water in ammonia, and has shown the existence of the compound $NH_4NO_3.3NH_3$[1] in the one case, and of the two hydrates $H_2O.NH_3$ and $H_2O.2NH_3$[2] in the other.

Experimental.

Melting Point.—The ammonium thiocyanate used was from Kahlbaum. It was purified by several crystallizations from water,[3] ground and kept over concentrated sulfuric acid. The melting point of this substance is variously given in the literature, ranging from 147° to 159°.[4] In a score or more of determinations made at various stages in our work, with salt taken both from water and from ammonia solutions, it melted constantly and sharply at 148°. The melting point was always determined in capillary tubes.

Absorptive Capacity for Ammonia.—The ammonia gas was obtained from pure concentrated ammonium hydroxide. It was dried over fused caustic potash, and by washing with its own liquid at its normal boiling point.

In two preliminary trials, made at approximately room temperature, ammonium thiocyanate absorbed 44.78% and 45.26% respectively of its own weight of ammonia. In each case the gas was passed into the salt till the weight of the latter showed no further increase. These proportions are almost exactly molecular, corresponding to 2.02 and 2.001 mols. of ammonia respectively. The product was an oily liquid, of specific gravity 0.981.

To determin whether a compound had actually been formed, or whether the molecular proportions were simply the result of an accidental choice of temperature, the absorptive power of the salt was tested at several

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[1] Kuriloff, *Z. physik. Chem.*, 25, 908–10 (1898).

[2] Rupert, THIS JOURNAL, 32, 748–9 (1910).

[3] Waddell has shown that the transformation of ammonium thiocyanate into thiourea practically does not occur in aqueous solutions, even when they are boiled for many hours. *J. Physic. Chem.*, 2, 527 (1898).

[4] 159°, Reynolds, *Ann.*, 150, 227 (1869). 148°–9°, Reynolds and Werner, *J. Chem. Soc.*, 83, 2 (1903). 149°, Findlay, *Ibid.*, 83, 407 (1904). 147°, Inghlieri, *Chem. Zentr.*, 1909, II, 905.

temperatures from 0° to 100°. At 0° the product was found to contain 43.10% of ammonia, at 25° 31.16%, at 50° 19.40% and at 75° 6.17%, while at 100° no ammonia was absorbed.

In Fig. 1 the circular plots represent direct absorption of ammonia, while the crosses represent values obtained by first saturating the salt at a lower temperature and then holding the product at the required temperature in a stream of ammonia gas till it no longer lost weight. It will be seen that the end result was sensibly the same by either method.

The percentages corresponding to molecular proportions are indicated on the axis of concentration.

Prolongation of the rectilinear upon which all of the plots lie cuts

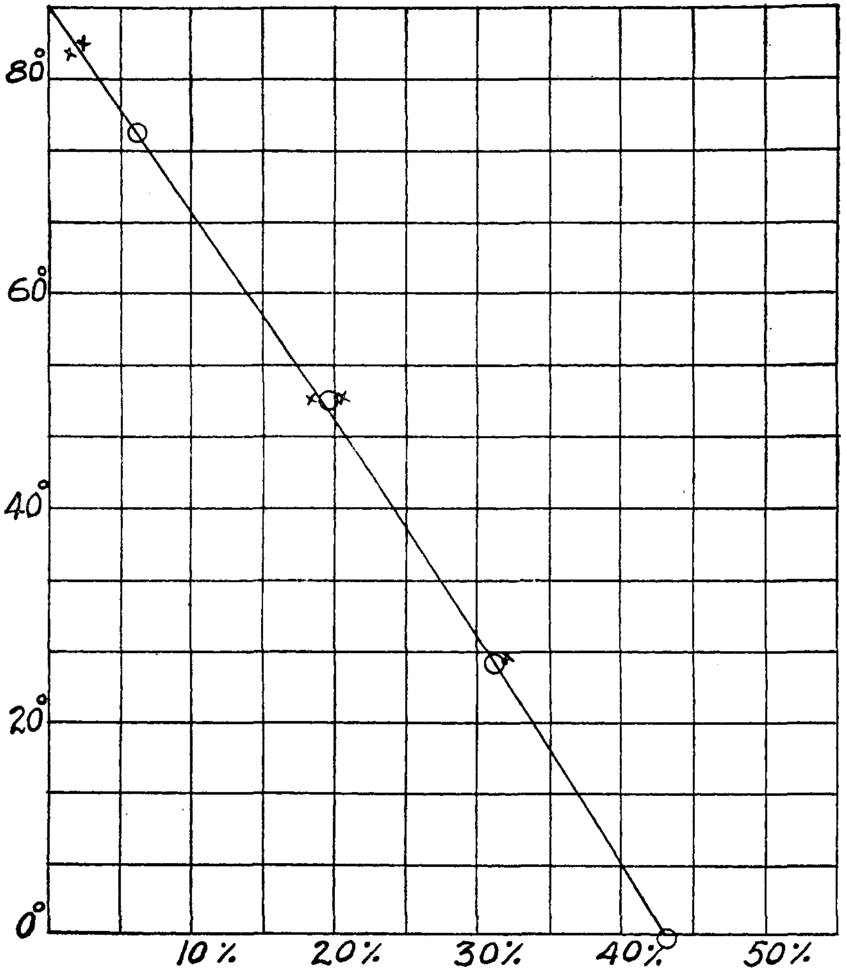

Fig. 1. Absorption curve.

the axis of temperature at 88°, which is thus the temperature at which ammonia ceases to be absorbed by ammonium sulfocyanate.

There is no basis in this curve for assuming the existence of compounds of ammonia and ammonium sulfocyanate at temperatures above zero.

Freezing-Point Curve.—Very different results were obtained at low temperatures by the study of the freezing points of solutions of ammonium thiocyanate in ammonia ranging in concentration from 0% to 100% of the latter.

The apparatus for this purpose consisted of a long-necked glass bulb of about 10 cc. capacity, provided with a steel cap as shown in Fig. 2.

A is a sleeve of such diameter as just to allow the slightly belled mouth of the neck to pass. B is a similar but smaller sleeve, split in halves in the direction of its length, fitting the glass neck as tightly as possible, and screwing into A above. Hard wax was melted into the free space between the top of B and the mouth of the neck, and the latter was held meantime in such a position as to project from A by an amount equal to about half the thickness of the glass. The wax, just before setting, was kept at the right height under the bell by screwing B up or down, as might be necessary.

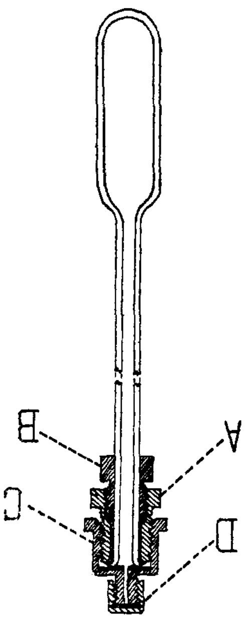

Fig. 2.

C is a cap provided within with a gasket of fiber or stiff rubber. It is perforated by a vent of small diameter and its gasket is likewise perforated. The vent in turn is closed by the little cap D, with its gasket. When C is screwed home, its gasket presses chiefly or wholly upon the glass.

In operation, the cap C was removed to charge the bulb with powdered salt and with ammonia. The latter was conducted to the bottom of the bulb by means of a narrow glass tube, the bulb meanwhile being held in the vapor of liquid air, at such a height above the liquid that the ammonia would condense as fast as it was delivered, but without freezing. The weight of the tube empty, the weight when charged with salt, and again when charged with both salt and ammonia, were the data for calculating the concentration of the solution.

The solution was then cooled to its freezing point by immersing the bulb in a bath containing about equal volumes of alcohol and ether. The increasing viscosity of alcohol, if used alone at the lower temperatures, would have interfered decidedly with the maintenance of a uniform temperature. The alcohol-ether mixture, contained in a deep cylindrical Dewar bulb, as shown in Fig. 3, was brought first, by means of liquid air, to a temperature slightly lower than the freezing point of the solution. The bulb having been inserted, a small portion of its contents froze, and melted again very slowly indeed as the bath warmed. During the latter process, both the solution and the bath were very effectively stirred by simply spinning the bulb by hand from above, the lower end of the bulb being kept centered the while, if necessary, by means of a simple arrangement of wire not shown. With the same object of thorough stirring in view, it was found advantageous to incline the Dewar bulb at an angle of about 45°. Just as the last crystals disappeared, the temperature of the bath was taken. Immediately after, liquid air was introduced into the well stirred bath, a few drops at a time, and the temperature was noted again just as the first crystals reappeared. If the interval between the disappearance and the reappearance of crystals was brief, there was no evidence of supercooling in the solution.

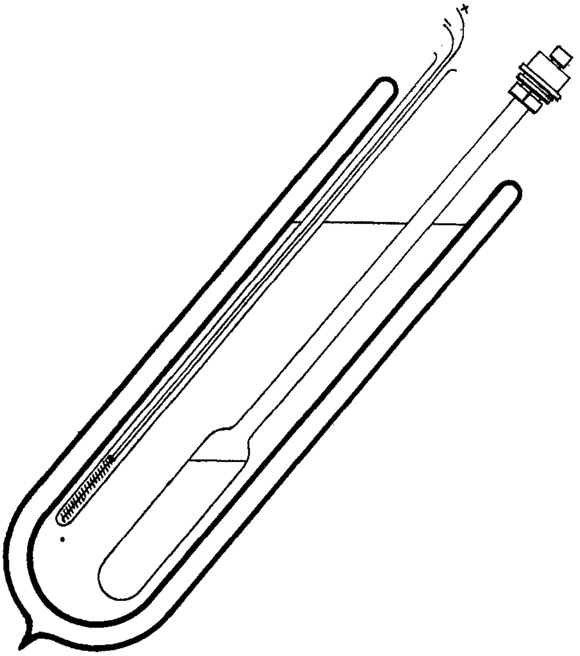

Fig. 3. Freezing-point apparatus.

Temperatures were read by means of a platinum resistance thermometer which had been thoroughly tried out in previous work, and which was standardized again for this immediate purpose by means of broken ice and a carbon dioxide-ether mixture (temperature 78.34 cor.).[1] This thermometer, protected by a thin-walled glass tube, was immersed several inches deep in the bath.

The arrangement of the thermometer, just described, suggests the likelihood of considerable lag in temperature, and this lag would have been realized no doubt if the temperature of the bath had been allowed to change too rapidly in either direction. By a not too cumbersome

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[1] Holborn, *Ann. Phys.*, [4] 6, 245 (1901).

combination of thorough stirring, and deft manipulation of the liquid air, it was found in practice that the difference between the melting and freezing points could be reduced to a fraction of a degree. That the thermometer moreover was practically unaffected by heat conducted in through the leads is shown by the fact that the freezing point of pure ammonia was found at 76.2°. Not less than three readings were taken of each freezing point of the solution for each concentration.

Having finished with one concentration, the tube was removed from the bath, carefully dried, and weighed again at room temperature as a check. The small cap D was then opened slightly, and a very small amount of ammonia was blown off, thus giving a new concentration. A considerable number of successive determinations could thus be made with a single initial charge, until the contents of the bulb were about half gone. At this point it was found desirable to begin with a new charge of suitably greater concentration than the first, for if the bulb was much less than half full, it became somewhat difficult to detect with sufficient precision the first appearance of crystals, or the exact moment of their disappearance.

For temperatures above that of the room, a bath of warm water was substituted for the alcohol-ether, and water warmer than the bath, for the liquid air.

Results.—The following table gives the data obtained and Fig. 4 shows the course of the curve.

Table of Freezing Points.

% NH_3.	F. p.	% NH_3.	F. p.	% NH_3.	F. p.	% NH_3.	F. p.
0.00	148	32.29	—39.8	56.18	—79.8	66.79	—95
9.89	77	34.01	—39.2	56.63	—76.8	67.30	—93
13.22	56	36.38	—38.8	57.43	—75.8	67.93	—91.8
16.55	32	38.76	—38.8	57.77	—79	68.25	—90.3
17.62	23	42.08	—41.3	58.62	—79.8	68.84	—89
19.40	10.3	44.08	—42	59.22	—79.8	69.65	—88
20.93	—0.3	45.40	—44	59.29	—79.8	71.00	—85.7
21.91	—5.8	47.33	—47.2	60.07	—79.8	73.77	—82.7
22.50	—13.8	48.76	—52.2	60.73	—84.7	76.18	—81.3
23.27	—18	49.75	—57	61.53	—86.3	78.75	—79
23.94	—20	51.08	—60.6	61.63	—84.3	79.38	—79.2
24.89	—22	52.20	—65.2	62.33	—87	83.18	—78.7
25.61	—24.3	53.96	—70.8	63.05	—87.2	86.78	—78
26.30	—25.8	54.65	—72.8	64.55	—87.3	90.01	—77
27.67	—29.8	54.90	—73	65.60	—88.3	93.50	—76.9
29.13	—34.8	55.13	—75.7	66.11	—89.3	94.78	—76.8
29.90	—39.8	55.52	—77	66.40	—90.8	94.90	—76.7
30.75	—42.8	55.91	—79.3	66.41	—91.3	100.00	—76.2

In Fig. 4, for convenience of reference, the percentages corresponding to molecular proportions are indicated on the axis of concentration.

It will be seen that the curve furnishes sufficient evidence of the existence of three compounds, at least. These are ammoniates containing three, six and eight molecules of ammonia respectively. The crests are well formed and the highest points correspond accurately enough to the theoretical molecular concentrations.

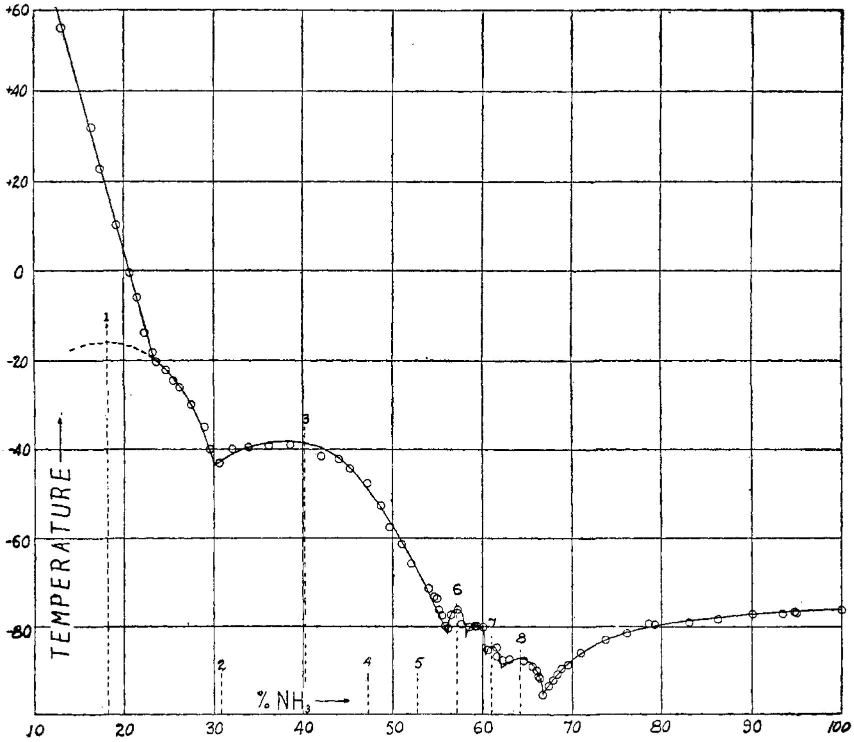

Fig. 4. Freezing-point curve.

That part of the curve which lies between 24% and 30% shows no crest. However, its prolongation would apparently culminate at about 18% ammonia, which corresponds to a mono-ammoniate. Provisionally, it will probably be safe to assume the existence of this compound, but if so, it forms only in the presence of a certain excess of ammonia. Cases of this sort are not at all uncommon.[1] Again, between 60% and 62% of ammonia there is doubtless a convolution corresponding to a hepta-ammoniate, but the numerical data are not as conclusive as might be desired. Intervals of concentration must be made much smaller before the course of the curve at this point can be considered certain. An important reason for assuming the existence of this hepta-ammoniate

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[1] *E. g.*, Kuriloff, *Z. physik. Chem.*, 23, 677 (1897).

is found in the fact that the crystals which form at this part of the curve are different from those which form on either side of it.

Finally, between 58% and 60% the plots are wholly ambiguous. Situated as they are, however, it is impossible that they should belong either to the convolution of the hepta-ammoniate on the left of them, or to that of the octo-ammoniate on their right. Clearly, also, they are poor material out of which to construct a new convolution between these two. Nevertheless, we are convinced that such a new convolution will be found here when data of sufficient accuracy come to hand, for, as in the previous case, the crystals which form in this section are distinguishable in appearance from those which form at concentrations immediately adjacent. Such a convolution would correspond to a compound, $NH_4SCN.6^1/_2NH_3$, or $2NH_4SCN.13NH_3$.(58.9% NH_3), which would be analogous to cases which occur frequently enough in salts with water of crystallization, *e. g.*, $FeCl_3.3^1/_2H_2O$ (= $2FeCl_3.7H_2O$). It remains only to add that while thus eight sorts of crystals could be distinguished by the eye it is a much more difficult, if not impossible, task to distinguish them by description. In general, however, the four sorts observed between 56% and 67% ammonia (the region of the four narrow convolutions) appeared as flakes, while the three below 56%, including ammonium thiocyanate itself, were granular. The solid ammonia, as it formed in small quantities, may perhaps best be described as jelly-like.

Considering the great complexity of the curve as a whole, it is highly desirable that the work be repeated with all possible refinements. Owing to the change of residence of one of us,[1] we shall unfortunately not be able to do this in the immediate future. It would also be interesting to determin the vapor pressure curve with a view especially to learn whether these compounds, or any of them, exist in solution at higher temperatures.

Summary.

1. Ammonium sulfocyanate is the most deliquescent substance in ammonia so far observed. It continues to deliquesce up to 88°.

2. The freezing-point curve has been determined in a preliminary way for solutions of ammonium thiocyanate in ammonia, at concentrations ranging from 0% to 100% NH_3.

3. The solvent forms three compounds certainly, and probably five, with the solute. The former contain respectively one, three and eight molecules of ammonia; the latter, seven and six and one-half molecules.

4. The melting points are approximately as follows: the mono-ammoniate, —16° (metastable); the tri-ammoniate, —38°; the hexa-ammoniate, —76°; the hepta-ammoniate, —84°; and the octo-ammoniate,

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[1] (W. B. A.)

about —87°. The ammoniate, $2NH_4SCN.13HN_3$, would probably melt in the vicinity of —80°.

5. The lowest eutectic point lies in the vicinity of —96°.

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MIDDLETOWN, CONN., Oct. 17, 1911.

A METHOD OF MEASURING ABSOLUTE VISCOSITY.

BY HAROLD P. GURNEY.

Received November 2, 1911.

The desirability of expressing the viscosity of liquids in absolute units cannot be too strongly urged. Unfortunately, most methods employed to this end are either not adapted to rapid commercial work, or are not capable of giving absolutely accurate results. The advantages that may be claimed for the following method are: (1) it can be made extremely accurate, (2) the manipulation is simple and rapid, (3) opaque liquids can be tested, (4) the apparatus can be set up in any chemical laboratory at short notice, taking but little time to calibrate, and (5) only a very small quantity of liquid is required.

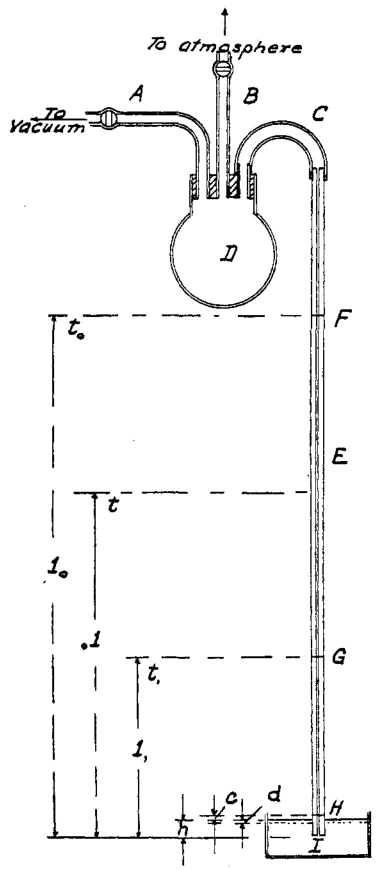

Fig. 1.

The apparatus is outlined in Fig. 1. The flask *D* is connected by a stopcock, *A*, to a vacuum pump and by rubber tubing, *C*, to a vertical glass tube, *E*, of capillary bore. A stopcock, *B*, connects with the atmosphere. A cup with vertical walls contains the liquid where viscosity is to be tested. There are three marks or etched rings around the glass tube at *F*, *G*, and *H*. In Fig. 2, the apparatus is shown with a jacket for temperatures other than room temperature.

The method of operation is simple. The cup *I* is filled with liquid until it just rizes inside the capillary to the line *H*. The stopcock *A* is opened and *B* is shut until the liquid has been sucked up above the line *F*. *A* is closed and *B* opened, thereby admitting atmospheric pressure above the liquid in the capillary tube. The level of the liquid in the capillary descends with but slightly