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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

Concentrated Solutions of NaSCN in Liquid Ammonia. Solubility, Density, Vapor Pressure, Viscosity, Thermal Conductance, Heat of Solution and Heat Capacity[1]

BY GEORGE C. BLYTAS AND FARRINGTON DANIELS

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The complete phase diagram of the NaSCN–NH_3 system has been determined. The formation of a stable compound NaSCN·3.5NH_3 (m.p. −6°), as well as a peritectic and two eutectic points, have been established. The densities of the liquid phase have been measured. Large negative partial molal volumes of solute have been noted at high temperatures and low concentrations of the electrolyte. The vapor pressures of the solutions up to 400 psia. are characterized by extreme negative deviations from Raoult's law. The viscosities have been measured over a wide range of temperatures and concentrations. At 12° the viscosities of solutions 68 and 35% NH_3 by weight are in the order of 0.5 and 6 centipoises, respectively. Thermal conductance data have been obtained by the hot wire method. They were found to be 3 or 4 times higher than that of the pure solvent. Finally, the heats of solution of NaSCN in liquid NH_3 at 0° were found to be exothermic to the extent of 12 kcal./mole at infinite dilution.

In emphasizing the importance of dilute aqueous solutions in the development of physical chemistry the interesting behavior of very concentrated nonaqueous electrolytic solutions has largely been overlooked. Bell[2] has pointed out the possibility of incomplete dissociation of strong electrolytes in very concentrated solutions due to short range attractive forces other than electrostatic. Unique situations may arise when there is not enough solvent present to form shells around the solute molecules. Progress in understanding these concentrated solutions may be made by regarding them as fused salts containing some of the dissolved liquid "solvent." For example the abnormally large heat conductance of very concentrated solutions of NaSCN in liquid ammonia reported here is characteristic of fused salts rather than of ammonia or aqueous solutions. Other physical properties of these concentrated solutions are reported here also in order to add to the very meager experimental data which are now available for the development of new theories of concentrated solutions. The data extend from −81 to 305°, from 10% NH_3 to 10% NaSCN corresponding to 25 molal solution and from pressures of a few millimeters to 400 pounds per square inch.

This particular system was chosen for study also because of its possible application in absorption–desorption refrigeration operating with solar heat. Engineering aspects of this application will be reported elsewhere. The NaSCN–NH_3 system is unusually favorable for such a purpose because it has high heats of vaporization, very high solubilities, low vapor pressures, low viscosities and high thermal conductances. It was chosen over some other equally favorable solutions because it is stable, safe and non-corrosive in steel. Ammonium salts which are highly soluble in ammonia corrode stainless steel and other materials which might be used for refrigeration and industrial operations.

A limited number of other salts in very concentrated solutions of ammonia have been studied with reference to solubility and vapor pressure, and they are described briefly in an accompanying contribution.

Liquid ammonia is an interesting solvent because its dielectric constant is high enough to permit extensive solubility of ionic substances and yet it is much lower than water. Much interesting work has been done by Kraus and others on the properties of dilute electrolytic solutions in ammonia at its boiling point −33.4°, but very little information is available for the concentrated solutions. These low temperature solubilities are limited and the temperature dependence of other physical chemical properties is unknown. At the

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[1] More complete details of the experimental procedure, the results and the theoretical interpretations may be obtained from the Ph.D. thesis of George C. Blytas filed in the Library of the University of Wisconsin in 1961.

[2] R. P. Bell, *Discussions Faraday Soc.*, **24**, 17 (1957).

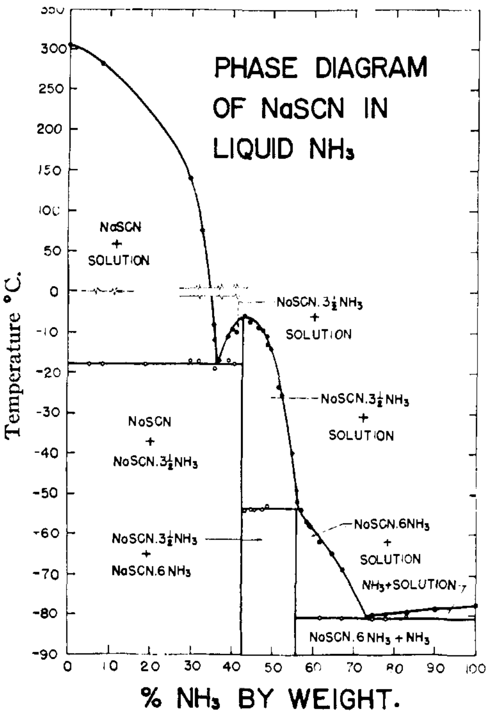

Fig. 1.

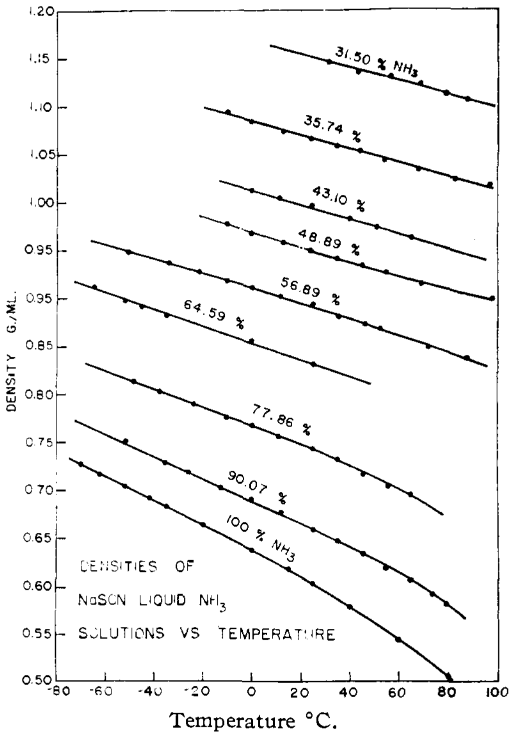

Fig. 2.

higher temperatures there is the inconvenience of handling solutions under high pressures of ammonia. On the other hand the solubilities are so great that it is possible to have solutions of liquid ammonia at room temperature with less than 1 atmosphere pressure, while the vapor pressure of liquid ammonia at the same temperature is 10 atmospheres.

In the course of this investigation it has been necessary to devise new apparatus capable of handling these solutions under difficult conditions.

Solubility

Experimental Procedure.—Solubilities were determined by observing the temperature at which phase transitions occurred in mixtures contained in sealed glass tubes. A 40 cm. section of Pyrex tubing having a 5 mm. inside and 7 mm. outside diameter was sealed at one end to a capillary tube to facilitate later sealing-off. The tubes were able to withstand pressures of a hundred atmospheres. The annealed glass tube was weighed, pure salt was quickly introduced through the wide (5 mm.) open end and the tube sealed off. After heating and evacuating for 2 hr. the tube containing the salt was weighed. Then the volume of purified ammonia necessary to give the desired concentration was distilled in and the capillary tube sealed off near the joint. The desired amount of ammonia was obtained by distilling ammonia from a trap containing sodium into a graduated tube cooled with solid carbon dioxide and acetone and then warming and redistilling a measured volume of this ammonia into the sample tube. The sample tubes were filled about two thirds full to allow for thermal expansion and after sealing they were weighed a third time. The uncertainty in composition was ±0.01% and the desired composition could be attained within ±0.2%. Chemically pure anhydrous sodium thiocyanate was heated and evacuated, pulverized and reheated and re-evacuated.

For temperatures above 90° the samples were thermostated in a small well bored in a tall vertical, thermally insulated brass cylinder. The cylindrical block was electrically heated and silicone oil insured good thermal contact with the brass. Because the pressures were very high at the higher temperatures the samples were manipulated behind a glass safety shield. They were drawn out of the well with a string on a "fishing pole," rapidly examined for the presence of crystals, and returned to the thermostat. For temperatures from 25 to 90° a water bath in a glass tube was placed behind a safety glass shield so that the meniscus could be read in position. For temperatures from 25 to −65° solid carbon dioxide and acetone were added together in the glass tube. From −65 to −90° petroleum ether was cooled by immersion in liquid air. Calibrated thermometers were used at different depths. For each solution the liquidus temperatures were recorded at which the last crystals disappeared with slow heating. This was better than trying to observe the temperature of the first appearance of crystals because of supersaturation on cooling. The solidus temperatures at which the last liquid disappeared on cooling or the first liquid appeared on heating were recorded also.

Results.—The liquidus points are given by the block circles and the solidus points by open circles in Fig. 1. The system shows the formation of a compound $NaSCN \cdot 3.5NH_3$ with a melting point of −6°. The eutectic point at lower concentrations of ammonia occurs at −18.5° at a composition of 36.0% ammonia. At higher concentrations of ammonia there is a peritectic point at −54° involving $NaSCN \cdot 3.5NH_3$ and $NaSCN \cdot 6NH_3$ and a eutectic point at −81° with a composition of 73.5% ammonia which involves $NaSCN \cdot 6NH_3$ and solid ammonia. The freezing point of pure ammonia is −77.7° and the melting point of the NaSCN was found in this investigation to be about 305°.

Densities and Partial Molal Volumes

Volume III of the International Critical Tables devotes over eighty pages to the densities of aqueous solutions and only a quarter of a page to the densities of liquid ammonia solutions, and these are at −33.4°. A knowledge of partial molal volumes is helpful in understanding the nature of concentrated solutions.

TABLE I

DENSITIES OF NaSCN SOLUTIONS IN LIQUID NH_3

NH_3, weight %	90.07	77.86	64.59	56.89	48.89	43.10	35.74	31.50
Mole fraction NaSCN	0.0230	0.0564	0.1033	0.1373	0.1800	0.2171	0.2741	0.3156
Temp., °C.								
100				0.823	0.897		1.012	1.099
75	0.588	0.682		.846	.912	0.953	1.028	1.117
50	.627	.712		.868	.929	.972	1.047	1.133
25	.658	.742	0.831	.878	.948	.991	1.066	1.149
− 0	.691	.768	.856	.910	.968	1.011	1.083	
−25	.718	.790	.875	.927				
−50	.746	.814	.897	.946				
−65			.912					

Experimental Procedure.—Sample tubes similar to those used for the solubility determinations were calibrated by filling to different heights with mercury and weighing. In a typical experiment the cc. per cm. of the Pyrex tube was found to be 0.17501, 0.17502 and 0.17507. The length of the solution column was determined by setting a tightly fitting ring of Tygon tubing 3 mm. wide, with sharp edges, around the sample tube at a suitable height. The glass tube thermostat previously described was adjusted until a temperature was reached at which the meniscus just touched the line of sight across the top of the Tygon ring. This temperature could be maintained to within ± 0.1°. The sample tube was then removed and the length of the column determined from the position of the ring. This length was determined within ±0.15 mm. corresponding in a 30 cm. column to 1 part in a thousand. This method of measuring densities gave values reproducible to only ± 0.07%, but it permitted rapid determinations over a wide range of temperatures.

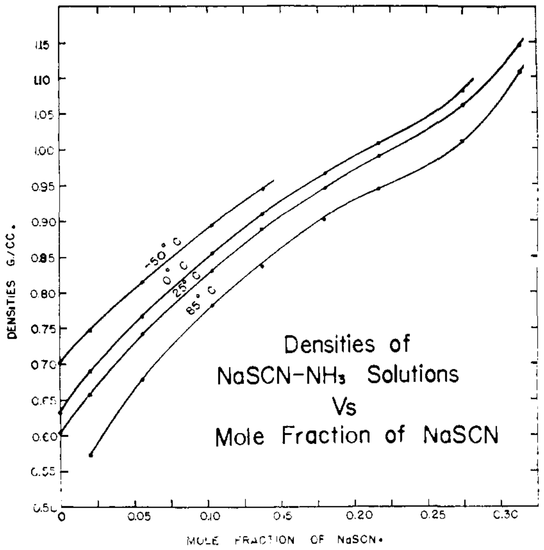

Fig. 3.

Results.—The densities are summarized in Figs. 2 and 3. Interpolated values of the densities are given in Table I and the partial molal volumes in Table II as obtained by the intercept method from a plot of the partial molal volume of the solution against the mole fraction of NaSCN.

Vapor Pressures

Extreme negative deviation from Raoult's law is an interesting characteristic of many salt solutions in liquid ammonia. A few measurements have been reported mostly at temperatures below 40°, but no experiments have been made on solutions of NaSCN.

Experimental Procedure.—The vapor pressure measurements were made with an Aschcroft Vapor Test Gauge reading up to 500 pounds per square inch in 2-pound divisions and calibrated with a dead-weight pressure tester. The calibrations ranged from 1 to 2 psi. and remained constant. At high pressures when liquid ammonia condensed in the gauge and the connecting tubes, heat was applied to vaporize the ammonia and maintain equilibrium conditions. At low pressures a mercury manometer was used.

The NaSCN-NH_3 solution was contained in a well 1.5 inches in diameter and 7.5 inches deep bored in an aluminum cylinder which was 5.5 inches in diameter. The cylinder contained three additional wells for a thermocouple, a Fenwal thermoswitch and a cartridge electrical heater. A stainless steel cover carrying the pressure gauge was bolted on and the apparatus and connections were made gas tight with Neoprene O-rings or Teflon gaskets. Depending on the temperature range the aluminum cylinder was placed in an insulated hot air thermostat, a water–glycol thermostat or a solid carbon dioxide–acetone bath of regulated temperature.

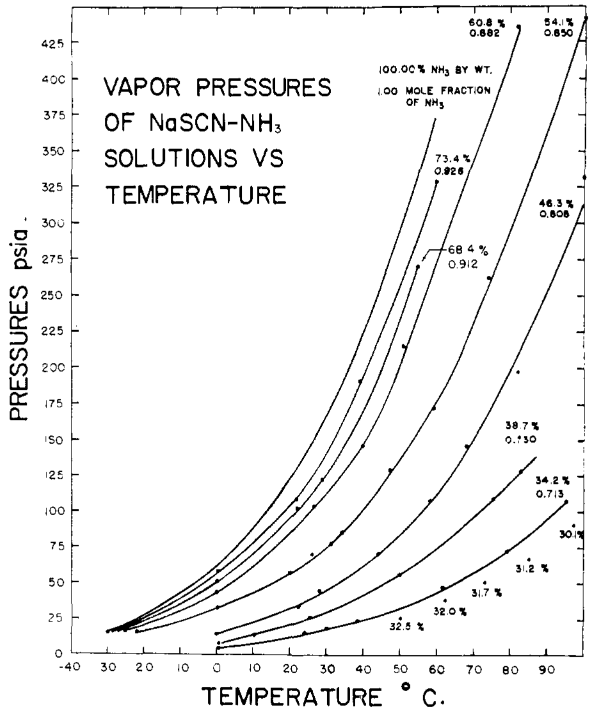

Fig. 4.

The solutions were prepared in the aluminum well by quickly introducing a carefully weighed sample of thoroughly dried and evacuated NaSCN, and then evacuating still further through a three-way valve. The desired quantity of sodium dried ammonia was distilled in from a cold graduated cylindrical reservoir while the aluminum cylinder was placed in a solid carbon dioxide–acetone bath. The greatest uncertainty was in the calculation of ammonia introduced,

TABLE II

PARTIAL MOLAL VOLUMES OF NaSCN AND LIQUID NH_3

Mole fraction of NaSCN	85°		25°		0°		-50°	
	$\bar{V}_{NaSCN}$	$\bar{V}_{NH_3}$	$\bar{V}_{NaSCN}$	$\bar{V}_{NH_3}$	$\bar{V}_{NaSCN}$	$\bar{V}_{NH_3}$	$\bar{V}_{NaSCN}$	$\bar{V}_{NH_3}$
0.025	-67.3	34.7	21.0	28.2	30.7	26.6	43.4	24.7
.050	- 2.5	32.3	30.7	28.1	35.6	26.4	44.2	24.2
.100	37.9	29.2	34.5	26.4	45.5	25.5	48.9	23.8
.150	49.1	27.8	51.9	25.5	50.5	24.8		
.200	51.8	27.3	52.2	25.3	53.7	24.2		
.250	49.4	28.1	49.6	26.1	49.7	25.3		
.275	43.7	30.1	45.1	28.3	44.2	27.3		
.300	23.1	38.3	23.9	36.2				

and it amounted to a maximum of ±0.2% in the 73% solution. Another uncertainty in the composition involves the presence of ammonia gas above the solution. This error was kept negligible by minimizing the volume of the vapor phase and applying a small correction.

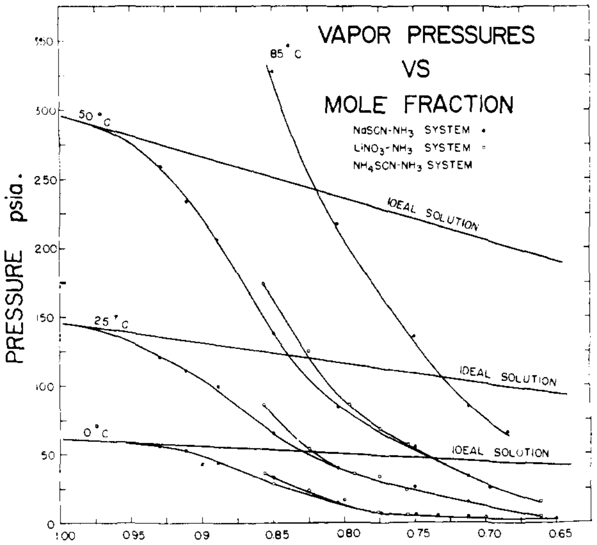

Fig. 5.

Results.—The experimental results are shown in Fig. 4 and the vapor pressures are plotted in Fig. 5 against mole fractions. In Fig. 5 a few data are given also for $LiNO_3$ and NH_4SCN solutions. Plots of logarithms of the vapor pressure against the reciprocal of the absolute temperature for solutions from 34.2% ammonia to 73.4 give excellent straight lines which are nearly but not exactly parallel, becoming slightly less steep in general, as the concentration of ammonia increases.

Interpolated data are summarized in Table III and the ratios of the vapor pressures of solutions to those of liquid ammonia are recorded in Table IV.

Viscosity

The determination of the viscosities of ammonia solutions is difficult on account of the high pressure of solvent, but the values are needed for design of refrigerating units and other equipment. Fitzgerald[3] determined the viscosities of KI, HgI, NH_4Br, $AgNO_3$ and $NaNO_3$ in ammonia at −33.4° and Planck and Hunt[4] determined the viscosities of pure ammonia at 5, 15 and 25°. In the present work the viscosities of NaSCN solutions were determined from −7 to 60° involving pressures up to 10 atmospheres.

Experimental Procedure.—The viscometer is shown in Fig. 6. It was designed to operate over a range of temperatures and pressures in an enclosed system and to permit easy rechecking of determinations and changing the composition of the solutions. There are two sections, the upper section of aluminum being a reservoir in which the NaSCN is placed and the purified ammonia distilled in from a graduated reservoir, thus permitting a calculation of the composition of the solution as previously described. After making determinations at one concentration more dilute solutions are prepared by distilling in additional measured amounts of ammonia.

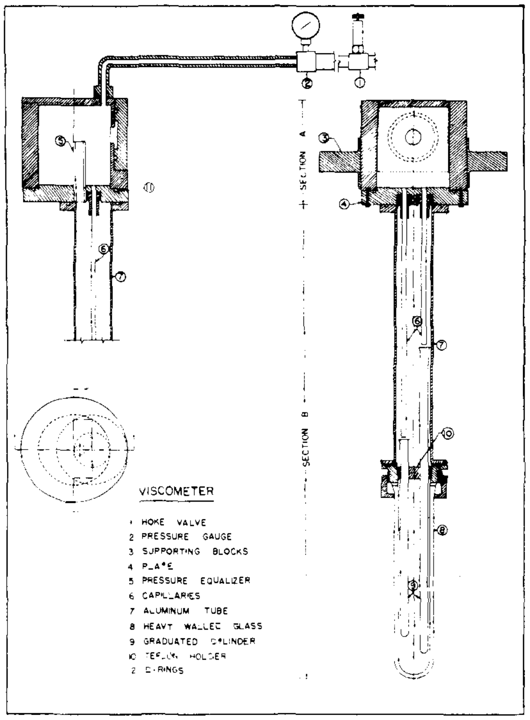

Fig. 6.

The lower part of the viscometer contained two capillary tubes through which the solutions flowed and two graduate cylinders to measure the volume of solution passing through in a given time. The graduated cylinders were enclosed in a heavy walled glass tube. When the viscosity measurements were to be made, the viscometer was set exactly vertical in a large insulated and illuminated thermostat of water and glycol kept within 0.05°. Before repeating a measurement or changing the composition of the solution the viscometer was inverted and the solution contained in the graduated cylinders was flown back into the reservoir. The total volume of the viscometer was 1650 cc. about equally divided between the top and bottom sections and the dead space took up more ammonia gas when the tem-

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(3) F. F. Fitzgerald, *J. Phys. Chem.*, **16**, 621 (1912).

(4) C. J. Planck and H. Hunt, *J. Am. Chem. Soc.*, **61**, 3590 (1939).

TABLE III

VAPOR PRESSURE OF AMMONIA IN PSI. FROM SOLUTIONS OF NaSCN

Mole fraction of NH_3 Temp., °C.	1	0.928	0.912	0.882	0.850	0.805	0.750	0.713
−20	27.59	25	24	21	16			
−10	42.18	39	35	31	24			
0	62.29	56	51	43.5	33	15	7.5	5
10	89.18	78.5	71.5	62	43	22.5	14	7.5
20	124.0	105	96	86.5	57	32	21	12.5
30	169.2	140	127.5	116.5	77.5	46.5	31	18.5
40	224.4	194	172.5	147	103	64	43	24.5
50	294.8	259	234	207	137.5	84	58	33
60	380	331	305	272	179	113.5	77	45
70	490			348	235	152	97.5	57
80	600			422	296	193	121	75
90	720				367	250	150	96

TABLE IV

RATIO OF VAPOR PRESSURES OF NaSCN SOLUTIONS TO PURE LIQUID AMMONIA

Mole fraction of NH_3 Temp., °C.	0.928	0.912	0.882	0.850	0.805	0.750	0.713
−20	0.908	0.870	0.763	0.585			
−10	.910	.829	.733	.561			
0	.900	.812	.700	.530	0.241	0.120	0.082
10	.879	.802	.695	.483	.247	.157	.085
20	.844	.772	.695	.458	.258	.171	.100
30	.826	.753	.688	.457	.270	.183	.109
40	.862	.765	.653	.458	.284	.191	.108
50	.878	.798	.702	.467	.285	.197	.112
60	.880	.802	.715	.472	.299	.202	.118
70			.710	.480	.308	.200	.117
80			.710	.495	.320	.202	.125
90				.051	.350	.210	.135

perature was raised. Thus the liquid phase of the most concentrated solution of NaSCN contained 34.72% by weight of ammonia at 59° while at 11° it contained 35.40%. Corrections were necessary and using two different methods they agreed within 0.15%.

Four different capillaries were used, the radii of which were determined at different lengths by weighing columns of mercury. They had the dimensions

I $r = 0.026422$ and $l = 35.60$ cm.
II $r = 0.026487$ and $l = 25.43$ cm.
III $r = 0.013713$ and $l = 35.60$ cm.
IV $r = 0.014114$ and $l = 25.43$ cm.

Capillaries I and II were used simultaneously and similarly III and IV.

Results.—The viscosity η was calculated with the Poiseuille formula as corrected by Hagenbach for kinetic energy

$$\eta = \frac{\pi P R^4}{8 v l} - \frac{m \rho v}{8 \pi L}$$

where P = pressure difference across the capillary tube, R = radius of the tube, L = the length of the tube and v = the volume of liquid flowing through in unit time, m is a constant 1.12 and ρ is the density of the solution as determined in a previous section. For capillary I this equation becomes

$$\eta = 0.018765\rho/v - 0.125177\rho v$$

when η is expressed in centipoises.

The purpose of the two capillaries of different length but of the same diameter was to help determine the magnitude and direction of corrections. As a first approximation the longer capillary gave a calculated viscosity 1.2% higher than the average of the two and the shorter capillary 1.2% lower. The flow was slow enough to be laminar and the kinetic effects were small. The viscometer was checked with ethylene glycol at 25° and the viscosities were nearly the same for the long and short capillary and both were less than 1% lower than the value given in the literature.[5] The rather complex corrections suggested by these results are analyzed elsewhere.[1] On the basis of this analysis, the corrected viscosities are from 2.2 to 5% higher than the average of those calculated from the two capillaries (including the 1% for calibration with glycol).

The minimum corrected viscosities in centipoises at different temperatures are plotted in Fig. 7 together with those by Planck and Hunt for pure ammonia. The composition changed slightly at the different temperatures due to the vaporization of ammonia as already explained and so the dotted lines are the more significant. They give the minimum corrected viscosities corresponding to the composition of the intersection of the dotted and the full line, throughout the whole temperature range.

In Fig. 8 the dependence of the viscosity on the mole fraction of ammonia is shown.

Thermal Conductance

Measurements of thermal conductance are not common in the literature of physical chemistry. Measurements of electrical conductance are much easier and more precise. Thermal conductance is of particular interest in the highly concentrated solutions which often have been regarded similar to fused salts. Should the thermal conductance of a concentrated solution be large, this similarity would be further substantiated. Moreover, the thermal conductance of $NaSCN-NH_3$ solutions is desired for the design of solar refrigeration units.

Early work on the thermal conductance of aqueous solutions, by Jager (1890), Budgman (1923) and Bates (1936) made use of "steady state" experimental techniques. A simpler method, the "line source" or "hot wire" method, has been developed[6-8] in which the temperature of a heated wire, immersed in the medium under investigation, is determined at successive times be-

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(5) Handbook of Chemistry and Physics, 32nd Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1950, p. 1831.

(6) B. Stalhane and S. Pyk, *Tekn. Tidskr.*, **61**, 389 (1913).

(7) A. Eucken and H. Engelert, *Zeit ges Kalte-Ind.*, **45**, 109 (1939).

(8) Van der Held and Van Drunen, *Physica*, **XV 10**, 865 (1949).

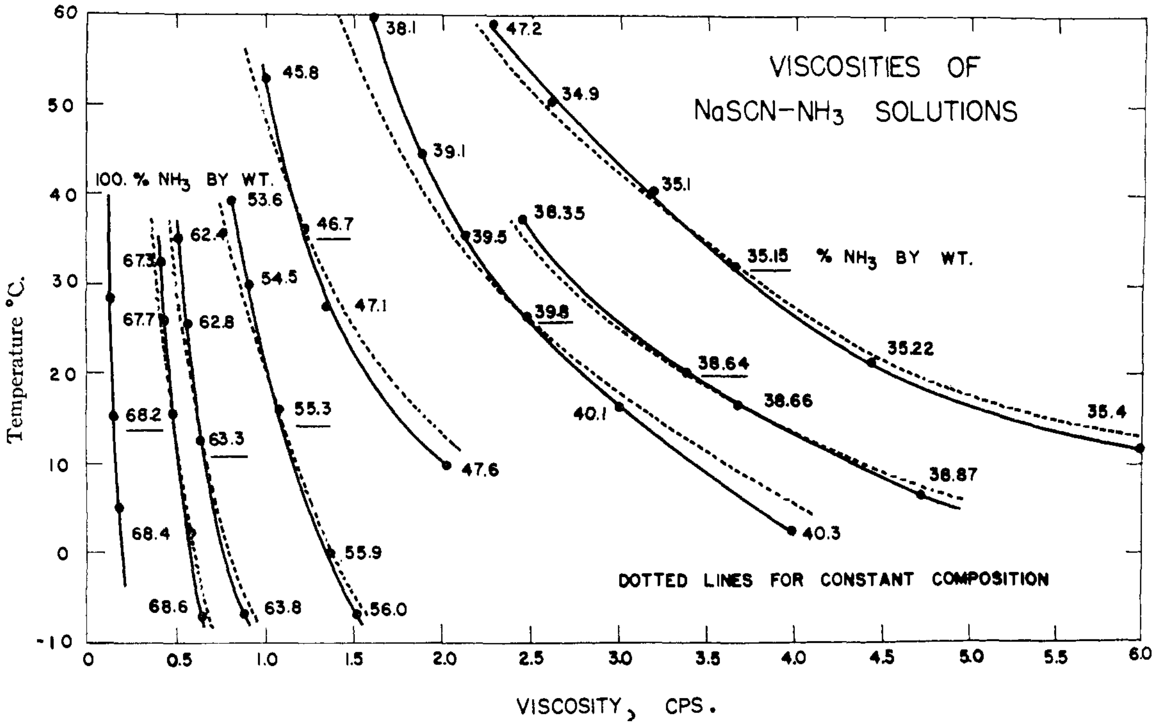

Fig. 7.

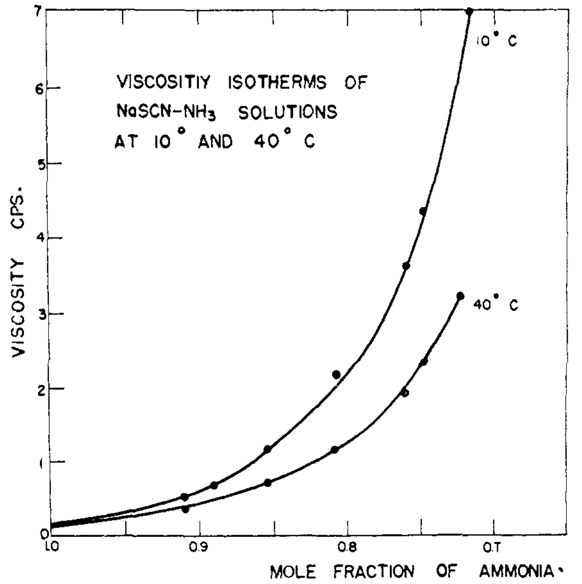

Fig. 8.

fore a steady thermal state is achieved and before convection sets in. Concentrated solutions with relatively high viscosities are suitable because loss of heat by convection is delayed. The formula used[1] was

$$T_{t2} - T_{t1} = \frac{q}{4\pi K} \ln \frac{t_2 - t_0}{t_1 - t_0}$$

where T is the temperature at time t, q is the heat produced per unit time, per unit length of heating wire, K is thermal conductance. In using this equation, it is necessary to have a sufficiently long wire and to measure the temperature of the wire in a central section well removed from the boundaries of the medium.

Experimental Procedure.—The thermal conductance cell was a heavy wall Teflon tube, 5 cm. i.d. and 15 cm. high. A nichrome wire heater (1.66 ohm per foot at 0° and 1.69 ohm per foot at 75°) was placed in the axis of the cell. At 6 cm. from the bottom a small iron-constantan thermocouple was soldered. The cold end of the thermocouple was kept in an ice bath. Teflon was chosen in order to minimize electrolytic conductance in the cell. The Teflon cell was fitted tightly into a brass cylinder to avoid deformation at high temperatures and pressures. The system was closed with a vapor tight stainless steel cover which was provided with a Hoke valve, a pressure gauge, and covar-in-glass electric leads for the heating wire and the thermocouple. The lower end of the heating wire was attached to an aluminum screw which made a vapor tight seal with the bottom of the Teflon container. The solution practically filled the Teflon cylinder and submerged the heating wire.

In order to fill the cell, a weighed quantity of dried NaSCN was placed in the cell, and a measured volume of ammonia was distilled in from a warmed steel cylinder containing ammonia and sodium. It was not possible to fill the apparatus as before by chilling it with solid carbon dioxide because the Teflon-metal contacts did not remain tight when cooled rapidly to very low temperature; thus the apparatus was kept in ice instead of in a Dry Ice–acetone bath.

A six-volt storage battery was used to supply current to the heating wire and to a standard resistance box connected in series. The thermal e.m.f. was measured with a potentiometer. The cell was set in the thermostat and allowed to come to thermal equilibrium and the potentiometer was set so that the galvanometer had a zero deflection. By changing the series resistance a constant current then was adjusted such that the temperature of the heating wire increased by 1 or 2 degrees in 15 to 25 seconds. In order to obtain the time interval required for a given temperature rise, the potentiometer dial was set to a reading corresponding to the higher temperature desired, and the switch closing the circuit was depressed simultaneously with the timer switch. The timer was stopped when the galvanometer read zero. One cause of uncertainty was the initial surge of the galvanometer in the thermocouple circuit. A correction was made for this by reversing the direction of the heating current.

Results.—The logarithms of the observed times were plotted against the corresponding temperature rises. The resulting line had a slight curvature, but a corrected straight line[9] could be found, which was a constant number of seconds away from the experimental curve. The constant time difference corresponds to the t_0 of the equation given above. The thermal conductance could then be obtained from the slope of this straight line. When, at longer times, convection sets in, the time required to obtain a given temperature increment rises sharply and is not reproducible.[10] In this work, the thermal conductance calculations are limited to measurements with shorter time intervals, before convection occurs. For the same reason only very concentrated solutions of appreciable viscosity were measured.

The uncertainty in the absolute values of the thermal conductance as measured here probably is about ± 4%. The trends in the thermal conductance measurements were not affected by changing the intensity of current and time of observations thus indicating that no systematic errors were important. A check measurement was made on ethylene glycol which according to the International Critical Tables has a thermal conductance of 0.00063 cal. sec.$^{-1}$ cm.$^{-1}$ at 0°. The value obtained in this work was 0.00063 at 20°.

The data are summarized in Table V. The fact that the more concentrated, *i.e.*, more viscous solutions, have a greater thermal conductance, suggests that convection errors were not important.

TABLE V

THERMAL CONDUCTANCE OF NaSCN–NH$_3$ SOLUTIONS

NH_3, weight %	Temp., °C.	I, amp	T_{max}, 0°C.	t_{max}, sec.	K, cal. sec.$^{-1}$ cm.$^{-1}$ deg.$^{-1}$
40.6	20	2.6	0.95	23.3	0.0052
40.6	69	1.850	1.80	13.1	.0054
46.0	20	0.957	1.04	17.8	.0038
46.0	60	.955	0.91	10.7	.0040
50.2	20	.957	.95	11.3	.0036
50.2	60	.955	.91	10.4	.0038

Heat of Solution

Previous calorimeter studies in liquid ammonia have been limited to measurements carried out at the boiling point −33.4°.[11] The best heats of solutions reported involve errors of the order of 0.1 kcal. per mole.[12]

Experimental Procedure.—The specially designed calorimeter had an effective volume of 360 cc. and very little space was available for ammonia evaporation. It was made of aluminum and had good thermal conductance, corrosion resistance and ability to withstand high pressures. The stirring of the solution was done by a propeller actuated through the tightly fitting cover with a horse-shoe magnet. The weighed quantities of dried NaSCN were contained in glass vials 2.2 cm. in diameter which were broken during a determination by screwing down a plunger through a Hoke valve sylphon bellows. There were three such sample breakers and sample vials to make possible successive determinations of heats of solution. Purified ammonia was introduced while the calorimeter was cooled with solid carbon dioxide and after plugging the ammonia inlet the amount of ammonia contained was determined by direct weighing. The calorimeter was set in 1420 g. of 200-silicone oil which was stirred with a propeller in a tube. The breaking of the samples, as well as the stirring of the solution and of the silicone oil bath were done by means of nylon shafts to reduce thermal leakage. The calorimeter and jacket were enclosed in a covered thermostat with suitable air gaps. For measurements at 0° the thermostat was filled with ice.

The energy input was derived from three 12-volt storage batteries in parallel and an electric heater of naked manganin wire immersed in the silicone oil. The voltage drop across the heater and across a standard resistance were measured with an accurate potentiometer. The temperature was measured with a 25 ohm platinum resistance thermometer having a sensitivity of 5×10^{-6}°.

With pure ammonia under pressure in the calorimeter at a temperature somewhat below that of the thermostated jacket a preliminary heating was carried out to determine the heat of stirring and other corrections. A thirty-minute heating period was then allowed for electrical calibration followed by another initial heating period for the measurements of the heat of solution. A sample was then broken and the temperature rise was observed again as a function of time over a period long enough to permit complete solution of the salt and the attainment of thermal equilibrium. The correct temperature rise was calculated from graphs using the Regnault Pfaundler method. After completion of the experiment another electrical calibration period followed and then a second sample of NaSCN was broken with a Hoke valve breaker and second determination made of the heat of solution. We are indebted to Professor J. L. Margrave and Miss M. Frisch for the use of the platinum resistance thermometer, Mueller bridge and galvanometer which were used with the calorimeter described here.

The integral heats of solution are given in Table VI.

TABLE VI

INTEGRAL HEATS OF SOLUTION OF NaSCN IN SOLUTIONS OF NaSCN IN LIQUID AMMONIA AT 0°

ΔH, kcal. per mole NaSCN		Moles NH_3 per mole NaSCN
−11.7	0.08	142.20
−10.2	.16	20.31
−9.8	.24	15.02
−7.0	.3	5.33

These data give a smooth curve which extrapolates to an integral heat of solution of 12 kcal. per mole of NaSCN at infinite dilutions.

Heat Capacities

The heat capacities of liquid ammonia solutions have never been studied before. The apparatus described in the preceding section is not very appropriate for measuring heat capacities on account of the large excess of silicone oil which must also be heated with the calorimeter. Nevertheless reasonably good values of the heat capacities were obtained with the electrical heating and the calorimeter in the course of the measurements of heats of solution just discussed.

Although the heat capacity determinations frequently were reproducible to within 0.3 and sometimes 0.1% there is uncertainty in the time lag from the heater and oil to the ammonia solutions. The determination of the heat capacity of pure liquid ammonia was too low by 4% when compared with published values for ammonia. After a correction of 4% to the present data it is believed that they are reliable to ± 2%.

The heat capacity of pure crystalline NaSCN or fused NaSCN has not been measured. By Kopp's additivity rule it is estimated to be 0.237 cal. deg.$^{-1}$ g.$^{-1}$. The experimental data are summarized in Table VII and compared with the heat capacities calculated by addition of those of the NaSCN and NH_3 assuming that they do not change in solution.

Discussion

In concentrated solutions of NaSCN, with percentages of ammonia less than about 55% by weight, the density decreases almost linearly with temperature as seen in Fig. 2. In the more dilute

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[9] W. M. Underwood and R. B. Taggart, Preprint Third Heat Transfer Conference, Am. Soc. Mech. Eng.-Am. Inst. Chem.-Eng., Storrs, Conn. (1959).

[10] D. G. Gillam and O. Lamm, *Acta Chim. Scand.*, **9**, 657 (1955).

[11] C. A. Kraus and F. C. Schmidt, *J. Am. Chem. Soc.*, **56**, 2298 (1934), and later contributions.

[12] W. L. Jolly, *Chem. Revs.*, **50**, 351 (1952).

TABLE VII

HEAT CAPACITIES OF NaSCN SOLUTIONS IN CALORIES DEG.$^{-1}$ GRAM^{-1}

NH_3, weight %	0° Obsd.	0° Calcd.	25° Obsd.	25° Calcd.
40.71	0.531	0.59	0.556	0.60
55.30	.600	.71	.630	.72
58.82	.680	.74	.670	.76
78.00	.745	.90	.820	.93

solutions of the electrolyte there is a slight curvature toward lower densities at the higher temperatures. The dependence of density on mole fraction is shown in Fig. 3. There is a change in the slope of the lines in the neighborhood of 0.22 mole fraction NaSCN. The phase diagram shown in Fig. 1 indicates that there is the formation of a chemical compound $NaSCN{\cdot}3.5NH_3$ at a mole fraction of 0.222 (42% by weight of ammonia). The difference in density trends at this concentration may indicate the existence of attractive forces which at lower temperatures become strong enough to cause the crystallization of the definite chemical compound from the solution. Again they may indicate that at this concentration there is a change in behavior from a solution of an electrolyte in a solvent of high dielectric constant to a solution of a system containing a fused salt in which "solvent" molecules are dissolved.

In the dilute solutions of NaSCN the partial molal volume of NaSCN decreases sharply with an increase in temperature and at 85° it reaches a large negative value, −67.35 cc. per mole as shown in Table II. Therefore, at high temperatures the addition of small amounts of the electrolyte NaSCN results in a pronounced decrease in the volume of the solution. The solute may be regarded as a binding agent which reduces the formation of "holes" in the structure of the liquid as the temperature approaches the critical temperature. This binding capacity of the electrolyte probably is enhanced at high temperatures by the thermal dissociation of ion pairs into ions which have a greater solvation tendency. Friedericks[13] found that several ionic salts follow the ammonia solvent into the gas phase in the critical region, indicating that there is a very strong attraction between ions and ammonia molecules even at elevated temperatures.

The vapor pressures of $NaSCN-NH_3$ solutions show large negative deviations from Raoult's law as indicated in Fig. 5 and Table IV. The deviations from ideal behavior of the solution is larger in the lower concentrations of ammonia. The non-ideality decreases with an increase in temperature except at high concentrations and low temperatures where the deviation first increases and then decreases. This change in the non-ideality with temperature occurs in a range of mole fraction of ammonia from 0.805 to 0.850 and in a temperature range from 30 to 40°. This concentration range is not far from the general region where at lower temperatures $NaSCN{\cdot}3.5NH_3$ precipitates out. A similar relation was noted in the temperature dependence of density.

All of the solutions studied, even those of the most dilute solutions of NaSCN, are still much too concentrated for application of the Debye–Hückel theory.

According to Bjerrum's theory of ionic associations, positive and negative ions form an ion pair when they approach to a distance q, which is characteristic of the solvent and the ionic valency. Ion pairs are in equilibrium with free ions and with charged or neutral ion clusters. In liquid ammonia q is of the order of 15 ångströms for 1–1 electrolytes. One cubic centimeter of 35% by weight solution of ammonia contains 4.8×10^{21} molecules at approximately 6 ångström units from each other. All of the ions then satisfy Bjerrum's electrostatic requirements, as in fact they do in all the solutions studied in this work.

Probably Coulomb's law on which the Bjerrum equation is based is not adequate to describe the system. Other short range forces and repulsions must be considered also. These short range forces probably do not extend beyond the first layer of the solvation shell, and it is to be noted that in many of the concentrated solutions studied here there are not enough solvent molecules present to provide complete solvation shells.

It is possible that in the concentrated solutions there are ion pairs and clusters which are less effective than the charged ions in causing deviations from ideality. They have less polarizing effect on the ammonia molecules due to the small charge to volume ratios. At higher temperatures some of these clusters and pairs are broken down and the non-ideality of the solution increases. This picture is in agreement with the data of Table IV. The linearity of the log P *versus* $1/T$ graphs is discussed elsewhere.[14]

The temperature coefficients of viscosity are higher at low temperatures and high salt concentrations. The viscosity of the solution is always greater than that of the solvent ammonia. Aqueous salt solutions in low concentrations generally have lower viscosities than water, suggesting a disrupture of the water structure. The temperature dependence of the viscosities of the concentrated NaSCN solution is similar to that of aqueous solutions of non-electrolytes.

The high thermal conductances of the $NaSCN-NH_3$ solutions, over three times that of organic liquids, can be explained by assuming that the concentrated solutions resemble a fused salt system. They decrease with an increase in concentration of solvent. Gambill[15] regards the thermal conductance of fused salts as intermediate between the thermal conductance of organic liquids, which is due to lattice contribution of short range atomic or molecular order present in the liquids, and the thermal conductance of liquid metals, which involves ionic and electronic drift. The thermal conductances of fused salts are about ten times as much as those of non-electrolytes. Another possible explanation of the high thermal conductance is the highly exothermic interaction of the NH_3 and the NaSCN, which at lower temperatures leads to compound formation. It is generally known that large molecular structures lead to lower thermal conductivities. This at first sight may seem con-

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(13) F. Friedericks, *J. Am. Chem. Soc.*, **35**, 1866 (1913).

(14) See accompanying paper, *ibid.*, **84**, 1083 (1962).

(15) W. R. Gambill, *Chem. Eng.*, **66**, Aug. 10, 129 (1959).

tradictory to a picture of the solution phase according to which forces leading to compound formation are present in the liquid phase. If, however, the loose bonds in the solution phase involve hydrogen, a high thermal conductivity may result, even with a highly ordered assembly of molecules. Perhaps the hydrogen bonding between the halogen-like thiocyanate ions and the ammonia protons is not unlikely. The relatively high conductance of water depends in part on the hydrogen bonding between the molecules.

The heat of solution of NaSCN in liquid ammonia is more exothermic than the heat of solution in water by 13 or 14 kcal. This larger evolution of heat in ammonia than in water is true of most salts and the difference may be due[16] to the requirement for energy absorption in the disruption of water clusters which are held together by hydrogen bonds.

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[16] S. P. Wolsky, E. J. Zdanuk, and L. V. Coulter, *J. Am. Chem. Soc.*, **74**, 6196 (1952).

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Concentrated Solutions in Liquid Ammonia: Solubility of $NaNO_3$ and KBr and Other Salts; Vapor Pressures of $LiNO_3$–NH_3 Solutions[1]

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The solubilities of several inorganic salts in liquid ammonia have been determined and the solubility curves of $NaNO_3$ and KBr over a limited concentration range are given. The KBr–NH_3 system has a negative temperature coefficient of solubility. Trends in solubility of salts are discussed in terms of polarizability and size of ions. The vapor pressures of $LiNO_3$–NH_3 solutions have been determined and are presented up to 200 psia.

In the accompanying paper[2] many physical properties of concentrated solutions of NaSCN in liquid ammonia are given together with a description of the experimental measurements and theoretical discussions. The same equipment and techniques were used in the present investigation in which phase diagrams of $NaNO_3$ and of KBr in liquid ammonia are presented. Solubilities of a few other salts are recorded and the vapor pressures of the system $LiNO_3$–NH_3.

The solid and liquid phase diagram of the $NaNO_3$–NH_3 system is shown in Fig. 1. A peritectic is formed which involves the compound $NaNO_3 \cdot 4NH_3$ with a melting point of −42.0°. There is a eutectic point at −81.0° at a composition of 78% by weight of ammonia. Hunt[3] has reported the freezing at 25° of a solution of 50.6% by weight of ammonia, whereas in this work there is a consistent evidence that the composition which first freezes at 25° is 43% ammonia.

The interesting but only partially complete phase diagram for KBr–NH_3 is given in Fig. 2. This system shows a negative temperature coefficient of solubility. The range of concentrations in this study was limited to solutions containing more than 67% by weight of NH_3 and more work should be done on this system. A similar behavior has been reported by Campbell[4] for Li_2SO_4 and water.

In Table I are recorded the liquidus points for several other salts in liquid ammonia.

The LiSCN–NH_3 system was chosen for study because it was anticipated that the salt would be highly soluble. The solutions however were so viscous that they were difficult to work with; in fact, at the higher concentrations of LiSCN the solutions were gel-like. The salt itself decomposed at 220 to 240°. Both in the case of the thiocyanate and the nitrate the lithium salts were more viscous than the sodium salts.

TABLE I

SOLUBILITIES OF SALTS IN LIQUID AMMONIA

Salt	NH_3, weight %	Moles NH_3 per mole salt	Temp., crystal disappearance, °C.
LiSCN	96.55	106.8	−75
	79.75	15.04	−82
	50.89	5.04	−64
	44.11	2.95	16
	33.91	1.96	20
LiBr	75.35	15.59	39
LiI	92.66	99.2	−76.5
	65.58	14.98	−37.5
NaBr	50.21	6.09	16.0
	42.0	4.38	25.0
NaI	40.40	5.97	14.5
KSCN	51.38	6.03	−59
KI	37.07	5.89	−49.5
KNO_3	94.36	99.42	−74
	71.69	15.04	100
AgSCN	38.25	6.04	−12

The solubilities of AgBr, AgI, $AgNO_3$, NH_4SCN, $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2$ and some other salts at 25° have been reported by Hunt.[3] The solubility of $LiNO_3$ in liquid ammonia has been studied by Portnow and Divilewitch.[5] The solubilities of NH_4I and NH_4NO_3 are also reported.[6]

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[1] More complete details of this research may be obtained from the Ph.D. thesis of George C. Blytas filed in the library of the University of Wisconsin in 1961.

[2] G. C. Blytas and F. Daniels, *J. Am. Chem. Soc.*, **84**, 1075 (1962).

[3] H. Hunt, *ibid.*, **54**, 3509 (1932).

[4] A. N. Campbell, *ibid.*, **65**, 2268 (1943).

[5] M. A. Portnow and N. K. Divilewitch, *Zhur. Obs. Khim.*, **7**, 2149 (1947).

[6] International Critical Tables, Vol. IV, 44 (1933).