ternary systems (two univariant, and two bivariant) studied. It is believed that the procedure adopted in this work might well be applied to the investigation of numerous other systems, containing hydrates, ammonates or other solvates, either pure or mixed.

## Summary

Pressure–temperature–concentration relations of the binary system, hydrazine trinitride–ammonia, and of other parts of the ternary system hydrazine–hydrogen trinitride–ammonia, have been investigated over ranges from 0 to 3200 mm., −50 to +80°, and 0 to 100% ammonia.

*Hydrazine trinitride hemiammonate*, $2N_2H_5N_3 \cdot NH_3$, the only solvate of the hydrazine salt found, is an extremely deliquescent, stable, white, crystalline solid, with vapor tension of ammonia of 5 mm. at 20°, and inversion point somewhat above 50°. In liquid ammonia it undergoes ammonolysis to an extent that varies directly with temperature and with concentration of ammonia

$$2N_2H_5N_3 \cdot NH_3 + NH_3 \rightleftharpoons 2NH_4N_3 + 2N_2H_4 \text{ (above } -9°)$$

$$2N_2H_5N_3 \cdot NH_3 + 5NH_3 \rightleftharpoons 2(NH_4N_3 \cdot 2NH_3) + 2N_2H_4 \text{ (below } -9°)$$

Definite boundaries between the fields of solvation and solvolysis have been determined and plotted.

ITHACA, N. Y. RECEIVED AUGUST 16, 1934

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[CONTRIBUTION FROM THE FERTILIZER INVESTIGATIONS UNIT, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

# The Solubility of Hydrogen in Liquid Ammonia at 25, 50, 75 and 100° and at Pressures to 1000 Atmospheres

BY R. WIEBE AND T. H. TREMEARNE

The investigation leading to this report is a continuation of the work in this Laboratory on the ammonia–hydrogen–nitrogen system. Larson and Black[1] measured the solubility of a 3:1 hydrogen-nitrogen mixture in liquid ammonia through a temperature range of −25.2 to +22.0° and at pressures of 50, 100 and 150 atmospheres. Wiebe and Tremearne[2] determined the solubility of nitrogen in liquid ammonia at 25° and at pressures to 1000 atmospheres. The solubility apparatus and procedure have been described in the preceding paper. The method had previously been checked by making a few determinations of the solubility of nitrogen in water. The results were in very good agreement with those obtained by the bubbling method.[3]

The hydrogen contained 0.1% of nitrogen and the synthetic ammonia 0.02% of water. A new 1500 atmosphere piston gage designed by J. R. Dilley of this Laboratory was used. This gage was calibrated against the 200 atmosphere gage previously described.[4] The latter was in turn compared with the piston gage of the Bureau of Standards.[5] For several pressures the maximum variation in the calculated effective area of the 200 atmosphere piston was less than two parts in 10,000 and for the 1500 atmosphere gage the variation was less than one part in 10,000.

At 100° the machine steel (0.15–0.25% C) used for the construction of the high pressure needle valves[6] became porous at the higher pressures. The ammonia–hydrogen mixture passed freely through the steel walls of the valves in numerous places.[7] A fine-grained chrome–vanadium steel (S. A. E. 6145) was secured from the Washington Navy Yard at the recommendation of Mr. L. Jordan of the Bureau of Standards and gave complete satisfaction as a material for making the valves.

## Discussion of Results

The results are plotted in Fig. 1. Pressures are given in international atmospheres, the local acceleration of gravity being 980.049. The solubility evidently increases decidedly with

(1) Larson and Black, *Ind. Eng. Chem.*, **17**, 715 (1925).

(2) R. Wiebe and T. H. Tremearne, THIS JOURNAL, **55**, 975 (1933).

(3) R. Wiebe, V. L. Gaddy and Conrad Heins, Jr., *Ind. Eng. Chem.*, **24**, 927 (1932), Table II.

(4) E. P. Bartlett, H. L. Cupples and T. H. Tremearne, THIS JOURNAL, **50**, 1275 (1928).

(5) C. H. Meyers and R. S. Jessup, *Bureau of Standards J. of Res.*, **6**, 1061 (1931).

(6) J. R. Dilley and W. L. Edwards, U. S. Dept. of Agriculture Circular No. 61; "Fixed Nitrogen," Edited by Harry A. Curtis, Chapter X, American Chemical Society Monograph Series, The Chemical Catalog Co., Inc., New York, 1932.

(7) For work on the action of hydrogen on various steels see, *e. g.*, Inglis and Andrews, *Engineering*, **136**, 613 (1933).

temperature. Zero solubility is reached at the vapor pressure of pure liquid ammonia corresponding to the particular temperature.

Table I gives the experimental results. As shown at least two independent sets of values were obtained at any one pressure. The probable error of the final values was calculated from the average values of the sets of runs. The fluctuations within the sets were at times considerably greater than the probable error of the final result would seem to indicate. We think that this is due to partial separation of the gas and liquid in the tube leading to the expansion valve and would probably depend on how far the valve was opened. In other words, we may consider the set as one big sample since the deficiency or excess in one measurement would be corrected in the following determination. The last meas-

TABLE I

THE SOLUBILITY OF HYDROGEN IN LIQUID AMMONIA (CC. OF HYDROGEN AT S. T. P. PER G. OF AMMONIA)

| Total press., atm. | Solubilities | | | | | | | Av. for set of runs | Final av. |
|---|---|---|---|---|---|---|---|---|---|
| | | | | At 25° | | | | | |
| 50 | | | | 4.403 | 4.441 | 4.469 | 4.472 | 4.453 | |
| | | | | 4.486 | 4.430 | 4.508 | | 4.475 | |
| | | | | 4.501 | 4.480 | 4.467 | 4.495 | 4.486 | 4.471 ± 0.011 |
| 100 | | 9.815 | 9.874 | 9.871 | 9.923 | 9.894 | 9.875 | 9.875 | |
| | | | 9.888 | 9.942 | 9.835 | 9.746 | 9.968 | 9.875 | 9.875 ± .000 |
| 200 | | 20.127 | 20.111 | 20.093 | 20.146 | 20.166 | 20.056 | 20.116 | |
| | | 20.107 | 19.729 | 20.158 | 19.858 | 20.100 | 19.978 | 19.988 | |
| | | | 20.366 | 20.132 | 20.122 | 19.962 | | 20.145 | |
| | | | 20.050 | 19.993 | 20.026 | 20.173 | | 20.060 | 20.077 ± .048 |
| 400 | | | 37.856 | 38.164 | 38.149 | 38.331 | 37.939 | 38.087 | |
| | | | 38.100 | 38.365 | 38.139 | 38.119 | | 38.180 | 38.134 ± .045 |
| 600 | | | | 53.668 | 53.691 | 53.811 | | 53.723 | |
| | | | 53.957 | 53.799 | 53.478 | 53.688 | 53.798 | 53.699 | 53.711 ± .011 |
| 800 | | | 67.55 | 67.88 | 67.70 | 67.45 | 67.59 | 67.63 | |
| | | | | 68.03 | 67.75 | 67.11 | | 67.63 | 67.63 ± .00 |
| 1000 | | | | 79.41 | 79.56 | 79.80 | 79.12 | 79.47 | |
| | | | | 79.70 | 77.82 | 79.82 | 79.25 | 79.15 | |
| | | | 80.13 | 78.81 | 78.91 | 79.89 | 77.88 | 79.12 | 79.25 ± .13 |
| | | | | | At 50° | | | | |
| 50 | | | | 5.088 | 5.105 | 5.079 | | 5.091 | |
| | | | | | 5.157 | 5.064 | | 5.110 | |
| | | | | 5.104 | 5.049 | 5.107 | | 5.087 | |
| | | | | | 5.088 | 5.119 | | 5.104 | |
| | | | | 5.052 | 5.159 | 5.099 | 5.131 | 5.110 | 5.100 ± .007 |
| 100 | | | 13.42 | 13.57 | 13.42 | 13.55 | 13.47 | 13.49 | |
| | | | | 13.51 | 13.47 | 13.47 | | 13.48 | 13.486 ± .007 |
| 180 | | | 26.27 | 26.46 | 26.20 | 26.49 | 26.32 | 26.35 | |
| | | | | 26.63 | 26.44 | 26.13 | 26.53 | 26.43 | |
| | | | | 26.34 | 26.19 | 26.26 | | 26.27 | |
| | | | | 26.33 | 26.33 | 26.38 | | 26.35 | 26.35 ± .05 |
| 200 | 29.51 | 29.26 | 29.30 | 29.41 | 29.78 | 29.23 | 29.21 | 29.39 | 29.39 ± .00 |
| 400 | | | | 59.21 | 57.91 | 58.61 | 58.00 | 58.43 | |
| | | | | 58.12 | 57.51 | 58.67 | | 58.10 | |
| | | | 58.54 | 58.33 | 58.55 | 58.30 | 58.18 | 58.38 | |
| | | | | 58.60 | 58.36 | 57.96 | | 58.31 | |
| | | 58.04 | 58.57 | 58.11 | 57.55 | 59.00 | 59.22 | 58.42 | 58.33 ± .09 |
| 600 | | | 83.08 | 83.75 | 83.09 | 82.93 | 83.75 | 83.32 | |
| | | | 83.68 | 83.78 | 83.30 | 82.89 | 83.62 | 83.45 | |
| | | 83.92 | 84.03 | 83.73 | 83.38 | 83.57 | 83.36 | 83.67 | 83.48 ± .12 |
| 800 | | | 106.88 | 105.51 | 105.65 | 105.11 | 105.78 | 105.79 | |
| | | | | 102.92 | 107.43 | 104.89 | 104.80 | 105.01 | |
| | | 107.57 | 104.88 | 105.70 | 104.80 | 105.64 | 103.67 | 105.38 | 105.39 ± .26 |
| 1000 | | | | 124.10 | 124.69 | 126.33 | 123.53 | 124.66 | |
| | | | | 124.20 | 125.72 | 126.02 | 125.40 | 125.33 | |
| | 123.97 | 126.39 | 123.73 | 124.66 | 125.49 | 123.62 | 125.32 | 124.74 | 124.91 ± .25 |

TABLE I (*Concluded*)

| Total press., atm. | Solubilities | | | | | | | Av. for set of runs | Final av. |
|---|---|---|---|---|---|---|---|---|---|
| | | | | At 75° | | | | | |
| 100 | | | | 16.41 | 16.30 | 16.33 | 16.17 | 16.30 | |
| | 16.41 | 16.41 | 16.44 | 16.44 | 16.57 | 16.45 | 16.55 | 16.47 | |
| | | | | | 16.27 | 16.29 | | 16.28 | 16.35 ± 0.07 |
| 200 | | | 41.21 | 41.44 | 41.56 | 41.52 | 41.45 | 41.45 | |
| | | | | 41.23 | 41.27 | 41.44 | 41.52 | 41.37 | 41.41 ± .03 |
| 400 | | 88.86 | 88.12 | 87.74 | 87.81 | 88.59 | 88.14 | 88.21 | |
| | | | | 88.36 | 88.55 | 88.27 | 88.66 | 88.46 | 88.34 ± .12 |
| 600 | | | | | | 130.90 | | 130.90 | |
| | | 130.93 | 131.14 | 130.87 | 130.55 | 131.00 | 130.90 | 130.90 | |
| | | | 131.50 | 131.42 | 131.19 | 131.04 | | 131.28 | 131.03 ± .15 |
| 800 | | | | 169.27 | 169.21 | 169.19 | | 169.22 | |
| | | | | 169.40 | 169.11 | 169.10 | | 169.21 | 169.22 ± .01 |
| 1000 | | | | 203.31 | 203.35 | 203.07 | 202.94 | 203.17 | |
| | | | | 203.39 | 203.44 | 203.43 | 203.55 | 203.45 | |
| | | | | 203.24 | 203.55 | 203.07 | 203.08 | 203.24 | 203.29 ± .10 |
| | | | | | At 100° | | | | |
| 100 | | | | 15.71 | 15.73 | 15.59 | 15.71 | 15.67 | |
| | | | | 15.71 | 15.72 | 15.66 | 15.54 | 15.66 | 15.67 ± .01 |
| 200 | | | | 57.16 | 57.14 | 57.11 | | 57.11 | |
| | | | | 57.14 | 56.96 | 57.12 | 57.10 | 57.08 | 57.10 ± .01 |
| 400 | | | | 140.77 | 140.49 | 140.53 | | 140.60 | |
| | | | | 140.82 | 140.66 | 140.48 | 140.44 | 140.60 | 140.60 ± .00 |
| 600 | | | | 224.63 | 224.03 | 224.40 | 224.10 | 224.29 | |
| | | | | 220.97 | 227.03 | 223.64 | 223.22 | 223.72 | |
| | | | | 224.21 | 224.04 | 223.95 | 223.81 | 224.00 | 224.00 ± .19 |
| 800 | | | | 305.3 | 305.1 | 303.0 | 307.0 | 305.1 | |
| | | | | 305.9 | 306.9 | 303.1 | | 305.3 | 305.2 ± .1 |
| 1000 | | | | 388.4 | 388.0 | 387.9 | | 388.1 | |
| | | | | 384.0 | 392.1 | 389.0 | 387.8 | 388.2 | 388.2 ± .1 |

urement of any one set may of course either have a deficiency or excess, as the case may be.

When plotting deviations from the equation

$$S = a(p - p_v) + b(p - p_v)^2 + c(p - p_v)^3$$

where $S$ = solubility of hydrogen in liquid ammonia in cc. of gas at S. T. P. per g. of ammonia, $p$ the total pressure and $p_v$ the vapor pressure of pure liquid ammonia, interpolated values were obtained. These interpolated values with the previous experimental ones are summarized in Table II. No correction was made for the nitrogen impurity. The experimental accuracy

TABLE II

SUMMARY OF EXPERIMENTAL AND INTERPOLATED DATA
The values marked * were obtained through interpolation

| Total press., atm. | 25° | 50° | 75° | 100° |
|---|---|---|---|---|
| 25 | 1.695* | 0.85* | | |
| 50 | 4.47 | 5.10 | 3.49* | |
| 75 | 7.20* | 9.33* | 9.95* | 5.80* |
| 100 | 9.88 | 13.49 | 16.35 | 15 67 |
| 150 | 15.08* | 21.60* | 29.00* | 36.35* |
| 180 | | 26.35 | | |
| 200 | 20.08 | 29.39 | 41.41 | 57.10 |
| 300 | 29.45* | 44.42* | 65.40* | 98.74* |
| 400 | 38.13 | 58.33 | 88.34 | 140.6 |
| 500 | 46.18* | 71.33* | 110.22* | 182.4* |
| 600 | 53.71 | 83.48 | 131.0 | 224.0 |
| 700 | 60.77* | 94.82* | 150.6* | 264.3* |
| 800 | 67.63 | 105.4 | 169.2 | 305.2 |
| 900 | 73.74* | 115.3* | 186.8* | 346.5* |
| 1000 | 79.25 | 124.9 | 203.3 | 388 2 |

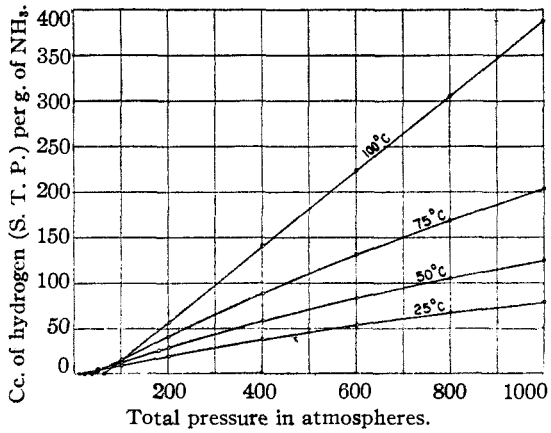


Fig. 1.—Solubility of hydrogen in liquid ammonia.

was greater at the higher temperatures because of slight improvements in apparatus and technique. The values are believed to be accurate within 2 to 3 parts per 1000.

Ipatiew and Teodorowich[8] measured the solubility of hydrogen in liquid ammonia at 25° and at pressures to 250 atmospheres. Their results are somewhat lower than ours over their whole pressure range.

Much additional information, some of which is now being secured, is needed before a thermodynamic treatment of the solubility of hydrogen in liquid ammonia can be given.

(8) V. V. Ipatiew and V. P. Teodorowich, *J. Gen. Chem.*, **2**, 305 (1932).

We wish to express our appreciation to Dr. C. H. Meyers for the generous assistance he has rendered in the course of the gage calibration.

## Summary

The solubility of hydrogen in liquid ammonia was determined at 25, 50, 75 and 100° up to 1000 atmospheres total pressure.

The solubility (cc. of gas at S. T. P. per g. of ammonia) increases with temperature.

WASHINGTON, D. C. RECEIVED AUGUST 16, 1934

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

# The Dielectric Behavior of Germanium Tetrachloride

BY JOHN G. MILLER

This paper presents a study of the dielectric properties of germanium tetrachloride as a liquid and in solution in carbon tetrachloride. The measurements indicate zero moment for this molecule while allowing very satisfactory calculation of its electronic and atomic polarizations.

## Experimental Part

**Apparatus.**—Capacitance measurements were made by a bridge method at frequencies in the broadcast band. A General Radio 516-A bridge[1] was employed with a General Radio 484-A modulated oscillator as power supply. The null indicator was a commercial superheterodyne receiver having a sensitivity of 10 microvolts and shielded in a copper-lined box. The voltage applied to the bridge never exceeded 1 volt; the null point heard on the loud-speaker was very sharply defined, even at very low power being within the backlash of the standard precision condenser, which was a General Radio 222-M instrument. The condenser and resistance units of the balancing arm of the bridge were kept in series throughout, although the resistances used were always extremely small.

The measuring cell was of the type designed by Smyth and Morgan[2] and was supported in a glass tray. Leads to the standard condenser were of stout brass arranged to give a constant minimum of inductance and capacity with one another. The cell was thermostated in an oil-filled bath kept constant within 0.05° for the temperatures 15 to 55°, while at 0° an ice-water bath was used. The cell was calibrated from time to time using benzene and air.

The inductance and parasitic capacity of the measuring circuit in shunt with the standard condenser were found to be quite low. The former was approximately 0.6 microhenry, while the latter, made up of the lead, stray and fixed capacities amounted to less than 7% of the circuit capacity when the cell was filled with air. Rather than evaluate the inductance in this circuit to correct the capacitance determinations, it was found more convenient and reliable to measure capacitance over seven or eight frequencies covering the broadcast range and to extrapolate these readings to zero frequency where inductance error drops out. The curves obtained were quite similar among themselves and to those obtained by assuming a value for the inductance of the circuit, indicating greater accuracy and convenience in this extrapolation method since the small inductance would be difficult to evaluate and keep constant from one circuit setting to another. The apparatus and method were tested with carbon tetrachloride from 0 to 55° and the results were extremely satisfactory.

Densities were determined with a pycnometer similar to that used by Smyth and Morgan[2] and having a volume of 25 cc. It was thermostated in the baths used for the dielectric cell. Refractive indices were measured with a Pulfrich refractometer. The cell and prism were thermostated by water pumped through their jackets from a thermostat kept constant within 0.02°. The room temperature was kept within 1° of the temperature used (30°).

The pure liquids used in all measurements were distilled into each measuring cell by means of an all glass distillation apparatus ground to fit the refractometer and dielectric cells as well as the pycnometer. The important body of this apparatus is shown in Fig. 1 attached to the refractometer cell. The material was distilled through an all glass three-ball Snyder column which fitted the receiver at the ground joint A. Stopcock B permitted distillation at reduced pressure or at dry air pressure. The carefully ground mercury-seal stopcock C allowed removal of undesired fractions through D and entrance of the desired material into the apparatus through E which conveniently extended below the ground joint on the outer jacket F. This outer jacket was equipped with a two-way cock G

(1) Burke, *General Radio Experimenter*, **7**, 1 (July, 1932).

(2) Smyth and Morgan, THIS JOURNAL, **50**, 1547 (1928).