With the heat of reaction as given above, this gives $\Delta F^\circ = -195{,}000 + (298.1 \times 123) = -158{,}000$ calories for the free energy of formation of oxalate ion.

Summary

The specific heat of $CaC_2O_4 \cdot H_2O$ has been measured from 19 to 300°K. and the entropy of the salt determined by graphical integration. Coupling this value with the entropy of solution and the entropy of calcium ion as herein calculated, the entropy of oxalate ion has been determined. A value for the free energy of oxalate ion has been calculated.

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Solubility of Nitrogen in Liquid Ammonia at 25° from 25 to 1000 Atmospheres

BY R. WIEBE AND T. H. TREMEARNE

Very few measurements have been made on the solubility of gases in liquid ammonia. The most extensive were made by Larson and Black[1] on the solubility of a 3 : 1 hydrogen–nitrogen mixture over a temperature range from −25 to +22° and up to 150 atmospheres. A rough incidental measurement of the solubility of hydrogen in liquid ammonia at −70° was made by Schlubach and Ballauf.[2] Aside from the practical importance, the knowledge of solubilities is of importance for any theory of solutions.

Apparatus and Procedure

Figure 1 shows the apparatus. Synthetic ammonia was fractionated and the middle portion was condensed into steel cylinder A of about 1400 cc. capacity. Nitrogen at a pressure somewhat in excess of the final equilibrium pressure was introduced and the steel cylinder after being disconnected, was shaken by means of the eccentric D. The shaking motion was stopped after a few hours and the pressure was adjusted to the final value through C which was connected both to the piston gage and the compression system. The apparatus was then shaken at this pressure and if necessary the procedure was repeated, until equilibrium was established as indicated by no further pressure change. Several independent sets of runs were taken at each pressure. No trend was observed in the results, showing that equilibrium must have been reached.

The receiving apparatus was evacuated up to the mercury seal maintained in the capillary between G and the buret system H. E was immersed in liquid air. Valve B was then opened slightly, permitting a mixture of ammonia and nitrogen to enter the receiving apparatus. The ammonia was condensed in E and the nitrogen expanded into the Toepler pump. When the sample was considered to be sufficiently large, valve B was closed and the Toepler pump G was operated in order to transfer the nitrogen into

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

[2] Schlubach and Ballauf, *Ber.*, **54**, 2825 (1921).

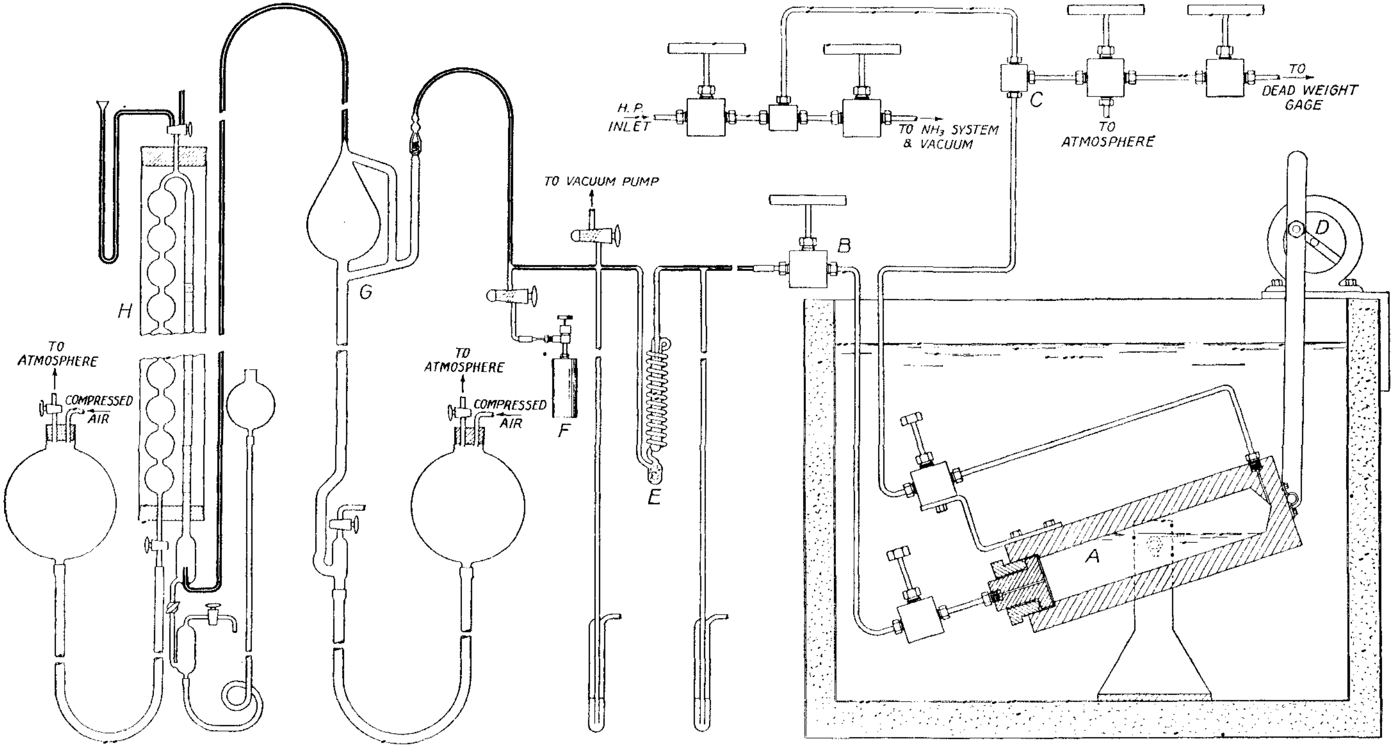
H.P. INLET
TO NH$_3$ SYSTEM & VACUUM
C
TO ATMOSPHERE
TO DEAD WEIGHT GAGE
TO VACUUM PUMP
B
D
A
E
F
G
H
TO ATMOSPHERE
COMPRESSED AIR
TO ATMOSPHERE
COMPRESSED AIR

Fig. 1.

the buret system H. The gas was measured partly in a 12-bulb buret, each bulb having a volume of approximately 25 cc., and the excess in a 50-cc. straight buret. Mercury was used exclusively.

The steel cylinder F, having a weight of approximately 190 g., was used to collect the ammonia through distillation from E. The steel cylinder was weighed empty before and after each measurement; the difference was ordinarily less than 2 mg. The average of the two values was used. Since in most cases the weight of ammonia ranged from 4 to 5 g., this uncertainty amounted to less than 0.05%. Small amounts of ammonia were carried through trap E by the nitrogen. These traces were later recovered by absorption in water and determined by titration. This correction was of importance at the lowest pressures where the total amount of gas was small; at higher pressures the correction was ordinarily less than 0.5%.

Pressures were measured by means of two piston gages described by Bartlett and co-workers.[3]

The nitrogen was 99.9% pure, the impurities being argon and traces of oxygen. The water content of the ammonia was 0.07%.

The apparatus was tested by measuring the solubility of nitrogen in water at 100, 200 and 300 atmospheres and 25°. The agreement with known values was within about a tenth of one per cent.[4]

Discussion of Results

Table I and Fig. 2 give a summary of the results.

TABLE I

Total pressure	Number of runs	Solubility in cc. of nitrogen (S. T. P.) per g. of ammonia
25	21	2.22
50	13	5.73
100	6	12.04
200	8	22.48
400	19	37.02
600	10	45.43
800	21	51.10
1000	16	54.83

The error is estimated to be several tenths of one per cent. and may be of the order of one per cent. at the lowest pressure. Sources of error were the impurities in nitrogen and ammonia, uncertainties in calibration, weighing, titrating and possibly changes in solubility due to slight pressure fluctuations during the run.

As will be noted from the curve in Fig. 2, zero solubility is attained close to ten atmospheres total pressure. The vapor pressure of liquid ammonia at 25° is 9.8955 atmospheres.[5]

Results for the amount of gas dissolved at any particular partial pressure of nitrogen could not be given for lack of adequate equations of state at the high pressures used.

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[3] Bartlett, Cupples and Tremearne, THIS JOURNAL, **50**, 1275 (1928).

[4] The values so obtained were published by Wiebe, Gaddy and Heins, *Ind. Eng. Chem.*, **24**, 927 (1932).

[5] Cragoe, Meyers and Taylor, Bur. of Standards Scientific Paper No. 369 (1920); also THIS JOURNAL, **42**, 206 (1920).

Lurie and Gillespie[6] have calculated the equilibrium pressure of ammonia in a nitrogen–ammonia mixture using an equation of state for mixtures up to 60 atmospheres total pressures and found satisfactory agreement with their composition measurements. Randall and Sosnick[7] applied the generalized Raoult's law[8] to gaseous solutions. They found that for solute gases below their critical temperature, the method led only to rough quantitative results and would therefore be of little use in this work.

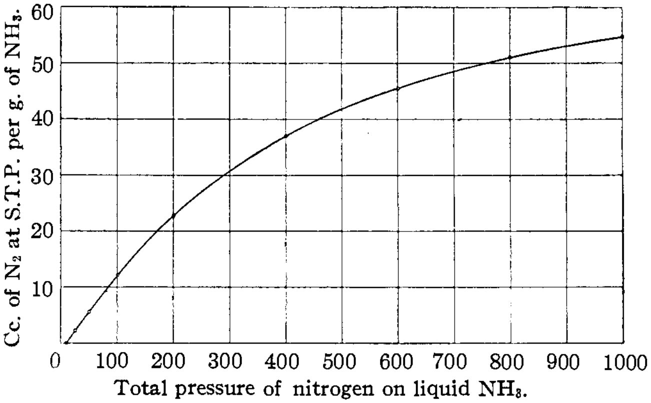

Fig. 2.

The authors are indebted to Mr. W. L. Edwards for the design of the shaking apparatus.

Summary

A satisfactory high pressure apparatus for measuring solubilities of gases in liquids having high vapor pressures has been described.

The solubility of nitrogen in liquid ammonia at 25° and from 25 to 1000 atmospheres has been determined.

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[6] Lurie and Gillespie, THIS JOURNAL, **49**, 1146 (1927).

[7] Randall and Sosnick, *ibid.*, **50**, 967 (1928).

[8] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 222.