[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

The Solubility in Liquid Ammonia of Hydrogen at 0° and of Nitrogen at 0, 50, 75, 90 and 100° at Pressures to 1000 Atmospheres. Critical Phenomena of Ammonia–Nitrogen Mixtures[1]

BY R. WIEBE AND V. L. GADDY

This work is part of a program to determine the physical properties of substances important in the production of fertilizers, such as ammonia, nitrogen, hydrogen and their mixtures.[2,3] The apparatus and method have been described previously. Pressures are given in international atmospheres. The results for hydrogen are given in Table I and Figs. 1 and 2. The points in Figs. 1 and 2 for the temperatures 25, 50, 75 and 100° have been included from a previous publication[3] to show the marked difference in the behavior of hydrogen and nitrogen in liquid ammonia in the same range of pressure and temperature.

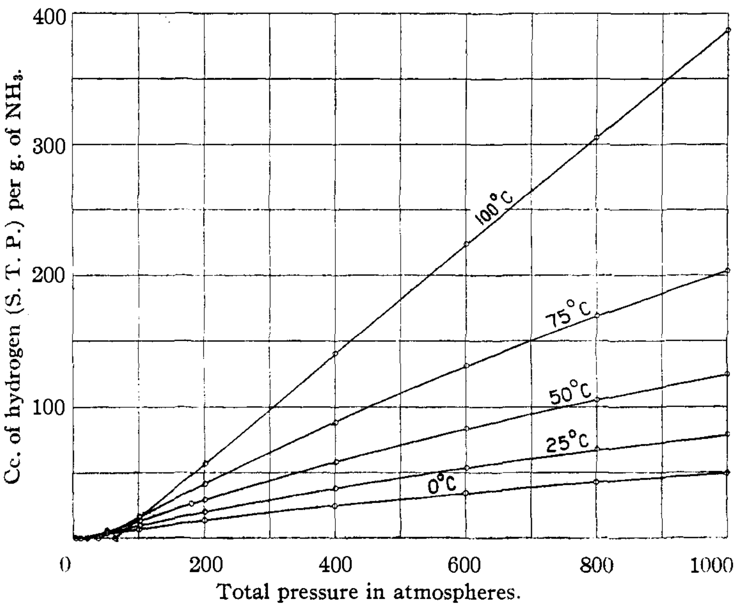

Fig. 1.—Solubility of hydrogen in liquid ammonia.

Table II and Figs. 3 and 4 give the results for nitrogen. At least two independent sets of values were obtained at each point. The accuracy of all the results except those in the neighborhood of the critical region is illustrated by the results at 200 atmospheres and 50°: 36.24, 36.24, 36.09, 36.17, 36.33, 36.35, 36.20, 36.28; average, 36.24 ± 0.02; all in cc. (S. T. P.) per g. of ammonia. The ± 0.02 is the probable error estimated from the eight observations. Zero solubility at any temperature is attained at the vapor pressure of pure liquid ammonia at that temperature.

TABLE I

THE SOLUBILITY OF HYDROGEN IN LIQUID AMMONIA AT 0°

Cc. of hydrogen at S. T. P. per g. of ammonia

Pressure, atm.	Number of runs	Solubility
50		(3.28)[a]
100	7	6.70
200	10	13.11
300		(18.96)
400	9	24.33
500		(29.27)
600	10	33.99
700		(38.25)
800	9	42.33
900		(46.20)
1000	8	49.77

[a] Figures in parentheses are interpolated values.

TABLE II

THE SOLUBILITY OF NITROGEN IN LIQUID AMMONIA EXPERIMENTAL RESULTS

Cc of nitrogen at S. T. P. per g. of ammonia

	0°		50°		75°		90°		100°	
P, atm.	No. of runs	Soly.	No. of runs	Soly.	No. of runs	Soly.	No. of runs	Soly.	No. of runs	Soly.
50			5	6.63						
100	7	7.90	6	17.19	2	21.38			7	20.50
200	6	13.73	8	36.24	3	55.48			6	86.32
300									6	193.16
325									4	235.95
350							4	165.50		
400	4	20.76	4	65.35	4	120.66			Single phase	
500							4	310.63		
550							6	430.8		
600	6	24.95	7	84.78	4	177.95				
700							Single phase			
800	11	28.06	7	97.20	4	218.99				
1000	11	29.69	7	104.59	4	241.75				

Table III gives interpolated values obtained graphically for different temperatures. The values, especially the higher ones, cannot claim a high degree of accuracy.

(1) Read at the meeting of the American Chemical Society, Rochester, N. Y., September 6 to 10, 1937.

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

(3) Wiebe and Tremearne, THIS JOURNAL, **55**, 975 (1933); **56**, 2357 (1934); **57**, 2601 (1935).

TABLE III

INTERPOLATED VALUES OF THE SOLUBILITY OF NITROGEN IN LIQUID AMMONIA

Cc. of nitrogen at S. T. P. per g. of ammonia

Total P, atm.	Temperature, °C. 0	10	20	30	40	50	60	70	80	90	100
50	4.10	4.55	5.45	5.85	6.30	6.63	6.35	5.20	2.7		
100	7.90	9.40	11.11	13.02	15.09	17.19	19.14	20.51	21.10	21.0	20.50
200	13.73	16.77	20.42	24.81	30.16	36.24	43.02	50.93	60.67	72.7	86.32
300	17.70	22.30	27.60	34.30	42.50	51.90	63.87	79.0	99.8	134.9	193.16
400	20.76	26.42	33.11	41.45	52.10	65.35	82.22	105.6	137.5	218.8	
500	23.00	29.50	37.20	46.85	59.45	76.07	98.05	129.4	197.0	310.6	
600	24.95	31.84	40.43	51.17	65.31	84.78	110.8	149.3			
700	26.60	33.87	43.07	54.75	70.35	91.70	120.4	165.1			
800	28.06	35.52	45.19	57.68	74.39	97.20	127.8	177.6			
900	29.00	36.75	46.95	59.95	77.35	101.25	133.6	186.7			
1000	29.69	37.93	48.53	62.02	79.89	104.59	138.8	194.3			

The measurements in the neighborhood of the critical curve are cumbersome both in the heterogeneous and homogeneous region. Shaking is not very effective. Constant temperature and pressure for long periods of time are essential for attaining equilibrium. The following example will illustrate some of the difficulties of knowing whether two phases or only a single phase was present. At 400 atmospheres total pressure and 100° results were obtained as follows. Any of the above sets is sufficiently constant and might have been mistaken for true equilibrium. The results of May 11 are slightly higher than the composition of the vapor phase on May 7. This is caused by the introduction of nitrogen to keep the pressure constant during sampling and by loss of liquid ammonia due to sampling itself. In order to make sure that enough ammonia was left to form a liquid phase, the pressure was reduced to 300 atmospheres at 100°. The following results were obtained

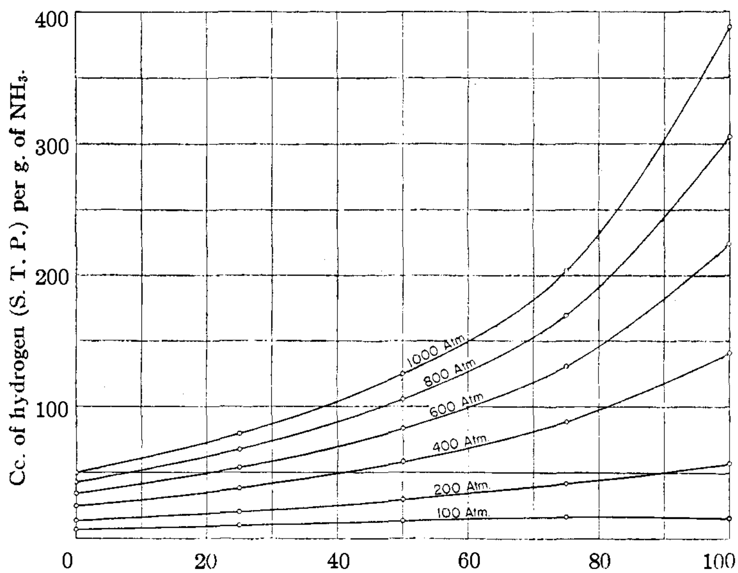

Fig. 2.—Solubility of hydrogen in ammonia.

COMPOSITION IN CC. OF N_2 AT S. T. P. PER G. OF NH_3

Time	Liquid phase			Vapor phase		
April 29	312.8	313.9				
April 30	375.0	375.7	376.4			
May 1	423.9	427.9	427.5			
May 5	515.1	513.4				
May 6	553.2	553.9	551.9			
May 7	561.8	566.1		591.7	590.4	596.5
May 11	599.3	600.9	599.6			

COMPOSITION IN CC. OF N_2 AT S. T. P. PER G. OF NH_3

Liquid	Vapor
197.55	836.9
190.79	855.1
190.38	855.9

Whether at 350 atmospheres a liquid phase was still present was not ascertained definitely.

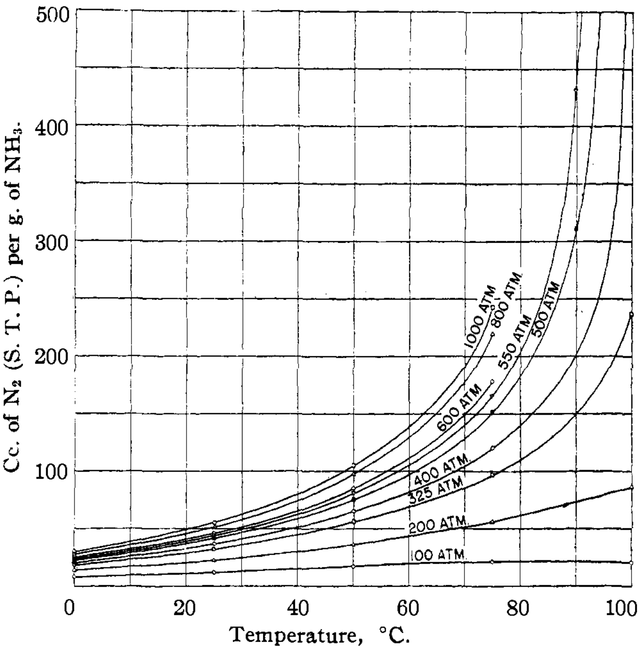

Fig. 3.—Solubility of nitrogen in ammonia, total pressure isobars.

From Figs. 3, 4 and 5 it can be seen that the critical pressure of the system ammonia–nitrogen at 90° is close to 600 atmospheres, while at 100° it has dropped to less than 400 atmospheres, thus rapidly approaching the critical point of pure liquid ammonia $p_c = 112.3$ atm., $t_c = 132.9°$. The critical phenomena had not been anticipated at pressures so low as 600 atmospheres and 90°, or 400 atmospheres and 100°, but were instead expected in the neighborhood of 1000 atmospheres at 100°. At that pressure and temperature the densities of nitrogen and liquid ammonia are very nearly the same, and due to mutual solubility the densities would tend to approach each other even more rapidly, as proved to be true. The critical condition is recognized most readily in Fig. 5. Here the vapor pressure of ammonia forms the lower boundary. The dotted line indicates the

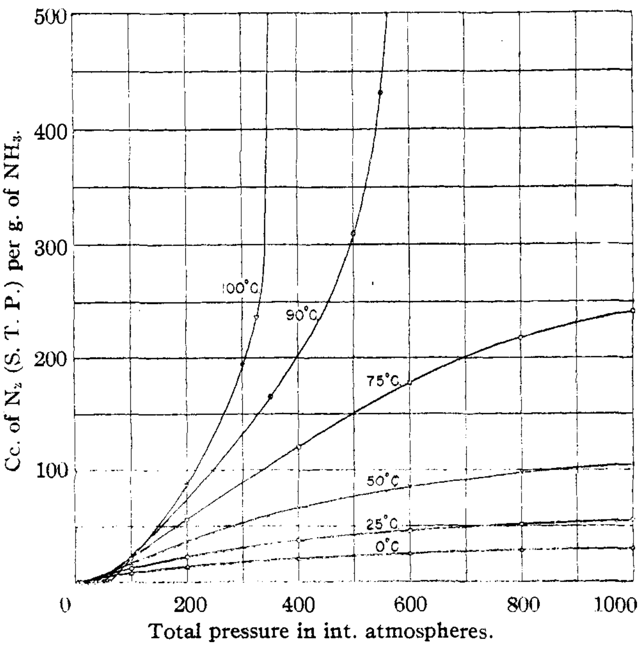

Fig. 4.—Solubility of nitrogen in ammonia.

probable trend of the critical curve of the mixture starting at the critical point of ammonia, rising to a very high pressure and finally curving back to end at the critical temperature $t_c = -147.1°$ and pressure $p_c = 33.5$ atmospheres of nitrogen. A number of constant composition curves for the liquid phase have also been drawn, the numerical values of which are given in Table IV. The data were obtained graphically. For illustration the "200," "250" and "300" composition curves have been extrapolated roughly to show the possible trend of the vapor branch. These extrapolations are of course highly qualitative. The curves for the other compositions will likewise come down and make contact of the first order with the critical curve (envelope), in somewhat the fashion depicted. The shape of the curves seems to indicate retrograde condensation of the first kind.[4]

TABLE IV

TEMPERATURES AT CONSTANT COMPOSITION IN °C.

Pressure, atm.	Composition in cc. N_2 (S. T. P.) per g. liquid ammonia 100	150	200	250	300
325	76.4	90.4	96.6	100.6[a]	
400	68.4	82.1	89.8	94.2[a]	96.6[a]
500	62.0	74.8	82.1	86.6	89.6
550	60.0	72.5	79.2	83.5	86.2
600		70.3			
800		65.3	72.9	77.5[a]	
1000		63.0	70.8	75.5[a]	

[a] These values are rather uncertain.

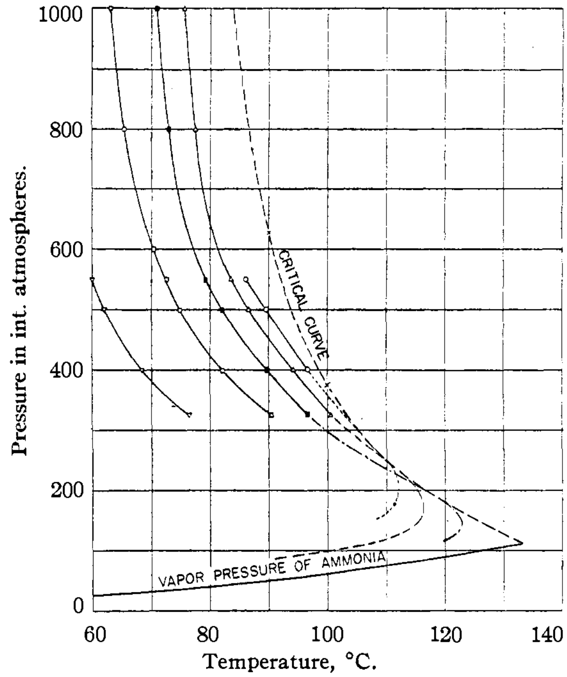

Fig. 5.—Constant composition curves and critical curve for nitrogen-ammonia mixtures, N_2 (S. T. P.) per g. of NH_3: ▽, 100 cc.; □, 150; ⊠, 200; △, 250; ○, 300.

Summary

The solubility of hydrogen in liquid ammonia was determined at 0° and at pressures to 1000 atmospheres. Over the same pressure range the solubility of nitrogen was measured at 0, 50, 75, 90 and 100°. Two critical points, one at 90° and about 600 atmospheres, the other at 100° and approximately 375 atmospheres, were found. The probable trend of the critical curve was sketched over a short range.

(4) For full discussion see, *e. g.*, Kuenen, "Theorie der Verdampfung und Verflüssigung von Gemischen," Joh. Ambrosius Barth, Leipzig, 1906.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE]

Thermodynamics of Lead Iodide[1]

BY JESSIE Y. CANN AND ALICE C. TAYLOR

The purpose of this investigation is to determine, by means of electromotive force measurements, the free energy of formation, ΔF, the change of entropy, ΔS, and the change in heat content, ΔH, of lead iodide.

In contrast to some previous investigators, *e. g.*, Gerke[2] who used 1 and 0.1 M solutions of electrolytes, we have used 0.1, 0.05 and 0.025 M solutions. Taylor[3] and Taylor and Perrott[4] have also studied lead iodide.

Method and Apparatus.—In this investigation the cell

$$PbHg_x, PbI_2(s), PbI_2(satd.) + m\ KI(aq.), AgI(s), Ag(s)$$

was measured. Pyrex H-tubes were employed, similar to those used by Gerke.[2]

The cell was placed in the usual oil thermostat, regulated at 25°, and measurements were made

(1) The experimental part of this paper is a portion of a thesis submitted by A. C. Taylor in partial fulfilment of the requirements for the degree of Master of Arts at Smith College.

(2) Gerke, THIS JOURNAL, **44**, 1684 (1922); and *Chem. Rev.*, **1**, 337 (1925).

(3) Taylor, THIS JOURNAL, **38**, 2295 (1916).

(4) Taylor and Perrott, *ibid.*, **43**, 489 (1921).