Using this apparatus, "adjustment" throughout a wider range of indicator concentrations and greater accuracy have been attained.

The product of the chloride-transference number and the corresponding equivalent conductance has been found to be constant for these substances within the experimental error. The bearing of this fact on the theory of the ionization of strong electrolytes is briefly outlined.

CAMBRIDGE A, MASSACHUSETTS

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE CONCENTRATION OF AMMONIA IN A COMPRESSED MIXTURE OF HYDROGEN AND NITROGEN OVER LIQUID AMMONIA

BY ALFRED T. LARSON AND CHARLES A. BLACK

RECEIVED JANUARY 19, 1925 PUBLISHED APRIL 4, 1925

In many of the technical adaptations of the direct synthetic ammonia process the ammonia formed is removed from the high pressure system by liquefaction and mechanical separation. It has been customary to assume that the concentration of uncondensed ammonia in the vapor phase is identical with the concentration of ammonia vapor over pure liquid ammonia at the temperature of the condenser. Harker,[1] for example, employs for this calculation the simple formula $X = (100/p)p_t$, in which X is the volume-per cent. of uncondensed ammonia, p the total pressure, and p_t the vapor pressure of pure liquid ammonia at the temperature of the condenser, t. In practice, however, the amount of uncondensed ammonia is much greater than that calculated by this expression. This excess may be due either to an incomplete adjustment of the equilibrium or to the operation of factors which the equation neglects, such for instance as the effect of total pressure and of the dissolved hydrogen and nitrogen upon the vapor pressure of the liquid ammonia and the effect of the hydrogen and nitrogen gas upon the partial pressure of the ammonia gas in the gas mixture.

With the exception of a single observation by Haber and Le Rossignol,[2] we have found no recorded measurement of the vapor concentration of ammonia in the presence of compressed nitrogen and hydrogen. These investigators found that the ammonia content of the gas phase at —79° and a total gas pressure of 190 atmospheres was about five times as great as corresponds to the vapor pressure of pure ammonia at this temperature. Accurate data of this sort are required for the design and operation of direct synthetic ammonia plants.

---

[1] Harker, "Physical and Chemical Data of Nitrogen Fixation," M. I. D. Research Laboratory, University College, London.

[2] Haber and Le Rossignol, *Z. Elektrochem.*, 19, 53 (1913).

Experimental Method.—The experimental method for the determination of the concentration of ammonia in a compressed mixture of hydrogen and nitrogen over liquid ammonia consisted in bubbling a 3:1 gas mixture of hydrogen and nitrogen through liquid ammonia contained in a steel bottle and determining the ammonia content of the effluent gas. The steel bottle was immersed in a thermostat filled with a saturated solution of calcium chloride, which was cooled by means of an ammonia expansion coil. The temperature of the bottle was measured with a mercury thermometer placed in the bath. Earlier experiments had demonstrated that the bath and the interior of the bottle are at practically the same temperature under the conditions of this experiment. The thermometer had previously been checked against a standard thermometer which had been calibrated at the Bureau of Standards.

The steel bottle was attached to the exit of a direct ammonia synthesis apparatus and ammonia was condensed by cooling the bottle in ice. The nitrogen-hydrogen gas mixture was prepared by burning electrolytic hydrogen and air in such proportions that the resulting gas mixture contained approximately 75% by volume of hydrogen. Pressures of 50 and 100 atmospheres were obtained by means of a standard gas compressor. Higher pressures were obtained by means of an hydraulic compressor. The water vapor added to the gas during this operation was removed by means of soda lime. The pressure of the gas was measured in each case by means of a calibrated piston-type (dead-weight) gage.

The ammonia content of the gas phase within the steel bottle was determined at intervals by passing the exit gas through an absorption bulb containing a measured amount of 0.1 *N* sulfuric acid slightly less than necessary to neutralize the ammonia in the sample taken. The excess of ammonia in the sample was then titrated with 0.1 *N* sulfuric acid, using sodium alizarin sulfonate as an indicator. The residual uncombined gases were collected in a compensating buret.[3] From the data obtained, the volume percentage of ammonia originally in the gas mixture was readily calculable.[4] All analyses were made at atmospheric pressure.

Results

In Table I are given the volume percentages of ammonia in the gaseous phase over liquid ammonia in the presence of hydrogen and nitrogen, at temperatures ranging from —22.5° to 18.7° and at pressures from 50 to 1000 atmospheres. In each case the hydrogen and nitrogen are present in the ratio of three to one. In the third column are recorded values, calculated by the usual method from the vapor pressure of pure liquid ammonia. The last column contains observed results. Each recorded value

---

[3] Tour, *Chem. Met. Eng.*, **23**, 1104 (1920).

[4] Values for molecular weights used in this calculation: NH_3, 17.03; H_2, 2.016; N_2, 28.02.

Table I

Results

Total press.	Temp. °C.	Vol. % NH_3 calcd. $X = \frac{100}{p} Pt$	Vol. % NH_3 obs.	Total press.	Temp. °C.	Vol. % NH_3 calcd. $X = \frac{100}{t} Pt$	Vol. % NH_3 obs.
50	−20.0	3.68	5.70	600	−22.0	0.27	1.18
	− 6.8	6.60	8.08		−14.0	.42	1.45
	0.0	8.52	10.00		− 8.6	.51	1.83
	10.0	12.00	13.97		0.0	.71	2.46
	18.7	16.20	19.26		15.5	1.22	4.32
100	−19.8	1.88	3.37	1000	−22.5	0.16	1.03
	− 7.6	3.20	4.52		−20.4	.18	1.08
	0.0	4.26	5.84[a]		−14.2	.25	1.33
	.0	4.26	5.78[b]		0.0	.43	2.09
	9.9	6.00	8.17		15.5	.73	3.67
	18.0	7.90	10.50				
300	−22.0	0.55	1.40				
	− 8.6	1.02	2.27				
	0.0	1.42	3.40				
	15.5	2.43	5.55				

[a] Equilibrium attained by saturation at higher temperature with subsequent cooling to 0.0°.

[b] Equilibrium attained by saturation at lower temperature with subsequent warming to 0.0°.

is the mean result of two to five independent analyses. The maximum deviation from the mean in any series of analyses was less than one part in sixty. The observed data are also given in the form of a graph, Fig. 1.

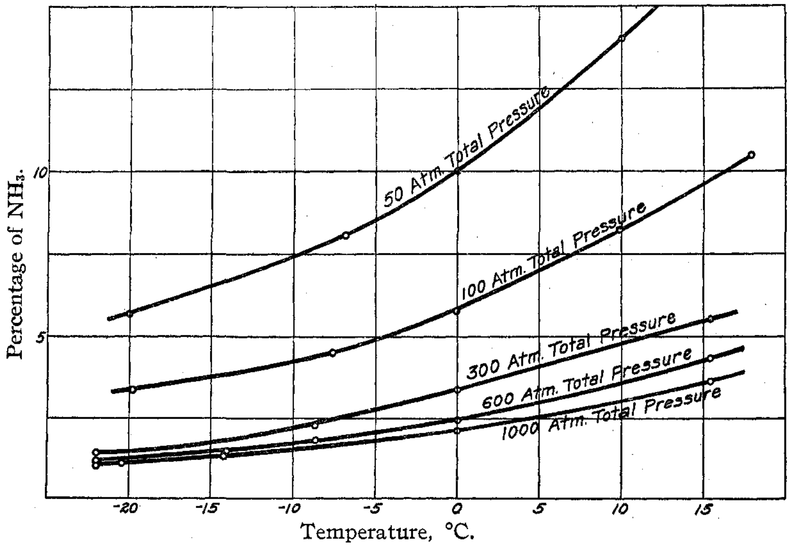

Fig. 1.—Volume percentage of ammonia in a 3:1 mixture of hydrogen and nitrogen saturated with ammonia vapor.

Discussion of Results.—The results of experiments at 0.0° and under 100 atmospheres' pressure definitely indicate that equilibrium is established between the liquid and gaseous phases of the system. The reproducibility of experimental results at all temperatures and pressures is further proof of the absence of variable influences such, for instance, as the formation of a mist. The high concentration of the ammonia in the vapor phase within the condensing coils may, however, be due to any one or to all of several probably closely inter-related phenomena.

1. The vapor pressure of pure liquid[5] is increased by the application of external pressure.
2. In a liquid-gas system of more than one component the presence of an indifferent gas, even though its critical temperature is below the temperature of the system, may cause an increased concentration in the vapor phase of the partly liquefied component. The magnitude of this effect appears to depend upon the mutual solubilities of the components.
3. The presence of an indifferent gas may cause an increased association of the molecules in the vapor phase of the partly liquefied component.

The effect of the first of these phenomena can be quantitatively determined if the pressure-volume relationships are known for liquid and gaseous ammonia. The compressibility of liquid ammonia has been determined by Cragoe and Harper.[6] Several equations of state for ammonia gas are available, notably those of Goodenough,[7] van der Waals,[8] and Keyes.[9] Results derived from the use of any of these equations may be invalidated, however, by the failure of the equation to represent the actual relationships of pressure and volume of ammonia in a gas mixture at temperatures and pressures at which pure ammonia can exist only in the liquid phase. Neglecting this possibility, calculations show that the vapor pressure of ammonia is raised three- to four-fold by applying an external pressure of 1000 atmospheres through the medium of an indifferent gas. This pressure is reduced by the nitrogen and hydrogen present in dissolved form in the liquid ammonia. On account of the slight solubility of the gases, however, the magnitude of this latter effect is small.[10]

The second phenomenon is identical with that observed in a two-com-

---

[5] Poynting, *Phil. Mag.*, [4] **12**, 32 (1881). Le Chatelier, *Z. physik. Chem.*, **9**, 335 (1892).

[6] Cragoe and Harper, *Bur. Standards Sci. Paper*, **420**, 314 (1921).

[7] Goodenough, "Properties of Steam and Ammonia," Wiley and Sons, **1917**, p. 23.

[8] Washburn, "Principles of Physical Chemistry," McGraw-Hill Book Co., **1921**, p. 39.

[9] Keyes, "Thermodynamic Properties of Ammonia," Wiley and Sons, **1916**, p. 20.

[10] The solubilities of nitrogen and hydrogen in liquid ammonia have been determined at pressures ranging from 50 to 150 atmospheres, and the results are soon to be published. Assuming that the solubilities continue to be proportional to pressure, the vapor pressure of ammonia under 1000 atmospheres total pressure and at 15.5° would be lowered 6% by the dissolved gases.

ponent liquid system, composed of two partly miscible liquids. The solvent effect of a compressed gas was first observed by Hannay and Hogarth[11] who dissolved solid potassium iodide in alcohol vapor heated above its critical temperature. Villard[12] verified this phenomenon by a large number of qualitative experiments with solid-gas and liquid-gas systems. Roozeboom[13] has provided a satisfactory theoretical explanation based upon Gibbs' phase rule, which has also been verified by the quantitative studies of Sander[14] on an ether-carbon dioxide system and of Pollitzer and Strebel[15] on hydrogen-water, air-water and carbon dioxide-water systems. It is apparent from these experiments that the "indifferent" gas acts as a solvent for the vapors from the liquid. As the pressure is increased, the liquid phase becomes richer in dissolved gases and the gas phase richer in vapor from the partly liquefied component. The two phases eventually become of like composition, and there results a one-phase bivariant system. Such critical phenomena were observed for the systems investigated by Villard and by Sanders. The critical data for ammonia in the presence of nitrogen and hydrogen are not yet available, but a similar phenomenon undoubtedly exists in this system. A further investigation of this system is being made, the results of which will be presented in a later paper.

Molecular association in the vapor phase of a system is a well-established phenomenon in the case of a number of substances such as sulfur and mercurous chloride. No experimental data have been published indicating this phenomenon in the case of ammonia vapor, although Walker[16] from a consideration of the critical data of ammonia and the size of the molecule has calculated a 9% degree of association under critical conditions. There is some evidence, however, that association exists in water vapor[17] and recently Keyes[18] has reported the presence of double molecules in carbon dioxide. In each of these cases the association is slight at atmospheric pressure. No study of the phenomenon has been made at high pressures.

Summary

The system, hydrogen-nitrogen-ammonia(gas)-ammonia (liquid), has been investigated within a temperature range from —22.5°C. to + 18.7°

---

[11] Hannay and Hogarth, *Proc. Roy. Soc.*, **30**, 178 (1880).

[12] Villard, *J. phys.*, [3] **5**, 453 (1895).

[13] Roozeboom, "Die Heterogenen Gleichgewichte," Braunschweig, **1904**, Vol. II, Part I, p. 99.

[14] Sander, *Z. physik. Chem.*, **78**, 513 (1912).

[15] Pollitzer and Strebel, *ibid.*, **110**, 768 (1924).

[16] Walker, *Phil. Mag.*, **47**, 111 (1924).

[17] Winkelmann, *Wied. Ann.*, **9**, 208 (1880). Wilsmore, *Trans. Faraday Soc.*, **3**, 85 (1907). Bose, *Z. Elektrochem.*, **14**, 264 (1908). Oddo, *Gazz. chim. ital.*, [1] **45**, 319 (1915). Kendall, THIS JOURNAL, **42**, 2477 (1920).

[18] Keyes, *ibid.*, **46**, 1584 (1924).

and a pressure range from 50 to 1000 atmospheres. The volume-percentage of ammonia in the gas phase within this range of temperature and pressure is presented in graphic and tabular form. At high pressures, concentrations of ammonia in the vapor phase have been found more than six times the concentrations calculated by the usual method from the vapor pressure of pure liquid ammonia.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE SEPARATION AND DETERMINATION OF THE ALKALI METALS USING PERCHLORIC ACID. III. NORMAL BUTYL ALCOHOL AND ETHYL ACETATE AS MIXED SOLVENTS IN THE SEPARATION AND DETERMINATION OF POTASSIUM, SODIUM AND LITHIUM

BY G. FREDERICK SMITH AND JOHN F. ROSS

RECEIVED JANUARY 29, 1925 PUBLISHED APRIL 4, 1925

n-Butyl alcohol and ethyl acetate as mixed solvents have been selected as one of the various combinations of organic solvents with properties best suited to the separation of the soluble from the insoluble alkali metal perchlorates by the extraction process.[1] *n*-Butyl alcohol has been used as solvent in the separation and determination of sodium and lithium by a process involving the precipitation and gravimetric determination of sodium as the chloride followed by the estimation of lithium by conversion to sulfate.[2] *n*-Butyl alcohol is not entirely satisfactory as extracting solvent to be used in the separation of sodium and lithium from potassium perchlorate because of the low solubility of sodium perchlorate. By the use of the mixed solvents given above, this objection is eliminated. The demonstration of imperfections in previously described methods and the development of an improved procedure for the extraction separation of the alkali metal perchlorates was the object of the second paper of this series.[3] The present paper applies the principles established in References 1, 2 and 3 to the quantitative separation and determination of potassium, sodium and lithium including the volumetric estimation of sodium using standard silver nitrate (Mohr's method).

The Method

The process, in brief, is as follows. The mixture of potassium, sodium and lithium chlorides is converted to perchlorates by evaporation of their solution with an excess of pure perchloric acid, the latter removed by evaporation to dryness twice with intermediate solution in water. Sodium

---

[1] Smith, THIS JOURNAL, **47**, 762 (1925).

[2] Willard and Smith, *ibid.*, **44**, 2816 (1922).

[3] Smith and Ross, *ibid.*, **47**, 774 (1925).