tetravalent state. The silver reductor offers many advantages over other reductors.

2. A method has been devised for the direct determination of iron in the presence of vanadium, titanium, chromium and manganese.

NEW YORK, N. Y. RECEIVED OCTOBER 7, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Vapor–Liquid Equilibria in the System Nitrogen–Water

BY ARTHUR W. SADDINGTON AND NORMAN W. KRASE

Introduction

Within recent years an increased amount of fundamental data on systems under pressure have been collected. Several papers upon the solubility relations of gases at high pressures in various liquids have appeared.[1] Among these is the work of Goodman and Krase,[2] who pointed out the existence at constant pressure of a minimum solubility point for nitrogen in liquid water at about 80°. Henry's law "constants" showed a wide variation and no definite trend. The most recent work has been reported by Wiebe[3] and his collaborators on nitrogen–water, hydrogen–water and nitrogen–liquid ammonia systems. These results for the first named equilibria did not agree closely with those of Goodman and Krase, but the evidence in favor of a minimum solubility point was further strengthened. Henry's law was of little value in predicting these results.

At various times reports[4] have appeared dealing with the vapor content of compressed gases in contact with the liquid phase. Recently Bartlett[5] published results showing the concentration of water vapor in compressed hydrogen, nitrogen and a 3:1 mixture of these gases in equilibrium with condensed water. As usually had been found in previous work, the water vapor concentration was much larger than that calculated by the ordinary methods. Poynting's relation did not predict the effect of pressure upon this system and the magnitude of the variation depended upon the nature of the indifferent gas. In the following year, J. J. Van Laar[6] using Bartlett's data demonstrated that his complex equation of state for gas mixtures in equilibrium with a condensed phase was able to predict the effect of the compressed gas upon the vapor pressure of water. Similar calculations have been made by Gillespie and his collaborators with the Beattie–Bridgeman equation of state and good agreement with experimental results was obtained where constants were available. A thermodynamic treatment of gas mixtures was given and it was shown that Dalton's law, the Gibbs–Dalton law and the Lewis and Randall fugacity rule were only approximations at elevated pressures. A method for the numerical calculations of the equilibrium pressures of a gas mixture was outlined.[7]

The various work mentioned above gives an incomplete understanding of the equilibrium relationships of the nitrogen–water system. In the present work an effort was made to extend this knowledge with the idea of bringing to light any basic quantitative laws. Measurements of gaseous and liquid phase compositions have been extended to about 240° at pressures to 300 atmospheres. Incidentally, an apparatus was designed capable of extending such researches to other systems.

A possible quantitative solution of the problem, however, seems to rest upon density measurements of both liquid and vapor phases. For example, the application of Poynting's relation to the gas phase depends upon the evaluation of β, the compressibility coefficient of the liquid. Actually a limited amount of data for pure water only is available. The method evidently falls into considerable error at this point for the compressibility of a solution of gas in a liquid cannot

---

(1) W. Sander, *Z. physik. Chem.*, **78**, 514 (1912); Frolich, *et al.*, *Ind. Eng. Chem.*, **23**, 548 (1931); V. Ipatiev, *et al.*, *Ber.*, **65B**, 568 (1932); B. Zuskend, *et al.*, *Z. anorg. allgem. Chem.*, **200**, 279 (1931).

(2) J. Goodman and N. W. Krase, *Ind. Eng. Chem.*, **23**, 401 (1931).

(3) R. Wiebe, V. Gaddy and C. Heins, *Ind. Eng. Chem.*, **24**, 823 (1932); **24**, 927 (1932); THIS JOURNAL, **55**, 947 (1933); R. Wiebe and T. Tremearne, *ibid.*, **55**, 975 (1933).

(4) H. Braune and F. Strassman, *Z. physik. Chem.*, **143A**, 225 (1929); A. Eucken and F. Bresler, *ibid.*, **134**, 230 (1928); A. Larson and C. Black, THIS JOURNAL, **47**, 1015 (1925); Pollitzer and Strebel, *Z. physik. Chem.*, **110**, 768 (1924); I. McHaffie, *Phil. Mag.*, [VII] **1**, 561 (1926).

(5) E. P. Bartlett, THIS JOURNAL, **49**, 65 (1927).

(6) J. J. Van Laar, *Z. physik. Chem.*, **137**, 421 (1928); **145**, 207 (1929).

(7) E. Lurie and L. J. Gillespie, THIS JOURNAL, **49**, **1146** (**1927**); L. J. Gillespie, *Phys. Rev.*, **36**, 121 (1930); H. T. Gerry and L. J. Gillespie, *ibid.*, **40**, 269 (1932).

be expected to equal that of the pure liquid. It is apparent, then, that measurements of the compressibility of the liquid solution must be made before the applicability of Poynting's equation can be tested rigorously.

Ostwald's coefficient for the solubility of nitrogen in liquids is defined as follows

$$\lambda = \frac{\text{g. } N_2 \text{ per cc. vapor phase}}{\text{g. } N_2 \text{ per cc. liquid phase}}$$

This coefficient has been evaluated to 100° from solubility data at 1 atmosphere pressure and it has been shown[8] that this offers the most likely method for the estimation of liquid phase compositions in the presence of compressed gases. However, this relation is applicable only over a limited temperature range (to 100°) and again assumptions must be made as to the density of the liquid solution. It is felt that the experimental determination of gas–liquid distribution coefficients calculated as the above on a volume basis offers a useful method for handling such systems. Similar coefficients on a weight basis, calculated from data reported here, show wide variations.

Experimental Method

Apparatus.—The necessary apparatus is shown schematically in Fig. 1. Commercial nitrogen was compressed from a large gasholder C through the calcium chloride tower E into three 1 cu. ft. cylinders. This capacity was great enough to ensure constant pressure conditions in the solubility apparatus during the course of an experiment. From these cylinders the gas was drawn through a charcoal absorption trap to the pre-saturating pipets 1 and 2, maintained at a temperature 10° higher than that of the solubility apparatus proper. These pipets were mounted in a copper thermostat H, a design previously used in this Laboratory. The copper block was wound with heavy electrical resistance wire in a manner to take full advantage of radiant heat. The furnaces were lagged by 5 cm. of magnesia insulation. The temperature was manually controlled by means of a lamp bank and varied less than 1° during average experiments. Supported in a second larger copper thermostat J of the same type were three additional pipets. The first of these, 3, acted as another saturating bottle maintained, however, at the temperature of the analysis and density systems. After bubbling through this series of pipets, kept half full of water, the saturated gases were usually led directly through valve P to the analysis pipet, 5. When necessary, by manipulating the valves N, O and P, the gases could also be passed through the density pipet, 4. The pressure tubing and valves connecting this series of five pipets were maintained at a temperature above that of the thermostats by the electrically heated air-baths K, L and M. The lower connections of the pipets in thermostat J were insulated and wound with electrical heating wire.

All of these pipets were machined from 18–8 chrome-nickel stainless steel since corrosion is an important factor and since high temperature work was contemplated. The saturators were constructed of heavy-walled tubing and had a capacity of about 150 cc. These tubes were closed at both ends by gasketed heads and the end-pieces bore the usual 6.2-mm. tubing connections. Both the analysis and density pipets were machined from solid stainless steel stock and differed from the saturators in having their lower ends turned down to form an expansion valve of the type usually employed in this work. The shaft, however, was elongated in order that the stem packing gland would be out of the heated zone.

The density and analysis pipets differed slightly in construction. In both cases the upper end was closed as with the saturating pipets. In the analysis pipet the gas was led in by way of the usual tubing connection through the lower shoulder of the pipet. To carry the bubble of gas above the exit to the sampling valve T a cylindrical tube 5 cm. long was tapped into the inside opening of this connection. In addition to the exit opening to the valve a second connection was made to the low pressure side of the valve seat. This connection carried dry nitrogen with which to remove all traces of liquid water after the sampling of the liquid phase. The head of the analysis pipet also carried a thermocouple well which projected to within 2.5 cm. of the bottom of the cylinder. A spray trap consisting of a tightly wound copper gauze filled the entire cross section of the upper 2.5 cm. of the pipet.

The density pipet had no inlet gas connections to its lower shoulder. The upper end piece was constructed to carry a long 6.4-mm. tube extending into the bottom of the pipet. The entering gases passed down through this tube and escaped back around its upper end through an outlet to the side of the pipet.

The valves N, O, P and R were constructed of stainless steel and differed from the usual design only in having elongated stems which permitted the packing gland to be located outside the hot air-baths. Water jackets on each valve permitted further cooling of these glands when necessary.

Temperatures were read by means of three chromel–alumel thermocouples located as shown in Fig. 1, a type K potentiometer and wall-type galvanometer. This system was sensitive to 0.005 mv. The thermocouples were checked against a Bureau of Standards calibrated thermocouple and readings were accurate to 0.5°. Temperatures of the two copper thermostats were recorded by thermocouples I and II. Number III was carried by the well of pipet 5 down into the liquid.

The pressure on the system was measured by a dead-weight piston gage. Two ordinary hydraulic pressure gages reading to 5000 and 10,000 pounds per square inch were connected to the storage manifold and aided in pressure control.

When desired, water was introduced into the density and analysis pipets by the use of a Cailletet hand pump, G. This consisted of a cylinder of about 150 cc. capacity in which was operated by hand a piston made water tight

---

(8) R. Wiebe, V. Gaddy and C. Heins, THIS JOURNAL, **55**, 947 (1933).

by the use of leather gaskets. A suitable manifold, not shown in the diagram, carried the distilled water to either pipets 4 or 5.

Liquid Phase Analysis.—The method employed in the determination of the composition of the liquid was essentially the same as that used by previous workers. Saturation was obtained by allowing gas to bubble through the analysis pipet for periods varying from three to twenty-four hours. Usually analyses were made after at least fifteen hours of such treatment. Several days were required to complete all the determinations at one temperature and pressure. The withdrawal of liquid and gas samples and recompression of the expanded gas were the only disturbing factors during this time. During any twenty-four hours the pressure gradually decreased about 1 to 2 atmospheres to its final value, after which gas was recompressed to the desired pressure. The withdrawal of liquid samples produced no noticeable change in pressure.

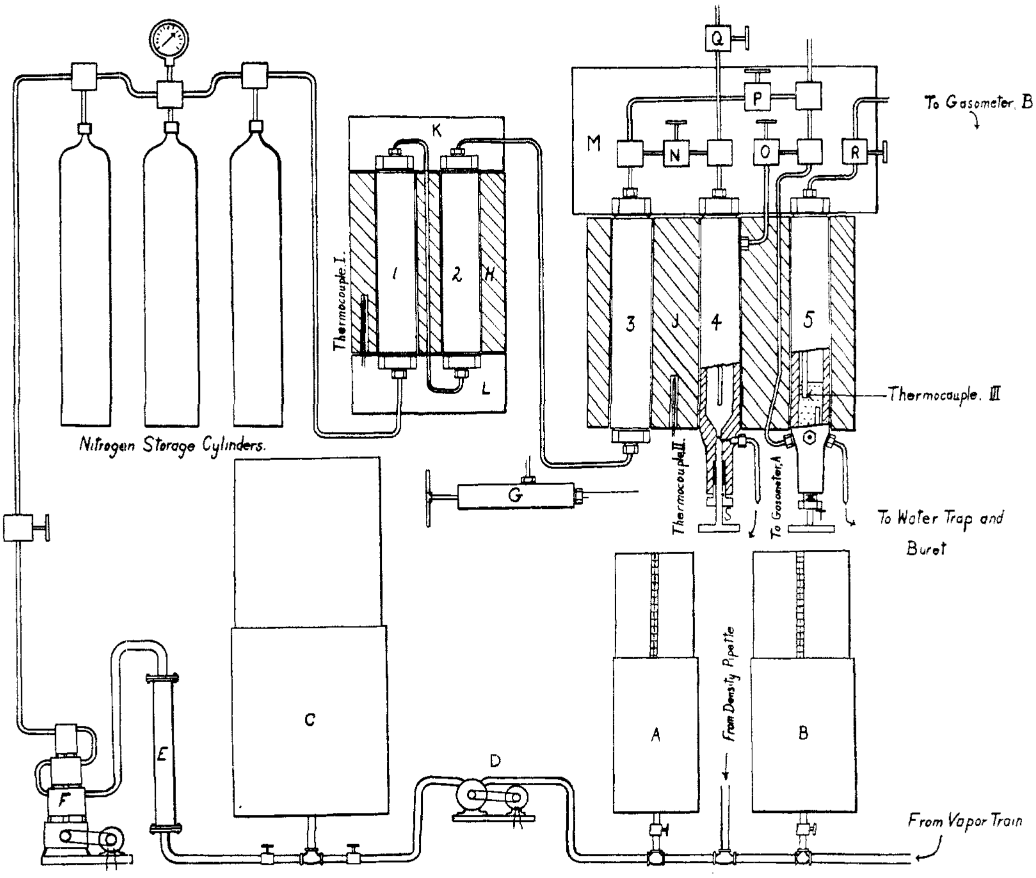

Fig. 1.

The analysis of the liquid phase was made by expanding 5 to 10 g. of water from the valve T into a combined trap, condenser and anhydrone drying train. This piece of apparatus fitted easily into a wide-mouthed thermos flask filled with cracked ice. Not only did this constant temperature bath serve to condense the steam rising from a sample but it also decreased changes in volume of the trap due to the hot water. These precautions were particularly necessary in the work at higher temperatures. The expanded gases were led to a gas buret of the usual type equipped with a compensator and jacketed by a glass water-bath. This buret having a capacity of 30 cc. was graduated in 0.05 cc. and easily read to 0.01 cc. The expanded water was allowed to stand for fifteen minutes or more to allow complete separation of the dissolved nitrogen and to permit cooling of the trap to 0°. After measuring the expanded gas volume dry nitrogen was passed through the exit tubing of the sampling line to carry over all the expanded water to the trap. This was then weighed. Pressure and temperature were recorded before and after every analysis.

Gas Phase Analysis.—The gas phase samples from pipet 5 were expanded through the valve R, which was kept at a temperature from 25 to 50° above that of the copper thermostats to avoid condensation from the compressed gases in the tubing connections and valve. If this condensate accumulated in the narrow gas passage it was blown out in appreciable amounts at irregular intervals. This tendency disappeared when the valve was heated. When heated in this manner a wide variation of the valve temperature produced no noticeable effect on the composition at any given temperature of the system.

The expanded gases were passed through a heated tube to the analytical train, consisting of three glass U-tubes weighing about 50 g. when packed. The first of these was packed with anhydrone and absorbed at least 95% of the water. The remaining 5% was condensed in two U-tubes packed with copper wool and immersed in liquid air. The volume of the expanded gas was measured over mineral seal oil either in a 5 cu. ft. or a 2 cu. ft. standard gasometers (A and B) which were kept in a constant temperature room maintained at 32.4 ± 0.1°. Volume measurements were made after adjusting the pressure of the expanded gas to that of the atmosphere and after allowing the gas to stand for fifteen minutes to reach thermal equilibrium. From the gain in weight of the U-tubes in the absorption train and the measured volume of nitrogen, the water content of the expanded gas was calculated. Pressure and temperature readings were made before and after every experiment.

While making an analysis the stopcocks of the U-tubes immersed in liquid air were protected from the condensing moisture of the room by fitting toy balloons snugly over them. An oil manometer placed at the head of the absorption train acted as a safety valve in the case of unexpected increases in the pressure of the expanded gas. The pressure in the absorption train was reduced to that of the atmosphere before and after every weighing. The loss of moisture from the copper wool of the condensers as they were warmed to room temperature was prevented by closing their stopcocks before a temperature of 0° was reached. The closed tubes were allowed to stand for at least a half hour at room temperature before weighing. The trapped gases in excess of the atmospheric pressure were then released by momentarily opening the stopcocks to the air. The loss of water vapor under such conditions was kept to a minimum. All weighings were made using a counterpoise and the results were reproducible to less than 0.5 mg. after hours of standing. The maximum error of weighing is not greater than 0.3 mg. and the average error on the three tubes must be less than 1.0 mg.

Anhydrone was not used in the liquid air condensers because of the tendency of other materials than water vapor to be adsorbed by its porous surface when at such low temperatures. The removal of adsorbed substances by flushing with pre-dried nitrogen involves a more complicated procedure than in the case of condensers packed with copper wool. Special tests indicated that adsorption on copper was negligible. It was found that the second of these condensers rarely changed in weight more than a few tenths of a milligram. The fact that the expanded gas velocity did not affect the results of similar experiments indicated that water vapor was not escaping as frozen spray. At the end of each analysis these condensers were dried by a stream of compressed air.

Gas Phase Density.—The density of the saturated vapor was determined by expanding the gases from a closed pipet of known volume. Two procedures were followed at various times in this work. Originally by manipulating the valves N, O and P of the high pressure manifold, the vapors from the pre-saturating pipets were allowed to flow through the density pipet, 4, before traversing the analysis pipet. Equilibrium was assured by sweeping out the density system with the compressed gases for twelve hours previous to an analysis. At the time of a determination valves N, O and Q were closed after the pressure of the system had been measured with the piston gage. The temperature of the system having been noted the contents of the closed density pipet were then allowed to expand through the valve S to the usual anhydrone–liquid air absorption train. The expanded nitrogen volume was obtained by leading the gas to the standard 2 cu. ft. gasholder A maintained in the constant temperature room. After measuring the gaseous contents of the pipet a stream of pre-dried nitrogen removed all the condensed water vapor from the pipet to the absorption train.

It was found with this procedure, however, that considerable condensation occurred on the walls of the pressure chamber. This was represented by an increased water content of the expanded nitrogen over the ordinary vapor analysis figures. The final procedure consisted in the careful expansion of the vapors of the pre-saturating pipets through the valve N to the closed, dry pipet, originally at atmospheric pressure. The small amount of dry gas introduced a negligible error as shown by the water content of the expanded gas.

The volume of the density pipet was determined by expansion of dry nitrogen at a known pressure and temperature from the closed system. After measuring the volume of these expanded gases the capacity of the pressure system was calculated from the compressibility coefficients of pure nitrogen.[9]

Results

Liquid Phase Composition.—The averaged results of the experiments comprising this phase of the work are shown in Table I. The solubility coefficient X is defined as the number of cubic centimeters of nitrogen at standard temperature and pressure that are required to saturate 1 g. of water.

TABLE I

THE SOLUBILITY OF NITROGEN IN LIQUID WATER

Pressure, atm.	Temp., °C.	X cc.(N.T.P.)/g.	No. of expts.	Av. dev. from mean, %
100	65.0	0.981	3	0.3
100	80.0	.977	3	.8
100	125.0	1.198	3	2.3
100	180.0	1.644	1	...
100	210.0	1.817	3	0.9
100	240.0	2.027	2	.9
200	50.0	1.806	6	.7
200	80.0	1.748	6	.7
200	100.0	1.825	7	.6
200	150.0	2.172	5	1.3
200	200.0	3.287	4	1.3
200	240.0	4.378	3	1.6
300	50.0	2.572	4	0.7
300	70.0	2.425	4	.7
300	105.0	2.598	2	2.6
300	135.0	3.128	3	1.3
300	165.0	3.905	3	0.3
300	230.0	6.062	3	2.3

The general trend of the liquid composition over the range of pressure and temperature investigated is best seen by an examination of Fig. 2.

---

[9] E. P. Bartlett, THIS JOURNAL, 50, 1275 (1928).

The average deviation from the mean in most of the results below 150° was in the neighborhood of 0.75%. This increased slightly at the higher temperatures to about 1 to 2.0%. Usually agreement with Wiebe is within the error of measurement, where the results are comparable.

where a is g. of N_2 per liter of compressed gas. A second equation is furnished by the gas phase analysis from which the ratio of W_c/a is readily evaluated. These relations may be solved and W_c evaluated. At the lower temperatures these two methods of calculation give check results.

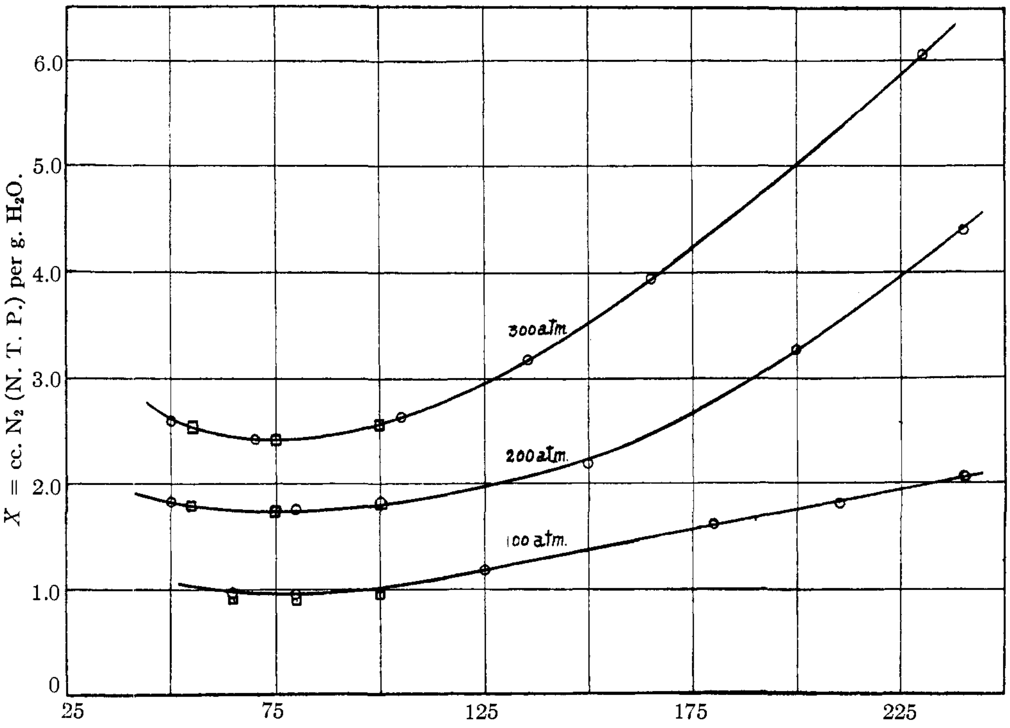

Fig. 2.—Temperature-liquid phase composition relations: ⊙, observed; ⊡, Wiebe.

Gas Phase Composition.—The average results from the analyses of the gas phase are shown in Table II for the range of temperature and pressure investigated. The term W_c is defined as the number of grams of water contained in 1 liter of compressed gas. Two methods were used in the calculation of this quantity. In the experiments below 100° the volume of the compressed gases was calculated from the expanded nitrogen volume using Bartlett's compressibility data for pure nitrogen. This assumption may also be used in the calculation of the gas phase density. But above 100° a comparison of these calculated figures with the observed densities showed a lack of agreement greater than the experimental deviation between like experiments. In the range of temperature above 100° the following method for W_c was used. If D_v be defined as the density of the gas phase in g./liter then

$$D_v = a + W_c$$

TABLE II

VAPOR PHASE COMPOSITION OF NITROGEN-WATER SYSTEM

Temp., °C.	Press., atm.	W_c in g. per l. of comp. gas	H_2O per g. of gas phase, g.	N_2 per g. of gas phase, g.	No. of expts.	Av. dev., %
50.0	100	0.1236	0.00118	0.9988	6	1.7
80.0	100	.3817	.00403	.9960	5	2.3
100.0	100	.6474	.00726	.9927	5	1.9
150.0	100	2.710	.0341	.9659	4	0.9
190.0	100	5.880	.0828	.9172	3	1.4
230.0	100	13.300	.1958	.8042	2	0.8
50.0	200	0.1463	.00085	.9992	5	2.6
85.0	200	.5116	.00290	.9971	3	0.6
150.0	200	2.960	.0203	.9797	4	2.1
190.0	200	7.550	.0564	.9436	3	0.4
225.0	200	14.840	.1180	.8820	3	.5
50.0	300	0.1975	.00073	.9993	4	2.2
75.0	300	.4607	.00262	.9974	3	3.0
100.0	300	.9126	.00372	.9963	2	1.9
115.0	300	1.450	.00629	.9937	2	3.5
145.0	300	3.240	.0155	.9835	3	2.4
165.0	300	5.320	.0259	.9741	4	1.0
230.0	300	16.400	.0933	.9067	3	2.2

The effect of temperature upon the water content of the gas phase is shown in Fig. 3. The marked increase of W_c with temperature accounts for the difficulty of checking similar analyses within 2%.

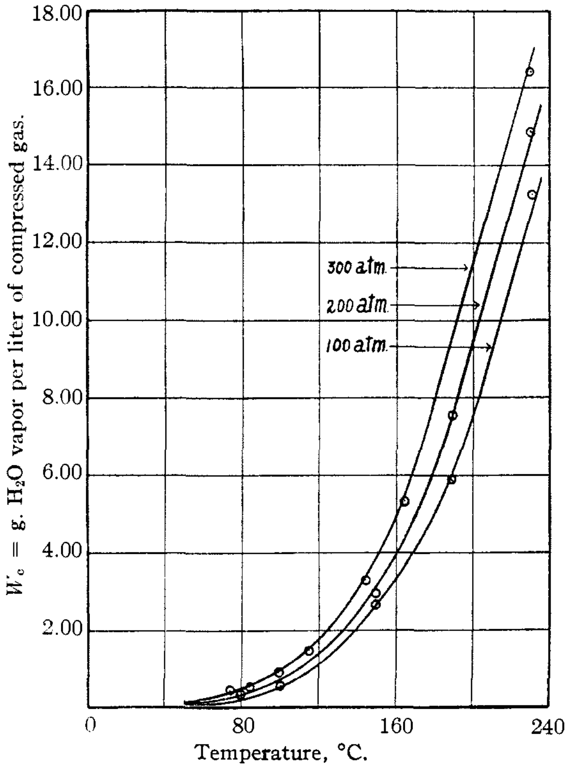

Fig. 3.—Effect of temperature on the water vapor content of one liter of compressed gas.

Gas Phase Density and Compressibility Factors.—The measurements of the density of the compressed gases in equilibrium with the solution of nitrogen in water are shown in Table III. The gas phase density, D_v, is recorded in g. per liter. The average deviation in these results is usually less than 0.5% but two sets of observations at 230° show a more marked variation. The trend of D_v with temperature is shown in Fig. 4.

From measurements of the gas phase density a compressibility factor for the gases may be calculated. Thus, the compressibility coefficient of the entire mixture, C_m, is defined as follows

$$C_m = PV/P_0V_0m$$

where P is the total pressure in atmospheres, P_0 is 1 atmosphere, V is the volume of the compressed gases in cc. and V_0m is the volume in cc. of the expanded mixture at 1 atm. and 0°.

Table III

Gas Phase Density and Compressibility Factors

Temp., °C.	Press., cm.	D_v, g. per l.	No. of expts.	Av. dev., %	C_m, obs.	C_m, calcd.
80.0	100	94.2	4	0.2	1.320	1.328
100.0	100	88.0	3	.7	1.417	1.411
150.0	100	76.8	3	.5	1.620	1.607
210.0	100	68.5	2	.4	1.755	1.799
230.0	100	67.7	3	2.6	1.773	1.814
50.0	200	196.8	4	0.5	1.272	1.273
80.0	200	176.7	3	.1	1.411	1.406
100.0	200	169.3	3	.1	1.470	1.495
150.0	200	145.8	3	.4	1.695	1.695
200.0	200	132.6	1	...	1.822	1.878
240.0	200	122.0	2	1.8	...	..
50.0	300	273.1	2	0.3	1.376	1.368
70.0	300	256.3	3	.5	1.468	1.460
100.0	300	237.2	1	...	1.586	1.596
115.0	300	225.0	1	...	1.656	1.658
140.0	300	212.1	1	...	1.761	1.760
170.0	300	198.3	2	0.1	1.863	1.877
230.0	300	176.4	1	...	2.007	2.0593
240.0	300	173.0	1	...	1.980	2.0773

The averaged values of this coefficient are shown in Table III, where it is compared with calculated values for C_m. The latter coefficient was calculated from the specific volume of saturated steam[10] and Bartlett's values for nitrogen, by taking a weighted mean of these figures. Experimental results for the vapor phase composition were

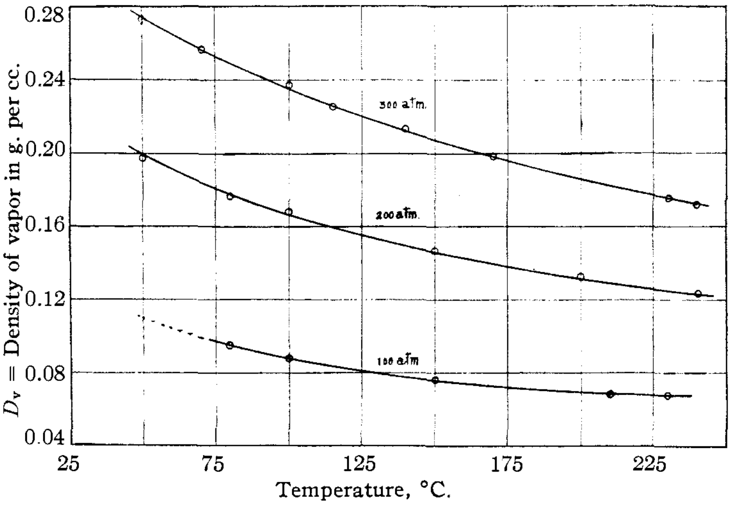

Fig. 4.—Relation between gas phase density and temperature for nitrogen–water vapor mixtures.

---

(10) G. A. Goodenough, "Properties of Steam and Ammonia," John Wiley and Sons, 1916.

employed. These comparisons are shown in Fig. 5, over a considerable temperature range.

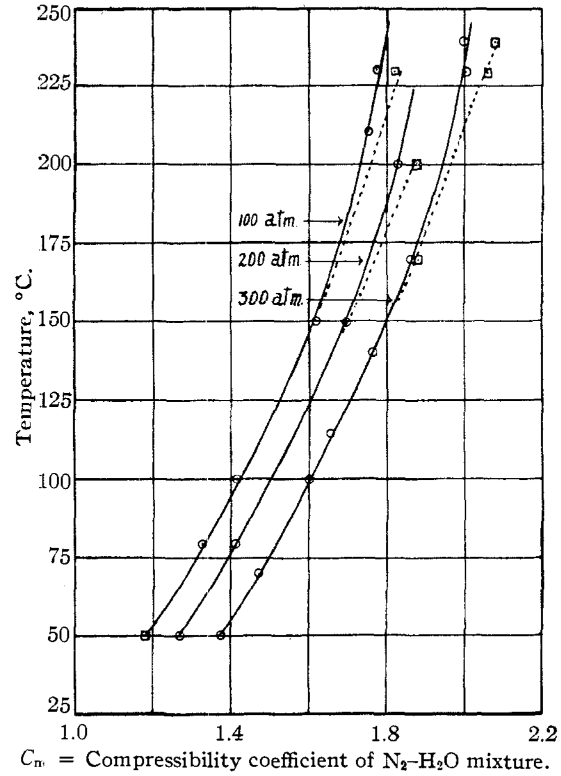

Fig. 5.—Comparison of calculated with experimental compressibility coefficients for nitrogen-water vapor mixtures: ○, observed results; ▣, calculated, additive rule.

Discussion of Results

Liquid Phase Compositions.—As is well illustrated in Fig. 2, the solubility of compressed nitrogen in water at any constant pressure decreases with temperature to a minimum at about 70 to 80°. Above this temperature the solubility increases slowly—very slowly when it is considered that the gas and liquid become miscible in all proportions at the critical point [$T_{C(H_2O)} = 374°$]. This phenomenon is well in accord with the general thermodynamic theory of Van der Waals and Keunen,[11] who have treated such systems at some length. Although such effects may be readily predicted qualitatively, it is difficult to apply quantitative laws since the various thermodynamic properties of the system are unknown.

That the effect of pressure upon the solubility of nitrogen in water is not quantitatively predicted by Henry's law is evidenced by the "constants" of Table IV, calculated from the relation $K = p_N/X_N$. The approximate validity of the relation, particularly at higher temperatures, is shown in Fig. 6.

TABLE IV

HENRY'S LAW "CONSTANTS"

T, °C.	1 atm.[a]	100 atm.	200 atm.	300 atm.
50	86.8	104.2	110.0	117.2
80	101.9	110.4	114.8	124.6
100	...	108.6	109.4	117.8
150	...	79.7	88.8	83.6
200	...	49.2	54.7	54.5
240	...	32.7	36.6	38.8

[a] From "Int. Crit. Tables."

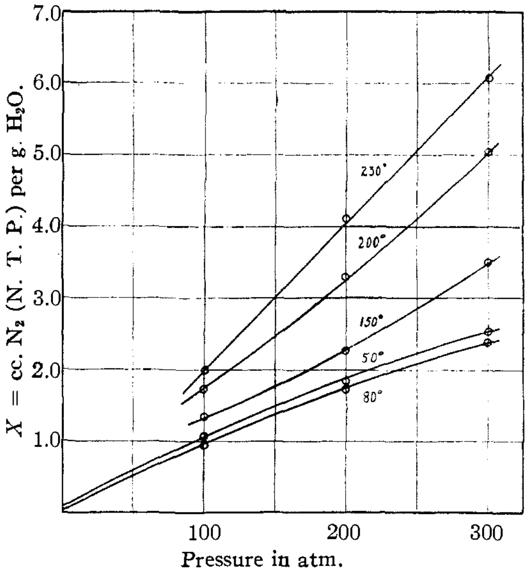

Fig. 6.—Pressure-liquid phase composition relations.

Gas Phase Compositions.—The general observation of all workers in this field that the water content of the compressed gases exceeds the theoretical values as predicted from equations such as Poynting's was found to hold for the results reported above. Figure 7 illustrates this effect of pressure upon the water content of 1 liter of compressed gas at constant temperature. The dotted line shown at several of the lower temperatures is, in every case, a plot of the Poynting relation, and this serves to emphasize the increasing "solubility" effect of a given volume of the compressed gases on water vapor as the temperature is raised. Bridgman's data[12] on the compressibility of pure water were used in these latter calculations. Above 80° these calculations have

---

(11) J. D. Van der Waals, "Lehrbuch der Thermodynamik," Verlag Johann Barth, 1906, p. 168; Keunen, "Verdampfung and Verflüssigung von Gemischen," Verlag Johann Barth, 1906, p. 82.

(12) P. W. Bridgman, "International Critical Tables," Vol. III, p. 40.

a doubtful value since it was necessary to extrapolate the compressibility data over a wide range of temperature. However, the slope of the observed W_c curves with pressure shows an increase at the higher temperatures. This also supports the conclusion that the effect of pressure upon the water content of a given volume of the gas phase becomes more marked as the temperature is raised.

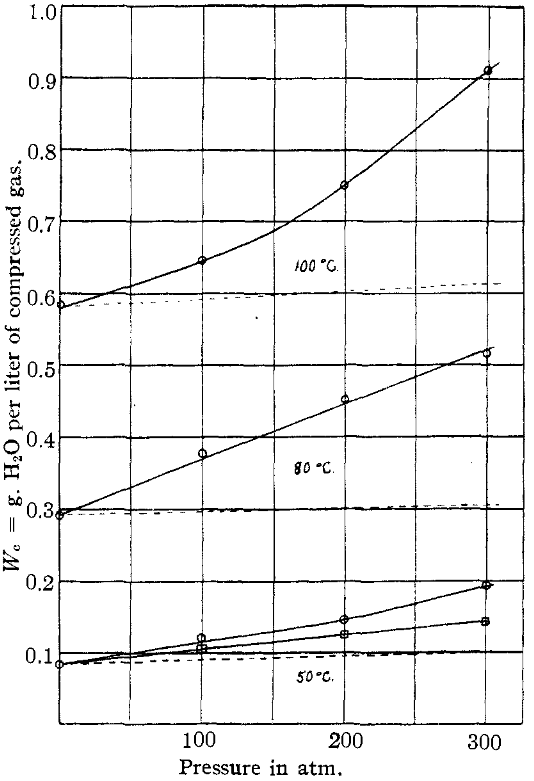

Fig. 7.—Effect of pressure on the water vapor content of one liter of compressed gas: – – –, Poynting relation; ☐, Bartlett; ○, experimental.

At 50° these results are compared in Fig. 7 with the determinations of Bartlett for this same system. A great discrepancy in these two sets of data is very evident. It is believed that such a disagreement depends mostly upon differences in the operating technique. In Bartlett's apparatus the expansion valve and the pressure tubing connections leading to it were maintained at the same temperature as the analysis pipet and foam trap. However, in this work, it was noted that water vapor tended to condense in the expansion valve under such conditions even at a temperature of 50°. This accumulated in the narrow gas passage and was blown out occasionally as evidenced by the sudden appearance of water in the absorption train, accompanied by noticeable fluctuations in the pressure of the expanded gas. To eliminate this effect it was necessary to insulate the air-bath surrounding the valve and to heat it to a temperature from 20 to 50° higher than that of the analysis pipet. When operating in this way no water vapor condensed in the expansion valve. Results were independent of the valve temperature at any constant temperature of the analysis pipet and successive experiments checked to within 1.5 to 2.0%. As the temperature of the valve was reduced to that of the thermostats the value of W_c tended to decrease, and at the same time the condensation of water in the valve produced wide variations in a set of successive analyses.

Gas Phase Density and Compressibility Factors.—As may be seen by the curves of Fig. 4, the density of the gas phase decreases with temperature at constant pressure. This effect is greatest at the highest pressure.

The observed measurements of the gas phase density were compared with values calculated from Bartlett's compressibility factors of pure nitrogen. Using these latter data and neglecting the influence of water vapor on the gas mixture, the volume of the compressed gases may be obtained from the expanded nitrogen volume obtained during a gas phase analysis. From this the gas phase density is readily estimated. Comparison of these results with observed data on D_v showed a good agreement at temperatures to 100°. At higher temperatures, however, the two sets of figures did not coincide, a deviation of 10–15% being noticed at 230°. At temperatures to 100°, then, the use of Bartlett's data in evaluating various properties of this system introduces no great error. But above 100° another method of calculation was necessary as outlined above.

A comparison of the compressibility factors for this gaseous mixture with those calculated by an additive rule from data on the pure constituents (Table III, Fig. 5) shows no great variations below 150°. It is interesting to note that the additive rule for the compressibility coefficient of gas mixtures does not hold very closely at the elevated temperatures. At the lower temperatures the water vapor concentration is too small to have much effect on the properties of the large amount of nitrogen present in the mixture.

Summary

A high pressure apparatus has been developed with which the equilibrium relations of liquid–

vapor systems may be examined in the presence of a compressed gas. Such measurements have been made to a temperature of 250° and pressures to 300 atmospheres for the nitrogen–water system.

As predicted by Keunen and others, the solubility of nitrogen in water passes through a minimum point. This occurs in the neighborhood of 70 to 80°. Pressure causes a decided increase in the amount of dissolved nitrogen but Henry's law does not explain this effect quantitatively.

The concentration of water vapor in a given volume of the compressed gases is decidedly greater than that calculated by the usual methods. This effect increases with both temperature and pressure.

A method for the determination of the vapor phase density and compressibility is presented. The vapor density decreases with rising temperature at constant pressure. At temperatures above 150° where the concentration of water vapor in the gas phase reaches fairly large values, an additive rule for the calculation of the compressibility coefficient of the mixture does not hold.

It appears that liquid phase density measurements should be made in order to test the applicability of Poynting's relation in calculating the vapor phase compositions from the compressibility of the solution. They would also permit a test of the constancy of Ostwald's distribution coefficient calculated on a volume basis.

URBANA, ILL. RECEIVED OCTOBER 9, 1933

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

A Study of Solutions of Methyl Alcohol in Cyclohexane, in Water and in Cyclohexane and Water

BY E. ROGER WASHBURN AND HOWARD C. SPENCER

Recent work has been concerned with the solubility relationships involved in ternary systems of water, an alcohol and a hydrocarbon.[1] The present investigation, using water, methyl alcohol and cyclohexane, is a part of this systematic study of solubility behavior.

Materials

Water.—Distilled water of conductivity grade was used throughout the work.

Methyl Alcohol.—Synthetic methyl alcohol obtained from Merck and Company was refluxed over freshly burned lime and then fractionally distilled from an all-glass apparatus. The final product had a specific gravity of d_4^{25} 0.78673 and a refractive index of n_D^{25} 1.32660.

Cyclohexane.—The cyclohexane was the best grade obtainable from the Eastman Kodak Company. This was subjected to repeated alternate fractional crystallizations and distillations. Finally, it was dried over sodium and distilled from an all-glass apparatus. The best sample had a specific gravity of d_4^{25} 0.77354, a refractive index of n_D^{25} 1.42370, and a freezing point of 6.10°. Samples of slightly lower specific gravity were found to give the same results as the better grade in solubility determinations and were used in a few cases.

Experimental

Determination of the Ternary Solubility Curves.—The ternary solubility curves were determined in a manner similar to the procedure used in previous investigations of such systems.[1] The flask containing the weighed amounts of two of the liquids was suspended in a hand controlled water-bath and the third liquid added by means of a "medicine dropper" which was thrust through a cork stopper substituted for the ground-glass stopper of the flask. The use of this apparatus reduced the loss from evaporation to a minimum, and also made it possible to introduce very small amounts of the titrating liquid. The flask was shaken after each addition of the third liquid and sufficient time allowed for equilibrium to be reached. In order to ensure complete saturation near the end-point, the bath was warmed a few tenths of a degree so that complete solution occurred and then cooled to exactly 24.8°.

Representative results of these titrations are tabulated in Table I and are shown graphically in Fig. 1. Titrations numbered 1 to X form one of the curves, while Y, 12, and 13 form the other curve which when drawn to scale is hardly discernible in the figure. The composition is expressed in terms of weight per cent. rather than the more common mole per cent. or mole fraction since in these solutions the molecular form of the components is not known.

While methyl alcohol and water are miscible in all proportions at 25° and water and cyclohexane are practically immiscible, methyl alcohol has *only a limited miscibility with cyclohexane.* The

---

[1] Washburn, Hnizda and Vold, THIS JOURNAL, **53**, 3237 (1931); Vold and Washburn, *ibid.*, **54**, 4217 (1932).