containing a high concentration of boric oxide have the same absorption band as is to be found in the water solutions of cobaltous salts or the sulfuric and acetic acid solutions and which is ascribed to the uncoördinated cobaltous atom. It is possible to prepare cobalt glasses with the proper concentration of oxides such that they will be pink at a given temperature and blue at a higher temperature. For this purpose potassium oxide is to be preferred to lithium and sodium oxides. With a given molar concentration, a more brilliant blue glass is obtained with potassium than with sodium or lithium oxides.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, FERTILIZER AND FIXED NITROGEN INVESTIGATIONS]

The Solubility of Nitrogen in Water at 50, 75 and 100° from 25 to 1000 Atmospheres

BY R. WIEBE, V. L. GADDY AND CONRAD HEINS, JR.

There is no reliable method by which the solubilities of gases in liquids at high pressure may be calculated or predicted. Carefully compiled experimental data, therefore, become of theoretical as well as immediate practical value.

Goodman and Krase[1] measured the solubility of nitrogen in water from 100 to 300 atmospheres over a wide range of temperatures while Frolich and associates[2] obtained the solubility of nitrogen in water at 25° up to 200 atmospheres. It will be seen that there is some disagreement between the various results. The data presented here are an extension of previous work.[3]

Apparatus and Method

The apparatus and method used are somewhat similar to those described previously.[4] Fig. 1 shows the apparatus. Cylinders A and B of 1000 and 300 cc. capacity, respectively, were filled with water to three-fourths capacity. For the high pressure approach gas was bubbled through A and B successively at a pressure above the final value in order to obtain supersaturation. The pressure was then lowered to the desired level and gas was bubbled through for several hours. The gas flow was then turned off and, after standing from two to fourteen hours, samples were taken. In the low pressure approach the water was saturated at a pressure below the final value and then gas was bubbled through at the final pressure for about three hours. Samples were taken only from B. A was used as a

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[1] Goodman and Krase, *Ind. Eng. Chem*, **23**, 401 (1931).

[2] Frolich, Tauch, Hogan and Peer, *ibid.*, **23**, 548 (1931).

[3] Wiebe, Gaddy and Heins, *ibid.*, **24**, 927 (1932).

[4] Wiebe, Gaddy and Heins, *ibid.*, **24**, 823 (1932).

reservoir to save time in saturation. In the low pressure measuring system the 30-cc. buret C measured the volume of water while the other two burets took care of the gas sample. The water sampling buret C could be read to 0.01 cc. Pressures were read on two piston gages described by Bartlett and co-workers.[5] The nitrogen was 99.9% pure, the impurities being argon and traces of oxygen.

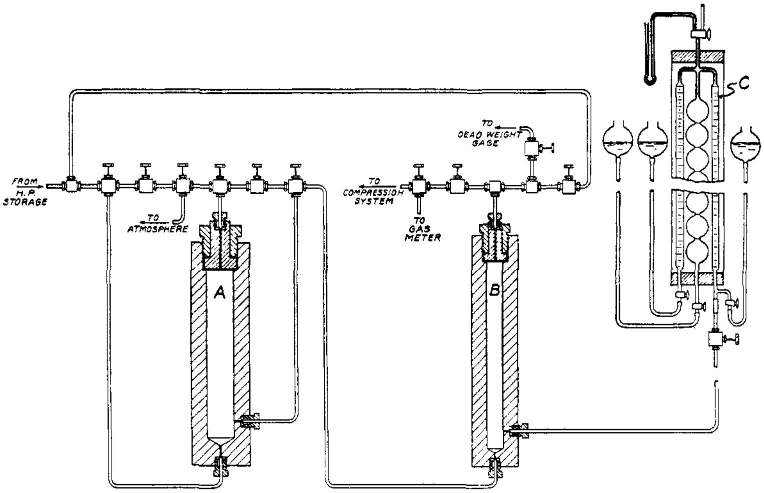

Fig. 1.

Discussion of Results

In Table I the experimental values are tabulated. The errors were calculated by means of the formula[6]

$$E = 0.6745 \pm \sqrt{\frac{\Sigma \Delta^2}{n(n-2)}}$$

and are shown in the third and fifth columns of Table I.

As will be seen, both approaches yield practically identical values, showing that equilibrium must have been reached. The final value was, therefore, obtained from an average of all observations. The absolute value may be different from the experimental by a few tenths per cent. due to the impurities and due to calibration errors of the burets and gages. The latter error will be greater at low pressures. The probable error naturally takes into account only accidental errors of observation. A slight error may also arise from the correction for the gas left in the water sample in the buret but this also becomes negligible at higher pressures.

A correction was made for the change of the partial pressure of water due to the total pressure. This correction is naturally most uncertain in the high pressure range of the 100° isotherm but in the worst case

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[5] Bartlett, Cupples and Tremearne, This Journal, **50**, 1275 (1928).

[6] Deming, *Phys. Rev.*, to appear.

TABLE I

ABSORPTION COEFFICIENTS (CC. OF GAS AT S. T. P. PER G. OF WATER) OF NITROGEN IN WATER

Press. of nitrogen in atm.	Number of runs for low press. approach	Av. for low press. approach	Number of runs for high press. approach	Av. for high press. approach	Final values
		25.00 ± 0.03°[a]			
25	10	0.348 ± 0.000	12	0.348 ± 0.000	0.348 ± 0.000
50	10	.673 ± .001	10	.675 ± .001	.674 ± .001
100	10	1.262 ± .001	7	1.268 ± .001	1.264 ± .001
200	6	2.253 ± .002	6	2.260 ± .002	2.257 ± .001
300	9	3.062 ± .004	15	3.060 ± .002	3.061 ± .002
500	14	4.436 ± .002	14	4.446 ± .003	4.441 ± .002
800	8	6.133 ± .01	19	6.135 ± .00	6.134 ± .003
1000	15	7.15 ± .00	18	7.15 ± .01	7.15 ± .00
		50.00 ± 0.03°			
25	9	0.273 ± 0.000	6	0.273 ± 0.000	0.273 ± 0.000
50	7	.533 ± .001	11	.533 ± .001	.533 ± .001
100	14	1.011 ± .000	5	1.011 ± .001	1.011 ± .000
200	7	1.829 ± .001	11	1.830 ± .001	1.830 ± .001
300	7	2.532 ± .001	10	2.535 ± .001	2.534 ± .001
500	5	3.718 ± .002	14	3.721 ± .002	3.720 ± .002
800	9	5.219 ± .003	7	5.223 ± .001	5.221 ± .002
1000	7	6.114 ± .006	7	6.131 ± .006	6.123 ± .005
		75.00 ± 0.03°			
25	8	0.254 ± 0.000	7	0.254 ± 0.000	0.254 ± 0.000
50	7	.494 ± .000	7	.494 ± .001	.494 ± .001
100	7	.946 ± .000	8	.946 ± .000	.946 ± .000
200	8	1.732 ± .001	6	1.731 ± .001	1.732 ± .001
300	7	2.414 ± .001	5	2.412 ± .001	2.413 ± .001
500	7	3.584 ± .001	5	3.583 ± .002	3.583 ± .001
800	8	5.064 ± .002	6	5.060 ± .002	5.062 ± .001
1000	5	5.927 ± .002	5	5.939 ± .004	5.934 ± .003
		100.00 ± 0.05°			
25	7	0.266 ± 0.000	9	0.265 ± 0.000	0.266 ± 0.001
50	7	.516 ± .001	7	.515 ± .001	.516 ± .001
100	7	.986 ± .001	8	.986 ± .001	.986 ± .001
200	9	1.822 ± .001	7	1.821 ± .002	1.822 ± .001
300	15	2.546 ± .001	12	2.546 ± .002	2.546 ± .001
500	14	3.799 ± .008	6	3.796 ± .003	3.799 ± .002
800	6	5.363 ± .005	6	5.367 ± .003	5.365 ± .003
1000	7	6.257 ± .008	7	6.255 ± .005	6.256 ± .004

[a] Some additional runs were made at 25° which introduced slight changes in some of the values previously published.

amounts to only about 0.1% so that even a 50% error would not change the absorption coefficient by more than 0.05%. The change of vapor pressure with total pressure on the liquid is given by the Poynting relationship[7]

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(7) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 183.

$$\left(\frac{dp}{dP}\right)_T = \frac{V}{v}$$

In this case p and P are the vapor pressure of water and the total pressure on the liquid, respectively, while V is the partial molal volume of water vapor and v that of water. Since the partial molal volumes are not known, the molal volumes were taken in each case. For the 100° isotherm the Callendar equation was assumed to represent the behavior of water vapor while for all others the perfect gas law was used. For the 100° isotherm the Poynting equation took the following form

$$A \ln \frac{P}{P_0} - B(p - p_0) = V_0(P - P_0) - aP^2 + bP^3 - cP^4$$ [8]

The data for the compressibility of water at 100° were taken from an extrapolation of the data of Bridgman.[9]

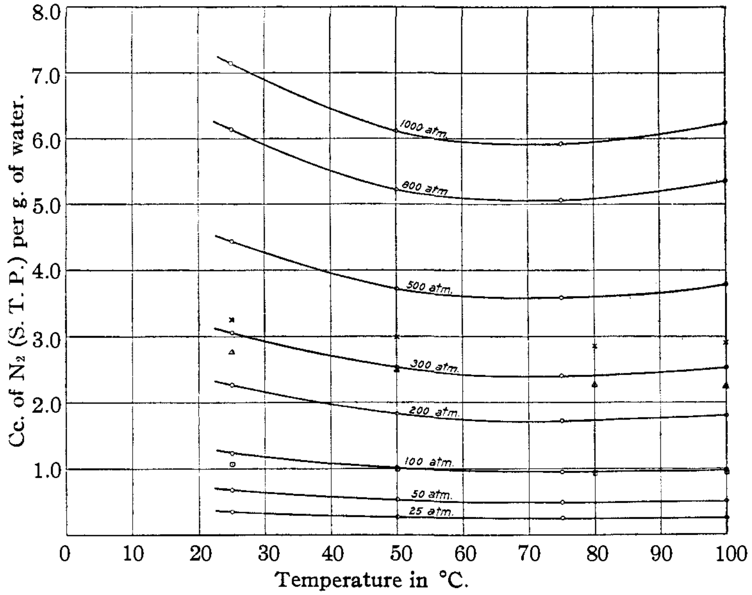

Fig. 2.—□, Goodman and Krase at 100°; △, Goodman and Krase at 200°; ×, Goodman and Krase at 300°.

The more recent data of Tammann[10] show a slightly different trend. The change of vapor pressure with total pressure has been discussed by Bartlett,[11] Lurie and Gillespie[12] and others. Bartlett measured the concentration of water vapor in compressed nitrogen and hydrogen in the presence of the condensed phase.

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(8) Dr. W. Edwards Deming suggested a convenient graphical method of solving this equation.

(9) Bridgman, "International Critical Tables," Vol. III, p. 40.

(10) Tammann and Rührenbeck, *Ann. phys.*, **13**, 63 (1932).

(11) Bartlett, This Journal, **49**, 65 (1927).

(12) Lurie and Gillespie, *ibid.*, **49**, 1146 (1927).

Isobars are plotted in Fig. 2. The data show a minimum at about 70° which becomes more pronounced as the pressure rises. The question of the actual existence of minima of solubility of gases in water has until quite recently been a controversial matter. Bohr and Bock[13] first found a minimum in the case of hydrogen, but their work was thought to have systematic errors.[14] Recently Ipatiew and co-workers[15] mention the possibility of a minimum for hydrogen between 65 and 75°. The minimum for helium that was thought to have been discovered by Estreicher[16] at about 25° has been discredited by Cady and associates[17] and more recently by Lannung.[18] Goodman and Krase[1] found a minimum for nitrogen but its location is not in very good agreement with the one in this work, as will be seen from Fig. 2. A comparison with the work of Frolich and associates was made previously.[3] Kuenen,[19] reasoning from the known behavior of mixtures, suggested that every gas should show a minimum of solubility and that for sparingly soluble gases this minimum should occur at low temperatures. The solubility of nitrogen in many organic substances increases with rise in temperature over the known range.[20] Figure 3 shows

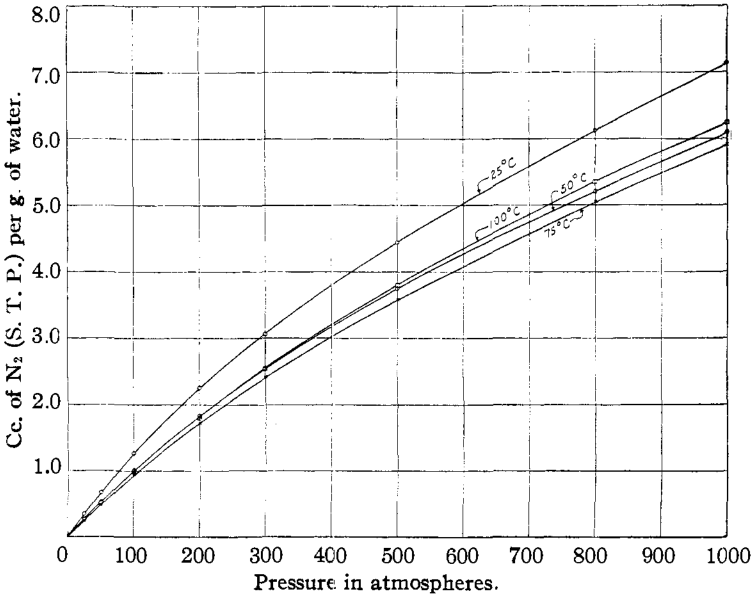

Fig. 3.

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(13) Bohr and Bock, *Wied. Ann.*, **44**, 318 (1891).

(14) Drucker and Moles, *Z. physik. Chem.*, **75**, 405 (1911).

(15) Ipatiew, Drushina-Artemowitsch and Tichomirow, *Ber.*, **65**, 568 (1932).

(16) Estreicher, *Z. physik. Chem.*, **31**, 176 (1899).

(17) Cady, Elsey and Berger, THIS JOURNAL, **44**, 1456 (1922).

(18) Lannung, *ibid.*, **52**, 68 (1930).

(19) Kuenen, *Proc. Roy. Soc. Edinburgh*, **23**, 312 (1900); Kuenen, "Verdampfung und Verflüssigung von Gemischen," Johann Ambrosius Barth, Leipzig, 1906, p. 82.

(20) Just, *Z. physik. Chem.*, **37**, 342 (1901).

more clearly the fact that at higher pressures the solubility of nitrogen at 100° is already greater than at 50°.

Figure 4 finally indicates the impossibility of predicting the solubility of gases at high pressures from any simple considerations. Henry's law

$$p = kc$$

where p is the partial pressure of the gas and c the concentration in the liquid does not hold as shown in Fig. 4. Substitution of fugacity for pressure actually makes the agreement worse at higher pressures. The dotted curve in Fig. 4 was calculated from the Ostwald absorption coefficient.

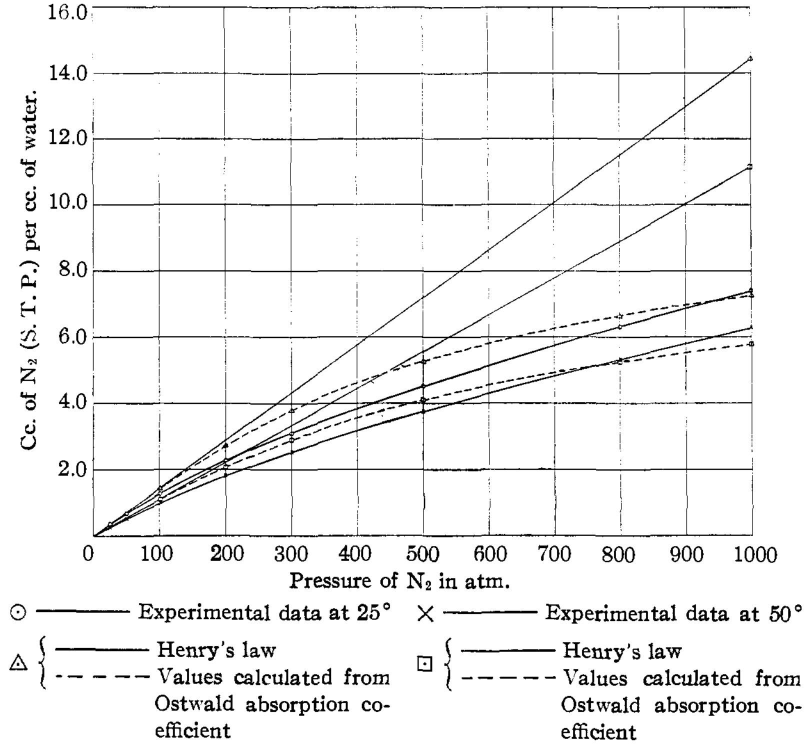

Fig. 4.

$$\lambda = \frac{\text{concn. in gas phase, g./cc.}}{\text{concn. in liq. phase, g./cc.}}$$

λ being obtained from the solubility at one atmosphere partial pressure.[21] The volume of water was corrected for compressibility, neglecting the solubility effect. The values calculated from the absorption coefficient are in much better agreement. The curves for 75 and 100° are not shown, but are of somewhat similar nature.

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(21) For calculation of the fugacities and densities of nitrogen, see Deming and Shupe, *Phys. Rev.*, **37**, 638 (1931).

Summary

A simple apparatus and method for obtaining solubilities of gases in water and similar liquids has been described.

The solubilities of nitrogen in water at 50, 75 and 100° from 25 to 1000 atmospheres were measured.

The absorption coefficient showed a distinct minimum at about 70° which became more pronounced with increase in pressure.

It has been shown that at present it is not possible to predict the solubility of nitrogen in water at high pressures from low pressure data with any degree of certainty.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE PHYSICAL LABORATORY, UNIVERSITY OF DENVER]

Luminescence and Crystalline Structure[1]

BY BYRON E. COHN

Many inorganic solids exhibit luminescence which may appear as fluorescence, phosphorescence or thermoluminescence. Small quantities of dissolved inorganic materials may confer upon these solids the ability to gather energy which may be emitted as luminescence. Such dissolved substances are termed activators. Lenard[2] has proposed the hypothesis that the absorbing and re-emitting center in luminescent solids consists of an atom or molecule of the activator linked with a definite number of solvent molecules. This investigator attributed each luminescence band to a different type of center. In recent years the hypothesis of Lenard has been transposed into a modified form in which it is stated that the manner of linkage of an atom of the activator with a definite number of solvent atoms occurs by substitution of the activator atom for one of the solvent atoms in a definite crystalline lattice.

Tiede and his co-workers[3] have presented some experimental evidence for the crystalline structure theory of luminescence. These workers find that the property of luminescence appears coincident with the occurrence of marked crystalline structure both in the case of calcium tungstate and boron nitride phosphors. On the other hand, Lenard and his students[4] stated that the Lenard phosphors (alkaline earth sulfides oxides or selenides) appear to be hardened glass-like materials. In view of the contradictory statements and the somewhat indirect evidence, information

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[1] Presented in part before the Physical and Inorganic Division at the 84th Meeting of the American Chemical Society, Denver, Colo., August 22 to 26, 1932.

[2] Lenard, *Sitz. Heidelb. Akad.*, 1917, 1918.

[3] Tiede and Schleede, *Z. Elektrochem.*, **29**, 305 (1923); Tiede and Tomaschek, *ibid.*, **29**, 303 (1923); Schleede, *Z. Physik*, **18**, 109 (1923).

[4] Pringsheim, "Fluorescenz und Phosphorescenz," Julius Springer, Berlin, 1928, p. 263.