Laboratory Note

Solubility of Nitrous Oxide in Water, 20–80 C

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Using a Van Slyke manometric apparatus, the solubility of nitrous oxide in water from 20 to 80 C was measured. Representative values for the Ostwald solubility coefficient are 0.693 at 20, 0.607 at 25, and 0.462 at 37 C, with standard errors 0.001 or less. All measured values were within 0.003 of those calculated from the third-degree polynomial curve which best fit the observed data. As expected for solubility of an inert gas in water, the data also very closely fit the equation $\log L = b_0 + b_1/T + b_2 \log T$, where T represents absolute temperature. (Key words: Nitrous oxide; Solubility; Ostwald solubility coefficient.)

MANY VALUES for solubility of nitrous oxide are available, but there are large discrepancies among them. Reported in the same journal in 1964 and 1965 are values of 0.367 and 0.478† for the Ostwald solubility coefficient of nitrous oxide in water at 37 C.[21,22] These inconsistencies led us to measure the solubility of nitrous oxide in water at 5-degree increments from 20 to 80 C. We have also reviewed the literature and catalogued solubility coefficients reported from 1855 to the present.

Methods

We designed a tonometer (fig. 1) from which water saturated with nitrous oxide could be transferred anaerobically into the extraction chamber of a Van Slyke–Neill manometric apparatus.† The procedure follows:

1) Water, twice distilled in glass, was freed of dissolved gas by boiling in a flask for 10 min and cooling under a vacuum.

2) By applying negative pressure to the tonometer gas outlet, gas-free water was aspirated from the flask through the tonometer pipette into the tonometer chamber previously filled with nitrous oxide. Initial temperature of the water was always lower than eventual temperature of saturation.

3) Nitrous oxide,§ entering through a sintered glass disc in the gas inlet, was bubbled through the water at 40–50 ml/min as the temperature rose toward that of the preheated, thermostatically controlled¶ water jacket.

4) When the water reached the temperature of saturation (t_s), measured with a mercury thermometer accurate to 0.1 C,** bubbling was continued an additional 20 min before analysis. The flow of nitrous oxide continued throughout this period and during the transfer of samples from the tonometer to the Van Slyke apparatus. The tonometer was shaken manually every 10 min during temperature equilibration and immediately before sampling.

5) For each determination, slightly more than 10 ml of saturated water was transferred through the tonometer pipette into the Van Slyke extraction chamber by lowering the mercury level slowly so that no air entered the tonometer through the open gas outlet. Prior to sealing the rubber-tipped pipette under mercury, the pipette was flushed with about 10 ml of saturated water. No bubbles entered the extraction chamber with the sample.

6) Sample size was measured against the 10-ml calibration line on the extraction chamber. Because water contracts with decreasing temperature, the extraction chamber was initially filled with more than 10 ml and the temperature allowed to fall to near 20 C, the temperature of calibration. Excess water was then emptied from the chamber to provide a 10-ml sample, and slight visual corrections in volume

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† Calculated from the Bunsen solubility coefficient.
‡ Arthur H. Thomas Company, Philadelphia, Penna., No. 3593-A, equipped with Thomas–Van Slyke–Folch absorption chamber No. 3599-Z.

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§ Ohio Medical Products, Madison, Wis.
¶ Heto Model T6K Circulator, The London Co., Cleveland, Ohio.
** Fisher Scientific Company, Pittsburgh, Pa., No. 15-00B.

were made for differences between actual and calibration temperatures. Thus, the volume of the sample was effectively measured at 20 C.

7) Nitrous oxide was extracted from the water by lowering the mercury column to expand the total volume of water and gas in the extraction chamber to 50 ml. The sample was agitated with a magnetic stirring bar for 3 min.

8) The water level was then raised gradually over 40–50 sec to the 10-ml calibration line and the manometer immediately read to within 0.2 torr, this pressure (P) related to the volume of extracted nitrous oxide. The temperature of extraction (t_e), accurate to within 0.1 C and almost always within 1 C of room temperature, was read from a mercury thermometer†† in the water jacket of the extraction chamber.

9) Blank pressure (P') was determined for every t_e by serially extracting gas from twice-distilled water in the Van Slyke apparatus, each time ejecting extracted gas from the chamber after reading the manometer at 10-ml gas volume. When three successive readings were identical, we assumed that all gas had been extracted. P', therefore, represented manometer zero plus pressure of water vapor at that temperature.

These manometric data permitted calculation of the volumes of dissolved gas in the samples. Constants and variables follow:

L, Ostwald solubility coefficient, defined as "the ratio of the volume of the absorbed gas to that of the absorbing liquid"‡
t_s, temperature of saturation
t_e, temperature of extraction
A, effective volume of extraction chamber
S, volume of liquid sample at 20 C
G, volume of gas in extraction chamber when pressure was measured
P, pressure reading after water vapor and extracted nitrous oxide were compressed to volume G at temperature t_e
P', pressure reading after water vapor was compressed to volume G at temperature t_e
B, barometric pressure
W, vapor pressure of water at t_s
L_e, Ostwald solubility coefficient at t_e

Volumes are expressed in ml, pressures in torr, and temperatures in degrees C.

We derived from Boyle's and Charles' Laws two formulas for transforming manometric to

†† Fischer Scientific Company, Pittsburgh, Pa., No. 15-00A.

volumetric data. Equation 4 was used when $t_e \neq t_s$, equation 8 when $t_e = t_s$.

The gas laws, with the left side of the equation representing conditions during saturation (subscript s), the right side conditions after extraction (subscript e):

$$\frac{P_s \times V_s}{T_s} = \frac{P_e \times V_e}{T_e} \quad (1)$$

where P is pressure, V volume, T absolute temperature. Substituting experimental variables for P, V, and T:

$$\frac{(B - W) \times L \times S}{t_s + 273.1} = \frac{(P - P') \times G}{t_e + 273.1} \quad (2)$$

Solving for L:

$$L = \frac{(P - P') \times G \times (t_s + 273.1)}{(B - W) \times S \times (t_e + 273.1)} \quad (3)$$

Correcting for nitrous oxide unextracted and remaining in solution:

$$L = \frac{(P - P') \times G \times (t_s + 273.1)}{(B - W) \times S \times (t_e + 273.1)}$$
$$\times \left(1 + \frac{L_e \times S}{A - S}\right) \quad (4)$$

Assuming $t_e = t_s$, $L_e = L$, and:

$$\frac{L \times (A - S)}{(A - S) + (L \times S)} = \frac{(P - P') \times G}{(B - W) \times S} \quad (5)$$

Inverting:

$$\frac{A - S}{L \times (A - S)} + \frac{L \times S}{L \times (A - S)}$$
$$= \frac{(B - W) \times S}{(P - P') \times G} \quad (6)$$

Solving for 1/L:

$$\frac{1}{L} = \frac{(B - W) \times S}{(P - P') \times G} - \frac{S}{A - S} \quad (7)$$

Establishing a common denominator and reinverting:

$$L = \frac{G \times (P - P') \times (A - S)}{S \times [(B - W) \times (A - S) - G \times (P - P')]} \quad (8)$$

Finally, we multiplied L by the ratio of specific gravity of water at t_s to specific gravity at 20 C to correct for having measured the volume of solution at 20 C rather than at t_s.[2]

Without this correction, solubility would have been overestimated by as much as 2.6 per cent at 80 C.

Both S and G were 10 ml for these experiments. A was found to be 49.15 ml by subtacting volume of the magnetic stirring bar from that of the extraction chamber. W at each t_s was read from appropriate tables,[3] while B was measured daily and corrected to 0 C.

Experiments in which $t_e = t_s = 20$ or 25 C were performed first, using formula 8 to calculate L for 20 and 25 C. Rectilinear interpolation between these temperatures, which bracketed all t_e, provided values of L_e for substitution in formula 4 to calculate L for t_s above 25 C.

Attempting to minimize both random and systematic error, we determined solubility at each t_s at least four times on each of two or more days. Conditions sometimes changed markedly, B as much as 11 torr, t_e as much as 3.2 C, and P′ as much as 4.8 torr.

Results

Results are listed in table 1 and plotted in figure 2.

The best-fitting third-degree polynomial equation relating solubility (L) to temperature (t), where $L = a_0 + a_1t + a_2t^2 + a_3t^3$, had the following coefficients:

$$a_0 = 1.161160589 \times 10^0$$
$$a_1 = -3.016537628 \times 10^{-2}$$
$$a_2 = 3.635864135 \times 10^{-4}$$
$$a_3 = -1.596736596 \times 10^{-6}$$

We chose a third-degree polynomial equation to represent the data, not because of theoretical considerations, but simply because it provided satisfactory fit and permits easy interpolation. The difference between observed and calculated solubilities (table 1) was no greater than 0.003 for any temperature, suggesting internal consistency of the measurements.

For theoretical reasons, we also fit the data to the equation

$$\log L = b_0 + b_1/T + b_2 \log T,$$

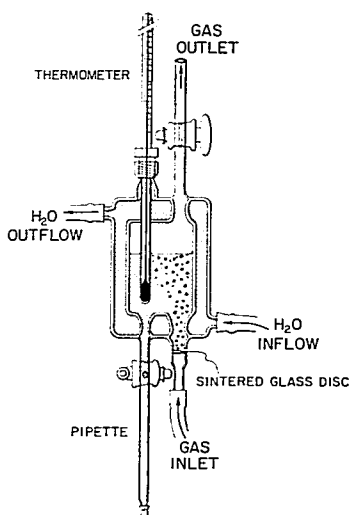where T represents absolute temperature. Coefficients were

FIG. 1. Tonometer designed for direct transfer of solutions to the extraction chamber of the Van Slyke apparatus.

$$b_0 = -7.497753348 \times 10^1$$
$$b_1 = 4.165337781 \times 10^3$$
$$b_2 = 2.456672318 \times 10^1$$

The variance ratio, $F = 41,472$, for the multiple linear regression, with two and ten degrees of freedom for greater and lesser mean squares, respectively, indicates exceptionally good fit. The solubilities of inert gases in water should follow this equation.[4]

Discussion

Figure 2 illustrates the results of more than a century of investigation of the solubility of nitrous oxide in water. The general pattern of solubility is clear, although there are wide individual variations. Our values tend to fall in middle ground.

The first to report solubility of nitrous oxide was Carius, who in 1855 published absorption coefficients for water at approximately 4 C increments from 2.5 to 24 C. A student

TABLE 1. Solubility of Nitrous Oxide in Water

Temperature (C)	Observed Ostwald Solubility Coefficient (L)		Number of Determinations	Ostwald Solubility Coefficient Calculated from Third-degree Polynomial Equation (Lc)	L − Lc
	Mean	SE			
20	0.693	0.001	20	0.691	0.002
25	0.607	0.001	12	0.609	−0.002
30	0.538	0.000	17	0.540	−0.002
35	0.482	0.000	13	0.482	0.000
37				0.462	
40	0.435	0.000	12	0.434	0.001
45	0.396	0.000	11	0.394	0.002
50	0.365	0.001	13	0.362	0.003
55	0.334	0.001	11	0.336	−0.002
60	0.316	0.000	9	0.315	0.001
65	0.298	0.000	12	0.298	0.000
70	0.282	0.001	12	0.283	−0.001
75	0.269	0.000	14	0.270	−0.001
80	0.259	0.000	11	0.257	0.002

of Bunsen, Carius fit his data to a second-degree polynomial equation, expressing solubility in terms of temperature, calculating coefficients to within 0.016 of observed values, and expanding six measured values into a table from which coefficients could be read throughout the range 0–25 C.[5, 6]

During the subsequent 81 years, 11 reports on the solubility of nitrous oxide in water appeared.[7–17] Each used modifications of Bunsen's and Ostwald's technique in which a known volume of gas-free liquid was saturated with gas from a reservoir of known volume. Isobaric and isothermal reduction in this volume during saturation was considered to represent gas absorbed by the liquid.

In 1937, Orcutt and Seevers first used a manometric method to determine solubility of gases in liquids. They showed how mathematically derived constants, without using empirically derived constants, could be made during Van Slyke analysis for gas not extracted from the solvent. Reporting few data, they emphasized that their purpose was to demonstrate the method and not to apply it in the most precise manner possible.[18] We have developed techniques of handling samples and analyzing data to facilitate application of the approach of Orcutt and Seevers.

Nunn, in 1958, used the Van Slyke apparatus to determine solubility of nitrous oxide in several solvents, including water. Instead of subtracting a blank pressure from the manometric reading at 2-ml gas volume following extraction, he expelled the extracted nitrous oxide from the chamber without losing solution and took a second reading at 2-ml gas
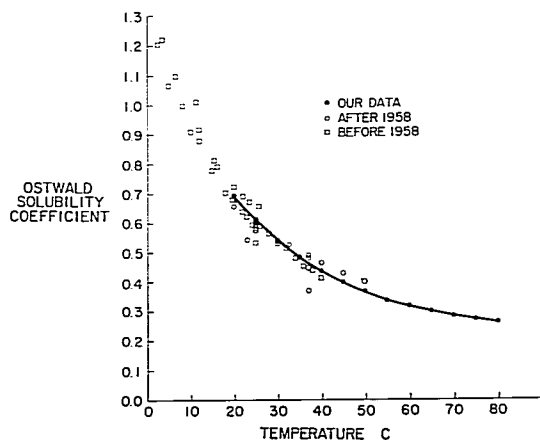

FIG. 2. Ostwald solubility coefficients for nitrous oxide in water, comparing our data with published values of others. The curve represents the third-degree polynomial equation which best fits our data.

TABLE 2. Ostwald Solubility Coefficients for Nitrous Oxide in Water

Temperature (C)	Carius, 1855*	Gordon, 1845*	Roth, 1897*†	Knopp, 1904*	Geffcken, 1904*	Siebeck, 1909*	Findlay et al., 1910*	Findlay et al., 1911*	Kunerth, 1922*	Manchot et al., 1924,1934	Killian, 1929*	Orcutt et al., 1937*	Markham et al., 1941*	Nunn, 1958*	Sy et al., 1961*	Bergstedt et al., 1965*	Stahlman et al., 1968*	Christoforides et al., 1970*
0.2 / 2.5 / 3.5	1.205		1.220										1.298					
5.0 / 6.4 / 8.1 / 8.2	0.999	1.012	1.100		1.067													
10.0 / 12.0	0.880		0.918		0.910													
15.0 / 15.5 / 15.8 / 16.2 / 18.0	0.792	0.811	0.813		0.778				0.703									
20.0 / 21.7 / 22.0 / 23.0 / 23.5 / 24.0 / 21.7	0.721 / 0.655	0.670	0.688 / 0.632	0.673	0.676	0.620			0.675 / 0.638 / 0.617		0.676			0.540			0.657	
25.0 / 26.0 / 28.0					0.591		0.592	0.585	0.587 / 0.561	0.531		0.599	0.589				0.591	0.612
30.0 / 32.0 / 32.5 / 31.0									0.530 / 0.513 / 0.478							0.538 / 0.525		
36.0 / 37.0 / 38.0						0.436			0.449						0.367	0.487	0.444	0.478
40.0													0.410			0.462		
45.0																0.425		
50.0																0.400		

* Calculated from Bunsen coefficients.
† Averages of two sets of data at slightly different temperatures.

volume, which he subtracted from the first. Nunn's Ostwald solubility coefficient of 0.540 at 23 C falls considerably below all other published values near that temperature (table 2 and fig. 2).[20] Additional nitrous oxide might have been extracted as pressure was reduced for the second reading at 2 ml. This would have led to a lower solubility coefficient, owing to a smaller difference between the first and second readings. To assure that blank pressure embodies only manometer zero plus vapor pressure of the solvent, multiple extractions should be carried out until no change in pressure occurs with further extraction.

Six years later, Sy and Hasbrouck attempted to apply Nunn's approach, coming up with another Ostwald coefficient which was well below the values reported by others (table 2 and fig. 2). They saturated water at 37 C with nitrous oxide, extracted and manometrically measured the volume of the gas at 25–28.5 C in a Van Slyke apparatus, and inappropriately calculated solubility with Nunn's formula, which requires that temperature of extraction equal temperature of saturation.[20, 21] Using Sy and Hasbrouck's published data, we were unable either to verify their basic calculations or to compute, correcting for differences

between temperatures of saturation and extraction, a solubility coefficient more in keeping with the findings of others.

Borgstedt and Gillies, in 1965, used gas chromatography to measure solubility of nitrous oxide in water between 30 and 50 C. Their solubility coefficients are equal to ours at 30 C but diverge with rising temperatures to become almost 10 per cent greater than ours at 50 C.[22] We suspect an error in method for converting integrated detector output to solubility, but their calculations are not described in sufficient detail for critical evaluation.

Using a Scholander apparatus for volumetric absorption, Saidman and colleagues[23] measured solubilities of several volatile and gaseous anesthetic agents. Their values for the Ostwald solubility coefficients of nitrous oxide in water at 20, 25, and 37 C are as much as 5 per cent lower then ours.[23] In contrast are the recent findings of Christoforides and Hedley-Whyte, who saturated water with about 74 per cent nitrous oxide at 25 and 37 C and found, using Van Slyke analysis, solubilities as much as 3.5 per cent greater than ours.[24]

Error in our results should be well below 0.5 per cent. Volumes measured in our Van Slyke extraction chamber are accurate to ± 0.01 ml at 10 ml and ± 0.1 ml at 50 ml.†† Maximum variation in A (± 0.1 ml) could lead to no more than 0.04 per cent error, while maximum variation in either S or G (± 0.01 ml) could theoretically lead to error of as much as 0.1 per cent in solubility. However, since G appears in the numerator and S in the denominator when calculating solubility, systematic errors in reading these volumes tend to cancel each other.

With Van Slyke analysis, two corrections must be considered: first, for volume of gas which cannot be extracted by negative pressure alone, for which we mathematically accounted in our formulas; second, for volume of gas which may redissolve when extracted gas is compressed for reading pressure. To show that no measurable amount of nitrous oxide redissolved in this study, we read pressure first at volume of extraction and then, without reextraction, at 10 ml. Volume of extraction

was 39.15 ml. i.e., volume of the extraction chamber reduced by that of the magnetic stirring bar (0.85 ml) and sample (10 ml). There were no consistent differences between solubilities calculated for the same sample from pressures read at 39.15 ml and 10 ml, respectively, showing that no nitrous oxide redissolved upon reducing volume to 10 ml.

Because gas pressures at 10 ml were four to five times those at volume of extraction, we could read pressure more precisely at 10 ml. This was manifested by smaller standard deviations in extracted volumes calculated from pressures read at 10 ml than at 39.15 ml. Therefore, we report only solubilities calculated from pressures read at 10 ml.

The hydrostatic head of the solution can theoretically increase gas tension on the floor of a tonometer. With our tonometer full, P_{N_2O} at the pipette outlet might have been underestimated by as much as 4.5 torr, causing as much as 1.1 per cent overestimation of the solubilities in some samples. The effect, however, would have been most apparent in the first sample withdrawn after refilling the tonometer, the subsequent five or six determinations becoming progressively less affected. We saw no such orderly progression as the tonometer was emptied, suggesting that this factor did not influence the results.

Neither was there an increase in measured solubility with time, attesting that saturation of the water with N_2O was complete by the time of initial sampling from the tonometer after 20 min of bubbling.

A potential source of error in solubility measurements is contamination of the test gas. Upon completion of this study, we asked the manufacturer to analyze contents of the approximately half-empty E cylinder from which we had taken nitrous oxide. The only contaminants were water, 75 ppm, oxygen, 50 ppm, and nitrogen, 200 ppm. (See Appendix for complete analysis.) Because water was the solvent studied, it can be ignored. In the temperature range under consideration, solubility of nitrous oxide is 10 to 40 times that of either oxygen or nitrogen,[25] making it unlikely that these gases contributed to the solubilities observed.

Solubility coefficients in this report are actually defined in terms of volume of solution rather than in terms of the "absorbing liquid" referred to in Ostwald's definition, since we have not corrected for expansion of solution produced by dissolved nitrous oxide. Measuring changes in density of solution before and after saturation with gas, Markham and Kobe[19] estimated that solubility may be underestimated by as much as 0.1 per cent because of volume changes caused by dissolved gas.

Assuming the correction to be negligible, we have not attempted to correct for alteration in the vapor pressure of water produced by dissolved nitrous oxide.

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Appendix*

Analysis of Nitrous Oxide E cylinder for Trace Contaminants

Test	Detectable Limit	Result
Carbon monoxide	1.0 ppm	None detected
Nitric oxide and nitrogen dioxide	0.1 ppm	None detected
Halogens	0.1 ppm	None detected
Carbon dioxide	10.0 ppm	None detected
Alkalinity (NH₃)	1.0 ppm	None detected
Water (vapor and liquid)	0.1 ppm	75 ppm
Oxygen (vapor phase, 70 F)	5.0 ppm	50 ppm
Nitrogen (vapor phase, 70 F)	5.0 ppm	200 ppm

* References 6 through 24 constitute a chronologic listing of reports on solubility of nitrous oxide in water published from 1855 to the present.

* Laboratory Report No. 2682, dated November 2, 1971, from Ohio Medical Products, 1177 Marquette Street, N.E., Cleveland, Ohio 44114.