Solubilities of Oxygen, Argon, and Nitrogen in Distilled Water

by Everett Douglas

Scripps Institution of Oceanography, La Jolla, California[1,2]   (*Received August 26, 1963*)

The solubilities of oxygen, argon, and nitrogen in distilled water from 5 to 30° have been determined microgasometrically with an estimated accuracy in α of ± 0.25 to 0.5%, dependent on the solubility of the gas. Comparison of the present results with those from previous workers show the oxygen values to be in good agreement with those of Winkler, whose values have been substantiated by Steen, Elmore and Hayes, and Klots and Benson, while the nitrogen values fall between those of Hamberg, Fox, and Adeney and Becker, but indicate those of Klots and Benson to be somewhat high. The argon values agree with those of Klots and Benson.

Introduction

In reviewing the literature for gas solubilities in distilled water, one is impressed by the nonconformity of values reported by various workers. Until recently, the values of Winkler[3,4] as used in the "Handbook of Chemistry and Physics"[5] and the values of Fox[6,7] were considered the standard values for oxygen. Fox's values are some 1–2% higher than Winkler's. Truesdale, Downing, and Lowden,[8] in determining the solubility coefficient for oxygen, reported values 4% lower than the accepted values. Since then the solubilities of oxygen have been redetermined and checked by different workers[9–13] using gasometric and titrimetric techniques of analysis, all agreeing within $\pm 1\%$ of the values of Winkler. Nitrogen has received less attention since it does not lend itself to titrimetric analysis. Fox's values[6,7] have been more or less accepted as the standard, with Winkler's values[14] lower and Hamberg's[14] higher. Since then several workers have redetermined the solubility values for nitrogen with resulting inconsistency of values still prevailing.[14–16]

Of the major atmospheric gases, argon has received the least attention. The various attempts show little uniformity with one another.[13,17–22]

The method as described below is similar to that used by Steen with several modifications. In view of these, a detailed description is given, although some parts will necessarily appear repetitive. The present microgasometric method has an estimated accuracy of $\pm 0.25\%$ for O_2 and Ar and $\pm 0.5\%$ for N_2.

Experimental

Principle of Method. The method takes advantage of the fact that the ratio of absorbed gas volume to

(1) Contribution from the Scripps Institution of Oceanography, University of California, San Diego, Calif.

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(3) L. W. Winkler, *Ber. Deut. Chem. Ges.*, **22**, 1764 (1889).

(4) L. W. Winkler, *ibid.*, **24**, 89 (1891).

(5) "Handbook of Chemistry and Physics," 39th Ed., Chem. Rubber Publ. Co., Cleveland, Ohio, 1957.

(6) C. J. Fox, *Intern. Hydrog. Comm. Publication de Circonstance* No. 41 (1907).

(7) C. J. Fox, *Trans. Faraday Soc.*, **V**, 68 (1909).

(8) G. A. Truesdale, A. L. Downing, and G. F. Lowden, *J. Appl. Chem.*, **5**, 53 (1955).

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(10) H. Steen, *Limnol. Oceanog.*, **3**, No. 4, 423 (1958).

(11) H. L. Elmore and T. W. Hayes, *J. Sanit. Eng. Div. Am. Soc. Civil Engrs.*, **86**, 44 (1960).

(12) J. C. Morris, W. Stumm, and H. A. Galal, *ibid.*, **87**, 81 (1961).

(13) C. E. Klots and B. B. Benson, *J. Marine Res.*, **21**, 48 (1963).

(14) J. H. Coste, *J. Phys. Chem.*, **31**, 81 (1927).

(15) W. E. Adeney and H. G. Becker, *Sci. Proc. Roy. Dublin Soc.*, **XV**, No. XLIV, 609 (1919).

(16) T. J. Morrison and F. Billet, *J. Chem. Soc.*, 3821 (1952).

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

(18) L. W. Winkler, *ibid.*, **55**, 345 (1906).

(19) A. von Antropoff, *Proc. Roy. Soc.* (London), **A83**, 474 (1910).

(20) A. Lannung, *J. Am. Chem. Soc.*, **52**, 68 (1930).

(21) T. J. Morrison and N. B. Johnstone, *J. Chem. Soc.*, 3441 (1954).

(22) H. Von König, *Z. Naturforsch.*, **18a**, 363 (1963).

liquid volume is constant at a given equilibrium pressure. In contrast to other methods, equilibration is rapid, 30 min., and takes place in a closed system under constant temperature and pressure. Gas-free water is brought into contact with pure gas and after equilibration the amount of gas absorbed by the water is measured volumetrically with a micrometer buret. This ratio gives α when the gas volume is reduced to $0°$.

Preparation of Gas-Free Water. Double-distilled water is boiled in a 500-ml. Pyrex suction flask for approximately 1 hr. The mouth of the flask is stoppered, leaving the side arm open for the steam escape, ensuring that no air is in contact with the boiling water. The water, still boiling, is drawn up into a syringe and the needle stoppered. A 10-cc. glass-tip syringe fitted with a blunt-tipped No. 23 needle is inserted through a vaccine stopper in a glass tube leading into the boiling water (Fig. 1a) and flushed several times to rid the dead space of any gas bubbles. The syringe is then filled with the

boiling water. Three syringes are filled from one boiling and stored in a pan of $90°$ water, thus preventing atmospheric contamination.

Apparatus. The absorption apparatus used (Fig. 1b) is modified from a 0.5-cc. analyzer.[23] It consists of only one side arm, enlarged to deliver approximately 4 cc. of water, to the main absorption chamber of 5-cc. capacity. The rubber stopper is replaced with a small polyethylene plug which is inserted tightly into the capillary of the side arm (Fig. 1c). This completely eliminates elasticity from the system. The water bath is thermoregulated within $±0.01°$ using a Bronwil regulator and all analyses are made in a constant temperature room.

Procedure. Filling the side arm with gas-free water involves having G and D filled with mercury (Fig. 1d), H, the thermobarometer, with water, and the stopcock S-1 closed prior to removing the plug, E. S-2 is in position I. The plug is now removed. No displacement of mercury will occur at this point. The sample syringe is taken from the storage pan and the stopper removed from the needle. The needle is fitted with a short polyethylene tubing adapter and inserted into the side arm (Fig. 1e). S-2 is now turned to position II and S-1 is opened. The side arm is flushed and left filled with gas-free water. S-2 is turned back to position I with S-1 remaining open. The needle is removed and the plug re-inserted. The gas-free sample is now in the side arm. The absorption chamber, G, is filled with mercury to the top of the capillary and the compensating chamber, H, is half-filled with water. A conventional gas-transfer pipet is filled with the pure gas and seated on the capillary. The gas meniscus is pulled down to the mark on the capillary, the micrometer connected to the leveling bulb, position III, and set to zero (V_0) and connected back to position I. To prevent pressure differences in the micrometer, the leveling bulb is always leveled with the mercury in the absorption chamber G. After about 20 micrometer units (mm.) of the gas is drawn into the absorption chamber, the transfer pipet is removed and the water sucked off, leaving an indicator drop in the capillary isolating the gas from the air in H.[24] S-1 is positioned and closed.

The volume of the gas is read (V_1) after approximately 2 min. when it remains constant. The gas-free water is then tilted in from the side arm.[25] Rapid mechanical shaking is then begun, avoiding bubble
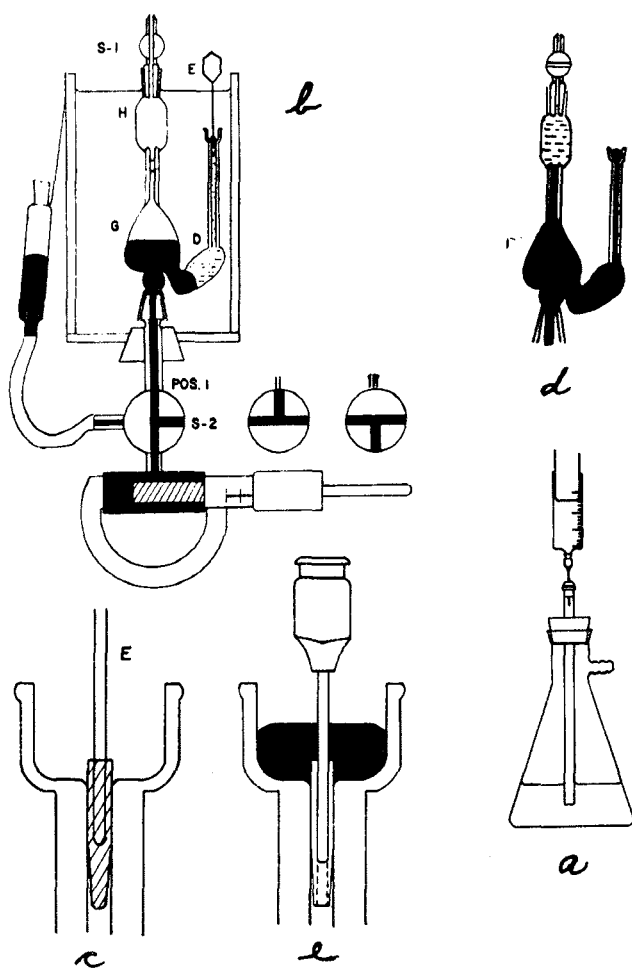

Figure 1.

(23)   P. F. Scholander, *J. Biol. Chem.*, **167**, 235 (1947).

(24)   For a detailed description, refer to the original paper.[23]

(25)   This is accomplished by first lowering the water level in the bath and then tilting in the sample water. The water bath level is then appropriately adjusted. The whole operation requires less than 15 sec.

formation, and the indicator drop kept at the mark on the capillary by screwing in the micrometer.

Absorption equilibrium is complete after about 15 min., but shaking is continued for 30 min., after which the volume of gas is read (V_2). Stopcock S-1 is now opened and removed, the indicator drop brought up and carefully drawn off by suction, and the gas expelled by screwing in the micrometer until the lower gas meniscus is at the mark for the reading V_3.[26]

The volume of the water, V_4, is measured by replacing it with mercury from the micrometer. This reading involved five repeated fillings of the micrometer and a common final reading is around 100 mm. Temperature measurements were made using a thermometer calibrated against two certified standards.

Calculation of Data. The equation used for the determination of α is

$$\alpha = \frac{\text{volume of gas absorbed (STPD)}}{\text{volume of water} \times \text{atmospheres of pure gas}}$$

or

$$\alpha_{\circ C.} = \frac{(V_1 - V_2)\left(\dfrac{B - b - w}{760}\right)\left(\dfrac{273}{273 + \,^\circ C}\right)}{(V_4)\left(\dfrac{B - b - w}{760}\right)}$$

where B is the uncorrected barometric reading, b is in brass correction units, and w is the vapor pressure of water. This equation is then reduced to its final form

$$\alpha_{\circ C.} = \frac{(V_1 - V_2)(273)}{(V_4)(273 + \,^\circ C.)}$$

It is a significant advantage that with this method, the equilibration pressure remains constant and therefore need not be known.

Results and Discussion

Oxygen. The present results for oxygen are shown in Table I and compared with the values of previous

Table I: Experimental Solubility Coefficients of Oxygen[a]

	Temperature, °C.	
8.00	19.94	29.15
0.03984	0.03095	0.02651
.03990	.03098	.02654
.03986	.03098	.02655
.03978	.03100	.02653
.03981	.03092	.02651
Av. .03984	.03097	.02653

[a] α is defined as the volume of gas (STPD) absorbed by a unit volume of water when the pressure of the gas is 760 mm.

workers in Table II. The greatest range of consecutive values at any single temperature was only 0.3% of α, showing the method to have good precision.

Figure 2 (top) shows the per cent difference of previous α values of oxygen from those presently obtained. The present values are in good agreement with those of Winkler and of most other workers, although Fox's values, which are used in "Standard Methods,"[27] are definitely higher, and those of Truesdale, *et al.*, are much lower except at the 29° mark. It is important to note the close agreement between the various workers from 5 to 20°, but from there the values begin to diverge. This would tend to indicate that 30° is the limiting temperature for some of these methods. It appears from the present determinations and previous work that Winkler's solubility values for oxygen as given in the handbook should remain the standard values.
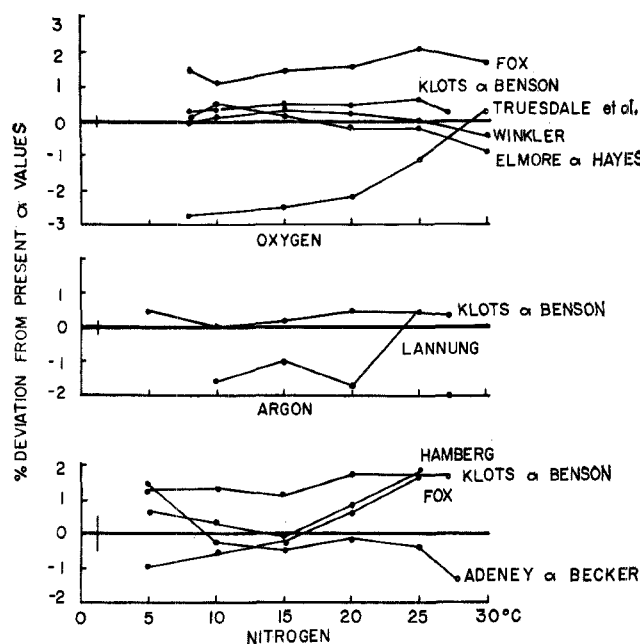

Figure 2.

Argon. Since the solubility coefficient for argon varied greatly between workers, analyses were made at 5° intervals from 5 to 30°. These results are shown in Table III and contrasted with those of the other workers in Table IV. The largest spread in consecutive argon

(26) In most cases V_3 is 0.000 on the micrometer although small amounts of water trapped on the chamber wall at the start would sometimes account for a reading of 0.010 to 0.015 for V_3. This could be ignored as it entered in the calculation of α in no way.

(27) "Standard Methods," 10th Ed., Waverly Press, Inc., Baltimore, Md., 1955.

Table II: Comparison of Previous α Values of Oxygen with Those Presently Obtained

| | Temperature, °C. | | | | | | |
	0	5	10	15	20	25	30
Winkler (1889)	0.04889	0.04287	0.03802	0.03415	0.03102	0.02831	0.02608
Fox (1909)	.04924	.04321	.03837	.03455	.03144	.02890	.02665
Truesdale, et al. (1955)	.04765	.04173	.03698	.03320	.03027	.02800	.02629
Elmore and Hayes (1960)	.04930	.04315	.03816	.03412	.03088	.02824	.02597
Klots and Benson (1963)	....	.04303	.03814	.03423	.03111	.02848	....
Present	....	....	.03797	.03403	.03095	.02830	.02620

Table III: Experimental Solubility Coefficients of Argon

| | Temperature, °C. | | | | |
4.62	10.00	15.04	20.00	25.20	29.70
0.04744	0.04178	0.03746	0.03407	0.03111	0.02895
.04741	.04169	.03749	.03399	.03115	.02907
.04748	.04182	.03753	.03407	.03112	.02900
.04749	.04182	.03750	.03405	.03115	.02898
.04747	.04189	.03751	.03408	.03114	.02905
Av. .04746	.04180	.03750	.03405	.03113	.02901

The comparison of the solubility coefficients of nitrogen, Fig. 2 (bottom), shows the present values to be in close agreement with those of Hamberg, Fox, and Adeney and Becker from 5 to 25°, where the values begin to diverge. The values of Klots and Benson remain systematically 1.5% higher.

Table VIII gives the α values of nitrogen from 3 to 30° as taken from a smooth curve.

Sources of Error. 1. Boiling water for 60 min., as

Table IV: Comparison of Previous Argon Values with Present Values

| | Temperature, °C. | | | | | | |
	0	5	10	15	20	25	30
Estreicher (1899)	0.05780	0.05080	0.04525	0.04099	0.03790	0.03470	0.03256
Winkler (1906)	.0530	....	.0420	....	.0350	....	.0300
Antropoff (1910)	.0561	....	.0438	....	.0379	....	.0348
Lannung (1930)	....	....	.0411	.0371	.0336	.0314	.0289
Morrison and Johnstone (1954)	....	....	.0417	.0367	.0335	.0308	.0282
König (1963)	....	.0353	.0328	.0302	.0263	....	....
Klots and Benson (1963)	....	.04713	.04182	.03759	.03421	.03137	....
Present	....	.04689	.04180	.03753	.03405	.03123	.02888

values was 0.4% experienced at 30 and 10°, while the others remained approximately 0.2%.

The present argon values are compared with previous values in Fig. 2 (middle). It is sufficient to say that the range of values among the various workers is wide. The present values are in good agreement with those of Klots and Benson.

Table VII lists the α values of argon from 5 to 30°. These were taken from a smooth curve fitted through the experimental points.

Nitrogen. Ten consecutive analyses of nitrogen solubilities were made at 7.83, 19.95, and 29.50° with checkpoints at 3.10 and 11.68°. A greater number of nitrogen values were determined at individual temperatures because of its lower solubility. The results for nitrogen are shown in Table V and compared with previous values from other workers in Table VI. The range in values for nitrogen was 1%.

Table V: Experimental Solubility Coefficients of Nitrogen

| | Temperature, °C. | | | |
3.10	7.83	11.68	19.95	29.50
0.02191	0.01953	0.01812	0.01556	0.01349
.02197	.01966	.01816	.01565	.01348
.02187	.01961	.01812	.01553	.01349
	.01957	.01817	.01559	.01363
	.01959	.01823	.01550	.01352
	.01951		.01557	.01351
	.01959		.01555	.01356
	.01956		.01559	.01356
	.01965		.01561	.01359
	.01963		.01561	.01359
Av. .02192	.01959	.01816	.01558	.01354

described, leaves no detectable amount of gas in solution. To confirm this, 10 cc. of the boiled samples was

Table VI: Comparison of Previous Nitrogen Values with Present Values

	Temperature, °C.						
	0	5	10	15	20	25	30
Hamberg[a]	0.02379	0.02105	0.01881	0.01703	0.01570	0.01468	....
Fox[a]	.02319	.02068	.01863	.01702	.01572	.01465	....
Winkler[a]	.02312	.02050	.01829	.01656	.01518	.01410	....
Adeney and Becker (1919)	....	.02122	.01870	.01696	.01555	.01435	0.01327
Morrison and Billet (1952)	....	....	....	.01743	.01595	.01481	.01377
Klots and Benson (1963)	....	.02118	.01899	.01724	.01584	.01466	....
Present	....	.02091	.01875	.01705	.01557	.01441	.01345

[a] These values were taken from Coste, ref. 14.

Table VII: Argon Values Interpolated from a Smooth Curve

Temp., °C.	α	Temp., °C.	α
3	.....	17	0.03604
4	.....	18	.03535
5	0.04689	19	.03468
6	.04584	20	.03405
7	.04473	21	.03342
8	.04369	22	.03284
9	.04272	23	.03228
10	.04180	24	.03174
11	.04086	25	.03123
12	.04000	26	.03074
13	.03915	27	.03027
14	.03833	28	.02981
15	.03753	29	.02934
16	.03677	30	.02888

Table VIII: Nitrogen Values Interpolated from a Smooth Curve

Temp., °C.	α	Temp., °C.	α
3	0.02198	17	0.01642
4	.02143	18	.01612
5	.02091	19	.01584
6	.02042	20	.01557
7	.01996	21	.01532
8	.01952	22	.01507
9	.01912	23	.01484
10	.01875	24	.01462
11	.01839	25	.01441
12	.01805	26	.01421
13	.01771	27	.01401
14	.01737	28	.01383
15	.01705	29	.01364
16	.01673	30	.01345

vacuum-extracted over mercury in a 500-cc. chamber, and showed that no gas remained in solution.

2. Diffusion of gas across the indicator drop was investigated. No net movement of the gas occurred across the drop over a period of 60 min., approximately twice the time limit of equilibration.

3. Complete saturation of the samples was verified by plotting % saturation vs. time, showing that the samples are from 90 to 98% saturated after 7 min. for argon, and 10 min. for nitrogen (Fig. 3). Equilibration time was set at 30 min. to allow for complete saturation.
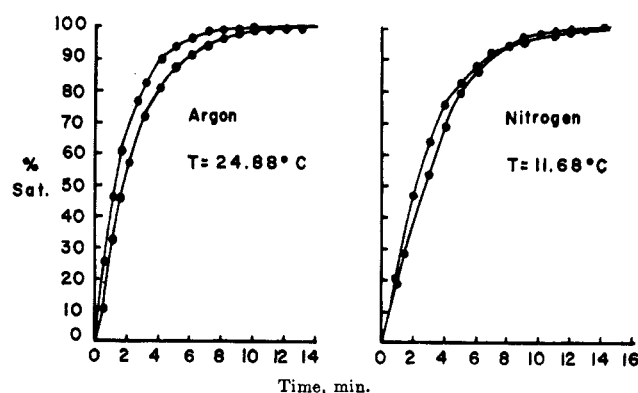

Figure 3.

4. The purity of the nitrogen and argon used was determined on a mass spectrometer, showing the nitrogen to contain 0.04% oxygen and less than 0.03% argon. The argon contained less than 0.1% nitrogen and less than 0.01% CO_2. The purity of oxygen was determined using the Scholander 0.5-cc. analyzer and microgasometric analyzer,[28] each showing the oxygen to be at least 99.5% pure.

Estimation of Accuracy. A temperature uncertainty of 0.05° causes an error of less than 0.02% in the values of α. The temperature is known, however, within 0.02°. The micrometer can be estimated to 0.001 mm. using a hand lens. The critical micrometer readings are those of V_0, V_1, and V_2. These three readings could lead to a ±0.15% discrepancy in α. The volume of

(28) P. F. Scholander, L. VanDam, C. L. Claff, and J. W. Kanwisher, *Biol. Bull.*, **109**, 328 (1955).

water measured by five stepwise micrometer readings is so large in relation to the others that only a negligible error of 0.04% in α can be introduced here. The temperature differential between the water bath and room temperature could account for a maximum change in α of 0.5%. In practice, however, the maximum error is 0.05% of α, experienced only at the very low temperature determinations. Assuming maximal additive errors, this gives a ±0.26% uncertainty in the determinations.

The Kinetics of Some Oxidation–Reduction Reactions

Involving Manganese(III)[1]

by H. Diebler[2] and N. Sutin

Chemistry Department, Brookhaven National Laboratory, Upton, New York   (Received August 27, 1963)

The kinetics of several oxidation–reduction reactions involving manganese(III) have been studied spectrophotometrically by the use of a flow technique. The free energies of activation for the oxidation of various substituted tris(1,10-phenanthroline) complexes of iron(II) by manganese(III) in perchloric acid and in pyrophosphoric–sulfuric acid media were found to be linearly related to the standard free energy changes of the reactions. The application of the Marcus theory to the reactions of manganese(III) with iron(II) and with various substituted iron(II)–phenanthroline complexes and to the reaction of cobalt(III) with manganese(II) in perchloric acid leads to an estimate of about $10^{-4}\ F^{-1}$ sec.$^{-1}$ for the rate constant of the manganese(II)–manganese(III) electron exchange reaction at 25.0°. Attempts to determine the rate constant for this exchange by a radioactive tracer method were unsuccessful.

Whereas numerous studies of the kinetics of oxidation–reduction reactions have been reported in recent years, very few have dealt with the reactions of manganese(III) in perchloric acid.[3] The paucity of data on such reactions is probably due to the belief that free manganic ions cannot exist in significant concentrations in aqueous solution.[4] Nevertheless, perchloric acid solutions of manganese(III) have been used in a few oxidation–reduction studies. For example, Adamson[5] has studied the electron exchange reaction between manganese(II) and manganese(III) in perchloric acid

while Ogard and Taube[6] have used perchloric acid solutions of manganese(III), prepared by the reaction

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) Chemistry Department, Stanford University, Stanford, California.

(3) For recent reviews of electron transfer reactions, see, for example: (a) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959); (b) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961); (c) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).

(4) W. A. Waters, *Quart. Rev.* (London), **12**, 296 (1958).

(5) A. W. Adamson, *J. Phys. Chem.*, **55**, 293 (1951).