

SOLUBILITY RELATIONS IN GAS-LIQUID SYSTEMS. IV*

THE SOLUBILITY OF OXYGEN IN WATER AS FOUND BY AN ANALYTICAL METHOD

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This investigation was undertaken to answer two important questions,

- (a) Are the results of analytical methods the same as those obtained by a method depending upon the measurement of the loss of volume of a gas when brought into intimate contact with water? and,
- (b) Is the amount of a gas dissolved by a liquid dependent upon the hydrostatic pressure in the liquid as well as upon the gaseous pressure?

Method

An Erlenmeyer flask (250 cc.) (A) and an iodine flask (300 cc.) (B) were fitted with two-hole rubber stoppers. Glass tubing and rubber tubing for flexibility connected the flasks (A) and (B). Both flasks were filled with gas free distilled water. About one-third of the water was displaced from (A) by inverting the flask while oxygen was being passed in. By inverting (B) in the same manner and continuing to pass oxygen through the apparatus, about one half of (B) was emptied.

By shaking both flasks in a thermostat, at 25°C., oxygen still passing through, saturation was obtained under the same conditions in both flasks. After fifteen minutes of saturation, flask (B) was filled by inverting (A) thereby forcing water from (A) into (B).

The iodine flask (B) was calibrated so that when the stopper was inserted the content of the flask was known.

Reagents—

48 grams $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in 100 cc. distilled water (E & A “tested purity”).

50 grams NaOH (by alcohol) in 100 cc. distilled water.

Saturated solution of KI in distilled water. (E & A “tested purity”).

New solution for each determination.

Sulfuric acid, 9 Molar from B & A, pure concentrated acid.

Standard thiosulfate—the sodium thiosulfate solution was standardized against twice recrystallized potassium dichromate.

Procedure

Five cubic centimeters of potassium iodide solution were added from a pipette, delivery being at the bottom of the flask. This enabled the saturated solution to remain at the bottom due to its heavy specific gravity. Five cubic

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centimeters of sodium hydroxide solution were added to the flask in the same manner as the potassium iodide. Five cubic centimeters of the manganese sulfate solution were introduced next. A creamy precipitate formed immediately in the bottom of the flask on addition of the latter reagent. The creamy precipitate which was formed, gradually changed to dark brown due to the oxidation by the oxygen dissolved in the water. Before disturbing the flask, the stopper was inserted. This was done in such a manner that no air bubble was caught in the flask but that it was completely filled with liquid and precipitate. The flask was shaken for five minutes to ensure complete mixing of the precipitate with the solution. The precipitate settled very quickly. Shaking was repeated until the precipitate had been shaken and settled three times. After a period of an hour after the last settling, the solutions were acidified with ten cubic centimeters of sulfuric acid. The acid was introduced into the flasks by pipette, delivery being made near the bottom, so as to cause as little stirring as possible and thereby preventing the precipitate from reaching the surface by agitation and being oxidized further by the oxygen in the air. The stopper was again inserted and the flask shaken to mix the acid with the solution. After standing five minutes, the stopper was removed and one hundred cubic centimeters of the iodine solution was drawn off by pipette. The solution remaining on the stopper was washed into the flask. The iodine was titrated with standard sodium thiosulfate. The titration was completed using starch as an indicator. The number of grams of oxygen equivalent to 1 cc. of the standard thiosulfate were known. From this was calculated the number of grams of oxygen in solution.

The formula for calculation is as follows:

$$q' = \frac{\text{Grams of O}_2}{\text{cc. of Thiosulfate} \times \text{equivalent to 1 cc. Thiosulfate} \times 760 \times \text{Flask Capacity}} \\ \frac{1}{[\text{Flask Capacity} - 100 \text{ cc.}] \times \left[\frac{\text{Barometer}}{\text{corrected}} - \text{v.p.} \right] \times [\text{Flask Capacity} - \text{reagents added}]}$$

q' = weight of gas in grams absorbed by 1000 cc. of solvent at a definite temperature and a partial pressure of 760 mm.

Approximate concentrations in flask

NaOH = 0.20 M

MnSO₄·4H₂O = 0.15 M

H₂SO₄ = 0.6 M

KI = 4%

Discussion

The Winkler Method¹ for the determination of oxygen in air dissolved in water is the fundamental principle of this method. The concentrations of reagents, and general procedures have been modified to eliminate the errors when a higher concentration of oxygen is present. By varying the concentrations, it was found that the concentrations recommended herein were the amounts which would give results which could be relied upon. The high concentration of potassium iodide is essential in order to keep the iodine liberated

¹ L. W. Winkler: Ber., 21, 2843 (1888); 22, 1764 (1889).

from vaporizing. Vaporization causes a considerable loss if these high concentrations are not used, due to the large amount of iodine liberated in the determination. The odor of iodine is very evident when lower concentrations of potassium iodide are used.

When the iodine had been liberated, the flask was disturbed as little as possible. The liquid was not stirred too violently during titration in order that iodine would not be lost by vaporization. This precaution was recommended by Theriault.¹

The 15 cc. of reagents added to the flask up to the time the precipitate forms must be subtracted from the total volume of the flask. The one hundred cubic centimeters of iodine solution which was taken from the flask just before titrating with the thiosulfate was also subtracted. It was found that the reagents did not contain sufficient oxygen to interfere with the determination.

While the precipitate was settling, the gutter around the stopper of the iodine flask was filled with water to prevent any air seeping between the stopper and the walls of the flask.

Care had to be taken that no air bubble was in the flask after the reagents were added and the precipitate was formed. If air had entered it would increase the value of the solubility of the oxygen due to further oxidation of the precipitate.

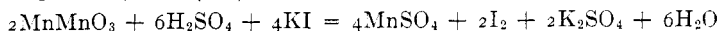
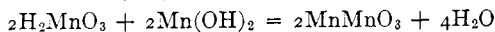
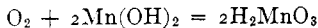
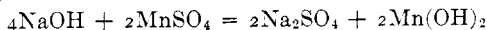
TABLE I
Oxygen Solubility in Distilled Water at 25°C.

Cubic Centimeters of Thiosulfate O ₂ equal to 1 cc. of Thiosulfate	Capacity of flask	Barometer Corrected	Grams O ₂ per liter q'
(0.001577 g.)			
48.06	307.8	749.7	.04084
47.87	307.8	747.6	.04080
47.60	307.8	748.2	.04054
47.82	307.8	747.7	.04075
47.25	307.8	746.8	.04083
47.85	307.8	745.2	.04092
49.63	307.8	758.7	.04092
(0.001676 g.)			
46.53	307.8	758.0	.04086
46.67	307.8	757.8	.04079
46.40	307.8	757.6	.04072
46.47	307.8	757.0	.04082
46.53	307.8	756.6	.04089
		Av.	.04080
		a.d.	.0473
		A.D.	.0421

¹ Theriault: Pub. Health Bull., No. 151 (1925).

The purpose of constructing the simple apparatus for saturation was to make certain that at no time was any oxygen saturated water, allowed to flow from one vessel to another unless in an atmosphere of oxygen and that atmosphere under a pressure at which the saturation took place. When a siphon was used, it was found that there was a loss of oxygen amounting to approximately three per cent.

Equations:



When the value $q' = 0.04080$ is compared with the result $q' = 0.04047$ of Morgan and Pyne¹ it was found that the analytical method gives results which compare favorably with the physical measurements.

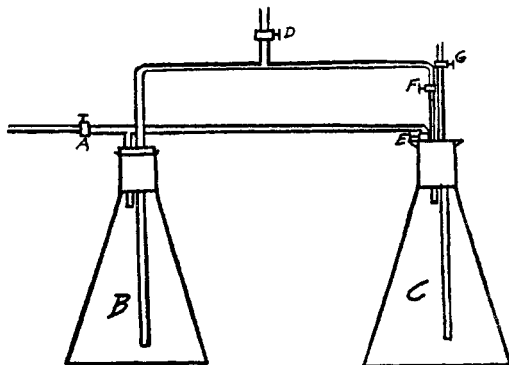


FIG. 1

The Solubility of Oxygen at Pressures Lower than Atmospheric

Henry's Law has always been taken as an approximation in the cases of most gases. Little experimental evidence has been evinced for its validity although many investigations have been carried out. Here an analytical method will be applied to the solubility of oxygen at pressures less than atmospheric in pure water.²

An apparatus (Fig. 1) was designed whereby the liquid could be saturated by shaking at a measured pressure less than atmospheric. The apparatus was designed in such a way that the liquid could be transferred from one vessel to another in an atmosphere of oxygen and under the pressure at which it was saturated. Although in Fig. 1, only glass connections are shown, rubber tubing was used in the connections between the flasks B and C. This enabled the flasks B and C to be shaken; or either to be inverted.

¹ Morgan and H. R. Pyne: *J. Phys. Chem.*, **34**, 1818 (1930).

² Henry: *Gilb. Ann.*, **20**, 147 (1805).

TABLE II
Solubilities of Oxygen in Water at Pressures less than 760 mm.

Partial Pressure of Oxygen	Grams O ₂ per liter q	l	K = G/P
174.7	0095	3158	5438
202.2	0107	3073	5292
240.7	0128	3088	5318
242.5	0128	3065	5278
280.7	0150	3103	5344
300.3	0160	3094	5328
349.0	0184	3062	5272
364.1	0196	3126	5383
396.1	0210	3079	5302
413.7	0220	3088	5318
433.3	0227	3042	5239
440.5	0233	3072	5290
446.7	0235	3055	5261
458.3	0243	3079	5302
478.1	0254	3085	5313
504.8	0265	3049	5250
511.4	0273	3107	5338
539.7	0283	3045	5244
559.3	0295	3063	5277
577.7	0303	3046	5252
610.2	0325	3093	5320
614.6	0327	3090	5320
639.7	0337	3059	5268
649.2	0342	3059	5268
738.7	0387	3042	5239
741.1	0394	3087	5317
741.1	0393	3080	5303
	Av.	3077	5299
	a.d.		.0319
	A.D.		.0440

Flasks B (250 cc.) and C (300 cc., another iodine flask) were filled with gas free water. This was siphoned into the flask with as little exposure to the air as possible. The apparatus was filled with oxygen before placing the flasks in position. At first the flasks were sealed at the stoppers with collodion but it was found that this was not necessary. The rubber stopper gave sufficient airtightness. Stopcock E was closed. Oxygen was allowed to enter through A forcing water from B to C. About one third of the volume of B was emptied. The water escaped from flask C at G which was open. Then E was opened and F closed. About half the water from C was allowed to escape through G. E was opened. Our system was then at atmospheric

pressures. Suction was placed on A to the approximately desired pressure. Stopcock D led to the manometer. This was opened while suction was applied to A, thus the approximate pressure could be determined. Flask B and C were shaken in the thermostat. The liquids were allowed to come to equilibrium and the manometer was read. With E and F open, B was inverted and the contents of the flask B allowed to fill flask C. E and F were closed. Flask C was removed from the apparatus. The reagents were immediately added as described above.

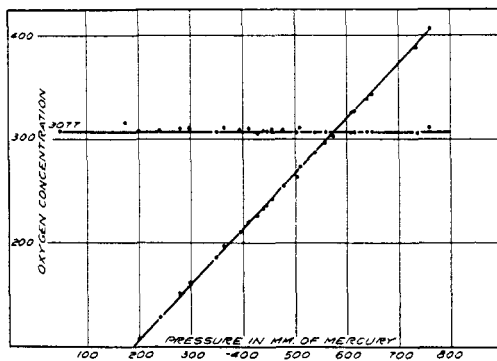


FIG. 2
The Solubility of Oxygen at 25°

In Table II, the last column gives the constant which is obtained by dividing the grams of oxygen per liter by the pressure at which the solution was saturated. It will be observed that the values obtained are constant. In column labelled "1" gives the Ostwald Coefficient which should be constant if Henry's Law is holding. The values are calculated by the following formula:

$$1 = \frac{224 \times 298 \times 760 \times q}{3200 \times 273 \times P}$$

It will be observed that there is an A.D. of 0.00004. These values may be considered to be a constant.

When pressure is plotted against solubility in grams per thousand cc., it is evident from Figure 2 that a linear relationship exists. When the Ostwald solubility coefficient is plotted against pressure the straight line obtained is parallel to the pressure axis. Therefore from experimental data, oxygen obeys Henry's Law when pressures are considered between 175 mm. and 760 mm.

Hydrostatic Pressure

When a bubble of gas is introduced under a column of water, the pressure when the bubble is released at the bottom of the column is more than the pressure when the bubble reaches the top of the column of water. Winkler¹

¹ J. W. Winkler: Ber., 22, 1764 (1889).

suggested that hydrostatic pressure entered into the solubility relationship, considering half the height of the column of water plus the atmospheric pressure as the pressure under which the solution was saturated.

Glass tubing of bore 1.7 cm. was attached to iodine flasks. Through this tubing was an inner tube of 0.5 cm. bore for conducting the gas to the bottom of the iodine flask. At the bottom of the outer tube was attached a smaller length of tubing of the same bore. The shorter length, about 15 cm. long, was connected to the longer length by gum rubber tubing. A rubber stopper was placed at the lower end of the shorter length of tubing which was inserted in the mouth of the iodine flask. Screw clamps were used at the rubber connections to prevent the water in the column from running out on disconnecting the flask. A battery of four columns and flasks were used for one saturation.

The columns and flasks were carefully filled with gas-free water and an even flow of oxygen was regulated in all flasks for a period of twenty hours bubbling up through the column. The heights of the liquids in the columns were measured, the flasks removed and oxygen content determined as recommended above.

Instead of introducing the sodium hydroxide before the manganese sulfate solution, it was found that less error was introduced by adding the manganese sulfate solution first. A noticeable evolution of gas occurred when NaOH was added, since the solution was supersaturated at the atmospheric pressure. If sodium hydroxide solution was added as the last reagent before closing the flask, there was little opportunity for the oxygen to escape, as the bubbles rose too slowly. All the reagent could be added before the bubbles reached the neck of the flask, allowing the stopper to be inserted before any oxygen could escape. Results of the experiments are given in Table III.

The column headed "temp" gives the temperature at which the water was saturated. It will be noticed that the temperatures are in groups of four. These four determinations were saturated at the same time and for the same length of time. The second column gives the pressure exerted by the column of water above the flask. The pressure of the column of water has been expressed in millimeters of mercury. The column of water was measured from the top of the flask to the level of the water in the column. The third column gives the pressure exerted by the column of water plus the atmospheric pressure minus 760 mm. This column really represents the pressure on the system in excess of standard pressure. Column four gives the actual grams of oxygen dissolved in one liter of water at the total pressure on the system. The pressure is really the pressure given in column three plus 760 mm. Column five gives the grams of oxygen at 760 mm. expressed as q' . This value was calculated from the corresponding value in column four, using Henry's Law. In column six, q' , is the value of the solubility of oxygen at the corresponding temperature as calculated from other data. By comparing the values of column five and six, it can be seen that the agreement is exceedingly close. In the column next to the last, the Ostwald coefficient is tabulated, as cal-

TABLE III
Effect of Hydrostatic Pressure on the Solubility
of Oxygen in Water at 25°C.

Temp.	MM of Hg	Total pres. -760	Grams O ₂ per liter	Grams O ₂ at 760 q'	q'	l	l
15.2	60.2	55.4	05438	05016	04873	3833	3335
15.2	95.7	90.9	05478	04865	04873	3717	
15.2	106.1	101.3	05582	04898	04873	3743	
15.2	165.9	161.2	05889	04891	04873	3737	
16.6	78.3	41.8	05346	04847	04741	3704	3623
16.6	132.1	95.6	05306	04520	04741	3454	
16.6	138.7	102.2	05441	04601	04741	3516	
16.6	163.5	127.0	05881	04840	04741	3698	
17.2	69.1	59.0	05198	04765	04677	3641	3574
17.2	107.6	97.5	05193	04549	04677	3476	
17.2	134.0	124.9	05553	04715	04677	3603	
17.2	158.7	148.6	05806	04803	04677	3670	
19.2	61.4	34.1	04890	04524	04507	3457	3444
19.2	107.0	79.7	05046	04423	04507	3380	
19.2	134.8	107.5	05305	04506	04507	3365	
19.2	165.0	137.7	05564	04511	04507	3447	
20.2	60.2	36.8	04716	04370	04427	3339	3383
20.2	117.2	93.8	05024	04352	04427	3326	
20.2	132.8	109.4	05036	04287	04427	3276	
20.2	148.3	124.9	05106	04272	04427	3264	
20.4	54.6	44.9	04796	04579	04412	3499	3371
20.4	106.8	97.1	05065	04441	04412	3394	
20.4	125.5	115.8	05193	04457	04412	3406	
20.4	154.0	144.3	05454	04451	04412	3401	
20.6	72.8	42.6	04796	04377	04404	3345	3371
20.6	127.2	97.0	05043	04320	04404	3301	
20.6	129.0	99.6	04972	04247	04404	3245	
20.6	161.7	131.5	05271	04346	04404	3321	
21.0	92.4	72.7	04926	04392	04365	3357	3335
21.0	98.7	79.0	04966	04395	04365	3358	
21.0	127.8	108.1	05056	04328	04365	3307	
21.0	153.8	134.1	05111	04251	04365	3248	
21.0	52.8	37.0	04684	04380	04365	3347	3335
21.0	85.4	69.6	04826	04339	04365	3316	
21.0	133.9	118.1	05123	04355	04365	3328	
21.0	150.9	135.1	05209	04346	04365	3321	
21.5	40.9	21.5	04580	04346	04327	3321	3314
21.5	74.2	47.7	04741	04320	04327	3301	
21.5	131.3	104.8	05078	04330	04327	3309	
21.5	149.8	123.3	05186	04332	04327	3310	

culated from the preceeding data. It will be observed that there is pronounced agreement between the Ostwald coefficient as calculated from the hydrostatic pressure data and the Ostwald coefficient from other data.

In Fig. 3, the pressure of the column of water in millimeters of mercury when measured from the top of the flask is plotted against α , the Ostwald coefficient at the temperature indicated. These points give a straight line

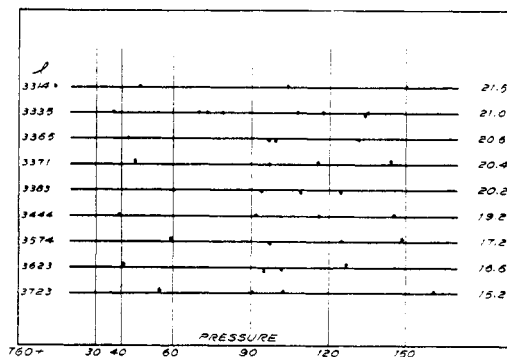


FIG. 3
Effect of Hydrostatic Pressure on Oxygen Solubility

for each temperature, parallel to the pressure axis. From these solubilities with varying heights of water above, it can be concluded that the solubility of oxygen is proportional to the hydrostatic pressure above the solution providing there is no mixing.

Due to the small-bore tubing, mixing of the water in the column with the water in the flask was very slight. Since the error in these determinations is larger than when the solubility is determined at atmospheric pressure, it seems highly probable that the mixing although slight would cause this larger error. The saturations were not conducted in a thermostat. Slight error would be introduced by this in one direction or another as equilibrium could not be reached if there was a sudden change in the temperature. There were little changes in temperature although local drafts might cause a slight variation. The error is not sufficiently large to prevent arriving at the conclusions.

Winkler was correct in assuming that the solubility at a greater depth was larger than at the surface of a liquid, for the hydrostatic pressure acts in the same manner on the solubility of gases as the atmospheric pressure. In vessels where we have mixing, it is not necessary however to take one half the hydrostatic pressure and add it to the atmospheric pressure in calculating the solubility. In cases of mixing, the height of the water column is considered zero. When a column of liquid two and a half meters in height was saturated, it could be seen that the difference in the amount of oxygen in the bottom of the column and that at the top was very small. Even when means were taken

to prevent undue stirring this difference was small. With even the slightest stirring the solubility difference between the top and the bottom seemed quite small. With a flask ten centimeters high, the height of the column would have little effect on the solubility. This is especially true when the oxygen is dissolved in the water by shaking methods. The part that is supersaturated in respect to the atmospheric pressure thereby establishes an equilibrium with the atmospheric pressure thereby losing its excess oxygen. Since there is no more oxygen available to saturate the lower layers, the lower layers become of the same composition as the upper layers and there is a uniform concentration of oxygen saturated at atmospheric conditions.

Summary

An analytical method for the determination of the solubility of pure oxygen has been developed. This is a modification of the Winkler Method using oxygen instead of air. Larger concentrations of reagents are necessary for the determination of the solubility of oxygen than in the Winkler Method. With small concentrations lower values for the solubility of oxygen were obtained. The proper concentrations have been determined for high concentrations of oxygen in solution.

The solubility for oxygen in water has been determined at 760 mm. and 25°C. by the modified method and found to be 0.04080 grams of oxygen per liter of water. The value is in agreement with values by other workers who measured the loss of volume of the gas when brought into intimate contact with water.

The solubilities of oxygen in water at pressures from 175 mm. to 760 mm. at 25°C. have been determined and found to conform to Henry's Law.

The solubility of oxygen in water was found to be proportional to a column of water above it, thereby making the solubility proportional to the hydrostatic pressure exerted by this column of water.

Appended is a bibliography where analytical methods have been used for the determination of oxygen existing in the air dissolved in water.

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