

# ON THE SOLUBILITY OF PURE AND ATMOSPHERIC NITROGEN IN DISTILLED AND SEA WATER

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The solubility of nitrogen in pure water has been investigated by several workers whose results are not very concordant. The case of sea water with its varying salt content has been studied by some of these workers with still less satisfactory agreement.

A very useful critical survey of then available data was made in 1886 by Hamberg<sup>1</sup> who wrote

"Da ich während der Expedition des Freih. von Nordenskiöld, 1883, ein kleines Material von Bestimmungen des Stickstoffgases in Meerwasser gesammelt hatte, musste ich zu deren Verwerthung einige Normalbestimmungen haben um sie damit zu vergleichen. Je mehr ich in die Kritik von Bunsen's, Dittmar's und Tornoë's Bestimmungen hineinkam, desto mehr wurde ich überzeugt, dass diese ganze Frage einer Revision bedürfe. Unter anderem hielt ich es für nothwendig, nicht nur die Wirkung der Temperatur, sondern auch die des Salzgehaltes auf die Menge des Stickstoffgases zu untersuchen."

Notwithstanding the considerable amount of work which has been done since 1886 those who need exact data will, like Hamberg, conclude that the whole question needs revision. In the following I have tried to discuss and collate the data available.

## The Effect of Argon on the Solubility of Atmospheric Nitrogen

The complication introduced by argon in absorptiometric determinations of the solubility of nitrogen seem first to have been realised by C. J. Fox<sup>2</sup> who, in 1907, discussed the question and deduced an expression for evaluating the error due to the greater solubility of argon than nitrogen. Bohr and Bock<sup>3</sup> and Winkler<sup>4</sup> in 1891 were unaware of the existence of argon, which was discovered in 1894. Winkler,<sup>5</sup> in 1901, referred to his work as being on atmospheric nitrogen and in a foot-note said "Unter atmosphärischem Stickstoff soll der, aus Luft dargestellte, Argon u. s. w. haltige Stickstoff verstanden werden." He does not seem to have realised that an error was thereby introduced into his results. The error is peculiar to the absorptiometric method in which a finite volume of water is agitated with a small, finite volume of gas. The

<sup>1</sup> Hamberg: J. prakt. Chem., **33**, 433 (1886). "Beiträge zur Chemie des Meerwassers."

<sup>2</sup> C. J. J. Fox: "On the Coefficients of Absorption of Nitrogen and Oxygen in Water and Sea Water and of Atmospheric Carbonic Acid in Sea Water." Trans. Faraday Soc., **5**, 68, (1909) and Internat. Hydrog. Comm. Publication de Circonstance, No. 41 (1907).

<sup>3</sup> Ch. Bohr and J. Bock: Wied. Ann., **44**, 318 (1891). "Bestimmung der Absorption einiger Gase in Wasser bei den Temperaturen zwischen 0° und 100°."

<sup>4</sup> L. W. Winkler: Ber. **24**, 3602 (1891). "Löslichkeit der Gase in Wasser."

<sup>5</sup> L. W. Winkler: Ber., **34**, 1408 (1901).

presence in the gas of two constituents of varying solubilities leads to the final equilibrium being obtained between water and a gas containing less of the more soluble than the original mixture. Two definite values may be desired, either the solubility of atmospheric nitrogen  $\alpha'$  or that of pure nitrogen  $\alpha_N$ . What is actually found in the absorptiometric experiment is something between the two,  $\alpha$ . Of these three values,  $\alpha'$  is the highest.

Fox gives an expression for the value of  $\alpha' - \alpha$  in any absorptiometric experiment in which the composition of the gas experimented with, and the ratio of volumes of gas to water =  $k$  are known. Substituting the proper numerical values and using  $\alpha_A$  at  $0^\circ = 0.0578$  and  $\alpha_N$  at  $0^\circ = 0.0230$  (Fox) we get

$$\alpha' - \alpha = 0.00001418/k + 0.0582$$

$k$  = volume of residual gas/volume of liquid. A few values of .1000 ( $\alpha' - \alpha$ ) which will be the correction in millilitres of gas for a litre of liquid are given below.

$k = 0$	.1	.2	.5	1.0	10
1000 ( $\alpha' - \alpha$ ) = 0.1243	0.09	0.05	0.02	0.01	0.001
Percentage error 1.06	0.39	0.22	0.09	0.04	0.004

In actual working the error would never reach the maximum value nor fall as low as the lowest given, since one could not use an experiment in which all the gas was absorbed nor measure with sufficient accuracy a volume of gas many times that of the liquid. It will be noted however that in the method of working by saturation of the liquid with an unlimited volume of gas and boiling off or pumping out the gas  $\alpha' - \alpha = 0$  that is the true absorption coefficient of the gaseous mixture is obtained. What, however, is the absorption coefficient of the pure gas, nitrogen =  $N_2$ ?

Fox shows, and indeed it is obvious, that

$$\alpha_N = \alpha' - 0.01185\alpha_A/0.098815$$

[0.01185 and 0.98815 being respectively the volumes of argon and nitrogen in one volume of atmospheric nitrogen]. Since  $\alpha_A$  = about  $2.45\alpha$  and  $\alpha'/\alpha_N$  we can simplify this to

$$\alpha_N = 0.9827 \alpha'$$

with an error of not more than, say,  $1/1000$ . We see therefore that the error, due to argon of an absorptiometric experiment cannot exceed 1% of the value determined and that the difference between the true values for  $N_2$  and atmospheric nitrogen is about 100 ( $1 - .9827$ ) or say 1.7 percent within a wide range of temperature. We can now consider actual results.

### Atmospheric Nitrogen in Distilled Water

Table I shows the results obtained by various workers from Bunsen down to Fox.

TABLE I

One litre of distilled water absorbs from atmospheric nitrogen at a pressure of 760 mm + tension of aqueous vapour millilitres of the mixed gas according to

At a temper- ature of °C	Bunsen	Dittmar	Hamberg	Bohr and Bock	Winkler	Fox
0	20.35	24.40	24.21	(23.88)	23.54	23.59
+5	17.94	21.62	21.42	(21.53)	20.86	21.03
10	16.07	19.43	19.15	(19.56)	18.61	18.95
15	14.78	17.65	17.37	(17.86)	16.85	17.31
20	14.03	16.18	15.98	(16.39)	15.45	15.98
25	—	14.95	14.94	(15.04)	14.34	14.89

Bunsen's<sup>1</sup> results are clearly inaccurate. As I wrote in 1918 his "work stands alone as that of a pioneer and cannot be criticized like that of other workers."<sup>2</sup>

Dittmar<sup>3</sup> was a careful worker but I am inclined to think that there were too many unprotected rubber joints in his apparatus. Most of his results are distinctly higher than those of the others. Hamberg saturated water with air and used a very good gas-extraction and gas-measuring apparatus. He considered air to contain 79.05% of the mixture he called nitrogen. Neither his results or Dittmar's are affected by error due to argon since in a bubbling process of saturation  $k$  is very large. Bohr and Bock used both absorptiometric and boiling-out methods but their results are not easily amenable to correction. Winkler's absorptiometric results given in Table I are not those he published but are corrected for the value of  $k$  which was fairly constant at  $1/4$ . The figures are taken from Landolt and Börnstein, Fifth edition, p. 765, Table 131b (1923). I have satisfied myself that the corrections are of the order required by Fox's expression. Fox's values are those given in Landolt and Börnstein and calculated from his values for the "nitrogen" in air. It will be seen that above 5° Hamberg and Fox agree well and the following rounded figures are probably fairly trustworthy.

One litre of water at	10°	15°	20°	25°C
dissolves	19.0	17.3	16.0	14.9ml.
	of atmospheric nitrogen.			

The disagreement between various workers at the lower temperatures is very remarkable. I note that the only tables given now in Landolt and Börnstein are Winkler's and Fox's, recalculated as above mentioned.

<sup>1</sup> R. Bunsen: "Gasometry" (Trans. H. Roscoe, 1857).

<sup>2</sup> J. H. Coste: J. Soc. Chem. Ind., 36, 846 (1917). The "Absorption of Atmospheric Gases by Water."

<sup>3</sup> W. Dittmar: "The Challenger Expedition, Report on Chemistry and Physics."

### Pure Nitrogen in Distilled Water

The only persons who appear to have determined directly the solubility of  $N_2$  in water are Braun<sup>1</sup> and Adeney and Becker.<sup>2</sup> Adeney and the late H. G. Becker published a few values incidentally in one of their papers on the rates of absorption. All the other workers used "nitrogen" from air and heated copper or air and phosphorus all but Fox and Winkler, believing this to be nitrogen. Fox corrected in some way to pure nitrogen but his results given on p. 73 of his paper (Faraday Society edition) do not agree with his correct formula for obtaining  $\alpha_N$  already mentioned.

In Table II Fox's results for atmospheric nitrogen calculated to  $\alpha_N$  by his formula are taken from Landolt and Börnstein. They differ from his published figures as will be seen; but those I have recalculated are certainly correctly reduced. Winkler's results are from the same source and Hamberg's figures have been multiplied by 0.9827.

TABLE II

One litre of distilled water absorbs from  $N_2$  at a pressure of 760 mm + tension of aqueous vapour millilitres of the gas.

According to	At 0°	5°	10°	15°	20°	25°
Hamberg	23.79	21.05	18.81	17.03	15.70	14.68
Winkler (L and B)	23.12	20.50	18.29	16.56	15.18	14.10
Fox (L and B)	23.19	20.68	18.63	17.02	15.72	14.65
Fox (paper)	23.00	20.64	18.54	16.84	15.54	14.43
Braun		21.73	20.03	17.89	16.21	14.32
Adeney and Becker		20.80	18.60	17.01	15.60	14.45

I have graphically interpolated Adeney and Becker's values which it will be seen agree well with Fox's and Hamberg's. Braun's results agree with those of no other worker.

We now come to the case of greatest practical interest, that of

### Atmospheric Nitrogen in Sea Water

Only four workers appear to have interested themselves in this matter and of these two, Dittmar and Tornøe left only the most casual record of the salt content of the water they used. Tornøe said he used a sea water of somewhat high density whilst Dittmar's artificial sea water was prepared" so as to represent about an average Challenger water." Hamberg, commenting on this uncertainty, informs us that he himself used waters of 1.7784%, 2.6580% and 3.5126% content of total salts whilst Fox used made up sea water containing about 7.5, 15.20 and 23 per mille Cl'. Hamberg used the following expressions

<sup>1</sup> L. Braun: Z. physik. Chem., **33**, 721 (1900). "Über die Absorption von Stickstoff und von Wasserstoff in wässrigen Lösungen verschieden dissociierter Stoffe."

<sup>2</sup> W. E. Adeney and H. G. Becker; Proc. Roy. Dublin Soc. (2) **15**, 44, 609 (1919). "The Determination of the Rate of absorption of Atmospheric Nitrogen and Oxygen by Water."

Water of salt content	Absorbs at 760 mm dry air pressure and the temperature to form atmospheric air the quantity of nitrogen in ccs.	
0.0%	19.139	$- 0.48616 t + 0.009307 t^2 - 0.000006353 t^3$
1.0%	17.712	$- 0.42828 t + 0.0078736 t^2 - 0.000005362 t^3$
2.0%	16.446	$- 0.38260 t + 0.0068794 t^2 - 0.000004698 t^3$
3.0%	15.342	$- 0.34922 t + 0.0063180 t^2 - 0.000004360 t^3$
3.5%	14.851	$- 0.33720 t + 0.006200 t^2 - 0.000004313 t^3$

and gave a table for the nitrogen content of water of these salinities for each degree of temperature from  $-3^\circ$  to  $+25^\circ$ . Fox used the following expression in calculating a table for atmospheric nitrogen at a dry pressure of 760 mm for each  $4^\circ$  from  $0^\circ$  to  $28^\circ$  and for each 4 parts of Cl' per thousand from 0 to

$$1000\alpha = 18.639 - 0.4304 t + 0.007453 t^2 - 0.0000549 t^3 \\ - \text{Cl}' (0.2172 - 0.007187 t + 0.0000952 t^2)$$

In order to compare the results of these two workers I have calculated from Knudsen's relationship—total salt content =  $1.805 \text{ Cl}' + 0.03$  the Cl' content corresponding to the salt contents for which Hamberg has given values and used Fox's correcting term for Cl' for the  $4^\circ$  intervals selected by this worker. The results are given in Table III.

TABLE III

Number of millilitres of atmospheric nitrogen absorbed from air at a pressure of 760 mm + tension of aqueous vapour by water of the salinity or chlorions content indicated at temperatures between  $0^\circ$  and  $24^\circ$ .

S‰	Cl'‰	0°	4°	8°	12°	16°	20°	24°
0.00	H	19.14	17.34	15.81	14.53	13.48	12.63	11.95
	F	0.00	18.64	17.02	15.63	14.45	13.45	12.59
10.00	H	17.71	16.12	14.76	13.61	12.66	11.87	11.23
	F	5.52	17.44	15.97	14.71	13.56	12.75	11.97
20.00	H	16.45	15.02	13.80	12.76	11.89	11.17	10.58
	F	11.06	16.24	14.92	13.80	12.85	12.05	11.36
30.00	H	14.34	14.04	12.93	11.99	11.19	10.54	10.00
	F	16.63	15.03	13.86	12.87	12.04	11.35	10.73
35.00	H	14.85	13.60	12.43	11.62	10.87	10.25	9.73
	F	19.37	14.43	13.34	12.42	11.65	11.00	10.43

H = Hamberg's values.

S ‰ = Total salts (gms) in 1000 gms.

F = Fox's values.

Cl' ‰ = Chlorions (gms) in 1000 gms.

It will be seen that the middle parts of the table agree well but that the two sets of figures are rather far apart at temperatures below  $8^\circ$  and for the higher temperatures at the higher salinities. The uncertainty as to saturation is only appreciable above 2% for distilled water and strong sea water at  $0^\circ$ .

On this point it may be recalled that Hamberg commenting on the difference of Tornøe's results from his says. "Für  $0^{\circ}$ , die Temperatur bei welcher die Unterschiede zwischen Tornøe's, Dittmar's und meinen Resultaten am grössten sind, ist die Zahl, welche ich gefunden habe die Durchschnittszahl von neun einfachen, gut mit einander ueberstimmenden Bestimmungen." This seems to point to the probable accuracy of the higher figure.

In 1923 I published a graph<sup>1</sup> showing the proportions of "nitrogen" and oxygen absorbed from air at a total pressure (air + water vapours) of 760 mm and varying temperature and salinities. In using this, which is based on Fox's values regard should be had to the likelihood that values in the regions just indicated are lower than they should be.

### Probable Causes of the Discrepancies between the Results of Different Observers

The differences which have been shown to exist between the results of workers who seem to have used great care are, when all corrections have been made, larger than one would be inclined to expect. I suggest the following causes as contributory.

1. The slowness of exchanges between gas and liquid phases as saturation is approached causes the differences of tension or volume of the gas phase to be so small that the human tendency to consider them insignificant may overcome sound judgment. The accuracy of an absorptionmetric experiment depends in the first place on the absolute freedom of the liquid from the gas or any gas at the beginning, that is, its tension should be exactly that of saturated water vapour, and secondly on the exact measurement of the loss of volume or tension of the gas. In a boiling-out or pumping-out experiment there seems to be no very exact criterion of the end of the exhaustion as aqueous vapour is ever present.

2. The changes in the properties of water towards the freezing point may have some effect: (a) the viscosity increases very rapidly as the water cools and the effect of agitation in mixing the liquid will no doubt be much decreased: (b) it seems probable that the region of maximum density may introduce some anomalies which a careful study would disclose.

3. The real difficulty of freezing water from air by boiling was pointed out by Leduc<sup>2</sup> in his work on the density of ice. He found it impossible (contrary to Bunsen's statement) to get a clear ice from water which had only been boiled and even after three freezings in vacuo under "huile de vaseline" found some cloudiness. The density of this ice was 0.0004 higher than that from boiled water. Leduc made the following

*"Remarque relative à l'analyse des gaz en dissolution dans l'eau.*

On voit, par ce qui précède, que l' eau longuement bouillie retiens une quantité de gaz fort appréciable, qu'elle abandonne au moins partiellement en se congelant. . . .

<sup>1</sup> J. H. Coste: 48, 433, (1923) "The Absorption of Atmospheric Gases by Water," Analyst.

<sup>2</sup> A. Leduc: *Compt. rend.*, 142, 149 (1906). "Sur la densité de la glace."

Il en résulte que l'analyse des gaz de l'eau, telle qu'elle se pratique toujours, est incomplète et par suite inexacte.

Si l'on admet que l'écart entre le nombre de Bunsen et le mien est dû uniquement à ce que ce savant a solidifié complètement de l'eau simplement privée de gaz par ébullition prolongée on arrive à cette conclusion que cette eau renfermait encore près de 1 cm<sup>3</sup> de gaz par litre mesuré sous la pression atmosphérique). . . ."

This observation of Leduc's shows that in the absorptiometric method there is some danger of incomplete preliminary removal of the gases of air from water. The result of this would be that less gas would be absorbed in the actual experiment than would have been absorbed by air-free water. A similar error is liable to affect the final extraction of gas in the boiling-out class of methods by reducing the actual volume of gas yielded by the water. It seems unlikely that the error should be as great as Leduc seems, on indirect evidence, to suggest.

The separation of dissolved gases from water when it freezes is one of the troubles of the maker of artificial ice. A clearer and more marketable product is obtained from gas-freed water. R. T. Gunther<sup>1</sup> has also called attention to the beautiful forms assumed by the chains of air bubbles which separate when water in a bottle is allowed to freeze slowly by exposure in frosty weather.

It would appear that the best way of extracting dissolved gases from water is to introduce the water into a vacuum vessel, boil, freeze, evacuate, melt, boil, freeze and again evacuate, repeating the cycle until a clear ice is obtained and no more gas can be collected. The low tension of aqueous vapour at 0° (4.579 mm) would prevent the volatilisation of much water during evacuation.

I hope as the time may allow, to make some determinations of the solubility of nitrogen, using the method of congelation for freezing the water from gas.

### Summary

When the proper allowances have been made for the effect of argon on the solubility of atmospheric nitrogen, considerable uncertainty exists as to the absorption coefficients of both this mixed gas and pure nitrogen in distilled water.

A similar uncertainty exists in the case of sea water.

Hamberg's and Fox's results obtained by different methods agree well in most cases. There is some reason for considering Hamberg's results more exact than Fox's at low temperatures (below 8°).

Congelation appears to be the best means of freeing water from dissolved gases.

*Teddington*  
*June, 1926.*

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<sup>1</sup> Nature, Jan. 11 (1917).