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THE RELATION OF DISSOLVED OXYGEN TO NITROGEN IN SOME ATLANTIC WATERS

By

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The use of the oxygen content of sea water to indicate the state of biological activity has become such common practice that one is apt to lose sight of the fact that it is subject to certain qualifications. Since it is based on the assumption that the water was originally saturated with oxygen, the momentary temperature and salinity must be observed, and results are often expressed in terms of "percentage saturation," the ratio of the present content of oxygen to that of water of the same temperature and salinity saturated with oxygen from the atmosphere. In this way, values for "percentage saturation" of more than 100% are frequently obtained. The conditions of this supersaturation must be kept in mind, however; the water is frequently under a very considerable pressure, preventing the actual escape of gas, except at the surface.

Assuming the water to have been saturated by contact with the atmosphere, any subsequent change in its temperature or salinity will produce an apparent change in its "percentage saturation." This may be the result of either the warming of the water from above or mixing with water of different temperature and salinity. A study of the solubility data for oxygen, or any of the other atmospheric gases, shows that the mixing of two water-masses at different temperatures, each saturated with gas, results in water with a gas content greater than the saturation content at the intermediate temperature.

On the other hand, the oxygen may actually increase, as the result of photosynthesis. It is also possible to bring about a state of supersaturation, although only to a slight extent, if the surface water is churned up with very small bubbles of air.

These various effects, however, are small compared with the observed differences in oxygen content of the water, so that the usual uncritical use of oxygen data is adequate for most purposes. But in the case of small oxygen differences it is necessary to have some means of evaluating the effects of the various physical factors if the real change in oxygen content is to be calculated exactly.

It is evident that this can be done by observing one of the more inert atmospheric gases, which is subject to the same physical and hydrographic

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influences as the oxygen, but which is really unchanged by either chemical or biological processes. Nitrogen would seem to be well adapted to this use, since its analytical determination, although more difficult than that of oxygen, is very much easier than that of any of the minor inert gases. Buch (1) has done this with some of the oxygen and nitrogen data in the earlier literature and has been able by this means to clear up the relation between assimilation and production of oxygen in some of the more obscure cases.

The increased attention which is now being given to the question of the oxygen minimum layer at deep sea stations, makes it more than ever necessary to be able to distinguish clearly between physical, hydrographic, chemical and biological influences upon the oxygen content.

The analytical determination of nitrogen gas in sea water is not easy, especially if one wishes to separate it from the inert gas fraction (argon, etc.) and not be satisfied simply with the "atmospheric nitrogen" left as residue after removing carbon dioxide and oxygen from dry air. Although this latter step may not be altogether necessary for the purposes described above, we have developed a reasonably simple method of doing so (3), primarily for use in some other studies, and have applied it to obtain the pure nitrogen content of water from several deep stations, for comparison with simultaneous oxygen determinations. The original development of such a method for obtaining real nitrogen values, rather than those by difference, was prompted by the feeling that there may very possibly be other inert gases than argon (such as hydrogen, hydrocarbons, etc.) present in some cases. That this was not altogether unwarranted will appear presently.

Buch (1) compared the oxygen and nitrogen solubility data from Fox' tables (2) and established a relation by which the saturation content of oxygen in water could be readily calculated from the temperature, salinity and nitrogen content. Assuming, then, that the nitrogen in the water has been unaffected by any chemical or biological changes since its original saturation, but that its apparent changes in "percentage saturation" are only the result of temperature and salinity variations in the water, it is possible to calculate a corresponding oxygen content which is the proper base-line from which to measure subsequent changes.

As we have pointed out previously (4), our own values for the solubility of pure nitrogen in sea water, as determined by our method, differ significantly from those for "atmospheric nitrogen" in Fox' tables. These revised values are reprinted in Table I. When these data are plotted against oxygen solubility at corresponding temperatures and chlorinities (taken from Fox) a linear relation is obtained between oxygen and nitrogen, which is independent of either temperature or chlorinity, over the range covered. This of course means that over this range the solubilities of both oxygen

and nitrogen are affected similarly by changes in temperature and chlorinity. As shown in Fig. 78, therefore, when the nitrogen content is known the corresponding saturated oxygen content may be calculated from the relation: $ccO_2 = .577 \times ccN_2 - .22$.

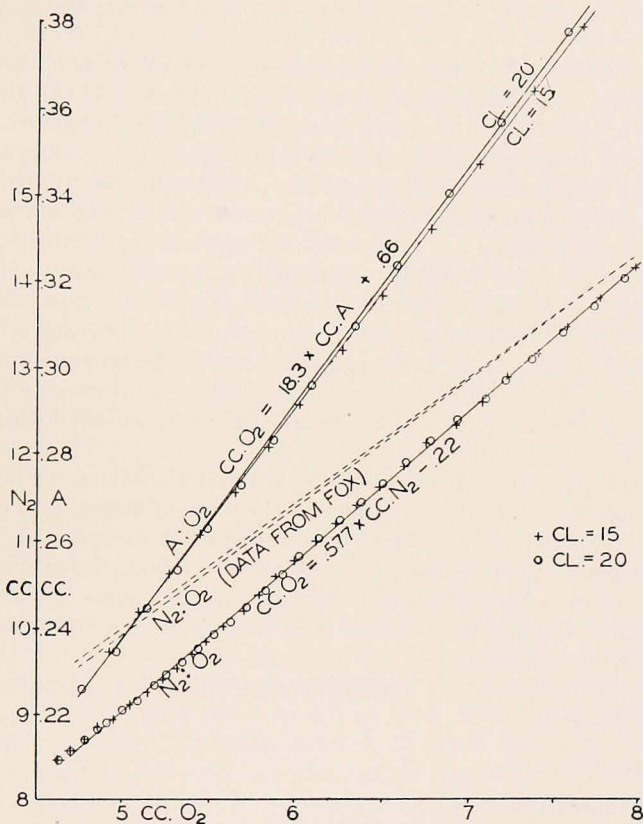


Figure 78. Relation of dissolved oxygen to nitrogen, and to argon, between 0° and 30° C., and chlorinities 15 to 20. Also showing the relation taken from Fox' data for "atmospheric nitrogen" (including argon).

The analytical determination of nitrogen leaves a residue which may also be measured and expressed as argon, although of course it includes any other inert gases as well. From these residual values we have also measured the solubility of crude "argon" in sea water (4) and have reprinted the results in Table II. The argon analyses are probably no more accurate than to about 5% under ordinary conditions, which must be kept in mind in the later discussion. However, these data have also been compared with the

solubility of oxygen at corresponding temperatures and chlorinities, and Fig. 78 shows a satisfactory linear relation between the two, but varying somewhat with chlorinity. We have accordingly used the "argon" figures also as a basis for the calculation of oxygen, although the results are more erratic and apparently not so well suited to the purpose as are those for nitrogen.

It must be kept in mind that the use of nitrogen values as a basis for the calculation of oxygen is predicated on the assumption that the nitrogen in the water is not affected by either chemical or biological changes. We are now carrying on a study to determine whether or not this is true, and while there are indications that free nitrogen may, under some conditions, undergo small changes, the regularity of the nitrogen content of deep-sea water and its close approximation to a condition of apparent saturation gives no reason as yet to doubt that it is substantially inert in the sea.

An example of this is found at Station 2899, at which the nitrogen content is almost identical with the saturation content at the temperatures throughout the whole water mass. It is evident that concentration equilibrium has been established along the whole column by diffusion of gas, and it would be exceedingly valuable to have a measure of the rate at which this process takes place.

Table III gives the data from several Atlantic stations, including the nitrogen values, obtained by the method mentioned above, as well as the "residual" figures for crude argon (containing other inert gases). Oxygen was determined by the customary Winkler method, for although the volume of dissolved oxygen is also measured in the course of the nitrogen analysis, these volumes will be lower than the true values, since the samples will have stood for some time.

The interpretation of the various symbols heading the columns in the table is as follows:

D = depth in meters

T = temperature in °C.

Cl = chlorinity pro mille

O_2 = observed oxygen content in ccs. per liter

O_2' = saturation oxygen content at the observed T and Cl (from Fox)

$\%O_2$ = "percentage saturation" of oxygen: $100 \times O_2/O_2'$

N_2 = observed nitrogen content

$\%N_2$ = "percentage saturation" of nitrogen: $100 \times N_2/N_2'$

A = observed content of residual crude "argon"

$\%A$ = "percentage saturation" of crude argon (as for N_2 and O_2)

O_2^N = original oxygen content, calculated from the observed N_2 , by the relation given in Fig. 78

O_2^A = original oxygen content, calculated from A , by the relation given in Fig. 78

Since physical and hydrographic factors affect the oxygen and nitrogen identically, then, if the nitrogen content has not been altered by chemical or biological changes, it should be possible accurately to calculate the original oxygen content from the nitrogen. The relation of the original oxygen to that observed may be expressed in several ways. A comparison of the "percentage saturation" of the two gases may be made. That of the oxygen will correctly indicate the production or assimilation of oxygen if that of nitrogen does not vary from 100%. It may be seen from the tables that such variation is indeed not great, being significant in a few cases only. The customary uncritical use of the "percentage saturation" of oxygen is therefore justified on the whole, particularly in deep water. In all such cases the difference between O_2 and O_2' is a close measure of the real change in oxygen content. On the other hand, O_2^N , calculated from the nitrogen content, is a more rigorous indication of the original oxygen. The difference between this and the observed oxygen is the corrected, true change in oxygen. Where this difference is positive oxygen has been consumed, where it is negative, as shown here in a few cases, oxygen has been produced in excess of its utilization. And in all such cases, of course, the "percentage saturation" of nitrogen will be greater than that of oxygen.

One of the important outcomes of this method of calculation is the revelation that this predominance of oxygen production over assimilation occurs more rarely than hitherto supposed. This should have some effect upon studies of the relation of photosynthesis to respiration in the sea.

Although similar calculations have been made from the "argon" content it is readily apparent that this function is much less reliable than the nitrogen content. Not only are the figures less accurate but they are erratic for another reason. In the data from Stations 2893 and 2899 the oxygen values calculated from the "argon" are higher than those calculated from the nitrogen in the upper levels, but lower than those calculated from the nitrogen in the deeper samples. It is reasonable to suppose that the "argon" values are somewhat too high in the shallower samples, due to traces of other gases (e.g. hydrogen or hydrocarbons), perhaps the result of the decomposition of plankton, which is present in larger amounts in those samples than the deeper ones.

The figures for the deeper samples at Station 2893 are also somewhat in error, due to another cause. When these samples were analyzed it was noted that small bubbles of air had come out of solution, as the sample-bottles had stood for some time and warmed up. This error, amounting

to nearly 5%, affects the nitrogen and "argon" values, but not the oxygen, since the latter had been obtained immediately by the Winkler method. Later, to avoid this, all the deeper, colder samples were stored under pressure, and at low temperature, until analysis, to prevent the escape of gas.

Figures 79, 80 and 81 have been drawn from the data for Stations 2643, 2899 and 2901 to show the relations between the various functions more graphically. It is believed that the curve for $O_2^N - O_2'$ shows the changes in the oxygen content of a water mass most conveniently and accurately.

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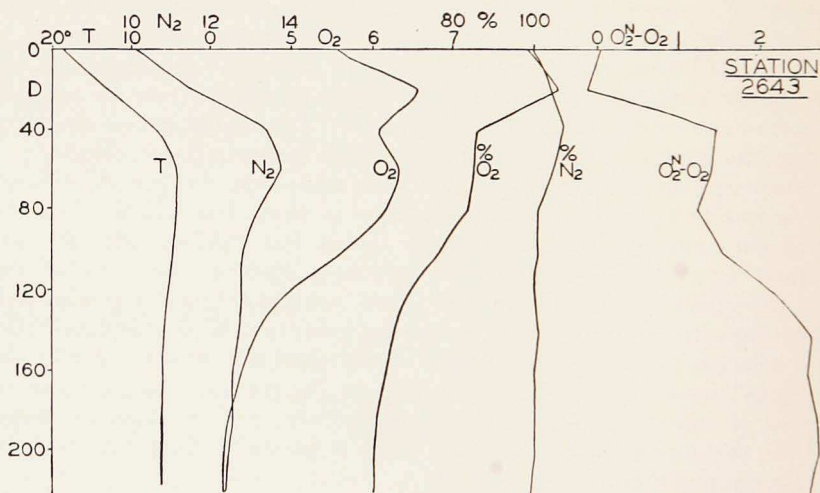


Figure 79. Vertical distributions at Station 2643 of Temperature (T), Nitrogen (N₂), Oxygen (O₂) and the difference between original oxygen contents calculated on the basis of nitrogen present and the observed oxygen contents ($O_2^N - O_2$). Nitrogen and Oxygen expressed in absolute values at the left and in per cent relative saturations at the right. Scales for absolute N₂, O₂ and $O_2^N - O_2$ in cc. per liter. Depths in meters.

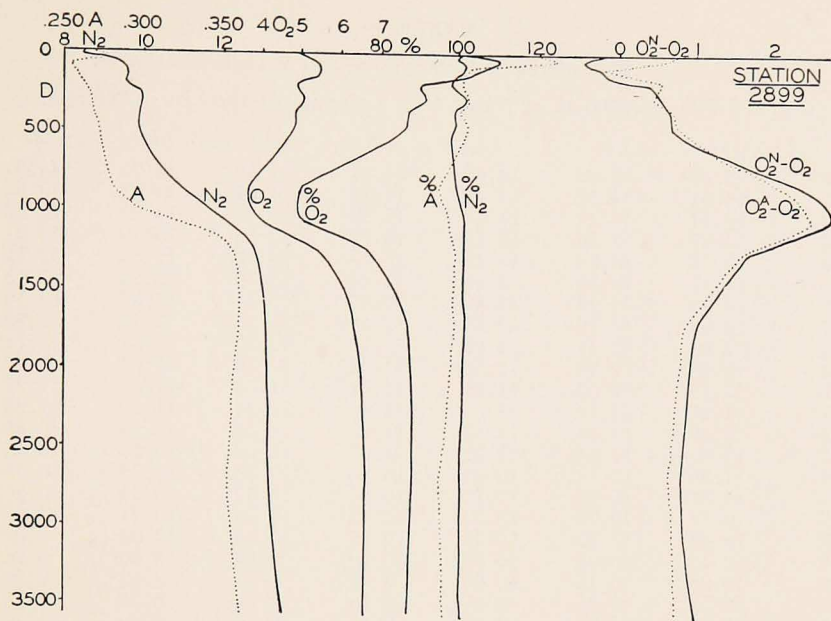


Figure 80. Vertical distributions at Station 2899. (A) Argon, $(O_2^A - O_2)$ difference between original oxygen contents calculated on the basis of Argon present and the observed oxygen contents. For further explanations see legend of Figure 79.

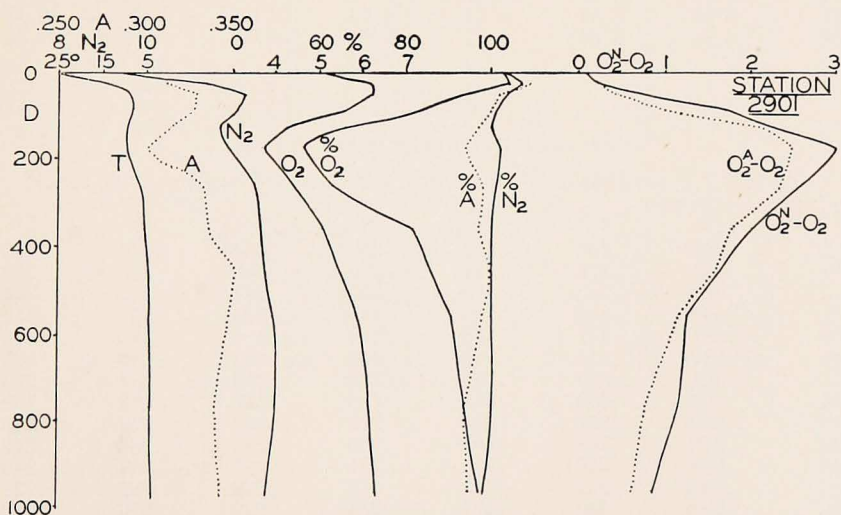


Figure 81. Vertical distributions at Station 2901. See legends of Figures 79 and 80.

TABLE I

SOLUBILITY OF NITROGEN IN SEA WATER

(Cc. at S.T.P. per 1000 cc. of Water, from a Normal Atmosphere of 760 mm.)

<i>T</i>	<i>Cl</i>	15	16	17	18	19	20	21
0°		15.22	15.02	14.82	14.61	14.40	14.21	14.01
1		14.81	14.61	14.42	14.23	14.04	13.85	13.66
2		14.43	14.24	14.06	13.88	13.69	13.51	13.33
3		14.07	13.89	13.72	13.54	13.36	13.19	13.01
4		13.73	13.56	13.40	13.24	13.06	12.89	12.72
5		13.43	13.26	13.10	12.94	12.78	12.62	12.45
6		13.14	12.98	12.82	12.67	12.51	12.35	12.19
7		12.88	12.72	12.56	12.41	12.26	12.10	11.95
8		12.62	12.47	12.32	12.17	12.02	11.87	11.71
9		12.38	12.23	12.08	11.94	11.79	11.64	11.49
10		12.15	12.00	11.86	11.71	11.56	11.42	11.27
11		11.92	11.78	11.63	11.49	11.34	11.20	11.06
12		11.69	11.56	11.42	11.28	11.13	10.99	10.85
13		11.47	11.34	11.21	11.07	10.93	10.79	10.65
14		11.25	11.13	10.99	10.86	10.73	10.59	10.45
15		11.04	10.92	10.79	10.66	10.53	10.39	10.26
16		10.83	10.72	10.59	10.47	10.34	10.21	10.08
17		10.63	10.52	10.40	10.28	10.15	10.03	9.91
18		10.44	10.33	10.21	10.10	9.98	9.86	9.74
19		10.26	10.15	10.03	9.92	9.81	9.69	9.58
20		10.08	9.98	9.87	9.76	9.65	9.54	9.43
21		9.91	9.82	9.71	9.61	9.50	9.39	9.28
22		9.75	9.66	9.56	9.46	9.35	9.24	9.14
23		9.60	9.51	9.41	9.31	9.20	9.10	9.00
24		9.45	9.36	9.26	9.16	9.06	8.96	8.86
25		9.30	9.21	9.11	9.02	8.92	8.82	8.73
26		9.16	9.07	8.97	8.88	8.79	8.69	8.60
27		9.02	8.94	8.84	8.75	8.66	8.56	8.47
28		8.89	8.84	8.72	8.62	8.53	8.44	8.35

TABLE II

SOLUBILITY OF ARGON IN SEA WATER

(Cc. at S.T.P. per 1000 cc. of Water from a Normal Atmosphere of 760 mm.)

<i>T</i>	<i>Cl</i>	15	16	17	18	19	20	21
2°		.405	.400	.395	.389	.384	.379	.373
4		.384	.379	.374	.369	.363	.358	.352
6		.365	.360	.355	.350	.345	.340	.335
8		.347	.343	.338	.333	.329	.324	.319
10		.331	.327	.323	.318	.314	.310	.305
12		.317	.313	.309	.304	.300	.296	.292
14		.304	.300	.296	.292	.288	.284	.280
16		.292	.288	.284	.280	.277	.273	.269
18		.282	.278	.274	.270	.267	.263	.259
20		.272	.268	.264	.260	.256	.253	.249
22		.262	.258	.255	.251	.247	.244	.240
24		.253	.249	.246	.242	.238	.235	.231
26		.244	.240	.237	.233	.229	.226	.222
28		.235	.231	.228	.224	.220	.217	.213

TABLE III

Station 2643				42°—19' N; 19°—20' W				August 10, 1936					
D	T	Cl	O ₂	O ₂ '	%O ₂	N ₂	N ₂	A	%A	O ₂ ^N	O ₂ ^A	O ₂ ^N -O ₂	O ₂ ^A -O ₂
0	18.3	17.6	5.58	5.63	99	10.13	100			5.61		.03	
20	13.0	17.8	6.56	6.17	106	11.50	104			6.42		-.14	
40	6.5	18.1	6.06	7.01	86	13.45	107			7.54		1.48	
60	4.2	18.2	6.32	7.38	85	13.8	105			7.74		1.42	
80	4.2	18.2	6.18	7.38	84	13.22	101			7.42		1.24	
100	4.5	18.4	5.66	7.31	77	12.85	101			7.20		1.54	
120	5.2	18.55	4.97	7.17	69	12.80	100			7.17		2.20	
140	5.7	18.7	4.60	7.08	65	12.76	101			7.26		2.66	
160	5.9	18.75	4.40	7.04	63	12.60	100			7.05		2.65	
180	6.1	18.9	4.24	7.00	61	12.58	100			7.03		2.79	
200	6.1	18.9	4.19	7.00	60	12.50	100			7.00		2.81	
220	6.1	18.9	4.21	7.00	60	12.42	99			6.95		2.74	
Station 2666				39°—00' N; 70°—00' W				September 3, 1936					
0	20.90	18.3	5.19	4.98	104	9.72	108			5.38		.19	
10	22.50	18.7	5.04	5.19	97	9.50	102			5.26		.22	
20	11.93	18.6	6.11	6.23	98	11.7	105			6.59		.48	
39	13.34	19.15	4.35	5.92	74	11.0	103			5.93		1.58	
59	12.46	18.85	4.29	6.13	70	11.0	100			6.16		1.87	
78	12.05	19.3				10.8	97						
87	12.31	19.0	4.04	6.16	66	11.1	100			6.18		2.14	
135	7.85	19.1	3.90	6.71	58	11.4	95			6.36		2.46	
183	9.57	19.3	3.20	6.48	49	11.7	101			6.53		3.33	
279	7.71	19.0	4.04	6.75	60	12.4	103			6.93		2.89	
375	5.23	18.9	4.84	7.13	68	12.6	99			7.05		2.21	
471	4.68	19.0	5.19	7.21	72	12.7	99			7.11		1.92	
552	4.69	18.95	5.31	7.21	74	12.5	97			6.99		1.68	
736	4.23	18.9	5.73	7.13	80	12.6	99			7.05		1.32	
921	4.02	19.2	6.02	7.31	82	12.5	96			6.99		0.97	
1105	4.12	19.3	6.08	7.31	83	12.8	98			7.17		1.09	
1381	3.58	19.0	5.90	7.40	80	12.8	97			7.17		1.27	
1845	3.34	18.8	6.21	7.44	84	13.0	98			7.28		1.07	
2762	2.56	19.05	6.24	7.58	82	13.3	98			7.45		1.21	
Station 2667				35°—31' N; 69°—15' W				September 5, 1936					
10	26.05	19.8	4.61	4.80	96	8.83	101			4.82		.21	
60	20.91	20.0	5.27	5.22	101	9.67	103			5.36		.09	
180	18.20	19.7	4.72	5.47	86	9.64	98			5.34		.62	
449	17.29	19.5	4.47	5.60	80	10.3	102			5.73		1.26	
719	14.77	19.4	4.10	5.83	70	10.4	101			5.88		1.78	
899	11.54	19.05	3.36	6.20	54	11.3	101			6.30		2.94	
1348	5.18	19.0	5.12	7.13	72	12.6	101			7.05		1.93	
3595	3.14	19.2	6.08	7.47	81	13.9	104			7.88		1.80	

TABLE III (Continued)

Station 2893				35°—30' N; 67°—17' W					July 12, 1937				
D	T	Cl	O ₂	O ₂ '	%O ₂	N ₂	N ₂	A	%A	O ₂ ^N	O ₂ ^A	O ₂ ^N -O ₂	C ₂ ^A -O ₂
0	26.5	20.07	4.65	4.73	98	8.8	102	.250	111	4.86	5.23	.21	.58
50	24.0	20.25	5.20	4.93	106	9.3	104	.260	110	5.14	5.41	-.06	.21
100	19.0	20.2	4.97	5.39	92	9.7	100	.270	109	5.38	5.59	.41	.62
150	18.5	20.2	4.86	5.43	90	9.9	101	.280	108	5.49	5.77	.63	.91
200	18.2	20.2	4.80	5.46	88	10.05	102	.290	111	5.58	5.96	.75	1.16
300	17.8	20.2	4.70	5.50	86	10.15	102	.320	120	5.64	6.50	.94	1.80
400	17.5	20.15	4.65	5.53	84	9.9	101	.290	108	5.53	5.95	.88	1.30
500	16.7	20.1	4.40	5.56	79	10.2	101	.295	109	5.66	6.06	1.26	1.66
600	15.5	19.95	4.10	5.74	72	10.4	101	.290	105	5.78	5.96	1.68	1.86
800	11.5	19.57	3.50	6.22	56	11.3	101	.315	104	6.29	6.41	2.79	2.91
1000	7.5	19.42	4.10	6.74	61	12.3	101	.335	101	6.87	6.78	2.77	2.66
1500	4.2	19.37	5.84	7.26	81	12.6	98	.340	96	7.01	6.68	1.17	1.02
2000	3.5	19.35	6.20	7.37	84	12.7	97	.345	94	7.10	6.95	.90	.75
2500	3.3	19.35	6.20	7.41	84	12.75	97	.350	95	7.13	7.04	.93	.84
3000	3.0	19.32	6.10	7.47	82	12.8	96	.350	94	7.16	7.04	1.06	.94
3500	2.8	19.32	6.07	7.51	81	12.9	96	.355	95	7.22	7.13	1.15	1.06
4000	2.5	19.32	6.00	7.56	79	12.95	96	.355	94	7.26	7.13	1.26	1.13
4500	2.3	19.30	5.90	7.60	78	13.0	96	.360	95	7.28	7.22	1.38	1.32
Station 2899				36°—01' N; 69°—57' W					August 8, 1937				
D	T	Cl	O ₂	O ₂ '	%O ₂	N ₂	N ₂	A	%A	O ₂ ^N	O ₂ ^A	O ₂ ^N -O ₂	C ₂ ^A -O ₂
1	27.37	19.99	4.79	4.67	102	8.60	101	.266	121	4.75	5.52	-.04	.73
23	27.06	20.05	5.05	4.70	107	8.52	100	.275	124	4.70	5.69	-.35	.64
46	25.54	20.14	5.28	4.82	110	8.75	101	.274	120	4.83	5.67	-.45	.39
93	20.97	20.21	5.51	5.20	106	9.51	102	.254	103	5.28	5.30	-.23	-.21
139	19.64	20.24	5.45	5.34	102	9.60	100		101	5.32		-.13	
185	18.84	20.20	4.88	5.40	90	9.52	98	.261	101	5.28	5.42	.40	.54
278	18.25	20.20	5.03	5.46	92	9.96	102	.266	102	5.53	5.46	.50	.43
371	17.89	19.43	4.83	5.54	87	9.89	99	.267	100	5.49	5.52	.66	.69
464		20.17	4.81	5.53	87	9.84	99	.271	102	5.46	5.54	.65	.73
556	16.87	20.11	4.61	5.60	82	9.92	98	.272	101	5.51	5.61	.90	1.00
861	12.36	19.70	3.63	6.09	60	10.80	99	.279	94	6.02	5.76	2.39	2.13
1076	7.78	20.19	3.89	6.62	59	11.95	101	.315	97	6.68	6.41	2.79	2.52
1291	4.98	19.37	5.52	7.12	77	12.82	101	.356	99	7.19	7.11	1.67	1.59
1722	3.96	19.36	6.31	7.29	87	13.05	101	.358	99	7.32	7.16	1.01	.85
2690	3.31	19.36	6.57	7.40	88	13.13	100	.353	95	7.36	7.20	.79	.63
3773	2.55	19.36	6.52	7.57	86	13.49	100	.362	96	7.57	7.27	1.05	.75
Station 2901				39°—40' N; 71°—43' W					August 11, 1937				
D	T	Cl	O ₂	O ₂ '	%O ₂	N ₂	N ₂	A	%A	O ₂ ^N	O ₂ ^A	O ₂ ^N -O ₂	C ₂ ^A -O ₂
1	25.05	17.78	5.14	5.01	103	9.43	104			5.23		.09	
25	14.62	18.46	6.18	5.93	104	11.42	107	.314	109	6.38	6.40	.20	.22
50	8.50	19.47	6.25	6.60	95	12.32	104	.329	102	6.89	6.68	.64	.43
87	8.42	18.79	5.59	6.66	84	12.10	101	.326	100	6.76	6.62	1.17	1.03
131	9.49	19.24	4.27	6.48	66	11.70	100	.314	100	6.53	6.40	2.26	2.13
176	9.22	19.38	3.64	6.51	56	11.91	102	.299	94	6.66	6.13	3.02	2.49
268	6.40	19.33	4.40	6.92	63	12.48	101	.332	98	6.98	6.73	2.58	2.33
363	5.40	19.33	5.06	7.07	72	12.62	100	.336	97	7.06	6.80	2.00	1.74
460	4.87	19.34	5.50	7.15	77	12.73	100	.352	100	7.13	7.10	1.63	1.60
560	4.48	19.39	5.87	7.21	81	12.89	100	.348	98	7.21	7.02	1.24	1.15
768	4.22	19.35	6.12	7.26	84	12.96	100	.340	94	7.26	6.87	1.14	.75
977	3.98	19.36	6.32	7.29	87	12.73	98	.343	95	7.13	6.93	.81	.61