

ON THE COEFFICIENTS OF ABSORPTION OF NITROGEN AND OXYGEN IN DISTILLED WATER AND SEA-WATER, AND OF ATMOSPHERIC CARBONIC ACID IN SEA-WATER.

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Dr. V. H. VELEY, F.R.S., in the Chair.*)

The object of the present series of measurements was primarily the determination of the absorption coefficients of nitrogen, oxygen, and atmospheric carbonic acid in sea-water. These coefficients have of late years acquired some special significance, notably in connection with that group of physical problems of which Arrhenius's work on the diathermancy of the atmospheric gases, particularly carbonic acid, and its effect upon terrestrial temperatures, is typical, and again in connection with those matters of biological interest which are concerned with the dynamic processes of pelagic life. In addition, the absorption coefficients of nitrogen and oxygen in distilled water are not known with great exactness, and it is believed that the present series of determinations will be of some interest from that point of view also.

1. NITROGEN AND OXYGEN.

The method employed for determining the absorption coefficients of nitrogen and oxygen is a modified form of Estreicher's adaptation of Ostwald's method.* The gas is admitted to the burette *A* (Fig. 1) through the tube *D*; its volume pressure and temperature are recorded. The bulb *B* containing the water freed from air is sealed on to the flexible glass spiral *C*, which is thereupon evacuated with a mercury pump and the tap *c* then closed. The volume between the three taps *a*, *c*, *b* is determined by allowing the gas to enter the spiral from the burette and measuring the resulting decrease of gas in the burette. The tap *b* is next opened and the bulb agitated until equilibrium between gas and liquid has been attained; the further contraction again resulting is a measure of the quantity of gas absorbed by the volume of water taken, at the pressure and temperature observed. The pressure and temperature are then varied at will, and further measurements made upon the same quantity of water and gas.

The object of the tube *G* in the present modification of the apparatus, which is in diameter and graduation identical with *A*,† is to enable the measurements to be made at any pressure, within about 30 cm. around atmospheric pressure, instead of having to measure the volume of the gas always just in equilibrium with the water just at atmospheric pressure. Estreicher employed the latter method, which is in practice by no means an easy thing to do exactly. The difference in mercury levels in the two tubes is, of course, a measure of the pressure at which the observation is made. The large beaker filled with water and fitted with a thermo-regulator serves as a

* Estreicher, *Zeit. für physikal. Chem.*, **31**, p. 176; Ostwald-Luther, *Physiko-chemische Messungen*, 2te Aufgabe, p. 274.

† In linear millimetres. The tube *A* was calibrated for volume by cutting it from the rest of the apparatus, sealing a tap on at the bottom, and then running out and weighing quantities of mercury in the usual way.

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thermostat and allows a telescope to be used for reading off the volume, pressure and temperature. Precautions were taken to eliminate every possible parallax error, by adjusting levels, perpendiculars, &c.

Estreicher, after having determined the volume and weight of the bulb, filled it with the water to be used (and a few c.c. of mercury to facilitate subsequent mixing with the gas), connected it directly by rubber tubing with an ordinary water-pump, and then boiled until about one-quarter of the water in the bulb had evaporated away; the tap was at this point closed and the bulb weighed again. On now shaking the bulb the water hits the glass in the vacuum with the characteristic crackle. As a matter of fact, however, an exhaustive trial showed that it is not possible to get complete evacuation

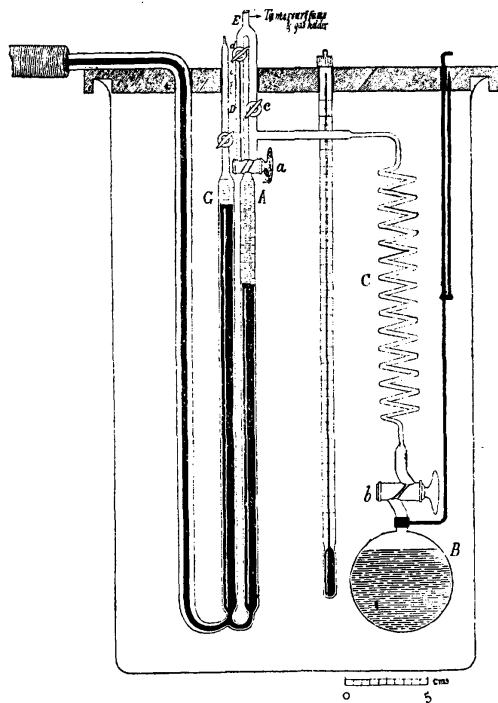


FIG. 1.

in this way, and the sound alone is not a satisfactory criterion at all. If the bulb really were air-free, it would be found upon opening under a mercury surface that mercury would enter and fill it; but a small residual bubble of air is invariably left, of volume about 0.01 to 0.10 c.c. at atmospheric pressure. It is difficult to get a water-pump to work quite evenly enough for this purpose; the water in the bulb bumps badly even when it is warmed gently in a lukewarm water-bath; a quantity of water condenses in the rubber tubing above, where it works up and down in effect like a piston, and this, no doubt, makes it difficult for the last traces of air to make their way out. It is suggested that Estreicher's values may be subject to an error on this account—in the case of argon of about 0.2 to 5 per cent., in the case of helium of 0.5 to 10 per

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cent. Winkler* as a result of some theoretical considerations, which are, however, admittedly not quite conclusive, has also suspected that these helium values are not quite so reliable as are those accepted for some other gases. It is therefore to be hoped that these determinations will be repeated.

In the present experiments the bulb was filled as follows (Fig. 2): By means of a piece of thick-pressure tubing the bulb *A* was connected to the bulb *B*, and *A* and about one-third of *B* was then filled with the water. The water-pump was applied to the upper end of *B*, the water in both *A* and *B* was kept boiling for 10–15 minutes; *A* was then, of course, quite full of air-free water. But it is desirable that it should not be too full, and in practice about 10 c.c. of air-free space is convenient. It is easily adjusted at that or any other value by deflecting and inverting the bulb for a moment during the boiling so that a bubble of steam instead of rising to the water surface in *B* may upon formation collect inside *A*. When the bulb is filled with the water in this way no residual air will be found upon subsequently opening under a mercury surface; and upon shaking, the water will be found to hit the glass in the vacuum with an intensity somewhat alarming, and much harder than is the case when the evacuation is carried out by the simple method adopted by Estreicher in his work.

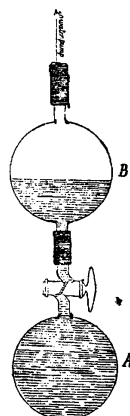


FIG. 2.

The nitrogen used in the determinations was obtained by several times passing air to and fro over warm white phosphorus,† soda lime, and P_2O_5 ; the oxygen was generated by heating $KMnO_4$ in a tube, and passed over soda lime, and P_2O_5 . All the apparatus was always evacuated and rinsed out with the gas several times before quantities for use in the actual measurements were finally collected in a glass gas-holder,‡ which was also connected further to the mercury-pump and the absorption apparatus. All joints were made with the blowpipe.

It is necessary to ensure that the residual undissolved gas in the burette is measured saturated with moisture; Estreicher attained this by so manipulating the bulb and the mercury level in the burette, that a drop of water passed over through the spiral. In the present apparatus the same end was served more conveniently by filling the fine capillary tubing between the taps *a* and *d* with water, before sealing the tube *E* on to the gas-holder and mercury-pump. Then when the gas was admitted through *d* and *a* to the burette, this known quantity of water was swept in before it; all the measurements were made with the gas moist, and allowance was made for the small quantity of water (about 0.015 c.c.), in calculating the results.

A. DISTILLED WATER—NITROGEN.

It must be noted here that to give values for pure nitrogen these measurements must be subjected to a correction dependent upon the fact that atmospheric nitrogen is a mixture of nitrogen and 1.185 per cent. argon. The solubility of argon is more than double that of nitrogen; and the result is that, under the conditions of the present observations, the ratio of their partial pressures does not remain constant and equal to that found in the open free atmosphere, and it is different at different temperatures.

* L. W. Winkler, *Zeit. für physik. Chemie*, 55, p. 344.

† Copper gauze was tried too, but it had to be reduced often, and the nitrogen prepared by passing over phosphorus gave quite the same values. After that had been established the more convenient phosphorus was always used.

‡ As illustrated in Travers, "Experimentelle Untersuchung von Gasen," Fig. 121.

Experiment I.

ATMOSPHERIC NITROGEN IN DISTILLED WATER.

Volume of bulb empty at $0^{\circ} = 138.686$ c.c. $= v_0$. Volume of water taken at $0^{\circ} = 123.498 = w_0$.
 Volume of gas taken N_2 (corrected) $= 17.630$ c.c. at 980° and 857.95 mm. $= 19.2124$ at 0° and 760 mm.
 Volume remaining in burette after opening first tap (corrected) $= 14.8495$ at 990° and 788.3 mm.
 \therefore Volume of spiral $= 4.244$ at $990^{\circ} = 4.243$ at $0^{\circ} = 4.248$ at 50° .*

t .	w .	v .	Burette Reading (in c.c.).	Volume Unabsorbed (c.c. at P).	$h =$ Pressure (Corrected).	Volume Unabsorbed (c.c. at P 760).	Volume of Gas taken (c.c. at P 760).	Volume Absorbed (P 760).	$1,000 a =$ Volume Absorbed by 1,000 c.c. at P 760 (c.c. at 0° 760).
0.53	123.510	138.689	2.410	21.832	Centimetres. 59.220	17.012	19.250	2.238	23.21
6.00	123.502	138.705	2.788	22.235	60.100	17.583	19.635	2.052	20.56
10.00	123.531	138.719	3.330	22.762	60.107	18.002	19.916	1.914	18.90
15.72	123.619	138.739	3.454	22.818	61.550	18.480	20.319	1.839	17.37†
20.60	123.732	138.754	4.184	23.440	61.489	18.965	20.662	1.697	15.76
24.90	123.857	138.769	4.254	23.401	62.750	19.321	20.965	1.643	14.73
29.88	124.030	138.786	4.559	23.561	63.020	19.537	21.315	1.578	13.83
34.99	124.236	138.802	5.394	24.117	63.460	20.138	21.675	1.537	13.12
41.49	124.536	138.823	6.113	24.647	63.680	20.652	22.132	1.480	12.31
46.79	124.867	138.841	6.817	25.099	63.822	21.077	22.505	1.428	11.63
49.89	124.928	138.851	7.277	25.438	63.700	21.321	22.723	1.402	11.33

* The cubical temperature coefficient of expansion of the glass used for the apparatus was found by experiment to be 0.0000239 between 0° and 50° .
 † This observation was rejected; it is affected by some exceptional error.

Experiment II.

ATMOSPHERIC NITROGEN IN DISTILLED WATER.

Volume of bulb empty at $0^\circ = 138.686 = v_0$. Volume of water taken at $0^\circ = 125.1995 = w_0$.
 Volume of gas taken N_2 (corrected) $= 18.250$ c.c. at 13.94° and 856.1 mm. $= 19.559$ at 0° and 760 mm.
 Volume remaining in burette after opening first tap (corrected) $= 15.501$ at 14.02° and 784.5 mm.
 \therefore Volume of spiral $= 4.420$ at $14^\circ = 4.419$ at $0^\circ = 4.425$ at 50° .

l	w_0	v_0	$v_{H_2O}^\circ$	Burette Reading (in c.c.)	Volume Unabsorbed (c.c. at P)	$P =$ Pressure (Corrected), Centimetres.	Volume Unabsorbed (c.c. at P 760).	Volume of Gas taken (c.c. at P 760).	Volume Absorbed (P 760).	$1000 a =$ Volume Absorbed by 1,000 c.c. at P 760 (c.c. at 0° 760).
0.39	125.213	138.687	1.5565	3.194	19.531	66.294	17.037	19.587	2.550	23.31
4.40	125.200	138.704	1.557	3.490	19.860	66.929	17.490	19.874	2.384	21.28
7.40	125.211	138.711	1.558	3.708	20.070	67.457	17.815	20.089	2.274	19.92
10.00	125.244	138.722	1.558	4.002	20.340	67.906	18.177	20.340	2.163	18.58
12.80	125.271	138.730	1.559	3.177	19.498	71.206	18.209	20.476	2.207	17.96
14.25	125.295	138.733	1.559	4.195	20.495	68.614	18.503	20.580	2.077	17.45
19.00	125.411	138.748	1.561	5.924	22.123	65.738	19.135	20.963	1.828	15.73
23.30	125.517	138.764	1.561	4.396	20.504	71.512	19.293	21.228	1.935	15.09
29.90	125.740	138.786	1.563	6.830	22.737	66.773	19.970	21.701	1.725	10.84
35.76	125.981	138.805	1.564	5.635	21.319	72.581	20.366	22.121	1.761	12.95
40.28	126.317	138.819	1.565	8.177	23.538	67.312	20.847	22.445	1.597	12.44
45.73	126.470	138.839	1.566	6.832	22.059	72.779	20.107	22.835	1.668	11.79
48.70	126.640	138.847	1.566	9.157	24.252	67.189	21.439	23.048	1.509	11.44
52.01	126.827	138.858	1.567	9.887	24.776	66.919	21.816	23.285	1.469	11.05

* In this experiment a small quantity of mercury was placed in the bulb before the water sample, with the object of helping mixing, in accordance with Estreicher's practice.

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