# 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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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.

## I. 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. Chemie*, **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.

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

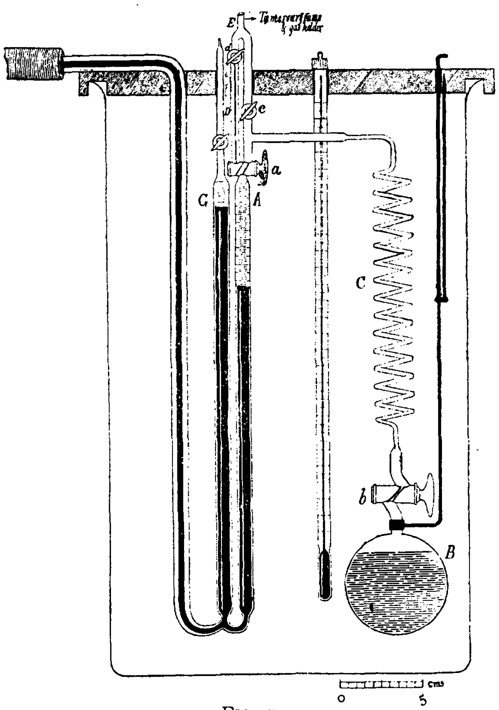


FIG. 1.

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 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.

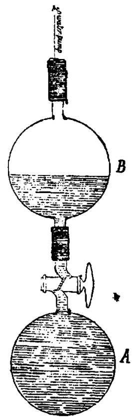


FIG. 2.

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 joins 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° = 138·686 c.c. = $v_0$. Volume of water taken at 0° = 123·498 = $w_0$.

Volume of gas taken $N_2$ (corrected) = 17·630 c.c. at 9·80° and 857·95 mm. = 19·2124 at 0° and 760 mm.

Volume remaining in burette after opening first tap (corrected) = 14·8495 at 9·90° and 788·3 mm.

∴ Volume of spiral = 4·244 at 9·90° = 4·243 at 0° = 4·248 at 50°.*

| $t$. | $w_t$. | $v_t$. | Burette Reading (in c.c.). | Volume Unabsorbed (c.c. at $t°p$). | $p$ = Pressure (Corrected). | Volume Unabsorbed (c.c. at $t°$ 760). | Volume of Gas taken (c.c. at $t°$ 760). | Volume Absorbed ($t°$ 760). | 1,000 $a$ = Volume Absorbed by 1,000 c.c. at $t°$ 760 (c.c. at 0° 760). |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Centimetres. | | | | |
| 0·53 | 123·510 | 138·689 | 2·410 | 21·832 | 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 | 5·304 | 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 | 124·807 | 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° = 138·686 = $v_0$. Volume of water taken at 0° = 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.

∴ Volume of spiral = 4·420 at 14° = 4·419 at 0° = $4{\cdot}425_5$ at 50°.

| $t$. | $w_t$. | $v_t$. | $v_{Hg}$.* | Burette Reading (in c.c.). | Volume Unabsorbed (c.c. at $t^0 p$). | $p$ = Pressure (Corrected). | Volume Unabsorbed (c.c. at $t^0$ 760). | Volume of Gas taken (c.c. at $t^0$ 760). | Volume Absorbed ($t^0$ 760). | 1,000 $a$ = Volume Absorbed by 1,000 c.c. at $t^0$ 760 (c.c. at 0° 760). |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Centimetres. | | | | |
| 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 |
| 10·90 | 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 | 18·269 | 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 | 19·976 | 21·701 | 1·725 | 10·84 |
| 35·76 | 125·981 | 138·805 | 1·564 | 5·635 | 21·319 | 72·581 | 20·306 | 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 | 20·167 | 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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