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.

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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

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. Chem.*, **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.

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Experiment I.

ATMOSPHERIC NITROGEN IN DISTILLED WATER.

Volume of bulb empty at $0^{\circ} = 138.686$ c.c. = w_0 . Volume of water taken at $0^{\circ} = 123.498 = w_0$.

Volume of gas taken N_2 (corrected) = 17.630 c.c. at 98.0° and 857.95 mm. = 19.2124 at 0° and 760 mm.

Volume remaining in burette after opening first tap (corrected) = 14.8495 at 99.0° and 788.3 mm.

$\therefore$ Volume of spiral = 4.244 at $99.0^{\circ} = 4.243$ at $0^{\circ} = 4.248$ at 50° .*

t .	w_0	w_1	Burette Reading (in c.c.).	Volume Unabsorbed (c.c. at p_0).	$p =$ Pressure (Corrected).	Volume Unabsorbed (c.c. at $p^0 760$).	Volume of Gas taken (c.c. at $p^0 760$).	Volume Absorbed ($p^0 760$).	$\frac{1,000 \cdot a}{1,000 \text{ c.c. at } p^0 760}$ (c.c. at $0^{\circ} 760$).
					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	1.486	12.31
46.79	124.807	138.841	6.817	25.009	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.

$\therefore$ Volume of spiral = 4.420 at 14° = 4.419 at 0° = 4.425_8 at 50° .

t .	w .	v_0 .	$v_{H_2O}^*$.	Burette Reading (in c.c.).	Volume Unabsorbed (c.c. at p/p).	p = Pressure (Corrected).	Volume Unabsorbed (c.c. at p/p).	Volume of Gas taken (c.c. at p/p).	Volume Absorbed (p/p).	$1,000 a$ = Volume Absorbed by 1,000 c.c. at p/p (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	18.209	20.476	2.207	17.96
14.25	125.295	138.733	1.559	4.105	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	20.366	22.121	1.761	12.95
40.28	126.317	138.819	1.565	8.177	23.338	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.

If p and $1-p$ be the partial pressures of argon and nitrogen in free atmospheric nitrogen ;

if $1, p_A, p_N$, be respectively the total pressure and the partial pressures of the argon and nitrogen after solution equilibrium has been attained ;

if a_A, a_N be the absorption coefficients for pure argon and pure nitrogen ;

a be the coefficient actually found in these measurements for the limited quantity of atmospheric nitrogen employed, and

a' be the true corrected coefficient for free unlimited atmospheric nitrogen ;

if v be the volume of water used in the bulb, and kv the volume of gas which remains undissolved, then—

$$a = a_A p_A + a_N p_N, \text{ and } a' = a_A p + a_N (1-p),$$

and—

$$x = a' - a = a_A (p - p_A) + a_N (1 - p - p_N).$$

But if after equilibrium is attained it is to be provided that nitrogen and argon still have the same ratio of partial pressures as they have in the atmosphere, then—

$$\frac{p_A (k + a_A)}{p_N (k + a_N)} = \frac{p}{1-p},$$

and—

$$p_A + p_N = 1,$$

whence by substitution it follows that—

$$x = \frac{(a_A - a_N)^2 (1-p) p}{k + a_A - p a_A + p a_N}.$$

For atmospheric nitrogen $p = 0.01185$, and $1-p = 0.98815$. k of course differed somewhat in the different experiments ; for present purposes, however, it is sufficient to use always its mean value, 0.140.

$$\therefore x = \frac{0.01171 (a_A - a_N)^2}{0.140 + 0.98815 a_A + 0.01185 a_N}.$$

This correction is always small ; for 1,000 c.c. of water it is 0.1 c.c. at 0° and 0.02 at 50° .

Further, since—

$$a' = a + x = 0.98815 a_N + 0.01185 a_A,$$

the absorption coefficient for pure nitrogen $= a_N = \frac{a' - 0.01185 a_A}{0.98815}$.

The observations (a) recorded above have been corrected accordingly ; the interpolation formula for pure nitrogen then calculated from them is—

$$1,000 a_N = 22.998 - 0.5298t + 0.009196t^2 - 0.00006779t^3,$$

and the values for each degree from 0° to 50° are given in Table I.

TABLE I.

	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
0	23.00	22.50	22.02	21.55	21.09	20.64	20.20	19.77	19.35	18.94
10	18.54	18.16	17.80	17.46	17.14	16.84	16.56	16.29	16.03	15.78
20	15.54	15.29	15.06	14.84	14.63	14.43	14.23	14.04	13.87	13.71
30	13.55	13.39	13.23	13.08	12.93	12.79	12.65	12.52	12.39	12.27
40	12.15	12.04	11.92	11.80	11.68	11.57	11.46	11.35	11.24	11.13
50	11.02	—	—	—	—	—	—	—	—	—

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Since the days of Bunsen's determinations, now only of historic interest, the absorption coefficients for nitrogen have been determined by Dittmar,* Tornøe,† Hamberg,‡ Pettersson and Sonden,§; but it is the determinations of Winkler || and of Bohr and Bock ¶ which are commonly regarded as the best values hitherto available. These determinations were evidently carried out with the utmost precision and care; but both were made prior to the discovery of argon. Winkler used atmospheric nitrogen and employed an apparatus theoretically analogous to that described here. The values published** must therefore be subjected to a correction in order to give values for pure nitrogen; his values refer to α and not to α' or α_N . Bohr and Bock's values differ appreciably from those of Winkler and the present writer. In making their determinations they usually bubbled a stream of atmospheric nitrogen through water, and then extracted and measured the quantity of gas absorbed; under these circumstances they must evidently have obtained not α_N or α but α' , and the values they have published, and which have since been copied into many works of reference, must therefore be corrected in order to give true values for argon-free nitrogen. (Argon is at 0° 2.46 times and at 50° 2.34 times as soluble as nitrogen.) Bohr and Bock's numbers must, therefore, be reduced accordingly in order to give values for pure nitrogen.

Corrected in this way, it will be seen that Bohr and Bock's values are higher than Winkler's and Fox's until about 30° , above which Fox's are highest.

	0° .	10° .	20° .	30° .	40° .	50° .
Winkler	23.14	18.29	15.18	13.20	11.65	10.82
Fox	23.00	18.54	15.54	13.55	12.15	11.02
Bohr and Bock ...	23.47	19.25	16.13	13.58	11.62	10.43

B. DISTILLED WATER—OXYGEN.

The observations made in the case of distilled water and oxygen are shown in Experiments III. and IV.

The formula and values for $1,000\alpha$ from 0° to 50° , calculated from these observations, are as follows (Table II.)—

$$1,000\alpha = 49.239 - 1.3440t + 0.28752t^2 - 0.0003024t^3.$$

TABLE II.

	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
0	49.24	47.94	46.65	45.45	44.31	43.21	42.15	41.15	40.19	39.28
10	38.37	37.51	36.75	35.98	35.26	34.55	33.88	33.21	32.58	32.01
20	31.44	30.91	30.38	29.86	29.38	28.90	28.42	27.94	27.51	27.08
30	26.65	26.27	25.90	25.54	25.19	24.85	24.52	24.20	23.89	23.59
40	23.30	23.02	22.75	22.49	22.24	22.00	21.77	21.55	21.34	21.14
50	20.95	—	—	—	—	—	—	—	—	—

* *Challenger Expedition, Physics and Chemistry*, vol. i., p. 172.

† *Den Norske Nordhavs Expedition, 1876–1878, Chemistry*.

‡ *Bihang til K. Svenska, Vet. Akad. Handlingar*, 10, No. 13, 1885.

§ *Svensk Kemisk Tidskrift*, 1889, p. 17.

|| Winkler, *Ber. d. deutschen Chem. Ges.*, 22 (1889), 1764; 24 (1891), 3602.

¶ Bohr and Bock, *Wiedemann's Annalen*, 44 (1891), 316.

** E.g., Landolt and Bornstein's tables.

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Experiment III.

OXYGEN IN DISTILLED WATER.

Volume of bulb empty at $0^{\circ} = 138.686 = v_0$. Volume of water taken at $0^{\circ} = 127.9645 = w_0$.
 Volume of gas taken O_2 (corrected) $= 19.370$ and 952.6 mm. $= 23.8078$ at 0° and 760 mm.
 Volume remaining in burette after opening first tap (corrected) $= 16.295$ at 15.43° and 993.7 mm.
 $\therefore$ Volume of spiral $= 4.8580$ at $15.43^{\circ} = 4.8565$ at $0^{\circ} = 4.8615$ at 50° .

t .	30° .	v_1 .	Burette Reading (in c.c.).	Volume Unabsorbed (c.c. at 0°).	$h =$ Pressure (Corrected). Centimetres.	Volume Unabsorbed (c.c. at 0°).	Volume of Gas taken (c.c. at 0°).	Volume Absorbed (0° 760).	$1,000 a =$ Volume Absorbed by 1,000 c.c. at 0° 760 (c.c. at 0° 760).
0.61	127.976	138.089	2.973	18.541	73.57	17.824	23.861	6.037	48.61
0.81	127.975	138.690	6.142	22.713	62.80	18.768	23.878	5.110	48.18
5.51	127.967	138.705	3.953	19.559	73.51	18.911	24.288	5.377	42.58
5.60	127.967	138.707	11.285	26.882	56.95	20.144	24.296	4.152	42.58
10.82	128.009	138.722	8.018	23.578	65.77	20.404	24.751	4.347	37.75
10.90	128.014	138.723	3.983	19.559	76.54	19.698	24.758	5.060	37.76
15.60	128.088	138.739	7.467	23.075	69.12	20.986	25.168	4.182	33.97
15.60	128.088	138.739	4.578	20.643	77.54	20.443	25.168	4.725	34.21
20.80	128.213	138.755	5.242	20.643	78.12	21.219	25.622	4.403	31.05
20.81	128.213	138.755	9.160	24.611	67.44	21.839	25.623	3.784	30.91
26.00	128.375	138.773	5.933	21.204	78.62	21.935	26.075	4.140	28.47
26.00	128.375	138.773	10.416	25.673	66.76	22.553	26.075	3.522	28.52
30.98	128.560	138.789	10.425	25.513	69.16	23.227	26.509	3.282	25.19
31.04	128.562	138.790	6.359	21.446	80.43	22.606	26.515	3.819	25.17
35.49	128.752	138.804	6.851	21.703	80.66	23.098	26.903	3.805	24.65
35.59	128.756	138.805	11.231	26.140	68.80	23.664	26.911	3.247	24.65
40.04	128.766	138.818	11.228	25.930	70.62	24.095	27.299	3.204	23.32
40.09	128.970	138.819	7.127	21.936	81.76	23.598	27.304	3.706	23.30
45.29	129.242	138.836	11.416	25.871	72.30	24.611	27.757	3.146	21.95
45.29	129.242	138.836	7.607	22.151	82.89	24.159	27.757	3.598	21.90
50.25	129.523	138.852	7.116	22.397	83.99	24.652	28.190	3.538	20.88
50.29	129.527	138.854	11.806	26.094	73.14	25.112	28.193	3.081	20.88

Experiment IV.

OXYGEN IN DISTILLED WATER.

Volume of bulb empty at $0^\circ = 138.2724 = v_0$. Volume of water taken at $0^\circ = 127.4260 = w$.
 Volume of gas taken O_2 (corrected) $= 19.965$ at 16.40° and 978.15 mm. $= 25.1071$ at 0° and 760 mm.
 Volume remaining in burette after opening first tap (corrected) $= 16.615$ at 16.54° and 900.6 mm.
 $\therefore$ Volume of spiral $= 5.060$ at $16.54^\circ = 5.058$ at $0^\circ = 5.062$ at 45° .

<i>l</i> .	<i>w</i> .	<i>v</i> .	Burette Reading (in c.c.).	Volume Unabsorbed (c.c. at <i>t</i> ^h).	<i>p</i> = Pressure (Corrected).	Volume Unabsorbed (c.c. at <i>t</i> ^h 760).	Volume of Gas taken (c.c. at <i>t</i> ^h 760).	Volume Absorbed (<i>p</i> 760).	$\frac{1,000 \alpha}{v} =$ Volume Absorbed by 1,000 c.c. at <i>p</i> 760 (c.c. at 0° 760).
1.63	127.432	138.278	3.930	19.834	Centimetres. 74.34	19.329	25.257	5.928	47.27
2.18	127.429	138.281	8.162	24.071	64.06	20.289	25.308	5.019	46.36
6.20	127.430	138.293	4.468	20.390	75.50	20.250	25.077	5.421	41.89
6.60	127.433	138.297	8.771	24.604	64.88	21.081	25.714	4.633	41.58
9.53	127.456	138.304	4.766	20.673	76.58	20.831	25.983	5.152	38.76
9.61	127.457	138.306	9.084	24.992	65.61	21.576	25.991	4.415	38.76
13.65	127.513	138.318	8.086	24.951	67.45	22.144	26.362	4.218	35.50
13.75	127.515	138.319	6.040	21.904	78.09	22.506	26.372	4.866	35.36
16.72	127.573	138.328	5.750	21.565	77.61	22.022	26.645	4.623	33.44
16.75	127.573	138.329	10.111	25.927	66.54	22.700	26.647	3.947	33.30
23.80	127.762	138.351	6.125	21.775	80.11	22.953	27.296	4.323	29.67
23.90	127.765	138.353	10.569	26.217	68.43	23.060	27.305	3.099	29.57
29.86	127.974	138.372	11.184	26.643	69.62	24.466	27.853	3.467	26.51
29.88	127.975	138.373	7.204	22.763	79.74	23.883	27.855	3.962	26.60
37.51	128.303	138.397	11.572	26.738	71.74	25.239	28.587	3.318	24.09
37.54	128.304	138.398	7.553	22.719	82.23	24.761	28.559	3.768	24.06
43.25	128.587	138.466	8.188	23.129	83.52	25.418	29.085	3.667	22.41
43.29	128.591	138.467	12.395	27.534	71.59	25.936	29.088	3.152	22.40

These values are intermediate between those of Winkler and Bohr and Bock.

	0°.	10°.	20°.	30°.	40°.	50°.
Winkler	48.90	38.02	31.02	26.08	23.06	20.90
Fox	49.24	38.37	31.44	26.65	23.30	20.95
Bohr and Bock	49.61	39.03	31.71	26.76	23.26	20.70

C. SEA-WATER.

Before using the sea-water for filling into the bulb, it is necessary to add acid, otherwise it is impossible to boil out all the carbonic acid or to prevent the precipitation of neutral carbonates. The very small quantity of acid which it is necessary to add was determined by heating 500 c.c. of the sea-water with excess of acid and then titrating back the excess, using phenolphthalein as indicator. The chlorine was determined by titrating the water in the bulb after the absorption observations had been completed, by Mohr's method. The sea-waters used corresponded to about 7.5, 15, 20, and 23 per mille Cl respectively; twenty-one duplicate observations were made in the case of each gas. The results were then combined with those given above for distilled water. The formula for nitrogen gives the quantity of nitrogen and argon absorbed by sea-water from a free unlimited dry atmosphere in which the nitrogen always contains a constant percentage 1.185 of argon. (Dry air assumed to be 79.10 per cent. N_2 and 20.90 per cent. O_2 .)

TABLE III.

Number of c.c. of Nitrogen (containing Argon) absorbed by 1,000 c.c. of Sea-water from a free dry Atmosphere of 760 mm. Pressure.

$$1,000 a = 18.639 - 0.4304t + 0.007453t^2 - 0.0000549t^3 \\ - Cl(0.2172 - 0.007187t + 0.0000952t^2).$$

Cl.	$t = 0^\circ.$	4°.	8°.	12°.	16°.	20°.	24°.	28°.
0	18.64	17.02	15.63	14.45	13.45	12.59	11.86	11.25
4	17.77	16.27	14.98	13.88	12.94	12.15	11.46	10.89
8	16.90	15.51	14.32	13.30	12.44	11.70	11.07	10.52
12	16.03	14.75	13.66	12.72	11.93	11.25	10.67	10.16
16	15.18	14.00	13.00	12.15	11.73	10.81	10.27	9.80
20	14.31	13.24	12.34	11.57	10.92	10.36	9.87	9.44

TABLE IV.

Number of c.c. of Oxygen absorbed by 1,000 c.c. of Sea-water from a free dry Atmosphere of 760 mm. Pressure.

$$1,000 a = 10.291 - 0.2809t + 0.006009t^2 + 0.0000632t^3 \\ - Cl(0.1161 - 0.003922t + 0.0000631t^2).$$

Cl.	$t = 0^\circ.$	4°.	8°.	12°.	16°.	20°.	24°.	28°.
0	10.29	9.26	8.40	7.68	7.08	6.57	6.14	5.75
4	9.83	8.85	8.04	7.36	6.80	6.33	5.91	5.53
8	9.36	8.45	7.68	7.04	6.52	6.07	5.67	5.31
12	8.90	8.04	7.33	6.74	6.24	5.82	5.44	5.08
16	8.43	7.64	6.97	6.43	5.96	5.56	5.20	4.86
20	7.97	7.23	6.62	6.11	5.69	5.31	4.95	4.62

2. CARBONIC ACID.

As is well known, the analyses of the salts of sea-water show an excess of base over acid—that is to say, when the CO_2 is left out of account in such analyses. This CO_2 (about 50 c.c. per litre) is of course in equilibrium with the excess of base, which is actually equal to about 40 mgms. OH per litre.* It would seem that the partial pressure of CO_2 very seldom, or never, exceeds 6 in 10,000, and the present work has been limited therefore to pressures of about 1 to 7 per 10,000.† For the determination of the absorption coefficients of CO_2 there are consequently four independent variables to be considered; that is to say, there is the influence of alkalinity, a chemical influence, in addition to the purely physical influences of temperature pressure and salinity. The CO_2 dissolved may for convenience be regarded as made up of two parts; namely, a small part, about 1 per cent. of the whole, dependent upon the physical influences alone, and therefore independent of the alkalinity, and a far larger part dependent upon the alkalinity pressure and temperature but independent of the salinity; the sanction for which arrangement will be found below.

The small physical effect, which is also dependent upon temperature and pressure of course, may be calculated from the measurements of Bohr on NaCl solutions.‡ For $p = 1$ per 10,000 a is given for 1,000 c.c. of water in Table V., the values for other pressures being, of course, directly proportional to these values in accordance with Henry's Law—that is, equal to pa . (Cl in grammes per mille, CO_2 in c.c. per litre.)

TABLE V.

t .	Cl = 0.	2.	4.	6.	8.	10.	12.	14.	16.	18.	20.
0	0'1713	0'1690	0'1667	0'1664	0'1621	0'1598	0'1575	0'1552	0'1529	0'1506	0'1483
4	0'1473	0'1453	0'1423	0'1403	0'1383	0'1363	0'1343	0'1323	0'1303	0'1283	0'1263
8	0'1283	0'1263	0'1243	0'1223	0'1203	0'1183	0'1163	0'1143	0'1123	0'1103	0'1083
12	0'1117	0'1103	0'1089	0'1075	0'1061	0'1047	0'1033	0'1019	0'1005	0'0991	0'0977
16	0'0987	0'0973	0'0959	0'0945	0'0931	0'0917	0'0903	0'0889	0'0875	0'0861	0'0847
20	0'0877	0'0867	0'0857	0'0847	0'0837	0'0827	0'0817	0'0807	0'0797	0'0787	0'0777
24	0'0780	0'0773	0'0766	0'0759	0'0752	0'0745	0'0738	0'0731	0'0724	0'0717	0'0710
28	0'0700	0'0690	0'0680	0'0670	0'0660	0'0650	0'0640	0'0630	0'0620	0'0610	0'0600

There remains, then, to be considered the chemical effect of the alkalinity, and the methods employed in this work for the determinations involved were as follows—

Chlorine was determined by titration with silver nitrate solution, with K_2CrO_4 as indicator. The OH was determined in 200–500 c.c. by adding a known quantity of acid in excess, boiling off the CO_2 , and then titrating the excess of acid with standard alkali, using phenolphthalein as indicator. The CO_2 pressure was determined by Pettenkofer's method, modified to suit the present requirements. In this method a known quantity of $\text{Ba}(\text{OH})_2$ solution is added to a bottle of known capacity, filled with the air to be analysed for CO_2 , and the excess of $\text{Ba}(\text{OH})_2$ is titrated after all the CO_2 has been absorbed and precipitated as BaCO_3 . The chief source of error in this method seems

* Dittmar and also Tornöe always gave this excess of base over acid, or alkalinity as they called it, in terms of the unnecessarily cryptic unit of quantity of CO_2 necessary to convert it into normal carbonate; and, unfortunately as it would seem, this practice has been followed ever since. The unit used here will, however, be gms. or mgms. OH per litre; the factor for transforming data published hitherto into gms. OH per litre is 0'001517.

† See Krogh, *Middeldeiser om Grönland*, Heft 6/7, 331–434.

‡ Bohr, *Ann. der Phys. u. Chem.*, 62 (1897), 614.

to be the action of the $\text{Ba}(\text{OH})_2$ on the glass, and a number of bottles (8–20 litres) of different glasses were examined from this point of view. Most of the measurements here recorded were carried out with two bottles

FIG. 3.

(12 litres) of Jena Geräte glass, which were found quite satisfactory. The measurements were therefore carried out as follows : 500 c.c. of sea-water was put into the bottle, which was then rotated by means of a motor, with its axis horizontal (Fig. 3), until the water was in equilibrium with the air above it. In this arrangement a thin

film of water is carried round, adhering to the walls of the bottle in rotation, which is continuously renewed ; equilibrium thus takes place quickly. If the CO_2 pressure required was that of the atmosphere, a current of air was drawn through the bottle during rotation with an ordinary filter-pump. If any other pressure was required the bottle was merely closed instead with a rubber stopper carrying two glass tubes (Fig. 4), which allowed the water to be drawn off after equilibrium had been obtained and then $\text{Ba}(\text{OH})_2$ solution to be added without disturbing the air inside.* In this latter case, too, it is necessary to add BaCl_2 solution as well as $\text{Ba}(\text{OH})_2$ in order to prevent the NaCl contained in the drops of water which still remain hanging to the walls of the bottle, after as much as possible has been run out, from reacting with the precipitated BaCO_3 ; this would spoil the end point of the titration with standard acid and phenolphthalein. The excess $\text{Ba}(\text{OH})_2$ was titrated as quickly as possible with standard succinic acid while still in the bottle, and the stopper was not removed until near the end point. The sea-water run out was analysed for total CO_2 (and OH) in the apparatus illustrated in Fig. 5, which the writer has used some years for extracting gases from liquids, and which has proved very convenient for the purpose. The sample of liquid for analysis, if sealed up in a tube, is admitted by way of *c* ; if in an open vessel it is drawn into the evacuated flask by way of *a* ; the quantity of water drawn in is determined by weighing the vessel before and after the water is admitted. A known quantity of standard acid is admitted through *H*, and after all the gases have been extracted the water is withdrawn, with the help of a filter-pump, into another empty flask by way of *a* again, and a titration of the excess of acid then gives a determination of the total alkalinity.

FIG. 4.

Before the water sample and acid are admitted to the apparatus, the flask *A* is evacuated by boiling in it some distilled water, by exhausting simultaneously with a filter pump applied at *I*, and finally with the mercury pump *B*, and by also washing out with an indifferent gas (usually hydrogen) generated in the pipette *C* and admitted by the tap *h* as required. A very efficient condenser is necessary owing to the low temperature of boiling, and the form known as Cribb's is very well suited to the purpose, especially as it takes up so little room. After the apparatus has been freed from air in this way, the sample to be analysed is admitted together with the acid, the gases

* In calculating *p*, it is necessary to apply a correction for the quantity of air which displaces the water as it runs out, and also for the CO_2 contained in the small quantity of water which remains behind adhering to the glass. A series of tests showed that these two corrections together could be kept down to about 5 per cent. of *p*.

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The temperature usually varied a little during the taking of a series of measurements, and in this case the mean of all was taken and the measurements subsequently reduced to that temperature ; it was found that for small temperature differences it was sufficient to assume the quantity of dissolved CO_2 proportional to the absolute temperature. Finally, it should be stated that many series of measurements were made, but several were for one reason or another

FIG. 6.

thought to be possibly less reliable than the others, and they were rejected ; only the most reliable ones are embodied in the conclusions given here.

In the first place the influence of OH upon the total quantity of CO_2 dissolved at constant pressure was determined, the constant pressure employed naturally being that of atmospheric CO_2 . In the case of the very dilute solutions here involved (40–50 mgms. OH per litre and up to about 90 c.c. CO_2) it is, of course, to be expected *à priori* that the second dissociation of H_2CO_3 into 2H^+ and CO_3^{--} is of no appreciable consequence. According to Bodländer * it is always 20,000 times less than the ionisation

* Bodländer, *Zeit. für physik. Chemie*, 35, p. 23.

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of the first H' , which is also, of course, very small itself. And, as a matter of fact, the present series of measurements showed that the ratio of OH to combined CO_2 is rectilinear. The measurements are given here, and the results are plotted in Fig. 6.

In accordance with Guldberg and Waage's law, the reaction is therefore represented completely by—

and no appreciable part of it can proceed according to the relation—

This having been established, it was then necessary in determining the influence of CO_2 pressure to use only one OH concentration; that selected was $OH = 40$ mgms. per litre, which is probably very near to the average alkalinity of the open ocean. Measurements were made at temperatures of about $0-27^\circ$ and pressures $1-6.5$ per 10,000; they are given below, together with those made in determining the influence of alkalinity. The formula calculated from using all the results together may be written in the form—

$$x = pa + yb,$$

or total CO_2 in c.c. per litre $= x = pa + y[0.9731 - 0.005382t + (0.08540 + 0.00113t)(p - 1) - (0.01587 + 0.000310t)(p - 1)^2 + (0.001254 + 0.00003455t)(p - 1)^3]$, where—

y = alkalinity in mgms. OH per litre.

a = factor depending upon Cl and t , and found tabulated in Table V.
i.e., for $p = 1$ per 10,000.

	Total OH per litre (y mgms.).	Total CO ₂ per litre (x c.c.).		t .	Free CO ₂ (x c.c.).	Total CO ₂ (x c.c.).		p .	Free CO ₂ (x c.c.).	Total CO ₂ (x c.c.).	
t p Cl pa	2.39 3.41 19.60 31.42 46.70 47.18 60.60	3.65 4.72 25.50 40.75 60.03 60.10 77.35	t Cl OH	$= 2.77^\circ$ $= 7.14$ $= 40.00$	1.03 1.66 3.21 3.65 5.48 5.53 6.15 6.64	0.15 0.16 0.47 0.54 0.80 0.81 0.90 0.98	t Cl OH	$= 15.04^\circ$ $= 19.46$ $= 40.00$	1.06 1.45 2.88 3.54 5.01 5.47	0.09 0.11 0.26 0.31 0.45 0.49	41.35 43.38 47.54 48.52 50.05 50.79
t p Cl pa	7.39 16.83 30.00 38.04 40.37 52.96 61.60 78.41	9.40 21.00 36.77 46.53 49.40 65.22 75.90 96.50	t Cl OH	$= 8.06^\circ$ $= 14.26$ $= 40.00$	0.73 1.12 1.18 3.11 5.37 6.26	0.08 0.13 0.13 0.35 0.61 0.71	t Cl HO	$= 20.96^\circ$ $= 14.36$ $= 40.00$	1.40 2.47 2.88 3.33 3.72 4.47 4.86 5.52 5.98	0.12 0.19 0.22 0.26 0.29 0.35 0.38 0.43 0.47	42.06 45.36 46.20 47.13 47.64 48.51 49.12 49.77 50.58
t p Cl pa	2.00 14.33 26.02 46.05 58.53 62.12 78.06	2.60 17.38 30.81 55.20 70.65 73.95 93.55	t Cl OH	$= 10.53^\circ$ $= 0.00$ $= 40.00$	0.77 1.16 1.19 1.63 1.79 2.70 2.79 3.61 3.70 3.97 4.12 4.14 5.31 5.92 6.63 7.02	0.09 0.14 0.14 0.19 0.21 0.33 0.33 0.42 0.43 0.46 0.48 0.48 0.62 0.69 0.78 0.82	t Cl OH	$= 24.18^\circ$ $= 0.00$ $= 40.00$	2.23 3.05 4.73 4.88 5.53	0.17 0.21 0.31 0.32 0.43	43.93 44.78 47.52 48.60 49.47
t p Cl pa	11.58 29.41 49.35 64.81	13.25 33.90 57.20 74.42	t Cl OH	$= 26.46^\circ$ $= 3.42$ $= 0.00$ $= 0.25$	4.12 4.14 5.31 5.92 6.63 7.02	0.48 0.48 0.62 0.69 0.78 0.82	t Cl OH	$= 28.49^\circ$ $= 19.48$ $= 40.00$	2.02 3.11 3.68 5.02 5.03	0.12 0.19 0.22 0.30 0.30	42.52 45.28 46.10 47.94 48.15

The first term pa , which represents the "free" CO_2 , has always a very small value (about 1 per cent. of the whole), and is independent of the alkalinity; the remainder (about 99 per cent.) is combined in the form of HCO_3' ions, and is independent of the salinity. Sea-water rarely contains more than $3\frac{1}{2}$ per cent. of salts, and its physical influence upon the chemical effect of the alkalinity is, as may be expected, practically nil; for the formula calculated from all the measurements taken together by ignoring the salinity (except as regards the first term pa) seems to fit the different series of observations about equally well. The data necessary for the calculation of pa in all cases have been given in Table V.; a tabulation of b for the most useful values of p when $y = 1000$ mgms. per litre is given in Table VI.

FIG. 7.

These values corresponding to $y = 1000$ mgms. per litre are, as shown, directly proportional to the alkalinity. All that is necessary therefore to find any value for any other specified alkalinity is to multiply the factor given in the Table for b , by the alkalinity expressed in mgms. Likewise from the Table it is possible to deduce the CO_2 pressure of a sea-water when x and y are known (pa is very small and nearly constant)—

$$b = \frac{x - pa}{y} = \frac{x}{y} \text{ approximately ;}$$

from which value, when t is known, p may be found from the Table. The value of p thus found is accurate enough for most purposes; but if not, it is easy from this value of p to put in the correct value of pa , and thus to calculate b accurately.

Some of the results, too, are given graphically (Fig. 7) for total CO_2 and varying pressure at $t = 0^\circ, 10^\circ, 20^\circ, 30^\circ$, and OH 10, 20, 40 mgms. per litre. In addition there are given also the values plotted for $t = 15^\circ$ and

TABLE VI.

$b = \text{c.c. combined CO}_2 \text{ in 1,000 c.c. sea-water for 1 mgm. OH per litre.}$

λ .	$l = 0$.	2.	4.	6.	8.	10.	12.	14.	16.	18.	20.	22.	24.	26.	28.
1.5	1.1	1.562	1.451	1.340	1.229	1.118	1.007	1.1.	0.785	0.674	0.563	0.452	1.	1.	1.
2.0	2.021	1.920	1.818	1.717	1.615	1.513	1.412	1.310	1.209	1.107	1.005	0.904	0.802	0.701	0.599
2.2	2.140	2.042	1.943	1.845	1.746	1.647	1.549	1.450	1.352	1.253	1.154	1.056	0.957	0.859	0.760
2.4	2.249	2.153	2.057	1.961	1.865	1.769	1.673	1.577	1.481	1.385	1.289	1.193	1.097	1.001	0.905
2.6	2.348	2.259	2.160	2.066	1.973	1.879	1.785	1.691	1.597	1.504	1.410	1.316	1.222	1.128	1.035
2.8	2.437	2.346	2.254	2.162	2.070	1.978	1.887	1.795	1.703	1.611	1.519	1.428	1.336	1.244	1.152
3.0	2.518	2.428	2.338	2.248	2.158	2.068	1.978	1.888	1.798	1.708	1.618	1.528	1.438	1.348	1.258
3.2	2.592	2.504	2.415	2.327	2.238	2.150	2.062	1.973	1.885	1.796	1.708	1.620	1.531	1.443	1.354
3.4	2.658	2.571	2.484	2.397	2.310	2.223	2.136	2.049	1.962	1.875	1.788	1.701	1.614	1.527	1.440
3.6	2.718	2.633	2.547	2.461	2.376	2.290	2.205	2.119	2.033	1.948	1.862	1.777	1.691	1.605	1.520
3.8	2.773	2.689	2.603	2.519	2.434	2.350	2.265	2.180	2.096	2.011	1.927	1.842	1.757	1.673	1.588
4.0	2.822	2.739	2.655	2.572	2.488	2.405	2.322	2.238	2.155	2.071	1.988	1.905	1.821	1.738	1.654
4.5	2.928	2.848	2.767	2.687	2.606	2.525	2.445	2.364	2.284	2.203	2.122	2.042	1.961	1.881	1.800
5.0	3.019	2.942	2.864	2.787	2.709	2.632	2.555	2.477	2.400	2.322	2.245	2.168	2.090	2.013	1.935
5.5	3.105	3.032	2.958	2.885	2.812	2.739	2.666	2.592	2.519	2.446	2.373	2.300	2.226	2.153	2.080
6.0	3.197	3.130	3.062	2.995	2.928	2.861	2.794	2.726	2.659	2.592	2.525	2.458	2.390	2.323	2.256
6.5	3.306	3.246	3.187	3.127	3.067	3.008	2.948	2.889	2.829	2.769	2.710	2.650	2.591	2.531	2.471

OH = 34.48 mgms. per litre ; the values for this temperature and alkalinity have been determined before by Krogh,* and this seems to be the only work done hitherto with which a comparison of the above Tables can be made.

Very little of the material hitherto published seems to be both complete enough and accurate enough to furnish useful information upon analysis with the help of these Tables. Of the five variables p , t , Cl, OH, CO₂ it is, of course, necessary to observe for every sample of water four at least, in order to obtain complete knowledge of the equilibrium ; if four are known the fifth can be deduced. Unfortunately the practice seems to have been to observe only three, namely, t , Cl, and CO₂ ; OH has been only very rarely determined. A great number of measurements were, it is true, made on the *Challenger* Expedition, but by obviously imperfect methods and often upon samples not very carefully stored, for years. Of all the material examined by the present writer, only the well-known series made in the Gullmar Fjord in July, 1890, by Frk. A. Palmquist, seems to be quite complete and at the same time obviously reliable ; the pressures calculated from those observations come out always between 1.5 and 4.0 per 10,000.

The chief interest of these measurements lies, however, in the fact that they for the first time allow a calculation to be made of the power of the sea to conserve the constancy of CO₂ pressure in the atmosphere ; a matter which, since the publication of Arrhenius's papers † on the effect of atmospheric CO₂ upon terrestrial temperatures has become of importance. The quantity of CO₂ required to change the CO₂ pressure of sea-water at constant temperature from p_1 to p_2 is given by—

$$c = y(b_{p_1} - b_{p_2}),$$

where y is the alkalinity and b_{p_1} b_{p_2} the factors in Table VI. corresponding to p_1 p_2 at t° . For $y = 40$ and $t = 12^\circ$, which are probably about the average numbers for the open ocean, and $p_1 = 3.5$ and $p_2 = 2.5$ per 10,000, c is equal to 1.76 c.c. per litre. In other words, it requires about 17.6 times as much CO₂ to raise the pressure by the same amount as for the same volume of air. In the case of CO₂, however, the effective volume of the atmosphere seems to be about eight times that of the ocean, ‡ and therefore when a quantity of CO₂ is poured into the atmosphere (e.g., by volcanic action) it will distribute itself between sea and air in the proportion of 17.6 to 8, or roughly $\frac{3}{8}$ and $\frac{1}{8}$ by total amounts, or 17.6 to 1 by concentration. And this is the measure of the ocean's capacity to conserve the constancy of CO₂ in the atmosphere. It is at the same time clear, however, that with insoluble carbonates on the sea-bottom and free CO₂ in the atmosphere at its surface, the ocean cannot finally be in equilibrium until either all the CO₂ or all the carbonate has gone into solution as HCO₃ ions. However, it takes time for this equilibrium to be established, and it is no doubt this time-factor which is geologically of

* Krogh, *loc. cit.*, carried his determinations up to $p = 352$ per 10,000, but he used only one temperature and one alkalinity.

† Arrhenius, on the influence of CO₂ in the air on the temperature of the ground, *Phil. Mag.*, 1896, pp. 237-276.

‡ According to Th. Schloesing, " Sur la Constance de la Proportion d'Acide Carbonique dans l'Air " (*Comp. Rend.*, 90 (1880), 1410), there are 4.7 kgms. CO₂ in the air above and 98 kgms. in the water beneath each sq. metre of ocean surface. On the other hand, there is 0.3 c.c. per litre in the air and about 50 c.c. per litre in the ocean. The effective volume of the atmosphere for CO₂ is therefore $\frac{4.7}{98} \times \frac{50}{0.3} = 8$ times that of the ocean.

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importance in this connection ; but at present nothing is known about its magnitude and exact influence.

In certain biological problems it is of interest to be able to calculate the concentration of the ions produced by the CO_2 . In the case of HCO_3 the concentration in gram equivalents per litre is given by—

$$\frac{0.002724}{61} x = 4.48 \times 10^{-5} x,$$

where x is the total quantity of CO_2 in c.c. per litre. As x is seldom more than 50, the concentration of HCO_3 will as a rule not exceed about 0.0022 gm. equivalents, or 0.13 gms. per litre.

The free CO_2 must exert its effect in increasing the concentration of free H^+ ions in the water, as a result of the formation of H_2CO_3 —

$$(\text{H}^+) \times (\text{HCO}_3') = 3.04 \times 10^{-7} (\text{H}_2\text{CO}_3).$$

If the free CO_2 be pa c.c. per litre, the concentration of H_2CO_3 is :—

$$\frac{0.00196}{44} pa \text{ gm. equivalents per litre,*}$$

or—

$$(\text{H}^+) \times (\text{HCO}_3') = 3.04 \times 10^{-7} \times \frac{0.00196}{44} pa = 1.36 \times 10^{-11} pa,$$

and—

$$(\text{H}^+) = \sqrt{1.36 \times 10^{-11} pa};$$

pa is practically always 0.2 to 0.5, and (H^+) consequently varies from 1.6 to 2.6×10^{-6} . For distilled water it is about 1×10^{-7} . In other words, sea-water reacts *in situ* very nearly neutral, and, in fact, just slightly more acid than distilled water. An attempt was made to measure this (H^+) concentration in sea-water directly, by means of E.M.F. measurements with the hydrogen gas electrode, but it was found very difficult to obtain constant values. However, the results at least pointed to some value between 10^{-5} and 10^{-7} . A similar result has already been obtained in the same way by Cottrell, on behalf of Loeb.†

And it seems probable that all naturally occurring liquids, whether of biological or geological origin, must, if neutral or alkaline initially, tend to become slightly acid in the same way ; owing to the all-pervading presence of CO_2 of low pressure. A liquid already acid to begin with will, of course, be practically unaffected.

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* This is not quite true, owing to the present insufficient knowledge of the equilibrium— $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$. It should be noticed, too, that H_2CO_3 reacts as a monobasic acid, and the equivalent of CO_2 is therefore to be taken as 44 and not 22.

† Pflüger's *Archiv.*, 99 (1903), 637.