## The Abnormal CO<sub>2</sub>-Percentage in the Air in Greenland and the General Relations between Atmospherie and Oceanie Carbonie Acid.

By

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Copenhagen. Printed by Bianco Luno. 1904. During a voyage round the Island of Disko in West-Greenland (lat. N. 70°) made in the summer of 1902, I undertook a series of analyses of the atmospheric air. The apparatus used, the accuracy obtained, as well as other details are given in the preceding memoir<sup>1</sup>), so I shall now proceed at once to a tabulation of the results. The localities mentioned lie along the northern and western coast of Disko, most of them being on the open sea-shore but a few also on the deep «fjords» of that coast.

As a supplement to the table containing my analytical results I record separately all the barometric observations made during the time. I cannot, however, find any connection between the variations of the pressure and the composition of the air.

Percentages of oxygen and carbonic acid in the air of Disko. (Hours from 6 p. m to 5 a. m. are printed in large type.)

Locality	Tin Date	ne Hour	Bar.	Win Direction		Weather	CO2 per cent	$O_2$ per cent	
Kuganguak	July 15	н	758.2	NW	2	Cloudy	0.05	20.93	At the sea.
	16	1	(701.0)	"	"	"	0.055	20.975	670 m. above the sea.
	"	3	756.2	"	"	"	0.07	20.95	At the sea.
Ingnagnak	20	2	765.0	NE	3	Overcast	{0.07 0.06	21.01 20.99	

<sup>1</sup>) KROGH: On the tension of carbonic acid in natural waters and especially in the sea. Medd. om Grønland, H. 26, pp. 333-405.

Locality	Tim Date	e Hour	Bar.	Wir Direction		Weather	CO2 per cent	$O_2$ per cent	
Napasiligsuak	July 21	3	771.1	NNW	1	Overcast	0.055	20.975 20.985	
	"	6	772.1	wsw	3	Overcast	0.05	20.975 20.98	
<del>–</del> 4.	"	"	"	"	"	"	{ 0.04 ( 0.04	20.94 20.94	Among the vegetation.
	"	"	"	n	"	Fog	0.05	20.92	80 m. above the sea.
Igdlorpait	27	1	758.6	NW	1-0	Overcast	0.05	20.96 20.945	- NOV
Avatarpait	29	8	750.1	s	3		0.05 0.05 0.055 0.055	20.975 20.975	$\begin{cases} Wind N 3-5 \\ during the \\ whole day. \end{cases}$
	30	7	755.2	wsw	3-6	Overcast, some rain	{ 0.05 0.04		The analysis a little un- certain.
Nordfjord	31	5	757.0	sw	1	Cloudy	{ 0.05 0.04	20.975 20.975	
	August 2	8	757.6	SE	2	Overcast	0.06	20.94	WindNW,1-3
	3	10	760.7		0	Bright	0.05		during the whole day.
	4	11	756.4	E	3-5	Rain, mist Overcast.	{ 0.035 0.03	20.94 20.90	
:	5	4	755.5	E	5-6	some rain	0.03	20.98	
	"	8	755.4	"	"	"	0.045	20.975	
- ,	"	8.30	"	"	"	"	0.04		(
	- 6	4	759.4	Е	3-5	Overcast	) 0.05 ( 0.045	20.965 20.975	Wind in the height S.
Ivisarkut Mellemfjord	10	6	757.8	S	4-5	Rain, mist	0.035 0.025	20.965 20.975	
	"	8	758 6	"	"	"	0.025	Sec.	
	11	8	762.4	S	2-3	Bright	0.02 0.03	20.975 20 955	

Locality	Tim Date	e Hour	Bar.	Win Direction		Weather	CO <sub>2</sub> per cent	O <sub>2</sub> per cent	
Ivisarkut Mellemfjord	August 11	2	763.4	s	1-2	Bright	{0.045 0.05	20.925 20.935	
meneninjora	"	9-	764.6	NNW	1	Overcast	0.045	20.95	Wind N since 4 o'clock.
	12 "	1 12	765.0 760.0	S	0 3-5	Cloudy Cloudy	0.05 0.025	20.955	Tp.16.5! Sci-
	13	3	762.8	SE	3-8	Cloudy Heavy	0.025	20.975 20.96	( rocco-wind. Tp. 13.8.
Head of		1	765.5	"	7-9	rain	0.045		Tp. 8.3.
Mellemfjord	11 12	9	765.8			Overcast	0.05	20.975 20.965	{ 120 m. above
Nakerdluk	17	11	765.5	W	1	Bright	0.06	20.84	( the sea.
Diskofjord	,	10	762.6	N	0-1	Bright	0.06	20.945 20.97	the fjord N.
	18	12			0	Cloudy	0.045	21.015	{ 500 m above the sea.
	.11	5	758.3	N	0-1	Cloudy	0.06 0.055	20.96 20,965	( Wind outside
	19	5	754.9	w	3	Fog	{ 0.065 0.07	20.915 20.935	the fjord said to be N.
Sioranguak Diskofjord	21	9	750.8	[E]	4	Rain	{ 0.065 0.07	20.95 20.93	
	22	7	748.4	[NE]	1-3	Rain	0.055		
Uvifak	25	12	753.2	WNW	3	Bright	0.055		

rs from	rs from 6 p. m. to 5 a. m. are printed in large type.)								
te	Hour	Barometer	Dat	te	Hour	Barometer			
15	11	758.2	July	28	11	756.4			
16	3	756.2		29	3	751.7			
17	12.30	753.3	-	"	8	750.1			
"	6	756.6	-	"	12	750.3			
"	9	758.5	-	30	9	750.8			
"	11	759.1	-	"	7	755.2			
18	1	759.3	-	"	10	757.3			
"	10.30	757,3	-	31	9	760.5			
"	1	754.9	-	"	5	757.0			
"	3.30	753.2	-	"	6	756.6			
"	7.45	751.1	August	1	11.15	754.4			
19	2	754.4		"	1	755.0			
"	6	755.2	-	"	6	756.8			
"	10	756.3	-	2	12.30	757.5			
"	2.30	757.2	-	"	12.30	756.9			
"	12	760.1	-	"	3.45	757.2			
20	2	765.0	_	"	8	757.6			
21	2	768.3	-	"	10.30	758.0			
"	9	770.2	-	3	8.30	757 8			
"	3	771.1	_	"	12.15	757.5			
"	5	771.7	-	"	5.45	7596			
"	6	772.1	_	"	10	760.7			
"	12	771.6	_	4	10	759.5			
22	8.30	772.8			2.30	758.3			
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Disko 1902. Barometric pressure at the sea-level. Hours e.)

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Date	Date Hour		Barometer I		Date H		Barometer
August	11	8	762.4	August	18	10.30	761.0
	"	2	763.4	-	"	1.30	759.8
	"	9	764.6	-		5	758.3
-	12	1	765.0		"	11.30	755.7
-	"	11	760.3	-	19	5	754.9
	"	12	760.0	-	20	8.30	753.2
-	13	3	762.8	_	"	2.30	752.4
-	"	1	765.5	-	"	6	753.2
	"	6	767.4	_	21	9	750.8
_	15	9	764.9		"	7	750.0
	17	11	765.5	-	22	7	748.4
-	"	10	762.6	_	25	12	753.2

Respecting the percentages of oxygen found by the analyses I have very little to say. They exhibit the usual variations: 21.015 to 20.92. An isolated observation of 20.84 is probably due to some very local cause or perhaps to an analytical error. Taking no notice of this one the average of the determinations comes out as 20.960, or slightly higher than that accepted for Europe, 20.93. REGNAULTS analyses indicate that the percentage in the Tropics is a little lower than in Europe.

The results of the  $CO_2$ -determinations are very remarkable and unexpected. Whereas everywhere else, in temperate Europe, in the Tropics and in the Southern Hemisphere, the percentage of carbonic acid is about 0.03 and varies from 0.02 to 0.04 at the utmost, I have found percentages up to 0.07 and variations from 0.025 to this figure.

I have, of course, tested these surprising results in every possible way and I must confess that I have tried again and again to explain them away as errors. But there is no such possibility.

The samples of air were sometimes taken directly into the analysis-apparatus, but in most cases they were taken into short test-tubes and analysed about half an hour later. The corks of the test-tubes were soaked in paraffine-wax. No detectable

413

traces of carbonic acid are eliminated from such corks and no difference was found in the double-determinations when one of the tubes was analysed immediately and the other preserved for a day or two.

Errors may arise, during the analysis itself, from the absorbing fluid, if this is not saturated with atmospheric air exactly at the temperature and barometric pressure obtaining (as mentioned in the preceding paper p. 346). When in Greenland I did not know this source of error, but very often (though not always) after a determination of carbonic acid I took the sample of air once more into the absorption-pipette and satisfied myself that no perceptible alteration of the volume took place. By the numerous determinations which I have made since then with more sensitive apparatuses I have never seen errors from this source amounting to more than 0.002 %. It is rather probable that several of my Greenland-determinations are infected with errors of this magnitude, because the temperature often varied considerably. In almost all cases, however, the temperatures at which the analyses were made were decidedly higher than those to which the absorption-fluid was exposed during the intervals. If anything, it would therefore be a little supersaturated during the analyses and give off a little air. If my analyses are infected by errors of this kind it must be admitted, therefore, that they do not reach 0,005 % and that they must, in almost all cases, have had a tendency to diminish the figures found for the carbonic acid.

During my stay in Greenland I wanted to test the results by means of another method, but my analytical outfit could not be transformed into a PETTENKOFER-apparatus or anything like it. I was very glad therefore to find in the literature a clear confirmation of my observations. During the *Discovery*-Expedition Dr. E. Moss<sup>1</sup>) made 3 determinations of carbonic acid

<sup>4)</sup> Notes on Arctic Air. Proc. Roy. Dubl. Soc. Vol. 2, 1880.

415

in the atmosphere of Grinnel-Land (Floebery Beach, Latitude N. 82° 27'). He applied the PETTENKOFER-method which is, according to TEICH (*Arch. f. Hygiene* Bd. **19** pp. 38-50), liable to give somewhat high results. It is very improbable however that the errors will exceed  $0.005 \ 0/0$ .

- Dcbr. 10. Wind NNW. Tp. 14.8° F. Quantity of air analysed 4735 cc. Percentage of CO<sub>2</sub>.... 0.0642
- 2. Jan. 18. Tp.  $-40^{\circ}$  F. Quantity of air analysed 9565 cc. Percentage of  $CO_2$ .... 0.0483
- 3. Febr. 29.

Quantity of air analysed 19128 cc. Percentage of  $CO_2$ .... 0.0536.

Even if these values must be diminished by 0.005 they are of quite the same order as my own, and though they are obtained from a place 750 miles north of Disko they may perhaps be due to the same local cause.

I shall not go into the problem of the biological and geological importance of the high percentage of carbonic acid which must certainly be very great<sup>1</sup>) but confine myself to the intricate question of the possible origin of the gas in the air.

It appears from my determinations that the direction of the wind had a distinct influence upon the carbonic acid. The percentage is generally higher from northern and western winds than from eastern and southern. There is only one serious exception to this rule, viz. the last analysis but two, made at *Sioranguak* in the Diskofjord, where a percentage of 0.07 was

<sup>&</sup>lt;sup>1</sup>) The assimilation of plants is, according to several investigators, directly proportional to the percentage of carbonic acid in the air, and there can be no doubt that the disintegration of the basalt is likewise much facilitated by a high percentage.

found during a strong easterly wind. It must be remembered however that the place lies at the head of a «fjord» surrounded on all sides by mountains; the real direction of the wind outside can therefore have been quite different. All other places mentioned lie on the open sea-shore or so near to the mouths of the «fjords» that the true direction of the wind could always be ascertained.

On the whole, it seems that Disko lies on the southern or eastern border of an area of intensive production of carbonic acid, since air, rich in the gas, oscillates to and fro over the Island according to the shifting of the wind. What can be the seat and source of this production or liberation of carbonic acid?

In order to solve this special question I have been obliged to take up the general problem of the carbonic acid of our atmosphere, and by bringing to bear upon this the principles of the tension of carbonic acid in the sea and of evasion and invasion, as set forth in the preceding paper, I shall be able, I hope, to throw some new light upon certain points in it.

## I. The carbonic acid of the atmosphere as a whole.

I we take 0.03 as the average percentage of carbonic acid in the air, what is probably a little too high, the total quantity of the gas present in the atmosphere comes out as  $2.4 \times 10^{12}$ tons. Is this quantity a fixed and unalterable one?

This question has been discussed by several Authors and valuable contributions have been made towards its solution, notably by  $H\bar{o}GBOM^{-1}$ ) and  $CHAMBERLIN^{2}$ ). I shall confine myself to a brief statement of the chief causes of consumption and production of the gas.

2) Journal of Geology, vol. 7, 1899.

<sup>1)</sup> Svensk Kemisk Tidskrift Bd. 6, 1894, p. 169.

The organic life. Carbonic acid is fixed and converted 1. into organic substances by the assimilation of green plants. It is liberated anew by the respiration of all living organisms and especially by the decay of organic substances. This circulation is generally performed in a very short time and cannot have any considerable effect (as pointed out by Högbom) on the quantity of carbonic acid present in the atmosphere. Only that part of the organic substance, which is deposited as such and in the course of the geological periods converted into carbon and hydro-carbons, is permanently, or at all events for a long time, withdrawn from the atmosphere. Through this deposition the organic life of the globe constantly tends to diminish the quantity of free carbonic acid. No small amount of carbon has, undoubtedly, been fixed in this way and stored up, partly in the layers of carbon and hydro-carbons, but, as CHAMBERLIN thinks, especially in the «disseminated organic matter in the sedimentary series». If the immense length of the geological periods is taken into consideration it would appear, however, that the amount of carbon fixed year by year must be comparatively small.

2. The formation of carbonate from «alkaline» silicates is a very important cause of diminution in the quantity of free carbonic acid and has been recognized as such by several Authors, who ascribe by far a greater influence to it than to the action of the organic life.

Högbom is of opinion that all carbonates on the earth are derived from this source and, estimating their quantity as the equivalent of a layer round the globe 100 m. thick (and probably more), he finds the quantity of carbonic acid contained in such a layer to be 25000 times that of our present atmosphere. He further estimates the total quantity of carbonates yearly carried to the sea by the rivers in the world at 3 cb. km. (corresponding to 4000 million tons of carbonic acid) of which only a small part can be derived from the decomposition of

27

silicates <sup>1</sup>). This method of estimating the production of carbonates from silicates must however give too small results, because it is highly improbable that all, or even the greater part of the carbonates produced, should be dissolved and carried to the sea. I have shown that, as the last trace of free carbonic acid is utilized in the decomposition of silicates, normal carbonates are formed and nothing is left to dissolve them and carry them away.

CHAMBERLIN (pp. 563—568) gives very good reasons for the opinion that the rate of decomposition of alkaline rocks is mainly dependent on the general elevation of the land. A great elevation must augment the volume and surface of rock exposed to the joint action of water and air and will greatly facilitate the circulation of the underground waters. As periods in the earths history of great general elevation he pronounces among others the Pliocene and Pleistocene.

The rate of decomposition of silicates must further be governed by the percentage of carbonic acid found in the atmosphere, whereby it acquires a certain regulating influence on the aforenamed percentage. A high percentage of carbonic acid must be accompanied and counteracted by an enhanced rate of combination of the gas with the rocks.

3. The exhalation of carbonic acid from the interior of the earth is the principal source by which the diminishing factors mentioned are checked. Carbonic acid issues forth from the ground in some places, notably in volcanic environs, in enormous quantities<sup>2</sup>). The origin of this carbonic acid is not known. Possibly it is partly derived from the decomposition

<sup>&</sup>lt;sup>1</sup>) T. MELLARD-READE (Adresses. Geol. Soc. Liverpool 1876 and 1884, quoted from CHAMBERLIN) estimates this part as corresponding to 270 mill. tons of carbonic acid.

<sup>&</sup>lt;sup>3</sup>) BISCHOF mentions for instance (*Lehrbuch der chem. und phys. Geol.* Bd. I p. 691) that a single mineral spring in Nauheim produces yearly about 500 tons of carbonic acid, whereas two others, at Meinberg, yield at least 650 tons pro year.

of carbonates at high temperatures by the action of silicic acid which, according to BISCHOF (*op. cit.* p. 42), is even capable of decomposing carbonates at  $100^{\circ}$ .

4. The combustion of meteorites is mentioned by Носвом and CHAMBERLIN as a possible source of carbonic acid. Nothing whatever is known about it quantitatively.

5. The combustion of coal by man is an ever-increasing factor that has in recent years reached very considerable magnitude. This factor can, unlike the others, be expressed in fairly accurate figures. The worlds production of coal amounted in 1902 to 700 million tons (according to statistics published in the *Times*), giving by combustion  $2.6 \times 10^9$  tons of carbonic acid or rather more than  $^{1}/_{1000}$  of the quantity present in the atmosphere. In the geologically insignificant period of 1000 years the percentage of carbonic acid could therefore be doubled by this cause alone, if all other factors remained unchanged.

While the action of the diminishing factors may be supposed to be fairly constant, so long as the climatic conditions and the percentage of  $CO_2$  in the air do not vary too much, the same obviously need not be the case with regard to the increasing ones. It is extremely probable that the exhalation of carbonic acid from the ground varies greatly, corresponding to the variable volcanic action, and we know that the quantity of coal burned by man is by no means an unalterable quantity. We have no reason, therefore, to think that the amount of carbonic acid present in the atmosphere is even approximately constant.

There exists, however, a great factor capable of acting as a *regulator* upon the variations by checking and retarding every increase as well as every decrease in the percentage in the atmosphere.

27\*

In a very remarkable paper<sup>1</sup>) SCHLOESING pointed out that the quantity of loose carbonic acid present in the bicarbonates of the sea depends upon the tension of the gas, and that, therefore, a decrease in the atmospheric carbonic acid must produce a dissociation of bicarbonates in the sea and, consequently, a liberation of the gas. SCHLOESING calculated that the amount of  $CO_2$  present in the air is 4.7 kgrs. to every sq. m. of the earth's surface, whereas the corresponding quantity in the sea is, according to him, 98 kgrs. He rightly concluded that, if equilibrium is once established, every alteration in the percentage in the atmosphere will be counteracted by the sea, which may give off or absorb comparatively large quantities of carbonic acid without any appreciable alteration in its tension.

By applying my recent determinations of tensions and quantities of carbonic acid in seawater we will get a still clearer insight into these processes. *The preceding paper* pp. 358-59.

According to "La grande encyclopédie" the total surface of the ocean amounts to  $3.74 \times 10^{14}$  sq. m. and its mean depth to 3500 m. (3300 in the Atlantic and 3800 in the Pacific). The total quantity of seawater is accordingly  $1.3 \times 10^{18}$  cubic meters. If we take the amount of free and loose carbonic acid at the tension of the atmosphere, 0.03 %, to be 50 mgrs. per l. we arrive at the enormous total of  $6.55 \times 10^{13}$  tons, or 27 times the quantity of atmospheric carbonic acid<sup>2</sup>).

If the  $CO_2$ -tension of the atmosphere is diminished or

<sup>&</sup>lt;sup>1</sup>) TH. SCHLOESING: Sur la constance de la proportion d'acide carbonique dans l'air. *Compt. rend.* T. 90, 1880 p. 1410.

<sup>&</sup>lt;sup>2</sup>) DITTMAR puts (in *Encycl. Brit.*) the average depth of the sea at 2000 fathoms and its total mass at  $1.322 \times 10^{18}$  tons. The total quantity of carbonate, calculated as normal carbonate of lime, is, according to DITTMAR,  $1.6 \times 10^{14}$  tons and from these figures I calculate the amount of free and loose carbonic acid (85 %) of the fixed quantity) to be  $5.98 \times 10^{13}$  tons.

augmented, carbonic acid will be liberated or absorbed to an extent which may be calculated from my determinations<sup>1</sup>).

Tension º/o	Quantity tons	Difference atmospheres
0.01	$4.57  imes 10^{13}$	5.5
0.02	$5.89  imes 10^{13}$	2.8
0.03	6.55 × 10 <sup>13</sup>	2.0
0.04	$7.04  imes 10^{13}$	1.3
0.05	$7.36  imes 10^{18}$	1.5

The differences given in the third column are expressed in terms of the present quantity of carbonic acid in the atmosphere and mean that if the percentage of carbonic acid in the atmosphere should sink, by the action of some  $CO_2$ -absorbing agent, from 0.03 to 0.02, this would not only involve the disappearance of 1/s of our present  $CO_2$ -atmosphere but the liberation from the ocean an subsequent disappearance of about 9 times as much. If, on the other hand, the production of carbonic acid should be augmented, the quantity of carbonic acid in the atmosphere must rise, but an increase from 0.03 to 0.04 0/o can only be attained by a surplus production of 1/s + 2 times the present amount of atmospheric carbonic acid.

The question here arises: Will not the absorption (or liberation) of carbonic acid by the sea be too slow a process really to exercise this influence? If the absorption of the quantity mentioned would take millions of years the regulating influence of the ocean, though doubtless existing, would not make itself very much felt.

By means of BOHRS determinations of invasion- and evasionconstants for water and solutions of chloride of sodium, quoted and explained in *the preceding paper* (p. 383), I shall be able to give an approximate answer to this problem of the *velocity* of absorption or liberation. If we take the coefficient of invasion

<sup>&</sup>lt;sup>3</sup>) Provisionally I assume for the sake of argument that the mean temperature of the earth is invariably  $15^{\circ}$ .

for seawater as 0.1 and calculate the invasion at a tensiondifference of only  $0.001 \, {}^{0}/_{0}$  of the atmospheric pressure we find that the ocean will absorb per year  $0.525 \, \text{cc.}$  of carbonic acid through every sq. cm. of its surface and, consequently, through the whole surface of 374 millions of sq. km.  $3.85 \times 10^{9}$  tons of the gas, corresponding to about  $1^{1/2}$  times the yearly output of coal<sup>1</sup>). If therefore our present consumption of coal should constitute a surplus-production of carbonic acid and destroy a state of perfect equilibrium between the atmosphere and the sea, we shall in a few years reach such a tension-difference that the ocean can absorb the surplus as rapidly as it is produced, and instead of being doubled in 1006 years, the percentage of carbonic acid in the air will, during this period, rise about  $0.005 \, {}^{0}/_{0}$  or probably less.

It follows from the enormous diffusion, that is brought about by extremely slight differences in tension between the atmosphere and the ocean, that a state of equilibrium — either stable or *sliding* — will in all cases very rapidly be attained. If the production of carbonic acid on the earth at a given time equals the consumption, the *mean* tension of the gas in the surface of the ocean must be equal to its *mean* percentage in the atmosphere<sup>2</sup>). If, on the other hand, the production of carbonic acid exceeds the consumption, the mean tension in the ocean-surface must be lower than the percentage in the

<sup>2</sup>) As the freshwaters on the earth are always engaged in transferring carbonic acid from the air to the sea, the state of equilibrium between consumption and production must — strictly speaking — correspond to a slight surplus-tension in the ocean-surface. The quantity of free and loose  $CO_2$  transferred yearly by the rivers of the earth is estimated by READE at  $1.35 \times 10^9$  tons or about 1/2 our consumption of coal. A surplus-tension in the sea of  $0.0003 \ 0/0$  would be sufficient to return this quantity to the atmosphere.

<sup>&</sup>lt;sup>1</sup>) The coefficient of invasion determined by BOHR is *possibly* too low, and in my calculation no account is taken of the waves and wavelets by which the absorbing surface is greatly increased. The figure found is therefore a minimum and possibly much below the mark.

atmosphere, and the difference will in a very short time become large enough to allow the surplus of production to be absorbed *almost* as rapidly as it is formed. This is what I call *a sliding* equilibrium. Quite analogous movements will take place in the opposite direction if the consumption of  $CO_2$  should exceed the production.

It has hitherto been absolutely impossible to ascertain whether the carbonic acid in the atmosphere was increasing or decreasing in quantity, or perhaps remained stationary, because the alteration itself must necessarily be too slow to be detected by direct analysis within a reasonable space of time. The method of tension-determination now furnishes a means of investigating this important problem, and certain data are already at hand indicating the probable result.

1. My series of tension-determinations across the Atlantic, from Cape Farewell to Fair Hill in the Shetlands, shows that the tension of the Gulf-Stream and, indeed, of all Atlantic surfacewater in this latitude was at the time distinctly lower than that of the atmosphere. (See my *preceding paper* p. 403).

2. The percentage of carbonic acid in the atmosphere has been found to be lower on the high seas or at the oceanborder than inland. Schulze in Rostock found for instance, by a series of determinations covering several years, a mean percentage of 0.0292 and THORPE found on the Atlantic from Brazil to England 0.0295 as a mean of 51 determinations. On the other hand, FITTBOGEN found in Brandenburg 0.0334 (average of 347 determinations) and FARSKY in Bohemia 0.0343 (average of 295 determinations)<sup>1</sup>). The same difference is observed when the extremely accurate English and French determinations by Armstrong<sup>2</sup>), REISET<sup>3</sup>), MUNTZ & AUBIN<sup>4</sup>) are compared with the

<sup>&</sup>lt;sup>1</sup>) These Authors are quoted from SACHSSE. Lehrbuch der Agrikulturchemie. Leipzig 1888.

<sup>2)</sup> Proc. Roy. Soc. Vol. 30 p. 343.

<sup>&</sup>lt;sup>3</sup>) Compt. rend. T. 90 p. 1144, p. 1457.

<sup>4)</sup> Compt. rend. 1881.

equally trustworthy Swedish by A. PALMQUIST<sup>1</sup>), the former giving for England and France values about 0.029 and very closely agreeing among themselves, while the latter give for the neighbourhood of Stockholm 0.032 as an average of 197 determinations.

3. The atmosphere of the Southern Hemisphere, where the area of the ocean is so great when compared with that of the continents, has an extremely low percentage of carbonic acid. MUNTZ & AUBIN<sup>2</sup>) found at Cape Horn the average value to be only 0.0256—260, and in Chile 0.0267—282. Even here the difference between the sea and the continent makes itself felt. MUNTZ & AUBIN found in Continental South-America a mean value of 0.0271, whereas G. TROILI-PETERSSON<sup>3</sup>) found 0.0240 as a mean of 19 determinations from the South-Atlantic (14 others, which however are not so trustworthy, gave 0.0222). The atmosphere of Patagonia showed according to the same Author 0.0270 (an average of 17 determinations).

These facts seem to indicate that the oceanic atmosphere always possesses a lower percentage of carbonic acid than the continental one, and as no other  $CO_2$ -absorbing agent exists on the high seas, this must mean that the ocean-water itself absorbs carbonic acid with considerable energy and, consequently, that the mean  $CO_2$ -tension of the sea is distinctly lower than the average percentage of the gas in the atmosphere. If this be so,

the atmospheric percentage of carbonic acid must at present be on the increase.

It cannot be denied however that the observational evidence, upon which this far-reaching conclusion is based, must be regarded as insufficient, and I have made out the case chiefly

<sup>1)</sup> Bihang Svenska Vet. Akad. Handlingar Bd. 18, 1892-93, Afd. II.

<sup>&</sup>lt;sup>2</sup>) A series of papers Compt. rend. 1881-1884.

<sup>&</sup>lt;sup>3</sup>) Über den Kohlensäuregehalt der Atmosphäre. Bihang Svenska Vet. Akad. Handlingar Bd. 23, 1897-98, Afd. II.

as a plea for a thorough investigation of the problem. In our times, when the greater part of the ocean is traversed day by day, throughout the year, by innumerable steamers, it ought to be possible to undertake such an investigation, which must of course be of an international character.

In all regions of the ocean samples of surface-water and also of atmospheric air must be collected at regular intervals throughout a whole year, and the corresponding temperatures and meteorological conditions observed. The manipulations are so simple and easy to perform that this part of the work could safely be intrusted to the hands of ships-officers. A number of suitably situated laboratories, marine or chemical, must further unite for the execution of the analyses, consisting chiefly in the determination of the tensions of carbonic acid in the water and in the air respectively. It is obvious that the general usefulnes of such an undertaking would be greatly enhanced, if the salinity and perhaps the alkalinity of the waters were simultaneously determined.

Before leaving this subject it will be necessary to add some words concerning the influence of the climate on the state of equilibrium and also the possible interaction between the atmospheric carbonic acid and the climate.

The influence of the temperature upon the tension-equilibrium between the ocean and the atmosphere is in its general features easily accounted for. The tension of carbonic acid in the ocean will rise and fall along with the mean temperature on the earth, and the percentage of the gas in the atmosphere must thereby be influenced. A decrease in the mean temperature on the earth amounting to  $3.2^{\circ}$  would cause a decrease in the tension of the ocean of about 1/10 of its value at the time 1) or from 0.03 to 0.027. The decrease of the ocean-tension

1) See the preceding paper pp. 363-65.

must involve the absorption of a corresponding part of the atmospheric carbonic acid. If such a decline in the mean temperature of the earth could take place in a few years, a perceptible tension-difference between the atmosphere and the sea would of course arise, and the results of the abovementioned general investigation of the state of equilibrium might be seriously vitiated. Nothing of the kind need however be feared. The tension-differences which may arise in this way are very much below the reach of our analytical methods <sup>1</sup>).

In 1896 ARREENUS<sup>2</sup>) propounded the hypothesis that the surface-temperature of the earth depends to a large extent upon the heat-absorbing power of the atmospheric carbonic acid. Taking as his base a series of determinations, published by LANGLEY, of the radiating heat received from the moon, he endeavoured to find out by elaborate calculations, the details of which I must confess myself unable to follow, the heat-absorbing powers of the atmospheric water-vapour and carbonic acid and to compute the influence upon the mean temperature of the earth-surface of definite alterations in the percentage of carbonic acid. He arrived at the extremely remarkable conclusion that a diminution of the percentage of carbonic acid from about 0.03 to 0.017 would cause a lowering of the temperature of  $4^{\circ}-5^{\circ}$  at the latitude of  $40^{\circ}-50^{\circ}$ , while, on the other hand,

<sup>1)</sup> If the temperature should fall at a constant rate of say 0.001° pro year, which I consider to be a high estimate, the tension of the sea would decrease yearly at the rate of  $\frac{1}{32000}$  of its present value and  $\frac{1}{32000}$  of the carbonic acid of the atmosphere (=  $7.5 \times 10^7$  tons) must be absorbed every year in order to maintain a sliding equilibrium. At a tensiondifference of 0.001 % the ocean will absorb (according to the calculations on p. 422)  $3.85 \times 10^9$  tons of  $CO_2$ , and  $\frac{1}{50}$  of this difference or  $0.00002 \ 0/0$  will therefore be amply sufficient for the absorption of  $7.5 \times 10^7$  tons and, consequently, for the maintenance of a sliding equilibrium. There is very little chance that we shall ever be able to detect tension-differences of this degree of magnitude.

<sup>2</sup>) On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground. *Phil. Mag.* 1896, pp. 237-276. a rise of  $8^{\circ}$ —9° together with a more uniform distribution of the heat over the globe would be produced, if the percentage of carbonic acid rose to 0.08 or thereabouts (p. 268).

In a second contribution<sup>1</sup>) ARRHENIUS published a series of experimental determinations of the absorption of heat by carbonic acid and revised his former calculations on this new basis, by which revision he obtained somewhat lower values for the influence of the atmospheric carbonic acid. It appears, however, from investigations by ÅNGSTRÖM<sup>2</sup>) that the density of of the gas has a very marked influence upon its absorption; 1 m. of  $CO_{2}$  at the pressure of 4 atmospheres absorbs 16.2 % of a dark radiation, whereas 4 m. at the pressure of 1 atm. absorb only 13.3 %. This effect of the pressure was not taken into account by ARRHENIUS, who made his determinations by means of varied pressures in a tube of unalterable length. His figures must therefore at all events undergo a considerable reduction, and it seems to me to be rather doubtful whether variation in the percentage of carbonic acid in the atmosphere will have any appreciable influence upon the climate. Angström expresses the opinion, for which he gives several reasons, that a rise in the percentage will have no influence whatever, while a decline will lower the temperature only if it is carried below 20 % of the present value.

TOLMAN (Journ. of Geol. vol. 7, 1899, pp. 610—16) discusses at some length the combined influence upon the ocean-tension of a decreasing percentage of carbonic acid in the atmosphere and the lowering of the temperature, which he supposes to take place in accordance with the original estimates of ARRHENUS. He arrives at the conclusion that the decline of the percentage of  $CO_2$  in

<sup>1)</sup> Svenska Vet. Akad. Förhandl. 1901, pp. 25-58.

<sup>&</sup>lt;sup>2)</sup> Ueber die Abhängigkeit der Absorption der Gase, besonders der Kohlensäure, von der Dichte. Svenska Vet. Akad. Förhandl. 1901, pp. 371-380 and: Einige Bemerkungen zur Absorption der Erdstrahlung durch die atmosphärische Kohlensäure. Ibid. pp. 381-89.

the air, which, of itself, would cause a liberation of the gas from the ocean, will be more than counteracted by the decrease in the temperature of the ocean-surface, and that therefore the result must be that the ocean «turns robber itself», absorbs carbonic acid from the air and thereby *aggravates* the direct climatic influence of the decreasing percentage.

As pointed out in the preceding paper (p. 352) the experimental basis of TOLMANS deliberations and calculations is very untrustworthy. If my figures are utilized, and if we assume (in accordance with the second paper by ARRHENICS) that a decrease in the percentage of carbonic acid in the atmosphere from 0.03 to 0.015 will lower the temperature  $3.2^{\circ}$ , we find that the tension in the different zones of the ocean will thereby be diminished as follows.

Original temperature	Original tension	Decreased temperature	Corresponding tension
20°	0.03 0/0	16.8°	0.0265
15°	"	11.8°	0.027
10°	"	6.8°	0.027
5°		1.8°	0.027

It is seen that the lowering of the tension is very nearly uniform throughout the whole range of temperatures and amounts to not more than  $0.003 \,^{0}/_{0}$ , while the percentage of carbonic acid in the atmosphere must, according to the hypothesis, be lowered by  $0.015 \,^{0}/_{0}$ . This proves that Tolmans conclusion is incorrect and establishes as a fact that the action of the ocean will retard and diminish any influence upon the climate, which the variations of the percentage of carbonic acid in the atmosphere might exercise. II. Local and temporal variations of the atmospheric percentage of carbonic acid, with special reference to the Arctic conditions.

It will be sufficient for my purpose here to enumerate the chief factors, which may in certain localities exercise an influence upon the percentage of  $CO_2$  in the air. The matter has been fully discussed in several papers of recent date<sup>1</sup>).

1. The organic life. Assimilation and dissimilation generally counterbalance each other pretty nearly. The percentage of carbonic acid in the air rises slightly during the night and decreases during the day, and a corresponding annual period has been found by some Authors, but the variations observed were very small. Amidst abundant vegetation the percentage may fall below the ordinary value, and in large towns it is always somewhat above it, though generally not higher than 0.04 to 0.05  $^{0}/_{0}$ .

In Arctic regions both the assimilatory and the dissimilatory processes only attain very small dimensions, but there can be no doubt that during the long uninterrupted summer-day assimilation exceeds dissimilation. The organic life cannot therefore have contributed in the least to the high percentages of carbonic acid observed in the Island of Disko during my journey.

2. Carbonic acid eliminated from the ground. The atmosphere of the ground is, as a rule, very rich in carbonic acid, chiefly produced by the decay of organic substances. Under certain conditions — low barometric pressure — considerable quantities may be given off to the air, but in most cases the gas is so rapidly removed by the wind and mixed with the

<sup>&</sup>lt;sup>1)</sup> PALMQUIST, Bihang Svenska Vet. Akad. Handl. Bd. 18 Afd. II. ANDRÉ, Öfversigt Svenska Vet. Akad. Förhandl. 1894 p. 355. SACHSSE, Lehrbuch der Agrikulturchemie. WILLIAMS, Ber. d. deutsch. chem. Ges. Jahrg. 30 p. 1450.

ordinary air that its influence cannot be detected by the analyses <sup>1</sup>).

As shown in the preceding paper the soil of Disko does not contain free carbonic acid or, at all events, the tension of the gas is distinctly lower than in the atmosphere, owing to the alkaline nature of the rocks. The freshwaters, likewise, absorb carbonic acid from the atmosphere instead of liberating it.

In many places, throughout Europe and elsewhere, carbonic acid issues forth from the depth in considerable quantities, which must be detectable by analyses of the atmosphere in the environs of such springs.

In Arctic countries, however, the deep layers of the ground are separated from the surface by an enormous sheet of frozen rock, which must generally be impermeable for the gases below. A few springs of hot water find their way through it, but even if these were saturated with carbonic acid, the amount of gas liberated would be too small to be detectable by analyses of the atmosphere. My investigations show, further, that the hot springs of Disko do not contain free carbonic acid.

It appears from the above that the cause of the high percentage of carbonic acid, observed in the air of Disko, is not to be found on land. We must therefore turn our attention to the sea.

3. Reasons have been given above for the contention that the  $CO_2$ -tension of the ocean-surface is generally lower than that of the atmosphere, but, notwithstanding this, it may very well be considerably higher in some places.

In the bottom-water of the Baltic I found a tension of carbonic acid of about  $0.16^{0}/_{0}$  (see *preceding paper* p. 389),

<sup>&</sup>lt;sup>1</sup>) The high percentage of CO<sub>2</sub>, often observed during fogs, is ascribed by PALMQUIST to the elimination of gas from the ground. It is supposed by this Author that the carbonic acid cannot, under such circumstances, be so rapidly dispersed.

and WALTHER & SCHIRLITZ<sup>1</sup>) noticed in some places in the Gulf of Naples that the bottom-waters contained a surplus of carbonic acid over and above that corresponding to fully saturated bicarbonates. This too must correspond to a very high tension. If waters, such as these, should rise to the surface and become dispersed over a considerable area, there can be no doubt that they would have a considerable influence upon the percentage of carbonic acid in the air above them.

Instances of this kind, it is true, are not yet known with certainty, but, as no tension-determinations except my own have been made, it seems reasonable to think that they will be found in the future, and I especially want to suggest the possibility that the abnormal percentages of carbonic acid in the air of Disko may be due to this cause.

Some slight evidence may be brought forward in support of this view:

1. I have made some determinations of the tension in the sea-water along the coast of Disko. In most places the seawater was mixed with water from the glacier-rivers and consequently more or less turbid; but in the southern part of the Disko-Fjord and off the south-western coast, where very few and small rivers come down from the mountains, it was found to be perfectly clear.

According to the analyses all turbid waters showed low tensions of carbonic acid  $(0.01 \text{ to}. 0.035^{\circ}/\circ)$ , while the clear waters showed high (0.035-0.06). The highest value was found 200 m. off Uvifak, where only one small river is found in a distance of more than 10 miles. It is perhaps reasonable to expect that still higher values would have been found in the open sea, had it been possible to examine this, but it must be remembered, on the other hand, that a sample of water

1 Zeitschr. der geol. Ges. Bd. 38. 1886.

taken a year later and about 60 miles to the south of Disko had a tension of about  $0.02 \, {}^0/_0$  only (see *preceding paper* p. 403, No. 1).

Locality	Salinity º/oo	Water	Тр.	Tension
Avatarpait	31.8	turbid	6.9°	3
Nordfjord	32.0	slightly turbid	7.9°	2
	31.3	1. S V.	7.5°	3.5
	30.8	_	7.1°	1.5
Mellemfjord	30.6		6.8°	1
Diskofjord	?	turbid	9.2°	2
	30.7	-	7.9 <sup>0</sup>	3.5
	19.3	clear	8.9°	4.5
	23.4	_	7.3°	3.5-4
Maligiak	31.9		6 5°	4
Uvifak	31.9	Nor _ And	6.8°	6

2. The state of the mussel-shells in a number of localities along the *East-Greenland* coast furnishes strong evidence that the surrounding water possesses a high tension of carbonic acid (see *the preceding paper* pp. 388-89), but if this water can possibly reach Baffin Bay and rise to the surface there, or if, perhaps, analogous waters may come down directly from the North, are not questions for me to decide.

With regard to the analyses of Moss there remains one very serious difficulty. How can the sea give off carbonic acid when it is covered for hundreds of miles in all directions with a solid sheet of ice, as it certainly must be on all sides of an observer in Grinnel-Land during the months of December, January and February?

I do not know, and I must leave this Arctic riddle of the carbonic acid unanswered, trusting that in these days of intense investigation of the extremities of our globe it will ere long be approached by others, and the solution some day brought to light.

## Summary.

1. A consideration of the  $CO_2$ -producing and  $CO_2$ absorbing factors of the earth shows that we have no reason to think that equilibrium will, as a rule, exist between them. The percentage of carbonic acid in the atmosphere must therefore be variable (pp. 416-19).

2. At the same tension  $(0.03 \, {}^{0}/{}_{0})$  the ocean contains free and loose carbonic acid to the amount of about 27 times that of the atmosphere. It must give off about  ${}^{1}/{}_{10}$  of this if the tension should sink to  $0.02 \, {}^{0}/{}_{0}$ , and absorb  ${}^{1}/{}_{15}$  if it should rise to  $0.04 \, {}^{0}/{}_{0}$ . The ocean is therefore capable of acting as a regulator on the variations of the carbonic acid in the atmosphere, provided the processes of absorption or liberation be sufficiently rapid (pp. 420-21).

3. These processes must be considered as extremely rapid since a tension-difference between the ocean and the atmosphere of only 0.001 % will cause the yearly absorption (or elimination) of upwards of 4000 million tons of carbonic acid, corresponding to  $1^{1/2}$  times the yearly output of coal by man (pp. 422-23).

4. By a comparison between the average  $CO_2$ -tension of the ocean-surface and the percentage of the gas in the atmosphere it will be possible to ascertain whether the latter is increasing or decreasing or perhaps stationary. The evidence now available points towards the first of these alternatives, but it is not sufficient to decide the question (pp. 423-25).

5. The action of the ocean will retard and diminish any alteration in the percentage of carbonic acid in the atmosphere

28

and any influence upon the climate, which the variations of this percentage may exercise (pp. 425-28).

6. The percentage of carbonic acid in the air of the Island of Disko in Greenland was found by analyses made in the summer of 1902 to be very great (up to  $0.07^{0}/_{0}$ ) and extremely variable ( $0.025-0.07^{0}/_{0}$ ), being high from northern and western winds and low from southern (pp. 409-16). This phenomenon cannot be explained by any enhanced production of carbonic acid from the land, but may possibly be due to a liberation of the gas from the sea, such as will take place if bottom-waters, possessing a high tension, should rise to the surface (pp. 429-32).

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