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by

August Lepp.



# On the Tension of Carbonic Acid in Natural Waters and especially in the Sea.

By

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## Definition and Introduction.

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If an unlimited quantity of water, in which carbonic acid and other gases are present, is brought into contact with a limited volume of air diffusion will of course take place, but after a sufficiently long time a stable equilibrium will be attained, and the partial pressure of each separate gas in the mixture will then indicate exactly the *tension* under which this gas is dissolved in the water. In the case of gases, that are only physically absorbed in the water, such as for instance nitrogen, this partial pressure, multiplied by the known coefficient of absorption, will give the exact amount of nitrogen present in the water. On the other hand, the tension can be found indirectly by determining the quantity of nitrogen in a sample of the water.

In the case of carbonic acid the conditions are quite different. This gas exists in natural waters, and especially in seawater, in very great quantities, but for the most part chemically combined as carbonates and bicarbonates. Nothing can therefore be ascertained about its tension from merely determining its quantity, and, as a matter of fact, up to the present time we know nothing whatever concerning its tension in the ocean or elsewhere in nature. Authors, who have dealt with the carbonic acid in the sea, have, as a rule, ignored the principle of tension or taken it for granted, that the tension in the sea must be equal to the partial pressure of carbonic in the atmosphere.



A thorough knowledge of the tension of carbonic acid, not only in the sea, but in streams and springs would however be of no small importance, since the solution of not a few problems of biological, hydrographical and perhaps geological and meteorological interest depends upon it. It is for instance most probable that the assimilation-energy of submersed plants and the phyto-plancton is directly proportional to the tension of carbonic acid in the water. It is certain that the rate of dissolution of molluscan shells is governed by the tension, and it must be considered as probable that thick shells and solid periostraca in some varieties of mussels may be accounted for by their being a protection against an especially high tension of carbonic acid in the surrounding water. From the  $CO_2$ -tension of springs some information may possibly be obtained about the strata through which they flow, and, last but not least, the tension of carbonic acid in the ocean is the factor governing the interchange of this gas between the air and the water, and when the average tension of the ocean becomes known, it will be possible to draw inferences respecting the actual state of equilibrium — or want of equilibrium — of this important component of our atmosphere<sup>1</sup>).

In the summer of 1902 I accompanied my friend Mr. M. PORSILD on an expedition to the Island of Disko on the west-coast of Greenland, under the auspices of the Danish *Commission for the Geological and Geographical Investigation of Greenland*. I intended to study the respiratory exchange of the organisms of the Arctic sea, and in order to do so I constructed an apparatus according to the principles mentioned above for the determination of the tensions of the dissolved

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<sup>1</sup>) Inferences have indeed been made already, for instance by CHAMBERLIN and TOLMAN, (*Journ. of Geol.* vol. 7. 1899 pp. 544, 585, 667), but from quite inadequate data, and it is a pity to see such vast masses of knowledge and such acute reasoning as are brought to bear by these Authors on assumptions that are really fictitious.



gases. At the same time I had in view the determination of the tensions in the surface-water of the sea and especially ascertaining as to whether the carbonic acid was really in equilibrium with the atmosphere.

The results I attained with regard to the last-mentioned question appeared to me to be so interesting that I devoted most of my time to it during my stay in Greenland, and I have since my return pursued it further.

In the present paper I intend to give:

I. A brief account of the methods originally applied and the modifications, which I have introduced, stating more fully the kinds of apparatus and details of method, which I have found most suitable.

II. The physico-chemical theory of carbonic acid in sea-water and freshwater and the relations between the quantity and the tension of the gas in ocean-water.

III. An account of my determinations of tension in Greenland and Danish freshwaters, in the Baltic and in the Ocean, together with the hydrographical, biological and geological considerations to which they give rise<sup>1)</sup>.

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<sup>1)</sup> The influence of the  $CO_2$ -tension of the ocean on the composition of the atmosphere will be discussed in a separate paper.

## Methodics.

My first apparatus for the determination of gas-tensions in water was a tonometer constructed on the principles of PFLÜGER<sup>1)</sup>: A stream of water is introduced through a narrow inlet at the upper end of a wide tube. When

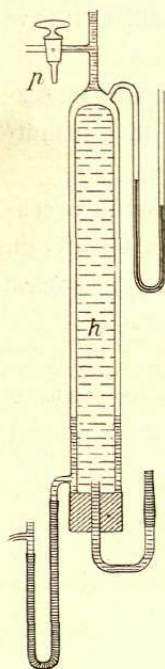


Fig. 1.

the velocity is suitably regulated it flows down covering the whole surface of the wall, and diffusion can take place through this surface with the air in the tube. The proportion of surface to volume of air is, however, in this simple apparatus much too small, if a rapid equalisation of tension between the air and the water is desired. I have therefore modified the apparatus by introducing an inner tube ( $h$  on the diagrammatic fig. 1) and allowing the water to flow down simultaneously on the inner wall of the primary tube and the outer wall of the second. By this means I have obtained a surface of 33 sq. cm. for every cubic cm. of air, whereas in PFLÜGER'S apparatus the corresponding surface was only some 2—3 sq. cm.

The details of my apparatus are of no importance for the determinations of the tension of carbonic acid, and they will be described elsewhere. Suffice it to say that the space between the two tubes is filled

<sup>1)</sup> *Arch. f. d. ges. Physiologie.* Bonn 1872 Bd. 6 p. 65.



at the beginning of a determination with atmospheric air which, after the diffusion is finished, is expelled through the three-way-tap  $p$  and either collected in a recipient or directly taken into the air-analysis-apparatus.

For the air-analyses I applied during the Greenland-expedition the extremely accurate and convenient HALDANE-apparatus with such modifications as were necessitated by the special conditions. The apparatuses were carried for about two months in an open skin-boat, they were often turned upside-down and sometimes roughly handled, when we had to land through the surf. Nevertheless, they did not get out of order and always worked admirably. The gas-burette contained 10 cc., and the part from 6.5 to 10 was graduated to 0.01 cc. I read it by means of a lens to 0.0005 cc., and the degree of accuracy for the carbonic acid corresponded as a rule to this figure.

Nearly all my analyses were made as double-determinations, and I thus have a very good test as to their accuracy. I give as an example the following quadruple-analysis of atmospheric air<sup>1</sup>).

29/vii. 8 p. m. *Avatarpait*. West-coast of Disko:

Volume taken . . . . .	6.584	6.6065	9.971	9.960
Absorption of $CO_2$ . . . .	6.5805	6.603	9.9655	9.955
Absorption of $O_2$ . . . . .			7.874	7.866
Percentage of $CO_2$ . . . .	0.055	0.055	0.055	0.05
Percentage of $O_2$ . . . . .			20.975	20.975

The method described for equalizing the tension in a sample of air with that of the water was only used during the first part of the journey, when comparatively few determinations were made. The apparatus was rather complicated and required a comparatively large quantity of water, which had to be carried

<sup>1</sup>) As will be seen from the analyses here cited the percentage of carbonic acid in the atmosphere was extremely high. This remarkable phenomenon will be dealt with in the following paper.

to the tent, as the apparatus could not be used in a boat except in a dead calm. Owing to these drawbacks, which made themselves very keenly felt, when it became necessary to travel quickly and to cut down the stays at most of the stations, I endeavoured to simplify the method as much as possible.

If you shake one liter of distilled water, at a temperature of  $15.6^{\circ}$  by which the coefficient of absorption is 1, with 100 cc. of air, free from carbonic acid, until equilibrium is attained, then it is obvious that the tension of  $CO_2$  in the water will only be diminished by  $\frac{1}{10}$  of its value on account of the carbonic acid given off to the air. If the coefficient of absorption is higher, as is the case at lower temperatures, or if the carbonic acid is not simply held in solution, but for the most part present in dissociable combinations, the diminution of the original tension will be even less.

I therefore thought it probable that I might determine without any appreciable error the tension in natural waters, which nearly always contain the greater part of their carbonic acid as bicarbonates, simply by shaking a sample of the water with a much less volume of air and subsequently analyse the air-sample for carbonic acid.

In order to test this method I made the following experiment:

1. The  $CO_2$ -tension of a sample of seawater was determined by means of the tonometer and found = 0.02 %.

2. 55 cc. of this water were shaken vigorously for five minutes with 20 cc. of air. The quantity of carbonic acid found in this air was likewise = 0.02 %.

3. 35 cc. of the water were shaken vigorously only for one minute, with 40 cc. of air. The quantity of carbonic acid in the air was = 0.02 %.

4. 40 cc. of the water were shaken for about five minutes as gently as possible — in such a way that the surface was



never ruffled. In the 35 cc. of air there was found a percentage of  $CO_2 = 0.03\%$ .

The percentage of carbonic acid in the atmospheric air used in these experiments was found by two analyses to be  $0.06\%$  or  $0.055\%$ .

It appears that seawater may be shaken with an equal volume of air and absorb  $\frac{2}{3}$  of the carbonic acid contained without the tension being perceptibly altered, and I therefore adopted the following method as perfectly reliable: The sample of water is taken into a bottle of 1 liters capacity and provided with a thermometer. So much air as will be sufficient for an analysis is left above the water, and the bottle is shaken vigorously for 2 minutes. The air is then transferred to the analysis-apparatus and the percentage of carbonic acid determined. The percentage found is the tension of carbonic acid in the sample of water at the temperature observed after the shaking. For the sake of convenience I take the  $\frac{1}{10000}$  of the normal atmospheric pressure as a unit. *A tension given in the present paper as 2.3 means therefore  $0.023\%$  of the normal atmospheric pressure.*

I hope that I shall be able to show in the present and the following paper that researches on the tension of carbonic acid in natural waters, and especially in the ocean, will very probably give important results, when they are extended over a larger area of the globe. For the sake of those who might wish to take up this subject I shall now proceed to give very full particulars regarding the most suitable methods, the precautions necessary in their application and the degree of accuracy desirable and obtainable.

The samples of water are taken into glass-stoppered bottles of one liters capacity. If the sample must be kept for some time I recommend the use of resistance-glass which has the

least possible influence upon the alkalinity of the water. A little air should be left above the water in the bottle, when it is not immediately analysed.

The taking of samples from the surface presents no difficulties whatever. Of course the samples, especially of fresh-water, should not be unnecessarily exposed to the air.

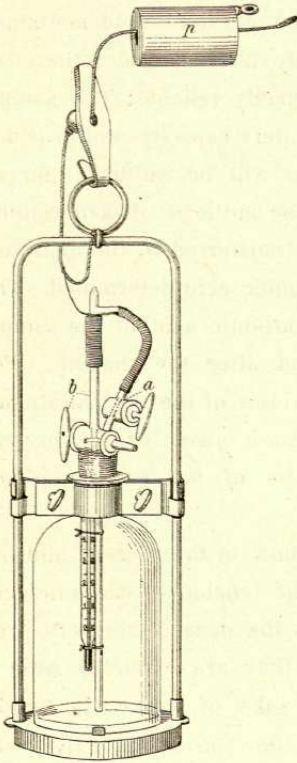


Fig. 2.

For the taking of samples from shallow depths up to 100 metres I have found the following method very convenient: The bottle is stoppered with rubber and provided with the two tubes (presently to be described) which are applied by the actual determination of tension. The taps are kept open, and the tubes are connected above as seen in the adjoined figure. The short piece of rubber-tubing fitting on to the vertical tube *b* must be thick-walled and should not be pressed down too hard. The whole apparatus is lowered to the appointed depth and then the lead *p* is allowed to drop. It is easily seen from the figure that the bumping of the lead will cause the disconnection of the tubes. The water will rush

in through *a* while the air escapes through *b*, and after a couple of minutes the sample may be hauled up and analysed. If it is read immediately the thermometer in the bottle will show with an accuracy of about  $\frac{1}{10}$  degree the temperature at the depth examined.

At greater depths than 100 m. a metallic water-bottle that



does not carry down air, for instance SIGSBEE'S, must be used in combination with a deep-sea-thermometer. As soon as the water-sample is on deck it should be transferred to a glass-bottle. No perceptible loss of carbonic acid need be feared, when this operation is performed by a rubber-tube of suitable bore conducted to the bottom of the bottle.

On the *preservation* of water-samples for a subsequent determination of the tension of carbonic acid I have not much to say, the more so, as perfectly reliable methods have not, so far, been discovered.

No perceptible increase of the alkalinity takes place at ordinary temperatures in resistance-bottles; it appears, on the contrary, from some of my determinations that the alkalinity may decrease, at least when the water is kept for some months.

Carbonic acid will sometimes be produced in the samples (presumably by bacteria) and consequently the tension will rise. In 18 samples from the Davis-Strait and the North-Atlantic, taken in new and clean bottles, this happened with 4, while the others remained unaltered. Most of these indeed became infected during the tension-determinations, and the tension in some of them rose considerably.

If 1 gr. of sublimate is added to each sample of 1 l. this formation of carbonic acid is completely avoided, but the presence of  $Hg Cl_2$  causes the tension of *normal* sea-water to rise 0.35 (0.0035 %).

I have not tried any other antiseptic, but I consider it extremely probable that, among the existing multitude of these substances, one or more may be found, capable of preventing the growth of carbonic-acid-producing organisms but free from any chemical action on the mineral constituents of seawater.

When the tension has to be determined the bottle is provided with a rubber-stopper pierced by two glass-tubes. One

of these tubes *a* reaches almost to the bottom, and to it the thermometer is attached. At the upper end it is provided with a simple glass-tap and terminates with a short piece of rubber-tubing. A glass-bulb *B*, holding about 15 cc. more than the gas-burette of the analysis-apparatus and likewise provided with a tap, can be connected with the tube by means of this rubber-tubing. The other tube *b* is short and of narrow bore and is

provided with a three-way-tap.

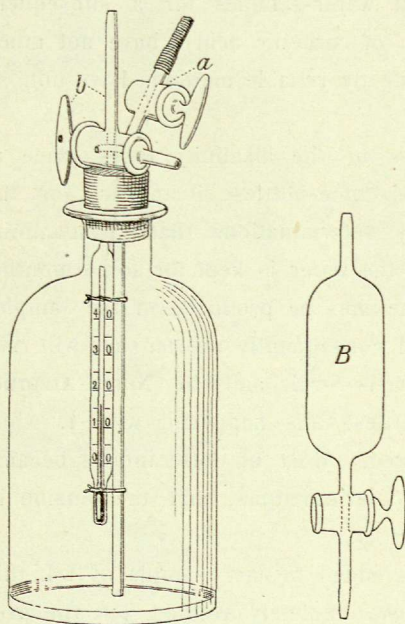


Fig. 3.

that of the atmosphere, and the shaking then repeated for another minute. The temperature of the water should not be allowed to vary more than  $\frac{1}{4}^{\circ}$  during the shaking, and the temperature of the bulb too should be kept fairly unaltered.

When the shaking is finished the bottle is connected with the analysis-apparatus and the bulb *B*. The manipulations are made in the following order (see fig. 4).

The gas-burette *e* is filled with mercury.

In order to take in the air-sample all taps are opened and water by way of *a* sucked into the bulb *B*, allowing it to be replaced through the tube *b* by pure atmospheric air. Then the taps are closed, the bulb disconnected, the thermometer read, and the bottle violently shaken for one minute or thereabouts. The tap *b* is thereupon opened for a moment in order to equalize the pressure in the bottle with



The tube *c* is connected with *b* and placed so that the connection at *d* can be made in an instant.

Then the bulb *B* is connected with the bottle, care being taken first to fill the space above the tap *a* with water from the bulb.

The tap *a* is now opened and the drops of water which have, during the shaking, found their way into the tube *b* are forced out through the tail-boring of the corresponding tap by opening it for a moment.

Thereupon the principal boring of *b* is opened, and the connection at *d* quickly performed. The mercury in the burette *e* is lowered and the sample drawn in.

If everything is correctly performed there will be at the finish a slight excess of pressure in the burette, the contents of which are therefore for a moment put into communication with the atmosphere by means of the tail-boring of *b* before the tap *f* of the burette is finally closed.

*The analysis of the air-sample.* As the amount of carbonic acid to be determined is always very small and often less than 0.03 % of the sample it is obvious that the utmost care must be bestowed upon the analyses.

As already mentioned, I used, during my journey in Greenland, a HALDANE-apparatus by means of which oxygen as well

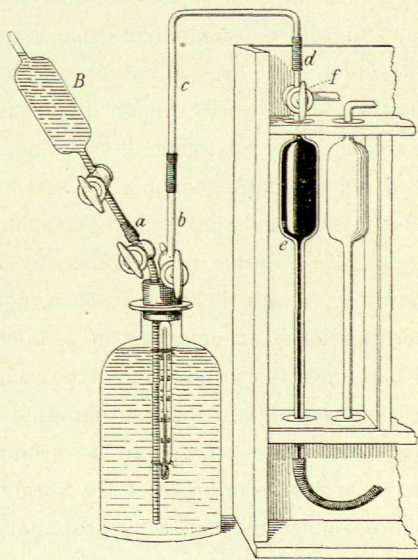


Fig. 4.

as carbonic acid could be determined with an accuracy of 0.02 and 0.005 per cent., respectively. This degree of accuracy was sufficient for my purposes at the time, and I think that it will suffice for some time to come for determinations of  $CO_2$ -tension in freshwaters. Generally, however, it will be of no use to be able to determine the percentage of oxygen, and I would therefore recommend the apparatus specially designed by HALDANE for the estimation of carbonic acid in air<sup>1</sup>). Its construction is very simple, the manipulations are easy when no greater accuracy than 0.005 % is wanted, and the apparatus is of very small compass ( $8 \times 13 \times 3$  inches) and weight (6 pounds) thus being easily portable.

I have found it possible to obtain by means of this apparatus, which I have made use of in the majority of my determinations, an accuracy of  $\pm 0.001$  %, but this is extremely difficult and I cannot therefore recommend the apparatus for the purpose of tension-determination in seawater or for determinations of the percentage of carbonic acid in the atmosphere. I have tried to improve it by augmenting the dimensions, but without success, because its principal defect lies in the pressure-gauge which is not sufficiently sensitive.

In the well-known apparatus constructed by PETTERSON and modified by SONDÉN this difficulty has been completely overcome by the application of a short, horizontal index of oil as pressure-gauge, and the numerous analyses of atmospheric carbonic acid, published by A. PALMQUIST<sup>2</sup>), G. TROILI-PETERSSON<sup>3</sup>) and others, abundantly show that an accuracy of 0.001 % is easily

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<sup>1</sup>) HALDANE: A rapid method of determining carbonic acid in air. *Journ. of Hygiene* vol. 1 1901 pp. 109—114. The apparatus is manufactured by Messrs. MÜLLER, ORME and Co. 148 High Holborn, London.

<sup>2</sup>) PALMQUIST: Atmosferens Kolsyrehalt. *Bihang Sv. Vet. Akad. Handl.* Bd. 18 Afd. II N:o 2.

<sup>3</sup>) TROILI-PETERSSON: Kohlensäuregehalt der Atmosphäre. *Ibid.* Bd. 23, II, 6.



attained<sup>1)</sup>. This apparatus, mounted for use in the laboratory and fitted with pipettes of 60 cc. capacity, may be obtained from GEISZLER of Bonn and perhaps also from other makers. The construction and use are fully described by PETTERSON<sup>2)</sup>, SONDÉN<sup>3)</sup> and PETTERSON & PALMQUIST<sup>4)</sup>, to whose papers I must refer.

In the figure 5 on p. 347 a modification is shown adapted for use when travelling and on board ships. It differs only in arrangement and points of detail from the original PETTERSON-apparatus. Whereas in the laboratory petroleum is the most suitable fluid for the index of pressure, it must be replaced on board ships by the more viscous paraffine-oil, and at the same time the index must be made as short as possible (about 2 mm.). When these precautions are observed, and the apparatus is suitably orientated with regard to the rolling or pitching of the ship it will be found possible to make accurate determinations when the movements are not too violent.

The following general hints with regard to the performance of the analyses and the possible sources of error may perhaps save others some of the trouble I have myself experienced.

The waterbath must be thoroughly mixed before each reading of the burette. The best way of doing this is to force a continuous stream of air-bubbles slowly through it.

The reading of the burette is facilitated by applying a simple lens mounted in a quadrangular piece of wood of suitable dimensions (see fig. 5, *m*).

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<sup>1)</sup> JOHANSSON: (*Skand. Arch. Physiologie* Bd. 8. 1898 p. 93) gives the probable error of one analysis as 0.000425 %. He has modified and enlarged the apparatus and thereby diminished the probable error to 0.0002 %, but so great an accuracy is rather difficult to obtain and cannot at present be considered necessary for hydrographic purposes.

<sup>2)</sup> *Zeitschr. anal. Chemie* Bd. 25 p. 467.

<sup>3)</sup> *Ibid.* Bd. 26 p. 592. *Zeitschr. für Instrumentenkunde* 1889 p. 472.

<sup>4)</sup> *Ber. d. deutschen chem. Ges.* 1887 p. 2129.

The gas-burette must always contain a little moisture, but care should be taken to avoid water in the narrow graduated part.

Before a series of  $CO_2$ -determinations the apparatus must always be tested by passing a sample of air several times to and fro between the burette and the absorption-pipette and seeing that the volume does not alter. If it does, the apparatus is either not air-tight, or else the soda-lye absorbs or gives off gases. This latter is not unfrequently the case when the temperature or the barometric pressure, or both, have varied considerably since the last analyses. If the fluid is not completely saturated with atmospheric air, at the pressure and temperature obtaining, it will give off or absorb (according to the circumstances) minute quantities of air during each analysis and thereby vitiate the results. Freshly prepared solutions of sodium-hydrate are always greatly supersaturated with air. The best remedy is to draw off the fluid into a large bottle and shake it vigorously for some time before recharging the apparatus.

If, as in my apparatus, the two bulbs of the absorption-pipette are connected by rubber-tubing it is very easy to empty them, but the rubber introduces a new source of trouble viz., that the soda-lye may in the course of time dissolve a little sulphur and thereby acquire the power of absorbing minute quantities of oxygen. A slight yellowish tint indicates this state of affairs and such solutions must be immediately renewed.

If the narrow part of the burette is graduated, as it ought to be, in  $\frac{1}{10000}$  parts the difference between the two readings gives the tension directly, and it is unnecessary to apply corrections even if the original volume is not exactly 10000. If great accuracy is desired, and especially if the determinations are made at greatly varying temperatures, it becomes necessary to make allowance for the varying tensions of water-vapour and



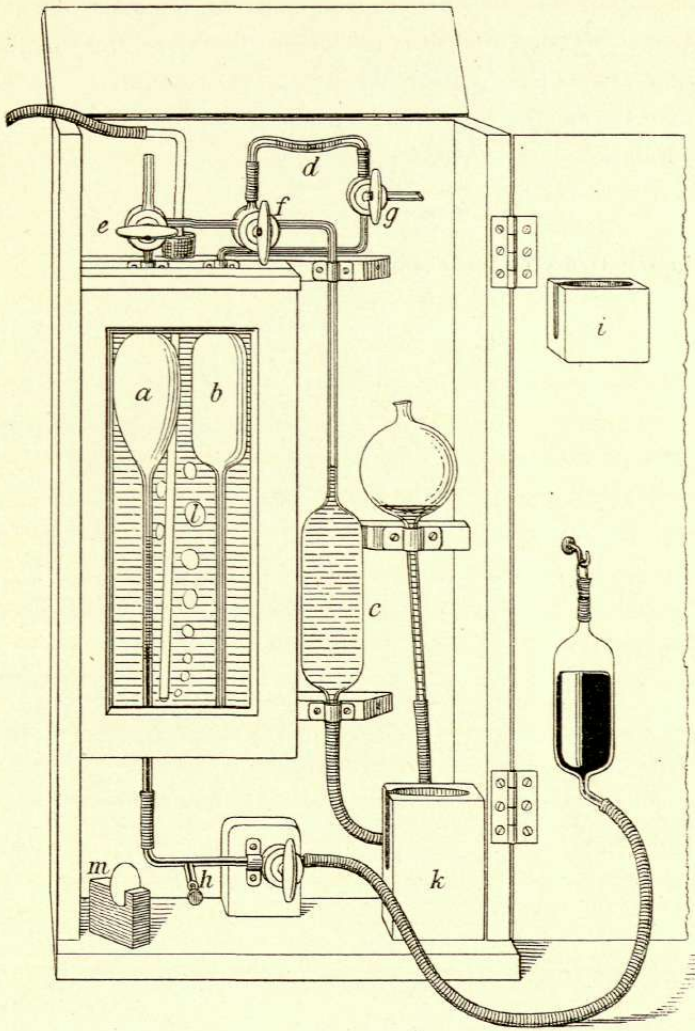


Fig. 5.

*a* graduated gas-burette, *b* compensation-burette, *c* absorption-pipette, *d* index of pressure, *e*, *f*, *g* three-way-taps; connection is established between the burettes and the index of pressure, *h* screw for the final adjustment of the pressure, *i* stand for the mercury-pipette, when the air has to be forced into the absorption-pipette, *k* ditto, when the apparatus is closed, *l* air-bubbles mixing the water-bath, *m* lens for reading the burette.

barometric pressures. Let a determination be made at the barometric pressure of 740 mm. ( $P$ ) and the temperature of  $15^{\circ}$  (tension  $f = 13$  mm.), then the real tension of  $CO_2$  ( $\theta$ ) is calculated from the observed tension ( $\theta' = 2.3$ ) by means of the formula

$$\theta = \frac{P-f}{760} \times \theta'$$

or, in the terms of the example,

$$\theta = \frac{740-13}{760} \times 2.3 = 2.2.$$


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## The Chemical Theory of the Tension.

The chemistry of the carbonic acid in seawater appears to have been very puzzling to the earlier investigators, and the problem has only been solved in comparatively recent years, through the labours of TORNØE<sup>1)</sup>, DITTMAR<sup>2)</sup> and, especially, HAMBERG<sup>3)</sup>. Independently of these authors, SCHLOESING<sup>4)</sup> appears to have had a clear and correct conception of it.

When the several mineral components of seawater are carefully determined it is seen that the bases ( $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$ ) are slightly in excess of the acids ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ), so that the water is in reality alkaline. This was discovered by DITTMAR (p. 20), and, at about the same time, TORNØE directly observed the alkaline reaction on litmus and rosolic acid. TORNØE found out, further, that the surplus alkali is combined with carbonic acid, and he devised an excellent method for the quantitative determination of the carbonic acid and the alkalinity, viz. to acidify a portion of water with normal sulphuric acid, to boil off the carbonic acid in a suitable apparatus, collecting the separated gas in normal baryta-water. After the boiling the quantity of carbonic acid is titrated in the baryta-solution,

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<sup>1)</sup> *The Norwegian North-Atlantic Expedition 1876—78. Chemistry.* 2. On the Carbonic Acid in the Sea-Water by H. TORNØE.

<sup>2)</sup> *Challenger Reports. Physics and Chemistry* 1. Report on the Composition of the Ocean-Water by W. DITTMAR.

<sup>3)</sup> Om kolsyran i hafsvattnet af AXEL HAMBERG. *Bihang K. Svenska Vet.-Akad. Handlingar* Bd. 10 Nr. 13. 1885. p. 31—50.

<sup>4)</sup> Sur la constance de la proportion d'acide carbonique dans l'air par TH. SCHLOESING. *Comptes rendus* 1880. T. 90. p. 1410.

while the alkalinity is determined by titration of the surplus acid in the sample of water.

TORNØE expressed his results with regard to the alkalinity, as well as to the quantity of carbonic acid, in units of carbonic acid, and he has been followed in this respect by all subsequent authors. The term alkalinity in the quantitative sense means therefore the quantity of carbonic acid (now as a rule given in cubic-centimeters) necessary to convert the surplus base in 1 liter of seawater to normal carbonate.

TORNØE found as mean values for the tract of the North-Atlantic investigated by him:

Alkalinity ..... 52.78 mgrs. = 26.86 cc. of  $CO_2$   
 Total quantity of  $CO_2$  ... 96.42 mgrs.<sup>1)</sup> = 49.07 cc.

The quantity of carbonic acid is insufficient to convert all the alkali present to bicarbonate but greatly in excess, on the other hand, of the amount necessary for normal carbonate. TORNØE, therefore, was of opinion that seawater contained a mixture of normal with bicarbonate, but that no trace of free carbonic acid could possibly be present. Accordingly, he supposed that the water must absorb carbonic acid from the atmosphere.

This last-mentioned supposition was disproved by DITTMAR.

This Author prepared an artificial seawater (*op. cit.* p. 109) by dissolving suitable quantities of chloride of sodium and sulphate of magnesia and adding a solution of magnesium-bicarbonate. The alkalinity corresponded to 53.54 mgrs. of  $CO_2$  per l., and the water was found to contain 104.5 mgrs. of  $CO_2$  (pp. 114—115). This water was shaken repeatedly; each time with 5 volumes of fresh air. After  $n$  such treatments the quantity of carbonic acid was found to be

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<sup>1)</sup> DITTMAR, who afterwards tested the method, found that, as a rule, the results proved 1—2 mgrs. too high (*op. cit.* p. 107).



$n =$	0	3	6	9
$CO_2 =$	104.5	99.3	94.8	90.7
Difference	5.2	5.0	3.6	

The water continued to give off carbonic acid, and DITTMAR clearly saw that this must mean that the dissolved bicarbonate possesses a *tension of dissociation*. On p. 212 he calculates the tension produced in the air, with which the water was shaken, and find it to be 5.7, 5.5 and 3.9 ten-thousandths of an atmosphere respectively<sup>1</sup>). Though these figures indicate a steady lowering of the tension DITTMAR calculated their mean = 5.0 and took this to be *the* tension of dissociation for the bicarbonate present in his artificial seawater, irrespective of the quantity of bicarbonate as compared with that of normal carbonate. DITTMAR was of opinion that, if the tension is only kept below this value, the bicarbonate will continue to give off carbonic acid, and he hoped «before long to be able to formulate the exact conditions of stability in seawater-bicarbonates as they exist when dissolved in real seawater, and amongst others to decide the question whether in this process they quite directly tend to become normal and do not perhaps more directly gravitate towards the state of sesqui-carbonate» (*op. cit.* p. 212).

As will be seen from the following this view of the question is fundamentally erroneous. One of the two chief factors on which the tension depends is the relation between the quantities of bicarbonate and normal carbonate present in the solution<sup>2</sup>).

In *Encyclopædia Britannica* (vol. 21 p. 612) DITTMAR has published some further experiments concerning the tension

<sup>1</sup>) There must be an error somewhere in DITTMAR's determination or calculations. He seems to have forgotten that the shaking with 5 volumes of air was repeated *thrice* between every two determinations of the quantity of carbonic acid. At least I find the tension in each case to be exactly  $\frac{1}{3}$  of the value given by DITTMAR.

<sup>2</sup>) The influence of the other factor, the temperature, was correctly recognized by DITTMAR, though he did not determine it experimentally.

found in seawater. They are made, as before, by determinations of the quantity of  $CO_2$  remaining in the water after repeated shakings with air. The figures, however, do not quite agree, but **TOLMAN** (*Journ. of Geol.* vol. 7, 1899 p. 610) has picked out "those that seem to correspond best with each other" for the construction of curves. These curves (as well as the figures themselves) represent the tension as being 0 at temperatures up to  $2^\circ$ , the quantity of carbonic acid being at the same time double that of the alkalinity, and, even at  $25^\circ$ , the quantity corresponding to a tension of 0 is not less than  $1.6 \times$  the alkalinity! These experimental results are in accordance with **DIETMARS** theoretical conceptions as given above in his own words, but they are absolutely incompatible with those of **TOLMAN**, who nevertheless proceeds to build upon them a very elaborate hypothesis concerning the interaction between the ocean and the atmosphere. That they cannot be correct will appear from the following experiments by **HAMBERG** and myself.

**HAMBERG** in a series of experiments conducted a stream of air with a constant percentage of  $CO_2$  through samples both of pure and diluted seawater, until equilibrium was attained, a method exactly the reverse of my own. The results are tabulated as follows:

Salinity ‰	Alkalinity cc. of $CO_2$ $\alpha$	Tempera- ture	Cc. of $CO_2$ per liter $\beta$	$\frac{100 \beta}{\alpha}$	Tension
35.13	26.96	0	49.11	} 182.8	2.7
		0	49.34		
		10	47.12	175.0	
		20	44.49	164.9	
26.58	20.26	0	37.40	184.7	2.7
		10	36.30	179.3	
		20	35.23	174.0	
17.78	13.47	0	26.08	} 193.1	2.7
		0	25.88		
		10	24.83	} 185.2	
		10	25.01		
		20	24.23		



This table shows that the quantity of  $CO_2$  decreases considerably with the rising temperature (or, in other words, if the quantity had been kept constant the tension would have risen) and that the quantity of carbonic acid relative to the alkalinity — *the saturation* — increases with the dilution. These important facts are rendered intelligible by looking at the whole process from the point of view of chemical mass-action, set forth by GULDBERG & WAAGE.

If two substances,  $A$  and  $B$ , can give rise by their mutual reaction to two other substances,  $A_1$  and  $B_1$ , then, if definite quantities of  $A$  and  $B$  are mingled, a mixture of all four substances,  $A$ ,  $A_1$ ,  $B$  and  $B_1$ , will result. In the state of equilibrium the numbers of molecules of  $A$  is dependent on the numbers of the other molecules, and these cannot be augmented or diminished unless the number of  $A$ -molecules increases or decreases accordingly.

In the case of seawater we have the surplus base and the carbonic acid in definite quantities, and hence a mixture must always be present of

$a$	$b$	$c$	$d$
free base	normal carbonate	bicarbonate	free, dissolved carbonic acid.

HAMBERG has re-tabulated his experiments in accordance with this view, calculating the quantity  $d$  from the percentage of  $CC_2$  in the current of air and the physical coefficient of absorption<sup>1</sup>), and disregarding  $a$  which he considered to be insignificant. If the alkalinity is called  $\alpha$  and the total quantity of carbonic acid  $\beta$ , while  $b$  and  $c$  are taken to mean, as above, the quantities of  $CO_2$  present as normal and bicarbonate, respectively, we must have:

$$b = 2\alpha - (\beta - d) \text{ and}$$

$$c = \beta - (d + b)$$

<sup>1</sup> The coefficients of absorption for carbonic acid in seawater were not experimentally determined, but HAMBERG deduced them from SETCHENOWS experiments on solutions of pure chloride of sodium.

Tp.	$\alpha$	$\beta$	$b$	$c$	$d^1)$
0	13.47	25.98	1.38	24.18	0.42
0	20.26	37.40	3.52	33.48	0.40
0	26.96	49.23	5.07	43.78	0.38
10	13.47	24.92	2.31	22.32	0.29
10	20.26	36.30	4.49	30.54	0.27
10	26.96	47.12	7.06	39.80	0.26
20	13.47	24.23	2.94	21.06	0.23
20	20.26	35.23	5.51	29.50	0.22
20	26.96	44.49	9.64	34.64	0.21

The influence of dilution as well as the temperature is now easily understood. Dilution will disturb the equilibrium, because  $\alpha$  decreases whereas  $d$  is slightly increased, and hence a number of molecules must pass from the state of normal to bicarbonate. A rise in the temperature, on the other hand, diminishes the coefficient of absorption and thereby lessens  $d$ , whereas  $\alpha$  remains unaltered. The result is that a number of molecules must pass from bicarbonate to normal carbonate<sup>2)</sup>.

Through the experiments of HAMBERG it has been established as a fact that there exists a definite relation between the alkalinity, the total amount of carbonic acid, the temperature and the  $CO_2$ -tension of seawater. Any one of these quantities is wholly defined by the other three. It is, however, impossible to calculate anything with accuracy from HAMBERGS tables, because his experiments are too few in number and because he has in all of them maintained a constant tension of 2.7.

If in the same sample of water and at a constant temperature a series of  $CO_2$ -tensions are produced and accurately

<sup>1)</sup> I have altered all the figures in HAMBERGS table from grms. to cubic-centimeters.

<sup>2)</sup> HAMBERG rightly supposed that a rise in the temperature has, likewise, a diminishing influence upon the affinity between the alkali and the carbonic acid.



measured, together with the corresponding quantities of carbonic acid, and if, further, the physical absorption of carbonic acid in the water is exactly known, it ought to be possible to ascertain by calculation, on the basis of the known laws of chemical mass-action, the real nature of the alkaline substances in seawater and the combination of carbonic acid with them. I have therefore resumed the problem and made several series of experiments with a «standard»-seawater from the North-Atlantic, viz.

1. An experimental determination of the physical absorption of carbonic acid at different temperatures.

2. A series of determinations of the total quantities of carbonic acid together with the corresponding tensions at a constant temperature.

3. Determinations of the variations of the tension with the temperature, while the quantity of carbonic acid remained unaltered.

1. *The coefficient of absorption of carbonic acid* was determined in water that was slightly acidulated by means of a few drops of muriatic acid (20 ‰). This slight alteration of the concentration has no perceptible influence upon the absorption, but it neutralizes the alkalinity and prevents the binding of  $CO_2$  by dissociation of some of the «insignificant» components of seawater.

The acidulated water was completely saturated with carbonic acid at the barometric pressure obtaining and at a known temperature, which was kept scrupulously constant during each determination. The quantity absorbed was determined by evacuation of 15—23 grms. of the water in the mercury-pump and subsequent analysis. For the reduction of the quantities of water weighed to cubic-centimeters, at the temperature of the experiment, I utilized DITTMARS determinations (*Challenger Reports, Physics and Chemistry* vol. 1, p. 74).

By this method I found that 1 cc. of seawater (salinity 35.19 ‰) absorbs at a tension of 760 mm. (dry pressure) of carbonic acid

at 0.0°	1.412 cubic centimeters
6.4°	1.119 — —
15.0°	0.853 — —
24.1°	0.659 — —

By means of these results the absorption-curve was constructed, and from this curve were the following values for the absorption from one degree to another of temperature obtained by graphical interpolation.

Tp.	Coeff. of abs. $\alpha$	Tp.	Coeff. of abs. $\alpha$	Tp.	Coeff. of abs. $\alpha$
0°	1.41	10°	0.99	20°	0.73
1°	1.35	11°	0.96	21°	0.71
2°	1.30	12°	0.93	22°	0.69
3°	1.25	13°	0.90	23°	0.675
4°	1.21	14°	0.875	24°	0.66
5°	1.17	15°	0.85		
6°	1.13	16°	0.82		
7°	1.095	17°	0.80		
8°	1.06	18°	0.775		
9°	1.025	19°	0.75		

If my figures are compared with those calculated by HAMBERG from determinations of the absorption in solutions of pure chloride of sodium, it will be seen that the similarity is remarkably perfect.

	$\alpha$ calculated by HAMBERG	$\alpha$ found
0°	1.42	1.41
10°	0.98	0.99
20°	0.77	0.73

For all ordinary purposes I do not think it necessary to make allowance for the variation of the salinity unless it falls below 32 ‰. The allowance for diminished salinities may be



approximately computed from HAMBERGS figures. He finds that if the salinity is diminished by the addition of distilled water from 35.1 to 26.6 or 17.8 ‰ the coefficients of absorption must be multiplied by 1.05 or 1.10 respectively.

2. The tensions at 15° of samples of the standard water, containing varied quantities of carbonic acid, were determined, according to the method described above, by shaking with air and subsequent analysis in the HALDANE-apparatus of this air. The determination was made twice with each sample of water. A recipient (*b* on the adjoined figure) of 225 cc.'s capacity, provided with two stopcocks, was thereupon filled with the water; care being taken to avoid loss or absorption of carbonic acid. This recipient was connected with the ordinary recipient *a* of the mercury-pump containing 10 cc. of decinormal muriatic acid. When this had been evacuated the tap *c* was opened, and the gas now liberated pumped out and collected. The quantity of carbonic acid in the collected gases was determined by analysis, and the mixture of seawater and muriatic acid was titrated with baryta for the determination of the alkalinity.

The alkalinity was found to be remarkably low, viz.  $A = 22.72$  cc. of  $\text{CO}_2$  per l. and I thought at first that I must have committed an error in the determination. A repeated determination of the normal acid, according to the extremely accurate method described by SØRENSEN<sup>1)</sup>, and a revision of the whole method

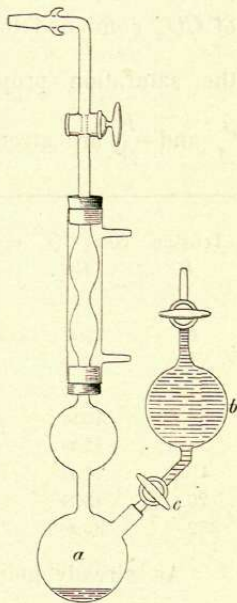


Fig. 6.

<sup>1)</sup> «Ueber die Anwendung des normalen Natriumoxalats in der Massanalyse». FRESENIUS' *Zeitschr. f. analyt. Chemie* Bd. 42 p. 333 and p. 512.

showed however that the result was substantially correct, and the following experiments will show that it is also in perfect agreement with theory.

The following table gives the values for the tension  $\theta$ , the total quantity of  $CO_2$  present in 1 l. of the water  $B$ , the quantity of free carbonic acid  $d$ , the quantity of carbonic acid combined with the alkali  $B - d = \beta$ , the difference between this quantity and the alkalinity or, in other words, the quantity of  $CO_2$  combined to form bicarbonates  $\beta - A = y$ , and, finally, the saturation proper  $\frac{\beta}{A}$ , and the approximate saturation  $\frac{B^1}{A}$ .  $\frac{\beta}{A}$  and  $\frac{B}{A}$  are given in the adjoined curves.

Tension $\theta$	Total $CO_2$ $B$	Free $CO_2$ $d$	$B - d =$ $\beta$	$\beta - A =$ $y$	Saturation $\frac{\beta}{A}$	Approxim. S. $\frac{B}{A}$
0.7	33.45	0.0595	33.39	10.67	1.470	1.472
1.15	36.69	0.0975	36.59	13.82	1.611	1.615
1.5	37.79	0.1275	37.66	14.94	1.658	1.663
2.95	40.98	0.2505	40.73	18.01	1.792	1.803
5.4	43.78	0.4585	43.32	20.60	1.906	1.927
13.9	46.14	1.180	44.96	22.24	1.979	2.035
29.5	48.76	2.520	46.24	23.47	2.035	2.146
352	83.96	29.90	53.46	30.74	2.353	3.668

As already pointed out by HAMBERG the quantity of alkali present as free base must be extremely small and negligible, and the reaction between the bases and the acid may be looked upon as a reversible interaction between normal carbonates and free carbonic acid. It follows from well-established chemical laws that all the bases of the seawater must form carbonates and take part in the reaction, but it is equally certain that they cannot do so to the same extent, owing to their varying quantities and affinities, and there are good reasons for believing, with DITTMAR, that the alkalinity is almost exclusively made up

<sup>1)</sup> This last-mentioned quantity is called the saturation by several Authors.



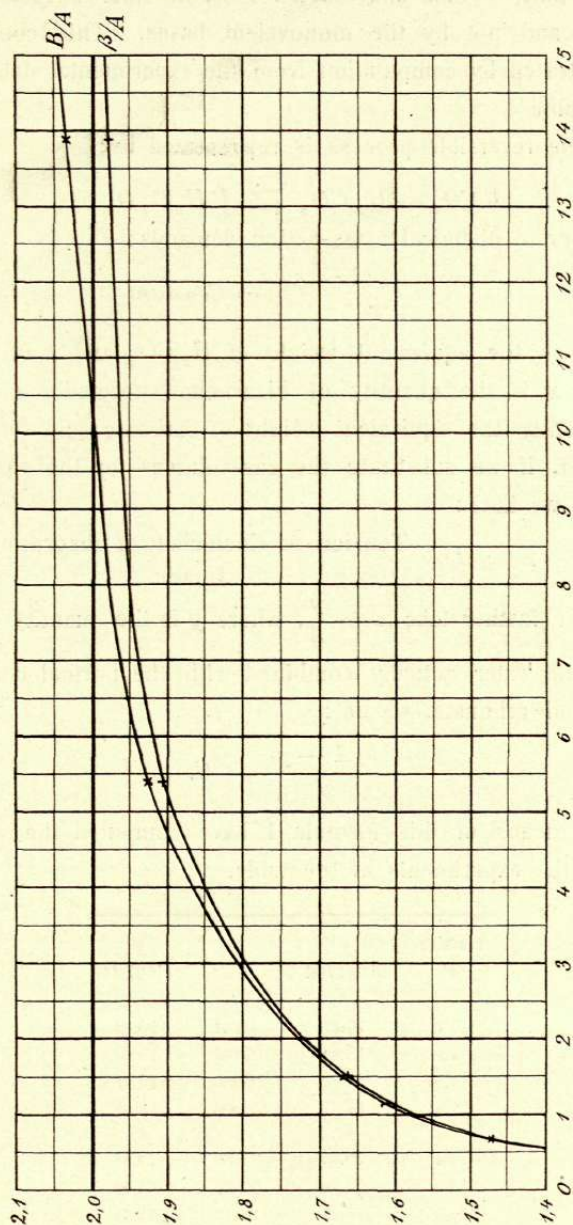
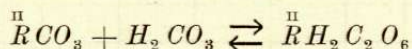


Fig. 7.

by carbonate of lime and magnesia or, in other words, by the divalent and not by the monovalent bases. This contention can be tested by computation from the experimental data given in the table.

If the reversible process is represented by:



the theory of chemical mass-action demands:

$$\frac{(a-x)(1-x)}{x} = \text{Constant}$$

where  $a$  is the equivalent weight of  $H_2CO_3$  and 1 of  $\overset{\text{II}}{R}CO_3$  whereas  $x$  is the quantity of bicarbonate formed.  $a-x$  is consequently the equivalent weight of carbonic acid remaining free, and, if we substitute the gas-volumes for the equivalent weights, we have:

$$a-x = d = \frac{\text{Tension} \times \text{Coefficient of absorption}}{10000}$$

If we further take  $x = \frac{y}{A}$ , where  $y$  is the quantity of  $CO_2$  in 1 l. of water actually combined with the normal carbonate to form bicarbonate, we get:

$$\frac{d(A-y)}{y} = C.$$

By means of this formula I have computed the value of  $C$  from the experiments of the table.

Tension $\theta$	$y$ observed	$C$	$y$ calculated
0.7	10.67	0.0671	10.82
1.15	13.82	0.0629	13.60
1.5	14.94	0.0663	15.01
2.95	18.01	0.0655	18.02
5.4	20.60	0.0472	19.88
13.9	22.24	0.0255	21.53
29.5	23.47	neg.	22.15
Average of four determinations		0.0655	



The degree of accuracy of the tension-determinations is not more than 0.1, and the values found for  $C$  up to and including the tension of 2.95 must therefore be said to correspond in a remarkable degree, but at the higher tensions the constant rapidly declines and has become negative at the tension of 29.5.

At the low tensions the result of the experiment is in strict accordance with the theoretical assumption, so that we may regard the loose carbonic acid as combined exclusively with carbonates of divalent bases, that is with lime and magnesia. At tensions above 3.0 the quantity of loose carbonic acid becomes greater than that claimed by the theory, and above a tension of 29 it exceeds the normal carbonate. In order to explain this remarkable phenomenon we must bear in mind the extreme complexity of the seawater-components and especially the small quantities of weak acids, boracic, phosphoric, arsenic etc., that are found in it. The salts of these weak acids must necessarily be partially decomposed by the free carbonic acid, the quantity and tension of which being thereby diminished<sup>1</sup>).

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<sup>1</sup>) During the writing of this chapter I began to suspect that there might be some connection between the alkalinity of the «standard» water and the excess of carbonic acid found at higher tensions over and above the quantities demanded by theory. If some weak (organic) acid is produced by the decay of organisms the alkalinity will be lowered, but a certain tension of carbonic acid will, on the other hand, cause a dissociation of the salts of such an acid. In order to examine the point in question I determined the alkalinity of a sample of «standard» water poisoned, when being taken, with 1 gr. of sublimate per l. It was found to be decidedly higher than that of the unpoisoned water, viz. 23.1, though the specific effect of sublimate upon the alkalinity causes it to decrease (the alkalinity of the standard water decreased from 22.7 to 22.0 upon the addition of 1 grm. of sublimate). The result indicates therefore that decaying organic substances may cause an appreciable decrease of the alkalinity of seawater, but the matter obviously needs further investigation.

The mean of the four first values gives the constant as 0.0655, and by means of this the values of  $y$  may be computed

$$y = \frac{Ad}{C+d}$$

In this manner the values given in the fourth column of the above table are obtained.

By substituting  $\beta - A$  for  $y$  the equations

$$C = \frac{d_1 (A - y_1)}{y_1}$$

$$C = \frac{d_2 (A - y_2)}{y_2}$$

and the analogous are transformed to

$$(\beta_1 - A)C = (2A - \beta_1)d_1$$

$$(\beta_2 - A)C = (2A - \beta_2)d_2$$

which can be utilized for a theoretical determination of the alkalinity  $A$ , desirable on account of the abnormal value found experimentally.

We obtain by transformation

$$A^2 - \frac{A}{2} \left( \beta_2 + \beta_1 + \frac{\beta_1 d_2 - \beta_2 d_1}{d_2 - d_1} \right) + \frac{\beta_1 \beta_2}{2} = 0$$

and the analogous equations from which are obtained the following values for  $A$

24.60, 22.99, 22.78, 21.32, 21.06, 22.77, Average 22.59

which agree sufficiently well with the figure found by direct determination 22.72<sup>1)</sup>.

<sup>1)</sup> All the determinations of tension and quantity given above apply solely to the state of equilibrium between the carbonic acid and the bases of the seawater. I have not specially studied the velocity of the reactions implied when this equilibrium is disturbed, but I have reason to believe that at ordinary temperatures it is extremely slow, and that experimental errors are apt to occur when this point is disregarded. The evidence in support of this view is as follows:

Solutions containing bicarbonate of lime or baryta are extremely difficult to evacuate by means of the mercury-pump. They continue to give off minute quantities of carbonic acid for 24 hours or more.

A rapid stream of  $CO_2$ -free air can be sucked through a sample



3. *The influence of temperature upon the tension.* Suppose that the tension of a water is determined at  $15^{\circ}$  and that it is thereupon cooled down to  $0^{\circ}$  in a closed vessel. If the chemical equilibrium remains unaltered by this process the quantity of free carbonic acid, as well as the alkalinity and the total quantity of  $CO_2$ , will remain unchanged. But the same quantity of free carbonic acid in the water will, at the altered temperature, correspond to a lower tension on account of the altered coefficient of absorption:

$$d = \frac{\alpha_{15} \theta_{15}}{10000} = \frac{\alpha_0 \theta_0}{10000}, \text{ hence } \theta_0 = \theta_{15} \frac{\alpha_{15}}{\alpha_0}$$

The formula indicates that if  $d$  is unaltered the tensions will vary in the inverse ratio of the coefficients of absorption.

By an experimental study of the variation of the tension with the temperature I have obtained the following results:

Temp. I	$\theta_1$	Temp. II	$\theta_{II}$	$\theta_1 \frac{\alpha_1}{\alpha_{II}}$	Correction
$0^{\circ}$	1.4	$6.4^{\circ}$	1.75	1.75	0
$\left\{ \begin{array}{l} 0.4^{\circ} \\ 0.8^{\circ} \end{array} \right.$	$\left\{ \begin{array}{l} 1.6 \\ 1.7 \end{array} \right.$	$\left\{ \begin{array}{l} 15.0^{\circ} \\ 15.0^{\circ} \end{array} \right.$	$\left\{ \begin{array}{l} 2.75 \\ 2.75 \end{array} \right.$	$\left\{ \begin{array}{l} 2.6 \\ 2.7 \end{array} \right.$	$\left\{ \begin{array}{l} + 0.15 \\ + 0.05 \end{array} \right. \} 0.1$
$0.4^{\circ}$	1.6	$24.0^{\circ}$	4.1	3.35	+ 0.75
$\left\{ \begin{array}{l} 0^{\circ} \\ 0^{\circ} \end{array} \right.$	$\left\{ \begin{array}{l} 2.6 \\ 17.7 \end{array} \right.$	$\left\{ \begin{array}{l} 20.0^{\circ} \\ 20.0^{\circ} \end{array} \right.$	$\left\{ \begin{array}{l} 5.4 \\ 34.2 \end{array} \right.$	$\left\{ \begin{array}{l} 5.0 \\ 33.9 \end{array} \right.$	$\left\{ \begin{array}{l} + 0.4 \\ + 0.3 \end{array} \right. \} 0.35$
$6.5^{\circ}$	8.9	$23.0^{\circ}$	15.1	14.7	+ 0.4
$6.7^{\circ}$	1.8	$23.8^{\circ}$	3.6	2.95	+ 0.75

of seawater for many hours without causing any appreciable decrease in the tension. It cannot be doubted that the free carbonic acid is by this process rapidly removed, but if we assume that it is very slowly renewed by breaking up of the bicarbonates the phenomenon becomes quite intelligible.

The results published by DITTMAR in the *Encyclopædia Britannica* must be explained in this way. DITTMAR found the quantities of carbonic acid corresponding to low tensions of the gas much too great, simply because the water did not, in his experiments, attain the state of equilibrium, and this explanation also accounts for the discrepancy between his several determinations.

The table indicates clearly that the chemical equilibrium is altered in such a manner that the affinity between the carbonic acid and the normal carbonates becomes less, and the tension consequently greater, at higher temperatures. The four last experiments, cited in the table, in which waters of very different tensions have been subjected to the same rise in temperature, show that no proportionality exists between the tension of the water at  $0^{\circ}$  and the increase caused by an increased temperature. On the contrary, a certain rise in temperature seems to cause an *additional* increase of a certain amount in the tension, irrespective of the original tension of

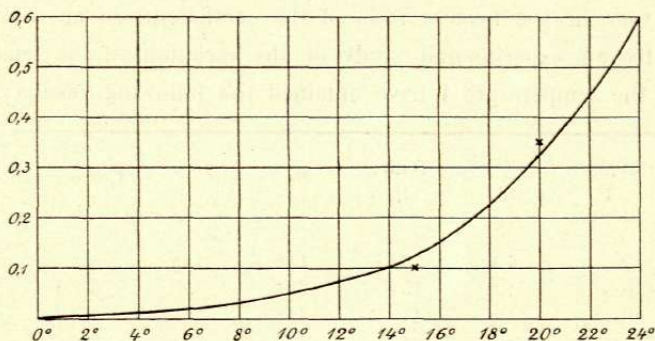


Fig. 8.

the water. It does not seem probable, that this rule will hold good for all tensions of carbonic acid, but it appears from the table that it has rather a wide range of application, and I therefore venture to express the results of the experiments in the form of the adjoined curve and table, by means of which the tension of a seawater-sample, observed at a known temperature, may be calculated for any other temperature between the limits of  $0^{\circ}$  and  $24^{\circ}$ , provided the tension at  $0^{\circ}$  is not lower than 1.0 and not higher than 15.

The table shows for every degree of temperature between  $0^{\circ}$  and  $24^{\circ}$  the additional increase in tension  $c$ , the coefficient



of absorption  $\alpha$  and the logarithm of this last quantity. It is used according to the formula

$$\theta_{t_2} = (\theta_{t_1} - c_{t_1}) \frac{\alpha_{t_1}}{\alpha_{t_2}} + c_{t_2}$$

Tp.	c	$\alpha$	log. $\alpha$	Tp.	c	$\alpha$	log. $\alpha$	Tp.	c	$\alpha$	log. $\alpha$
0°	0	1.41	0.1492	10°	0.05	0.99	9.9956	20°	0.32	0.73	9.8633
1°	0	1.35	0.1303	11°	0.06	0.96	9.9823	21°	0.38	0.71	9.8513
2°	0	1.30	0.1140	12°	0.08	0.93	9.9685	22°	0.45	0.69	9.8388
3°	0.01	1.25	0.0969	13°	0.09	0.90	9.9543	23°	0.52	0.675	9.8293
4°	0.01	1.21	0.0828	14°	0.10	0.875	9.9420	24°	0.60	0.66	9.8195
5°	0.02	1.17	0.0682	15°	0.12	0.85	9.9294				
6°	0.02	1.13	0.0531	16°	0.15	0.82	9.9138				
7°	0.03	1.095	0.0394	17°	0.19	0.80	9.9031				
8°	0.04	1.06	0.0253	18°	0.22	0.775	9.8893				
9°	0.04	1.025	0.0107	19°	0.27	0.75	9.8751				

Example: Given the tension of a water at  $20^\circ = 3.4$ .  
Sought its tension at  $5^\circ$ :

$$\theta_{20} = 3.4$$

$$c_{20} = 0.32$$

$$\theta_{20} - c_{20} = 3.08 \quad \log. (\theta_{20} - c_{20}) = 0.4885$$

$$\log. \alpha_{20} = 9.8633$$

$$0.3518$$

$$\log. \alpha_5 = 0.0682$$

$$(\theta_{20} - c_{20}) \frac{\alpha_{20}}{\alpha_5} = 1.92 \quad 0.2836$$

$$c_5 = 0.02$$

$$\theta_5 = 1.95$$

It would of course be possible to treat the influence of the temperature upon the tension theoretically and to determine the equation of the reaction-isochore, but I do not think the experimental data, so far obtained, sufficiently numerous or, indeed, sufficiently accurate for such treatment, and I therefore

prefer to confine myself to the above remarks and to the curve and table which are purely empirical.

By means of the constants determined in this chapter, viz. The coefficients of absorption, the constant of dissociation at  $15^{\circ}$  and the additional corrections for the temperature, it ought to be possible to utilize the determinations of alkalinity and total  $CO_2$  in seawater, that are found in literature, for the purpose of tension-determinations. For several reasons I cannot, however, recommend such a course. Firstly because my «standard» seawater has proved itself to be, in the course of the investigation, rather abnormal with regard to the alkalinity, but still more so, because the older determinations are rather unreliable. The alkalinity is, as a rule, very accurately determined, but it is by no means certain that the quantities of carbonic acid are always directly comparable with the alkalinity. Rather often, I think, have the cubic-centimeters or milligrammes of  $CO_2$  been slightly different from the corresponding units for the alkalinity, and even very slight differences of this kind will prove disastrous for a computation of the tension. I am inclined to think that some error of this kind must have infected the otherwise so remarkably accurate experiments of HAMBERG. At least they do not agree, when treated theoretically, either with my own or indeed among themselves.

Nearly all the investigators have stored the water-samples for some time before analysing them, and we cannot be sure that they have avoided infection or diffusion of carbonic acid either to or from the atmosphere. The water-samples of the Ingolf-Expedition were certainly examined immediately, but KNUDSEN expresses the opinion that the values of the quantities of carbonic acid found are inaccurate, owing to absorption in the analysis-apparatus. (*The Danish Ingolf-exp. Hydrography* p. 34).



If direct determinations of the carbonic acid, or other gases, in seawater are to be made in the future I must recommend the use of the mercury-pump as the only really accurate and convenient apparatus for the extraction of gas. There can be no serious difficulty in its adaptation for use on board ships.

If my experiments are repeated with really «normal» seawater and a final value obtained for the constant of dissociation the easiest, and for all practical purposes a sufficiently accurate, method of quantity-determination will be to determine the tension and alkalinity of the water and to compute the quantity by means of the formulas given above.

*The carbonic acid of freshwater.* With regard to freshwaters very little theoretical work has been done. The chief alkaline, and in most cases the chief saline component also, is carbonate of lime. SCHLOESING (*Compt. rend.* T. 74 p. 1552, T. 75 p. 70) has studied the solubility of this salt in pure water and in water, saturated at varying tensions with carbonic acid, and has arrived at the following results.

Carbonate of lime is soluble in water to a certain extent irrespective of the carbonic acid present — 1 l. of water at 16° is, according to SCHLOESING, capable of dissolving 13.1 mgrs. of  $\text{CaCO}_3$ <sup>1)</sup> — but beyond this the salt is dissolved as bicarbonate

<sup>1)</sup> ANDERSON (*Proc. Roy. Soc. Edinburgh*, vol. 16, 1889, p. 324) has determined the solubility of calcspar, coral powder and amorphous calcium carbonate in distilled water and found that 1 liter dissolves 25.1, 28.5 and 248 mgrs., respectively. Though his results are *perhaps* vitiated by atmospheric carbonic acid and therefore too high, I have no doubt that SCHLOESING'S figure is too low.  $\text{CaCO}_3$  is certainly not less soluble than  $\text{BaSO}_4$ . It is probable that SCHLOESING has experimented upon crystalline carbonates and that, on this account, his results are not directly applicable to solutions of the amorphous lime.

by the action of the carbonic acid. SCHLOESING found out the following empirical formula:

$$x^m = ky$$

in which  $x$  stands for the tension of  $CO_2$  expressed in atmospheres and  $y$  for the quantity of  $CaCO_3$  dissolved, whereas  $m$  and  $k$  are constants. For carbonate of lime he found  $m = 0.37866$  and  $k = 0.92128$ , whereas for carbonate of baryta  $m$  was  $= 0.38045$  and  $k = 0.534726$ . In view of the close resemblance between the two values for  $m$  SCHLOESING expressed the opinion that this constant is of fundamental importance and will hold good for all carbonates of small solubility.

I have not myself studied the relations between the quantity and tension of carbonic acid and the alkalinity of freshwater, but I am of opinion that the same laws will hold good as those found for the seawater. Where no other base, but  $CaCO_3$ , is present, the simple dissociation-formula for bicarbonates of divalent bases must govern the process up to very high tensions.

I have made a single determination of the influence of rising temperature upon a tension which was indeed very high previously.

Tp. I	$\theta_I$	Tp. II	$\theta_{II}$	$\theta_I \frac{\alpha_I}{\alpha_{II}}$ <sup>1)</sup>
2.5°	$\begin{cases} 43 \\ 43 \end{cases}$	20.2°	74	75.5

The tension at the higher temperature agrees very well with the calculated figure, and it appears therefore that by such high tensions the alteration of the chemical equilibrium, which no doubt takes place, has no perceptible influence on the tension.

<sup>1)</sup> The values of  $\alpha$  are taken from BOHR. *Ann. der Physik und Chemie.* Neue Folge Bd. 68. 1899, p. 504.



The theoretical results of the present chapter may be summarized as follows:

The alkali in seawater consists almost exclusively of carbonates of alkaline earths, especially of lime and probably in a less degree of magnesia. To a certain extent these carbonates are chemically combined with carbonic acid, and bicarbonates are thus formed. The tension of the water at a given temperature depends upon the relation between the quantities of bicarbonate and of normal carbonate, and up to a tension of about 3 (at a temperature of  $15^{\circ}$ ) the process is in perfect agreement with the theoretical dissociation-formula. At tensions above this point secondary processes come into play. These secondary processes involve the chemical combination of more carbonic acid than demanded by theory, and they most probably consist in the partial replacing of certain weak acid by carbonic acid, in their salts.

The tension of a given seawater rises with the temperature, chiefly because the coefficient of absorption and consequently the tension corresponding to a given quantity of free carbonic acid is thereby altered, but also, partly, because the affinity between normal carbonate and free carbonic acid decreases with the rising temperature.

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## The Influence of the Soil upon the $CO_2$ -Tension of Freshwaters.

### Investigations in Greenland.

The freshwaters on the Island of Disko in Greenland are almost exclusively surface-waters, directly derived from the rain or from the melting of the snow and ice. The obvious reason for this fact is that the mean temperature of the year is below 0 and that, consequently, the ground is permanently frozen from a depth of less than 1 m. downwards. The very numerous rivers and brooks are of two different kinds, viz. The glacier-rivers, obtaining the bulk of their water-supply from the glaciers, and the ordinary rivers and brooks, depending solely on the rain, the melting snow, and, certainly, to no small extent on the melting of ice in the ground. The water of these last-mentioned rivers is almost always perfectly clear, while the glacier-rivers are extremely turbid and of a red, almost brick-red, colour, caused by the enormous quantities of débris which they hold in suspension and carry to the sea. Organic life is scarce in the ordinary rivers and practically, perhaps absolutely, absent in the glacier-rivers, though their temperature, near the mouths at least, rises very nearly to that of the atmosphere. Both kinds of rivers cease to flow during the winter. The height of the island varies from about 700 m. in the South to 2000 m. in the North, and as its area is only about 8300 sq. km. nearly all the rivers have an extremely rapid current, and not a few of them consist of an unbroken series of waterfalls.



It follows from what is here stated that every particle of water is almost continuously exposed to the atmosphere. It comes down as rain or snow, it oozes through at most 3 feet of loose earth, very often devoid of organic life, and then runs and falls in shallow streams into the sea. Considering this, one might reasonably expect that the tension of the carbonic acid in these waters would be equal to that of the atmosphere, and it is a little surprising to find that this is far from being the case.

As already mentioned (p. 337) the quantities of carbonic acid present in the air of Disko were extremely high: 4, 5 or even 6 tenthousand-parts. The tension of the river-water was always far below that. Instead of citing the whole series of my analyses I prefer to give some typical examples:

1. In a spring coming out of a terrace near the sea and showing a temperature of  $3.1^{\circ}$  the tension at the source was found = 0.

2. In a glacier-river rushing down a thousand feet, mostly as foam and dust, a tension of 2.5 was found. The temperature was  $7.1^{\circ}$ .

3. It often happens in calm weather that the freshwater from a glacier-river spreads out over the surface of the sea in a very thin layer, easily distinguishable by its colour and opaqueness and sometimes stretching several miles out. In such a layer of perfectly fresh water I once examined the tension of carbonic acid and found it by two analyses 2.5—3 while, at the same time, the tension of the atmosphere was found = 6.5—7.

It cannot be doubted that the water under the circumstances obtaining in examples 2 and 3 must absorb large quantities of carbonic acid from the atmosphere. But why does not the tension rise higher?

Only one explanation is possible. The carbonic acid absorbed must be chemically combined with some substance in

the water, and this substance must moreover be present in, practically, infinite quantities, because it would otherwise very soon be saturated with carbonic acid at the tension of the atmosphere.

Such a substance is found in the rocks above and through which the water flows and the particles of which it holds in suspension. Almost the whole of Disko is basaltic<sup>1)</sup>, and the carbonic acid, as the stronger of the two, tends to replace the silicic acid in its salts. In this particular instance the basalt is decomposed by the formation of carbonate of lime and free silicic acid.

The phenomenon has been investigated by BISCHOF (*Lehrbuch der chem. und phys. Geologie*, Bd. I, 2. ed. Bonn 1863) who has made several very convincing experiments.

If for instance a stream of carbonic acid is conducted through a solution of silicate of potassium or sodium a considerable quantity of carbonate is formed, but the decomposition of the silicate never becomes complete. A state of equilibrium will be attained in which acid silicates as well as carbonates are present (p. 31).

Silicate of lime, suspended in water, is very readily decomposed by a stream of carbonic acid, and a precipitate consisting of  $\text{CaCO}_3$  and free silicic acid is formed (p. 36).

Silicate of magnesia on the other hand is not in the least affected by carbonic acid (p. 37).

In perfect accordance with the experiments BISCHOF found that basaltic rocks, of which silicate of lime forms the chief constituent, very often show effervescence of carbonic acid when treated with dilute muriatic acid. This effervescence is an important sign of the decay of the rocks, and it is sometimes

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<sup>1)</sup> On the southern and eastern coast of Disko gneiss and sedimentary rocks with coal-beds are found. I have only examined waters from the basalt.



present before the decay is in any way visible to the eye<sup>1)</sup> (p. 46).

The presence of carbonates, indicated by the reaction, must of course be due to the carbonic acid of the water oozing through the rocks. In almost all regions, but the Arctic, this gas will be present in rather considerable quantities produced, as it is, mainly from organic sources, and its tension may rise to 3 per cent or even higher. It cannot be inferred therefore from BISCHOF's experiments (carried on at a  $CO_2$ -tension of 100 %) or observations whether a certain tension of carbonic acid be necessary for the action on silicate or not, but at first sight it would seem probable that it was so. My determinations of the tension in Disko-waters show however that it is not, and reveal the fact that basaltic rocks will absorb carbonic acid down to a tension of less than 0.5 tenthousand-parts. All the observations I have made on the carbonic acid in Disko-freshwaters serve to confirm this conclusion.

Before I invented the shaking-method of tension-determination I made some analyses of air-bubbles from the bottom of rivers and small ponds. A glacier-river very often forms a tract of comparatively level ground at its mouths, and by running over this is sometimes shifts its course from hour to hour. Considerable quantities of air become hereby enclosed in the loose sand of the bottom, and after some time tension-equilibrium will be established between the bubbles of air and the surrounding water. If this is at rest the tension may become 0, if it is rapidly renewed from above, the tension

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<sup>1)</sup> Some Authors (EBELMEN: *Ann. des Mines*, sér. 4, T. 7, 1845 and HUNT: *American Journ. of Sc. and Art.* 1880) have held that all silicates must be decomposed by carbonic acid, but this opinion, on which HUNT bases some very fantastic speculations concerning the carbonic acid in the atmosphere, is entirely hypothetic and was disproved, several years before HUNT wrote, by BISCHOF who found the effervescence of carbonic acid only in such rocks as contained silicate of lime (oligoclase and anorthite)

will generally be somewhat higher. I have found a tension of 0 in the bottom of a little creek on the river Kuganguak, where the water was perfectly at rest. In the bottom of rapid-flowing glacier-rivers I have found varying tensions up to 3. The percentage of oxygen in the air-bubbles is generally a little below that of the atmosphere — 20.75 %.

Peculiarly instructive are some analyses of air-bubbles from a very small pond, about 1 foot deep, which had, probably for a couple of months, been shut off from the Kuganguak. In this pond the bottom was covered by a thick and rather solid organic pellicle protecting the water of the pond from contact with the basaltic soil. The pellicle was covered with innumerable, small air-bubbles, a sample of which was collected and analysed. When the pellicle was removed bubbles of air could be collected from the bottom itself, and by means of a stick I succeeded in collecting air-samples from a depth of about 1 foot. The analyses showed:

	$CO_2$ ‰	$O_2$ ‰	Tp.
Air from the organic pellicle.....	5	24.60	11.1°
Two samples of air from the bottom...	$\left\{ \begin{array}{l} 2 \\ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 20.83 \\ 20.07 \end{array} \right.$	$\left. \right\} 11.1^\circ$
Air from the depth of one foot.....	7	2.14	

Though assimilation, as seen from the percentage of oxygen, was distinctly preponderant over respiration in the water of the pond the tension of carbonic acid was hardly below that of the atmosphere, while in the basaltic bottom it was much lower. In the deeper stratum organic life, probably bacteria, must, I suppose, have been the cause of the comparatively high tension of carbonic acid as well as the extremely low percentage of oxygen.

The influence of vegetation on the tension of carbonic acid is shown by some analyses. Bogs are of very common



occurrence on the lower slopes of the mountains, and they are often intersected by brooks. If the tensions of carbonic acid in the latter are examined, at the points of their entering and leaving a bog, it will be found that a considerable rise is caused by the passage:

	Tension	Tp.
Brook with numerous waterfalls just above a bog . . . . .	3	7.0°
The same brook below the bog . . . . .	14	5.1°
The same brook below the bog, after heavy rain . . . . .	8	5.6°

The rise may partly be due to the respiration of the roots among which the water flows, and partly to their secretion of acid which will combine with the alkali in the water and set free the carbonic acid.

At the beginning of this chapter I stated, that *almost* all the freshwaters in Disko are surface-waters and gave the reason for it, viz. That the earth at a depth of less than 1 m. is frozen all the year round. The sheet of ice which thus separates the surface from the deeper strata, where the temperature is again positive, is certainly very thick, and it is absolutely inconceivable that water from the surface should find its way through it.

In some places, nevertheless, water rises from the depth and forms the so-called «Unartut» or hot springs. The word «hot spring» must, however, not be taken too literally, for the temperature of some of them is not more than 2—6°<sup>1)</sup>, but they are distinguished by their flowing continuously during the winter, when all other streams are dry or frozen.

I have examined a spring on the south-coast of the Disko-

<sup>1)</sup> The hottest spring, known in Disko, was found by STEENSTRUP in Mellemfjord on the west-coast of the Island. Its temperature was 18.8° (*Medd. om Grønland*, Hefte 24 p. 287).

Fjord, formerly visited by RINK and also by STEENSTRUP (*Medd. om Grønland*, Hefte 24 p. 299). It rises vertically through several mouths, situated at the top of a slight elevation of the ground. At the time of my visit, <sup>24</sup>/viii 1902, the temperature varied in the different mouths from 11.33° to 11.65°. RINK found in June 1849 12.5°, and STEENSTRUP on the <sup>5</sup>/ix 1898 in the three hottest points 12°, 11.3° and 9° respectively, while on the following day, after some rain and snow, the highest temperature recorded was only 7°<sup>1</sup>). The water issues forth through fine sand, and in several places I observed bubbles of air, amounting I think to about 100 cc. each time, coming out of the sand at regular and very short intervals (about every 15 seconds). From two points these bubbles were collected and analysed, and in addition the CO<sub>2</sub>-tension of the water was determined in the ordinary way.

The air-analyses showed for the carbonic acid 0 and 0 and for the oxygen 14.47 and 13.64 % respectively. In two samples of the water a tension was found of 2 and 2.5 respectively. I explain the results in the following manner.

From very deep strata a stream of water finds its way through the covering sheet of frozen rock and ice. I suppose that this rising must take place with considerable velocity through a narrow fissure or channel, as the spring comes up artesian-like through the loose earth above the ice, and because the temperature, sometimes at least, may be remarkably high. A portion of the water must, however, be stopped by the loose earth and attempt to flow along the surface of the ice in the ground; but thereby the ice will be melted and a sort of wide funnel, as shown in the diagrammatic figure 9, will be formed.

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<sup>1</sup>) GIESECKE (*Mineralogische Reise in Grønland*, Copenhagen 1878, p. 25) mentions an Unartok in Southern Greenland with a temperature of 40°. During his stay it began to rain, and in a quarter of an hour the temperature fell to 30°. The temperature of the hot springs in Greenland always seems to be lowered by rain-fall.



In this funnel ordinary surface-water, flowing along the ice, must necessarily be collected and partly mixed with the hot water of the spring, and this accounts for the variability of the temperature, because the available quantity of surface-water is dependent on the state of the weather and will be augmented by rain in a short time. It is very improbable that the water of the spring itself should contain dissolved oxygen, as this gas is so easily combined with many minerals, but the surface-water is of course saturated with oxygen at the pressure present in the atmosphere. If gas-bubbles are formed<sup>1)</sup> and equilibrium obtained the oxygen-tension of such bubbles must

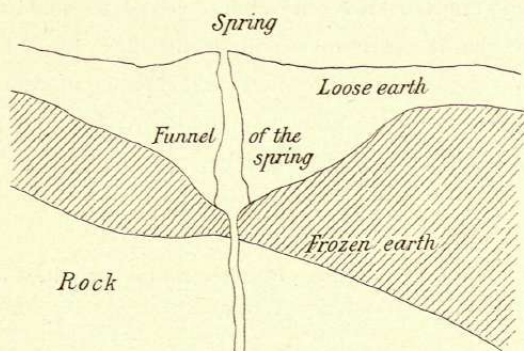


Fig. 9.

correspond to a mixture of oxygen-free water with common surface-water. This is exactly the result of the analyses.

At the depth where the bubbles are formed the tension of carbonic acid is evidently 0 but at the mouth of the spring it is about 2. This fact is not surprising, for at the mouth the water is mixed with more surface-water and with that portion of the surface-water which has just obtained a high

<sup>1)</sup> The formation of gas-bubbles indicates in itself that a mixture of hot water with cold may have taken place, because such mixtures, provided that each water was saturated beforehand with a gas (for instance nitrogen), will always be supersaturated and therefore liable to the formation of gas-bubbles.

tension of carbonic acid by passing between the roots of the abundant vegetation, surrounding the «Unartok».

It may be safely deduced from the determinations that the water from the depth does not contain any trace of free carbonic acid, and I venture to predict that, if this spring should be examined in winter-time, the temperature will be found to be higher, the tension of carbonic acid = 0, and the percentage of oxygen in the air-bubbles — if air-bubbles there are — very insignificant or probably 0.

*Summary.* The general feature of the carbonic acid in the freshwaters of Disko is the influence of the soil. The basaltic rocks may rightly be characterized as alkaline; when moist they absorb carbonic acid from the atmosphere and, indeed, from any source, and they are capable of reducing the tension of the gas to 0 and consequently of dissociating bicarbonates of alkalis and alkaline earths.

This powerful influence is so easily observed because the climate in arctic. The organic production of carbonic acid in the soil is comparatively insignificant and altogether unable to mask the influence of the soil itself.

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## Dissolution and Deposition of Lime by Natural Waters.

### **The tension of carbonic acid in Danish freshwaters.**

In a country with a temperate climate and a fertile soil the influence of organic life upon the tension of carbonic acid in freshwater becomes overwhelming, and the other factors are often masked.

Interwoven, as they are, with the roots and mycelia of plants, constantly burrowed by earthworms and other animals, full of organic remains on which the countless myriads of bacteria can prey, the upper strata of the ground are the source of an abundant production of carbonic acid. The numerous analyses of the atmosphere of the soil give ample evidence of this fact<sup>1)</sup>.

The rainwater oozing through the ground and moistening particle after particle of earth readily takes up the carbonic acid formed and becomes completely saturated with it at the tension existing. But as a consequence the water acquires strong dissolving powers, and every grain of lime or alkaline silicate, met with, is attacked.

At a certain depth, variable according to the nature of the soil, organic life decreases and thereupon almost totally ceases, and from this point downwards the tension of carbonic acid cannot increase further. It may become stationary or it may decrease according to the properties of the soil.

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<sup>1)</sup> SACHSSE: *Lehrbuch der Agrikulturchemie*. Leipzig 1888, pp. 142—146.

I have made only a few determinations of the tension in springs and wells and all of these in that part of the country where the deep layers consist of limestone, while the upper strata are generally rich in this mineral, but they are sufficient to demonstrate the very high tensions that may obtain in waters which have oozed through limestone for so long a period that they must be supposed to be completely saturated with calcium-carbonate.

	Date	Tp.	Tension	$Ca\ CO_3$ <sup>1)</sup> mgrs. per liter
Well carried down in the upper strata of the solid limestone. Water very abundant .....	26/9 02	10.0°	131 <sup>2)</sup>	13 + 211
The same well .....	5/8 03	11.0°	105	13 + 194
Another well very near the first but not so deep. Yield of water rather small	5/8 03	12.2°	270	13 + 279
Copenhagen Water-works .....	30/9 02	9.8°	48	13 + 145
	3/5 03	12.5°	60	13 + 157

Considerable quantities of  $Ca\ CO_3$  are carried away by waters such as come from the limestone-rocks, and the spacious caves found everywhere in such rocks are thereby easily accounted for. At the same time the problem arises: Whither is this carbonate of lime carried, where and when is it deposited?

<sup>1)</sup> The quantities of dissolved carbonate of lime are computed from SCHLOE-SINGS formula (given above p. 368) on the assumption that the waters were saturated with the salt at the tension found. It must however be remembered that it is uncertain whether the formula holds good for solutions of amorphous limestone, and that the figure 13 for the physically dissolved  $Ca\ CO_3$  is certainly too small.

<sup>2)</sup> On seeing these high figures for the tension of waters coming from limestone I suspected that the rock itself, being of organic origin, might possibly contain bicarbonates and give rise to a tension of its own when treated with pure,  $CO_2$ -free, water. I therefore tested my suspicion on fresh limestone, obtained from a quarry, and on pulverized shells of mussels, but the result was absolutely negative. The shells, as well as the limestone, did not contain any bicarbonates.



As shown in the preceding chapter basaltic rocks must have the power of precipitating  $\text{CaCO}_3$  from the bicarbonate-solutions, because they combine with the free carbonic acid and constantly diminish the tension.

In Denmark however, where basaltic rocks are not to be found, the dissolved carbonate of lime is not deposited, until the water arrives at the surface of the ground, where several causes will produce a diminution of the tension of carbonic acid and consequently the deposition of a corresponding quantity of lime. The most important of these causes is the atmosphere, towards which the surplus of carbonic acid readily diffuses<sup>1</sup>). Well-known instances of this process are the petri-fying springs which sometimes give rise to extensive layers of amorphous limestone<sup>2</sup>), but also the chalk-marl-deposits in many lakes owe their origin mainly to it.

Not a few investigators have studied the formation of these last-mentioned deposits, but though many valuable observations have been made concerning the special forms of the deposits, the general problem involved seems to have been somewhat overlooked, and some of the papers published have, no doubt, done more to confuse the question than to solve it.

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<sup>1</sup>) BISCHOF (*Lehrbuch* . . . I pp. 100—108) has made a series of experiments in order to investigate this process. He prepared solutions of bicarbonate of lime by saturating water with carbonic acid and carbonate of lime, but he also experimented upon natural waters from wells. He found that all these waters deposited carbonate of lime, when atmospheric air was allowed to bubble through them for a sufficiently long time. It is remarkable, however, that the greater part of the free carbonic acid was thereby got rid of in a comparatively short time, whereas large quantities of air were often necessary in order to cause precipitation of the lime. In these cases the deposit was sometimes crystalline and continued to appear after the stream of air had ceased.

I cannot satisfactorily explain these phenomena, but I think they must be due either to a formation of supersaturated solutions of  $\text{CaCO}_3$ , or to the probably very small reaction-velocity for the dissociation of  $\text{CaH}_2\text{C}_2\text{O}_6$  as previously mentioned (p. 362).

<sup>2</sup>) See BISCHOF: *Op. cit.* vol. I p. 545.

Taking a broad view of the matter we may contend that all the carbonate of lime is carried to a lake by the feeding streams and is either held in suspension or dissolved as bicarbonate. Matter held in suspension in a stream will, of course, be almost totally deposited in a lake. With this mechanical deposition my argument has nothing whatever to do.

In the lake two different organic processes are supposed to cause a deposition of dissolved lime.

The first is the assimilation of plants by which carbonic acid is withdrawn from the water and combined to form the organic material of the plants, and through them the animals that prey upon plants. About the equivalent weight of  $\text{CaCO}_3$  to the  $\text{CO}_2$  thus combined in organic compounds (2.3 grms. of  $\text{CaCO}_3$  for each gr. of  $\text{CO}_2$ ) will be deposited, provided the water of the lake be on the whole saturated with calcium-bicarbonate at the tension existing. But nearly all, and for the sake of argument I will presently suppose that all, this organic material is in due course again decomposed, whereby the carbonic acid is completely recovered. If nothing else takes place this carbonic acid must redissolve all the carbonate of lime deposited.

The second process is the formation of shells by mussels. These animals absorb calcium-bicarbonate, probably through the gills; they retain the monocarbonate, but the carbonic acid forming bicarbonate is liberated and will increase the tension of the water causing it to dissolve from the lime-deposits of the bottom, from dead shells and, indeed, from whatever source exactly the quantity of lime which the living mussels have taken from it.

In the long run, therefore, organisms are altogether incapable of either adding to or diminishing the lime-deposits in a lake<sup>1)</sup>,

<sup>1)</sup> In a lake where permanent organic deposits are formed these may give rise to the deposition of 2.3 grms. of  $\text{CaCO}_3$  for each gr. of carbonic acid deposited as organic material. The organic material that is not



and we must evidently look for a cause which will not fix carbonic acid in some form or other for a shorter or longer period but will permanently displace it from the lake. This cause can be no other than the diffusion of carbonic acid which takes place between the water of the lake and the atmosphere.

In order to show that this cause is amply sufficient to explain the formation of the lime-deposits in lakes I must go into a small calculation. BOHR<sup>1)</sup> has defined as the evasion-coefficient of a gas from a fluid that quantity which leaves the fluid through 1 sq. cm. of the surface when the density of the gas in the fluid is 1, that is to say, when 1 cc. of the fluid holds absorbed 1 cc. of the gas. For carbonic acid in water he has found the coefficient of evasion at 8°  $\beta = 0.108$  and the corresponding coefficient of absorption  $\alpha = 1.28$ . If we take the surplus tension of carbonic acid in the water of a lake to be only  $\frac{1}{10000}$  (tension in the water 4 and in the atmosphere 3) the active density will be  $D = 1.28 \times 10^{-4}$ , and the quantity leaving during one year ( $T = 5.25 \times 10^5$  minutes) and 1 sq. cm.

$$Q = \beta DT = 1.08 \times 10^{-4} \times 1.28 \times 10^{-4} \times 5.25 \times 10^5 = 7.25 \text{ cc.}$$

To this quantity will correspond a certain amount of carbonate of lime deposited on each sq. cm. of the bottom, depending upon the state of saturation of the water entering the lake. The maximum amount will be  $7.25 \times 1.96 \times 2.3 = 33$  mgrs.<sup>2)</sup>,

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redissolved is however a very small quantity in most lakes and completely inadequate to account for the abundant deposits of lime.

<sup>1)</sup> BOHR: Definition und Methode zur Bestimmung der Invasions- und Evasionscoefficienten bei der Auflösung von Gasen in Flüssigkeiten. Werthe der genannten Constanten .... *Ann. der Physik und Chemie*. Neue Folge Bd. 68. 1899, pp. 500—525. It is possible that the values found by BOHR are somewhat too small.

<sup>2)</sup> In this calculation no account is taken of the waves which will of course greatly augment the surface and thereby also the evasion of carbonic acid.

I need hardly say that it is not my opinion that the whole of such

which is, indeed, no small deposition on the area of 1 sq. cm. In the Danish lake Fure-Sø with an area of 9 sq. km. it would correspond very nearly to 3000 tons of lime pro year.

In the summer of 1903 I examined the tensions of carbonic acid in the waters of the Fure-Sø and obtained the following results:

Date	Depth of the water m.	Depth of the sample m.	Tp.	Tension	Annotations
23/6	0.5	Surface	17.5°	3.5	In a shallow bay "Store Kalv". Abundant vegetation. Bright and calm weather.
	3	2.5	16.5°	7.5	
		Surface	17.5°	3.5	
24/6	36	34	9.2°	11	Deepest part of the lake. Vegetable plankton in the surface. Bright and calm weather.
		38	9.2°	10.5	
		28	9.2°	8	
	38	19	9.3°	?	
		10	16.2°	15	
		Surface	17.2°	5	
28/9	4	Surface	20.1°	5.5	Samples taken near the shore. Bright weather, fresh breeze.
		Surface	20.1°	5.5	
4/7	38	34	9.2°	12.5	Bright and calm weather.
		28	9.3°	9.5	
		28	9.3°	11	
		10	17.2°	9.5	
		Surface	18.0°	5	
5/7	6	5	18.0°	5	On a bank in the middle of the lake. Abundant vegetation. Various points in the southern part of the lake. Rain.
	11	11	14.0°	7	
	17	10	15.0°	7.5	
	24	24		11.5	

The analyses show that the tension of carbonic acid in the surface of the lake is higher than that of the atmosphere.

a deposit is directly formed by the evasion of  $CO_2$  to the atmosphere. Possibly a very great part may be *formed* by organic forces, but it is due solely to the removal of carbonic acid by the atmosphere that this part is not redissolved.



This point is very essential, since the whole evasion of carbonic acid depends on the surplus tension in the very surface of the water. The difference found on different days in the open part of the lake amounts to 2 and would therefore, if maintained throughout the year, account for a yearly deposition in the lake of about 6000 tons of lime. I have some reason to believe, however, that the figure found is a minimum, or very nearly so, because the weather during the investigation was exceedingly favourable to the assimilation of the vegetable plankton.

As seen by the first entries in the table the tension in shallow creeks with abundant vegetation may be somewhat lower, but still it is higher than that of the atmosphere.

The tension is found to increase pretty regularly with the depth. This is only what we must expect when the carbonic acid is chiefly set free at the bottom and removed through the surface.

It appears from the above that lakes will act to a great extent as *decalcifiers* on the water that flows slowly through them, but the phenomenon no doubt deserves to be more thoroughly studied, and I am of opinion that quantitative results of some importance with regard to the deposition of lime could be obtained by series of tension- and alkalinity-determinations comprising at least a whole year.

In rivers and brooks the conditions are far more complicated than in lakes, because the water is continuously renewed and also because organic material as well as particles of lime, when such are formed, are carried away by the stream and deposited elsewhere, perhaps in a lake or perhaps in the sea. As I have but very few observations at my disposal I shall not enter upon any discussion on these points but will only mention the fact that the tension in a river, with an abundant vegetation of *Potamogeton*, *Ulva* and other plants, is extremely variable and may sink far below that of the atmosphere as will be seen from the following analyses:

Grenaa river. All the samples taken at exactly the same spot near the middle of the stream.	Date	Tp.	Tension
	25/9 02	11°	{ 9
	26/9 02	11.6°	8.5
	14/8 03	17.1°	2.3
	18/8 03	16°	{ 1.5
	20/8 03	13.9°	1.7
			3.2



## The Tension of Carbonic Acid affecting the Structure and Preservation of Molluscan Shells.

### Investigations in the Baltic.

I have made some determinations of the carbonic acid-tension in the Baltic in order to test a suggestion made by Mr. AD. JENSEN of the Copenhagen Zoological Museum. Mr. JENSEN had observed that some species of Bivalves from certain High-Arctic localities, notably along the east-coast of Greenland, presented very marked peculiarities with regard to the structure and thickness of the shells. I shall enumerate some of the most striking examples leaving it to himself to treat the matter adequately from a malacological point of view.

The periostrakum of *Astarte borealis* is in these localities extremely thick and bast-like. In the Danish seas Dr. JOH. PETERSEN found that this was likewise the case in the Baltic, while the same species, living in the Kattegat, has a normal, thin periostrakum. Mr. JENSEN thinks it probable that this thickness of the periostrakum may act as a protection against dissolution.

*Tellina calcaria*, whose shells are normally rather solid, is found in the same High-Arctic localities and also in the Baltic, around Bornholm, with extremely thin and fragile shells, often bearing strong indications of their having been exposed to chemical attack from the water.

Dead shells, which everywhere else greatly outnumber the

living specimens, are comparatively scarce in these same localities and such as are found are generally in a bad state of preservation.

The specimens of *Saxicava arctica* from the East-Greenland locality Heklahavn [Hekla-Harbour] have, as a rule, lost the periostrakum almost completely, and Mr. JENSEN found that the shells are either extremely thick, so as to completely disfigure the animal, or else they are thin and extremely fragile. He is of opinion that this indicates that a struggle is going on between the animals and some lime-dissolving agent, and that some of them are able to hold their own in this struggle by a greatly enhanced production of shell-substance, while others succumb.

Carbonic acid is obviously the only dissolving agent that can be present in normal seawater, since all stronger acids, if by any chance they were formed, must immediately combine with the alkali and liberate carbonic acid. If therefore a high tension of  $CO_2$  should be demonstrated in those localities, where the bivalves possess the characters observed by Mr. JENSEN, his views would be thereby corroborated.

The only locality which I was able to examine at the time was the Baltic near the Danish Islands of Bornholm and Christiansø.

The table on page 389 shows that from a depth of about 50 m. downwards the tension of carbonic acid rises rapidly and attains a considerable height at the bottom. It is in perfect agreement with this fact that dead shells are readily dissolved and that some, at least, of the living Molluscs protect themselves by means of a thick periostrakum.

The correctness of Mr. JENSEN'S opinion cannot of course be finally established by observations in one locality but it seems to me that he is most probably right and that interesting results are likely to be obtained by combined examinations in many localities of the tensions of carbonic acid and the structure



Position	Depth m.	Depth of sample m.	Salinity	Temp.	Tension	
NE-point of Bornholm SSW, 3 miles	41	37	0.79	6°	4.4	} Bottom «clay»
	41	19	0.77	15.2°	3.9	
	60	51	1.02	7°	10.1	
	60	0	0.77	16.5°	4.0	
Near Christiansø	13	13	0.72	16.0°	2.4	} Bottom granite, with vegetation
	28	28	0.70	10.2°	4.2	
Christiansø N, 1 mile	95	75	1.3	Thermo- meter lost	16.0	
	95	56	1.1		7.8	
	95	0	0.7		2.8	
«Taarnrende»	10	10	0.7		2.1	} Rich vegetation
	10	0	0.7		3.1	
Narrow creek Græsholmen	3	3	0.7		1.6	} Very rich vegetation

of Molluscan shells. It is almost certain that the rapidity with which dead shells are attacked and dissolved is a simple function of the  $CO_2$ -tension, and the fact, that also in the Arctic localities already referred to, the dead shells are scarce and badly preserved, furnishes therefore a strong argument in support of Mr. JENSEN's views<sup>1)</sup>

The last analyses in the table show the influence of abundant vegetation and clear sunlight on the tension. Especially in the small and narrow creek on Græsholmen, where the water is probably not so rapidly renewed, the tension reaches a very low value. It is a well-known fact, that the assimilation of higher plants in air is directly proportional to the percentage of carbonic acid, at least at the ordinary low percentages. So

<sup>1)</sup> I think it possible that, by a collection of data in this direction, definite relations might be established between the state of preservation of sub-fossil shells and the tension of carbonic acid obtaining during their deposition.

far as I know, the flora of the sea has not been examined in this respect, and it is obvious that a comparison would be very misleading if it were based on the *quantities* of  $CO_2$  present in the water and in the air, respectively. If the law holds good for marine Algae the assimilation must be proportional to the amount of free carbonic acid — that is to the tension<sup>1)</sup> —, and the growth of the plants must not unfrequently be seriously hampered by want of carbonic acid, though the gas may be present in considerable quantities.

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<sup>1)</sup> An experimental investigation of this problem will now be comparatively easy if my method of tension-determination be adopted.

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## The Alkalinity and the Carbonic Acid of the Ocean.

A great many determinations of alkalinity and carbonic acid in seawater have been made since the time of the Challenger-expedition but very few general results have been obtained. The alkalinity and still more the quantity of carbonic acid have been found to be «variable»; the carbonic acid being present, as a rule, in quantities insufficient to form bicarbonates with all the alkali.

It is obvious however that neither the alkalinity nor the quantity of carbonic acid can vary spontaneously, and I shall now endeavour to enumerate and to exemplify the circumstances which will cause alterations of these quantities.

### *Causes which govern the alkalinity.*

1. *Alkaline substances.* When flowing along the bottom the water will in many places be in close contact with alkaline substances: carbonate of lime, carbonate of magnesia and silicate of lime. If the water contains an excess of carbonic acid it is certain that it will readily dissolve these substances and that the alkalinity will increase (DITTMAR: *op. cit.* p. 130), and even when the water is in its natural state it also seems to be capable of dissolving carbonates. DITTMAR made two experiments (p. 130—131) with water from the Irish Channel, containing 97.7 mgrs. of  $\text{CO}_2$  per l. with an alkalinity of 50.2 mgrs. (corresponding probably to a tension at  $15^\circ$  of 4.5—5). He digested 260 cc. of this water at ordinary temperature with 2 grms. of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ , respectively. In the first case he found that the

alkalinity *decreased* from 50.2 to 47, a result which he however suspects being due to an observational error, while in the second it increased from 50.2 mgrs. to 60.8.

IRVINE & YOUNG (*Proc. Roy. Soc. Edinburgh* vol. 15, 1887 p. 316) made some further experiments and found that the seawater from the «German Ocean», on which they experimented, was always capable of dissolving more lime from the remains of different organisms as well as from crystallized and amorphous carbonate of lime. The quantities taken up vary very much, according to the material used, from 32 mgrs. of Coral sand to 649 mgrs. of precipitated carbonate of lime.

ANDERSON (*ibid.* vol. 16. 1889, p. 319) studied the solubility of carbonates in solutions of different salts and found that these, with the exception of  $CaSO_4$ , dissolved more carbonate of lime than distilled water. In artificial seawater, free from carbonates or carbonic acid, very nearly as much was dissolved as natural seawater will take up in addition to its original alkalinity. The Author arrives at the conclusion, by no means borne out by his experiments, that the solubility of carbonate of lime «has nothing to do with the existence of free carbonic acid or bicarbonates». His experiments prove, however, that certain seawater-salts, especially the  $MgCl_2$ , play an important part with regard to the solubility of carbonate of lime and that therefore SCHLOESINGS formula, quoted above (p. 368), by which it ought to be possible to compute the quantity of  $CaCO_3$  corresponding to any given tension, cannot be used in the case of seawater.

By boiling in vacuo or in a current of  $CO_2$ -free air seawater rapidly loses its dissociable carbonic acid and becomes turbid <sup>1)</sup>, but, on the other hand, no trace of turbidity became visible at ordinary temperatures or, indeed, up to 80° in my experiments with very low tensions (0.7—1.15), and the direct determinations of the alkalinity showed no decline.

<sup>1)</sup> By this fact the conclusion of ANDERSON is disproved.



It appears from the experiments cited that seawater cannot be regarded as saturated with alkali and that it will take up more if brought into contact with a suitable bottom<sup>1</sup>).

How much it will take up we do not know, however, with any accuracy, and in order to ascertain this a series of experiments ought to be made on the lines initiated by DITTMAR, but connected with accurate determinations of tension and temperature. Such experiments will be very easy to perform by means of my method of tension-determination, and I would take up the problem myself if I did not fear that the abnormal alkalinity of my present stock of seawater would vitiate the results. As it is I must leave it to other investigators who may be in a position of more easily obtaining the necessary supplies of pure ocean-water.

It appears with certainty from DITTMARS determinations of alkalinities in the ocean that bottom-waters are, as a rule, more strongly alkaline than surface-waters and waters from intermediate depths, but the exceptions to this rule are rather numerous. When the experiments above referred to have been made it will, in all probability, be possible to explain some of these exceptions and to learn something about the influence of the bottom upon the alkalinity by a comparative study of the alkalinities and the chemical composition of the corresponding bottom-samples.

From the tables of the *Ingolf-Expedition* I have extracted the following figures for the alkalinities at depths about 1000 Danish fathoms or more. The first series of stations (47—67) comprises the deep sea south of Iceland and east of the high barrier «Reykjanæs-Ryg» stretching in a south-westerly direction from the SW-point of Iceland. In all the samples of bottom-water from this tract a very high alkalinity is found. The

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<sup>1</sup>) The remarkable fact that calcareous deposits do not exist at the greatest depths of the ocean (beyond 2800 fathoms) points to the same conclusion (*Challenger, Narrative*, vol. I p. 920—926).

stations of the second series (91, 12—20) lie west of Reykjanæs Ryg between this barrier and Greenland and the third series is obtained from the Davis-Strait. The alkalinity of these parts is markedly lower than that found east of the great barrier. In the present state of our knowledge I cannot give any explanation of these differences but I think it probable that they may be due to some bottom-influence.

Station	Depth	Tp.	Salinity	Alkalinity
47	950	3.2°	35.01	27.0
48	1150	3.2°	35.10	29.4
49	1030	3.4°	35.34	28.0
65	1089	3.0°	35.27	29.9
67	975	3.0°	35.18	31.6
Mean				<b>29.2</b>
91	1236	3.1°	35.01	26.2
12	1040	0.3°	35.05	26.9
18	1135	3.0°	35.07	26.9
19	1566	2.4°	35.09	26.4
20	1695	1.5°	34.97	26.5
Mean				<b>26.6</b>
21	1330	3.4°	34.72	26.9
36	1435	1.5°	34.93	25.6
37	1715	1.4°	34.63	25.8
38	1870	1.3°	34.60	26.7
Mean				<b>26.3</b>

2. *The organic life* has, I think, a comparatively small influence upon the alkalinity. Nothing definite can, however, be said about it quantitatively. It may be summed up as follows:

a. Formation of organic substance. Among the mineral components absorbed by plants, when growing in a culture-solution, the acids are slightly in excess of the bases and the alkalinity of the remaining liquid therefore increases. We do not know whether this also holds good for marine macroscopic and microscopic plants on which no experiments have been



made, but, even if it does, I am of opinion that the effect upon the alkalinity of the sea will remain below our analytical power<sup>1)</sup>.

Under this heading must also be mentioned the possibility that the assimilation of the plants may sometimes so greatly diminish the tension of carbonic acid in the seawater that a precipitation of carbonates can take place. My experiments show, however, that such precipitation requires so great a diminution of the tension that it is practically impossible, except perhaps in narrow bays where there is an abundant vegetation as in the example mentioned on p. 389.

*b.* Decomposition of organic substance. Whereas the formation is practically confined to the upper layers of the sea, where the water is constantly mixed and the physical and chemical conditions are well defined, disintegration may take place everywhere and through the most different intermediate stages. No fixed rule with regard to its influence upon the alkalinity can therefore be given, and observation and experiment must decide everything. I think it probable that in stagnant, or, in comparatively stagnant waters, where oxygen is scarce, organic acids and perhaps sulphuretted hydrogen may be formed and the alkalinity thereby appreciably diminished. On the other hand the abundant production of carbonic acid under such circumstances will enhance the solution of carbonates, if such be present<sup>2)</sup>, and there is also the possibility of a formation of ammonia.

A fine example of the influence of decaying organic substances in the presence of  $CaCO_3$  and  $MgCO_3$  is given by WALTHER & SCHIRLITZ (*Zeitschr. Deutch. Geol. Ges.*, Bd. 38, 1886,

<sup>1)</sup> At a very moderate estimate an additional alkalinity of 0.1 (cc. of carbonic acid) obtained in this way would correspond to a production of 0.1 gr. of dry organic substance in 1 l. of water.

<sup>2)</sup> In *Challenger, Narrative* vol. 1 p. 917 it is stated that the Blue Mud forming the most extensive deposit around the continents often contains sulphuretted hydrogen while calcareous remains are sometimes quite absent.

p. 331): In the depressed parts of the Bay of Naples the bottom consists of a soft mud containing carbonates and decaying material, mostly from plants, and on this bottom the alkalinity rises to 59.6, 58.3 and 58.8 mgrs., whereas in the corresponding surface-waters it is only 52.4, 54.2 and 52.3. The Authors are of opinion that the alkalinity is partly made up by ammonia but they give no satisfactory proof of this contention.

c. Deposition of silicic acid in the shells of the Diatoms and other organisms must undoubtedly increase the alkalinity, but in the ordinary method of alkalinity-determination all the silicic acid is precipitated and variations in its quantity cannot, therefore, show themselves. Besides, they are certainly very small and probably altogether below the range of our analytical powers.

d. The deposition of lime in the shells of many organisms is certainly the most important organic factor connected with the alkalinity.

We are accustomed in the case of the higher animals to look upon the food as the sole source of the mineral as well as of the organic components of the animal organism. If this view were correct for marine animals we might discard the accumulation of lime by animals as having no bearing upon the problem of the alkalinity. The investigations of IRVINE & WOODHEAD (*Proc. Roy. Soc. Edinburgh*, vol. 16, 1890, p. 324—354) proved however that crabs are able to utilize the calcium-salts of the seawater directly and independently of the food<sup>1)</sup>. BISCHOF had previously (*op. cit.* p. 585) expressed the same opinion with regard to the mussels but without proof and appa-

<sup>1)</sup> From a physiological point of view a more detailed study of this function would be very interesting. Nothing is known about the ways and the mechanism of the absorption. It is extremely improbable that it takes place through the intestinal tractus, as we have not the slightest evidence that crabs *drink* the enormous quantities of seawater required (1 gr. of  $\text{CaCO}_3$  is contained in 10 l. of water), nor, indeed, that the drink at all. Most probably the absorption takes place through the gills.



rently without perceiving the physiological difficulty. He calculated that the amount of carbonate of lime present in the shells of a single oyster corresponds to 172—293 kgrs. of seawater or 28000 to 76000 times the weight of the animal. There can *now* be no doubt that BISCHOF was right in supposing that such large quantities of lime must be absorbed directly from the water circulating within the mantle, and if we venture to extend the results obtained by IRVINE & WOODHEAD to all the marine lime-producing organisms<sup>1)</sup> we must conclude that their combined action will have some diminishing influence upon the alkalinity of the ocean.

According to MURRAY (*Challenger narrative*, vol. 1, p. 980) as much as 16 tons of  $\text{CaCO}_3$  may be present in the shells of organisms in a mass of ocean-water possessing an area of 1 sq. mile and 100 fathoms deep from the surface. This seemingly large figure corresponds however to only 0.025 mgrs. of lime per l. or to the alkalinity of 0.01 mgrs. About twenty times must the formation of this quantity be reiterated in the same mass of water and the shells removed by sinking, before the result is detectable by the alkalinity-method.

3. *Evaporation* concentrates the surface-waters and augments the alkalinity which remains, however, during this process strictly proportional to the salinity.

4. *Dilution* with freshwater is easily detected and quantitatively determined by its influence on the salinity or the percentage of chlorine, but its influence on the alkalinity is more complicated.

a. Freshwater produced by melting ice. It is probable, though I do not know that it has been experimentally verified, that ice formed in the sea is much less alkaline than the

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<sup>1)</sup> It must be admitted of course that some lime is in all probability derived from the food, and some organisms are perhaps reduced, more or less, to this source of lime. WESENBERG-LUND maintains (*Medd. Dansk Geol. Foren.* Nr. 7, 1901) — on rather inadequate grounds — that this is the case with all Gasteropods.

seawater, or that it is perhaps neutral. Freshwater from this source will therefore *perhaps* diminish the alkalinity in nearly the same proportion as the salinity.

b. Freshwater from the continental rivers generally possesses an alkalinity of its own, and the alkalinity of the sea will therefore be diminished by it in a less proportion than the salinity or it will not be diminished at all.

I have been able to extract a good example of this kind from the INGOLF-tables. A series of determinations have been made in the surface of the Davis-Strait where the seawater is diluted, principally with river-water from the west-coast of Greenland. A comparison of these with others from the surface of the Atlantic, south of  $63^{\circ}$  N. L., shows that the alkalinity in the Strait has absolutely decreased but has increased relatively to the salinity.

Longitude W $> 45^{\circ}$ Latitude N $> 60^{\circ}$				Longitude W $< 45^{\circ}$ Latitude N $< 63^{\circ}$			
Station	Salinity S	Alkalinity A	$A \cdot \frac{35}{S}$	Station	Salinity S	Alkalinity A	$A \cdot \frac{35}{S}$
25	32.97	25.9	27.5	17	35.26	26.8	26.6
26	32.90	25.5	27.1	18	35.05	28.0	27.95
27	33.01	25.2	26.7	19	35.16	26.9	26.8
28	32.91	26.5	28.2	20	34.96	26.2	26.25
29	33.65	26.9	28.0	21	34.79	27.6	27.75
30	33.28	26.1	27.45	39	35.38	25.8	25.5
31	33.36	25.9	27.2	40	35.30	26.2	26.0
32	33.04	25.4	26.85	41	35.35	27.3	27.05
33	33.56	27.1	28.25	42	35.41	26.7	26.4
34	32.97	26.6	28.25				
35	32.76	26.3	28.1				
36	33.56	25.8	26.9				
37	33.80	26.1	27.05				
Mean	33.21	$26.1 \pm 0.15$	$27.5 \pm 0.15$		35.18	$26.8 \pm 0.2$	$26.7 \pm 0.25$

If it were permissible to assume, which of course it is not, that it was the surface-water from the examined area of the



Atlantic that was carried up into the Davis-Strait and diluted with freshwater the figures would indicate that the average dilution amounted to 5.6 per cent of freshwater with an average alkalinity of 14.3 or about the half of that of the seawater.

In WALTHER & SCHIRLITZ' paper (quoted above) an examination of brakish water taken near the mouth of the Volturno in the Bay of Gaëta is mentioned. Unfortunately, the salinity is not given, but the very high alkalinity — 68.5 mgrs. — is rightly attributed by the Authors to the river-water coming down from the extensive beds of limestone in the Appennines.

When we try to consider the alkalinity of the ocean as a whole we find two causes of augmentation, viz. The alkali of the bottom and the alkali of the freshwater, carried to the sea, and one of diminution, the fixation of lime by the marine organisms.

It is generally stated that the ocean must have attained, during the immense space of time, a stable equilibrium. This may be true with regard to the salinity but we have not sufficient reason to believe that it also holds good for the alkalinity. A large part of the carbonates no doubt perform a regular circulation being fixed by the organisms, converted into rocks of limestone and dolomite, dissolved by the meteoric waters and again carried to the sea<sup>1)</sup> but the several phases of the process are absolutely independent of each other, and the velocity of the motion as a whole may, for all we know, be very variable.

Alongside the circulation runs a constant production of carbonates from alkaline silicates and even should this process

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<sup>1)</sup> The yearly amount of lime carried to the sea by the rivers of the earth is variously estimated:  $1.3 \times 10^9$  tons (*Challenger narrative* vol. 1 p. 980)  $3.1 \times 10^9$  tons (*Journ. of Geol.* vol 7 p. 569). The figures are probably not very reliable, but they may indicate that the real quantity is something of this order of magnitude.

be in some measure rotatory as the carbonates may be broken up at greater depths in the earth and converted into silicates, the absolute independency of the two phases is incontestable.

We may therefore regard the total alkalinity of the ocean as a quantity that has probably been subject to considerable variations during the geological periods, but it must be admitted on the other hand that the variations must go on very slowly, because the altering factors are insignificant compared with the total amount of alkali present in the ocean at any one time. There is at present found about  $1.6 \times 10^{14}$  tons of alkali (reckoned as carbonate of lime) which according to the CHALLENGER-estimate, is 120000 times the quantity added yearly by all the rivers on the earth.

I am well aware of the very imperfect character of my remarks upon the alkalinity, but perhaps they may be useful as indicating some points which require clearing up, and the study of which may prove of some hydrographical value. It ought to become possible to draw some conclusions from the alkalinity respecting the former travels of a sample of water.

### *Causes which govern the quantity of carbonic acid.*

1. *The influence of the organic life* is very easily accounted for. Assimilation causes decrease, and dissimilation causes increase in the quantity of carbonic acid. Broadly speaking we may say that the quantity varies inversely as the quantity of oxygen present in the water. This was first observed by KNUDSEN (*Ingolf Expedition, Hydrography* p. 153) who found that the average quantity of carbonic acid for the samples, possessing a higher oxygen-tension than the atmosphere, was 39.8, whereas for the others, showing an oxygen-deficit, it was 41.7. KNUDSEN showed that the variations of the oxygen, as well as the carbonic acid, were due to the plankton and depended upon its vegetable or animal character.



2. DITTMAR mentions (*Challenger, Physics and Chemistry*, vol. 1, p. 213) the possible existence in the sea of veritable *springs* of carbonic acid. That such springs may exist in the sea as well as on land is, indeed, extremely probable but, so far as I know, none have as yet been discovered.

3. The *river-water* entering the ocean no doubt contains a considerable part of its alkali in the state of bicarbonates, and the amount of loose carbonic acid contained in these is a source of gain to the sea. MELLARD READE (*Journ. of Geol.* vol. 7, 1899, p. 569) estimates the yearly quantity as  $1.35 \times 10^5$  tons.

4. *Interchange with the atmosphere.* Any difference in tension existing between the surface of the sea and the atmosphere will give rise to diffusion, the rate of which may be determined from BOHR'S formulas and constants of invasion and evasion (quoted above p. 383) when the tension-difference is known. In this respect the ocean may be compared with the freshwater-lake mentioned above, but there is this great difference that, while the total amount of carbonic acid in the lake is extremely insignificant compared with that of the atmosphere, the amount of loose and free carbonic acid in the ocean is many times greater than in the air. If differences in tension are found the interchange of the gas between the sea and the atmosphere will therefore have by far the greater influence upon the latter, and I must refer for a more exhaustive treatment of the matter to the following paper on the composition of the atmosphere. Here I shall confine myself to give only the tensions actually found in a series of water-samples from the Davis-Strait and the North-Atlantic collected in Septbr. 1903 during the home-voyage of a steamer.

The first of these tables contains the tensions as they were actually observed in the samples of water at  $12^{\circ}.5$ . Two samples of water were always collected simultaneously, and 1 gr. of sublimate was added to one of them.

The tensions of the pure-water-samples, given in the first

column, do not keep unaltered and are not always trustworthy, because they become infected by bacteria. All figures regarded as untrustworthy are put in brackets.

The tensions of the sublimate-samples are arranged in the second column, marked *S*. The sublimate causes an increase of the tension, probably because some monocarbonate of mercury is formed, and the differences between the reliable figures in the two columns are therefore given in the third. These differences vary only between 0.25 and 0.4, their average being 0.35. This average is taken as the specific increase in tension produced by the chloride of mercury; the figures for the sublimate-samples are diminished by 0.35 and the final values for the tensions at 12.5° are computed and given in the last column.

The second table contains the dates and positions of the samples; the state of the weather at the time of their collection, and the salinities, temperatures and  $CO_2$ -tensions of the waters in situ.

Number	Tension	Tension <i>S</i> .	Diff.	Adopted tension
1	2.1, 2.0	2.4, 2.4	0.35	2.05
2	2.4	2.7	0.3	2.4
3	[2.7, 2.6, 3.4]	2.6, 2.8		2.4
4	2.9	3.3	0.4	2.9
5	3.0	3.4, 3.3	0.35	3.0
6	2.5 [3.4]	2.8, 2.7	0.25	2.45
7	3.2	3.5	0.3	3.2
8	2.6	3.0	0.4	2.6
9	1.9, 3.3]	2.9, 2.9		2.55
10	2.6	2.9	0.3	2.6
11	2.2	2.6	0.4	2.2
12	[1.9, 2.3, 3.5]	2.5		2.15
13	[2.4]	2.4		2.05
14	2.2	2.6	0.4	2.2
15	2.2	2.6	0.4	2.2
16	[2.7, 2.8]	2.7		2.35
17	[3.6]	2.5		2.15
18	[3.5, 3.5]	3.3		2.95
Average.....			0.35	



Date	Hour	Lat. N.	Long. W.	Wind		Weather	Water			Number
				Direct.	Force		Salinity ‰	Temp.	CO <sub>2</sub> Tension	
August 31	6 p. m.	68° 28'	54° 17'	N	1	Bright	33.46	5.2°	1.55	1
Septbr. 1	8 a. m.	65° 20'	53° 58'	NNE	2	Bright	32.75	4.2°	1.75	2
—	1 8 p. m.	63° 52'	52° 07'	N	2		32.38	4.5°	1.8	3
—	2 8 a. m.	62° 26'	50° 38'	N	2	Overcast	33.55	5.8°	2.25	4
—	2 8 p. m.	61° 04'	48° 58'	N	2	Overcast	34.16	6.5°	2.4	5
—	3 8 a. m.	59° 45'	47° 11'	N	3	Overcast	34.29	6.0°	1.9	6
—	3 8 p. m.	59° 14'	46° 54'	SE	2	Bright	34.92	7.0°	2.7	7
—	4 8 a. m.	58° 46'	44° 03'	N	3	Bright	34.94	8.7°	2.25	8
—	4 8 p. m.	59° 13'	41° 15'	ESE	1	Bright	34.95	9.0°	2.2	9
—	5 8 a. m.	59° 24'	38° 29'	ENE	1	Bright	34.96	9.5°	2.3	10
—	5 8 p. m.	59° 27'	35° 58'	NNE	2	Bright	34.92	9.6°	1.95	11
—	6 8 a. m.	59° 28'	33° 09'	SE	2	Overcast	35.05	10.0°	2.0	12
—	7 8 a. m.	59° 32'	27° 50'	NE	4	Cloudy	35.19	10.5°	1.9	13
—	8 8 a. m.	59° 35'	22° 07'	NNE	4	Cloudy	35.25	11.0°	2.05	14
—	9 8 a. m.	59° 36'	17° 03'	NW	5	Cloudy	35.25	12.9°	2.25	15
—	10 8 a. m.	59° 50'	11° 29'	N	3	Cloudy	35.35	11.5°	2.25	16
—	10 8 p. m.	59° 25'	8° 29'	N	3	Cloudy	35.37	11.7°	2.1	17
—	11 8 a. m.	58° 50'	6° 00'	NNW	3	Rain	34.91	12.0°	2.9	18

The percentages of carbonic acid in the atmosphere have not been determined, as they certainly ought to be, along with the tensions, but we may feel sure that they were distinctly higher than these and that *a copious absorption of carbonic acid took place in a very considerable area of the North-Atlantic and Davis-Strait during the first half of September 1903.*

It cannot be gathered, of course, from this single series of tension-determinations whether such will prove to be of direct hydrographic value, but it appears to me that they will deserve a fair trial in this respect.

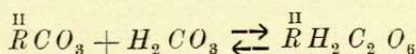
## Summary of the Results.

1. *Definition.* The tension of carbonic acid in natural waters is the percentage of the gas in air being at ordinary pressure in diffusion-equilibrium with the water. It is determined simply by shaking a sample of the water with a little air and determining by analysis the percentage of carbonic acid in the latter.

2. *Theoretical.* The carbonic acid is present in natural waters chiefly in combination with carbonates and forming dissociable bicarbonates. At low tensions the relation between the tension and the quantity of the gas corresponds exactly to the formula

$$\frac{(a - x)(1 - x)}{x} = \text{Constant.}$$

Hence it follows that the equilibrium is expressed by the formula



and that the bicarbonates present are those of alkaline earths, chiefly lime (pp. 357—62).

3. *Tension and temperature.* The tension varies with the temperature inversely as the absorption-coefficient of the water (determined on p. 356) and *besides* it rises a little with rising temperature owing to increased dissociation (pp. 363—66).

4. Basaltic rocks absorb carbonic acid and are transformed into carbonates. They are capable of reducing the  $CO_2$ -



tension to 0. The very low tension in the freshwaters of Disko is hereby explained (pp. 370—75).

5. The waters of the «hot springs» of Disko become mixed in their «funnel» with greatly varying quantities of surface-water. The unmixed water contains no trace of free carbonic acid (pp. 375—78).

6. Danish freshwaters are, as a rule, rich in carbonic acid and dissolved carbonate of lime (pp. 379—80).

7. The deposition of carbonate of lime in lakes is almost exclusively due to «*evasion*» of carbonic acid from the surface of the lake to the atmosphere. The yearly deposition of lime may be estimated from the average tension-difference between the surface of the lake and the atmosphere. For the Fure-Sø a tension-difference of 0.02 % will correspond to a yearly deposition of about 6000 tons of lime (pp. 381—85).

8. The dissolution of calcareous remains of organisms is a simple function of the tension of carbonic acid in the surrounding water (pp. 388—89).

9. In the Baltic and certain other localities some species of mussels seem to protect themselves by various means against attack from waters with a high tension of carbonic acid (pp. 387—389).

10. The alkalinity of a sample of ocean-water is determined by a series of augmenting and diminishing factors, and the same being the case with the total alkalinity of the ocean this cannot be regarded as invariable (pp. 391—400).

11. The  $CO_2$ -tension of the ocean-surface often differs from that of the atmosphere and may cause considerable absorption or elimination of the gas (pp. 401—403).

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