nu*m*erous analyses of North Sea water, found from 90 to 100 milli­grammes per litre ; hut he also observed that only a small portion of the carbonic acid is eliminated on boiling : the rest comes out only when the water is distilled to dryness. He presumed that the gas was retained chemically by the chloride of magnesium. Buchanan, who inquired into the subject synthetically, arrived at the conclusion that it was the sulphates @@1 in sea water *(qua* sul­phates) which retained the carbonic acid. Accordingly in his numerous carbonic acid determinations he liberated the gas by distilling the water down with an excess of chloride of barium. Tornöe was the first to prove that the carbonic acid in sea water is present as carbonate, and that, in the northern part of the North Atlantic at least, the total carbonic acid, while considerably greater than the quantity which would convert the surplus base into normal, falls short of that which would be required to produce fully saturated acid carbonate.

Even without Tomöe’s discovery it would have been necessary to find the true interpretation of the results of the numerous carbonic acid determinations made during the voyage of the “Challenger” by Buchanan. Dittmar had no difficulty in prov­ing the non-existence of the alleged affinity of sulphates for car­bonic acid, and naturally concluded that the chloride of barium used in the processes liberates the *loose* part of the carbonic acid by converting the normal carbonate part into a precipitate of carbonate of baryta, thus—R"CO3 + *x*CO2+BaCl2=R"Cl2+BaCO3 + xCO2. A series of synthetical experiments showed that this is substantially, though not exactly, correct. If Buchanan’s *modus operandi* be rigorously followed, the carbonic acid obtained, as a rule, falls somewhat short of the actual amount of loose carbonic acid present, while on resuming the distillation after addition of fresh water an appreciable part of fixed carbonic acid passes away as gas. Yet, Buchanan’s results being of great value, Dittmar discussed them (conjointly with his own alkalinity determinations) on the basis of the assumption that they afforded a fair approximation to the proportions of loose carbonic acid in the respective waters. His gen­eral conclusions are as follows. Taking “alkalinity ” as meaning the “weight” of the carbonic acid, CO2, in the normal carbonate part of the carbonate present per 100 parts of total solids, the alka­linity in the water samples analysed (omitting a few obviously abnormal cases) was found to be as follows (Table IV.) :—

|  |  |  |  |
| --- | --- | --- | --- |
| Alkalinity ranges from | Number of Cases. | Alkalinity ranges from | Number of Cases. |
| 0·1400 to 0·1439 | 9 | 0·1640 to 0·1719 | 6 |
| 0·1440 ,, 0·1479 | 34 | Alk. = 0·1731 | 1 |
| 0·1480 ,, 0·1519 | 40 | „ - 0·1888 | 1 |
| 0·1520 , 0·1559 | 19 | " - 0·2079 | 1 |
| 0∙1560 „ 0·1599 | 12 |  |  |
| 0·1600 ,, 0·1639 | 4 | 0·1400 to 0∙2079 | 127 |

Values above 0.16 are obviously exceptional ; hence the normal range may be said to be from 0.14 to 0.16. The most frequently occurring values were found to be about 0146 in the case of surface or shallow sea water, and in the case of bottom water about 0·152. In regard to the loose carbonic acid a full discussion of Buchanan’s results led to the following conclusions :—(1) carbonic acid rarely occurs in the free state ; as a rule it falls short of the quantity which would produce bicarbonate ; (2) in surface waters it is relatively high where the natural temperature is relatively low, and *vice versa ;* (3) within equal ranges of temperature it seems to be less in the surface water of the Pacific than it is in that of the Atlantic Ocean. Of the 195 samples of sea water which Buchanan analysed for carbonic acid only 22 contained fully saturated bicarbonate, and only 2 out of these are proved by the analyses to have contained free carbonic acid in addition to bicarbonate. In all the remaining 173 samples the “carbonic acid deficit” (meaning the proportion of carbonic acid which was wanted to completely transform the carbonate into bicarbonate) assumed tangible and often considerable values. We are probably safe in concluding that the ocean as a whole will have to continue taking in carbonic acid for thousands of years before its carbonic acid deficit has been reduced to nothing. But it is as well to observe that at its surface in the warmer lati­tudes the attainment of this condition is a physical impossibility as long as the percentage of carbonic acid in the air retains its present low value.

A solution of a bicarbonate when shaken, say in a bottle, with

pure air (free of carbonic acid) at summer heat gives up its com­ined carbonic acid to the air space in the bottle until the partial tension of the acid gas there has come up to a limit value *p,* which is called the dissociation tension of the bicarbonate at the prevail­ing temperature *t.* General experience concerning such phenomena warrants the presumption that, up to a certain (low) temperature *t*o, *P* = 0 and thence onwards, *p* increases with *t.* It does not follow that the bicarbonate in a solution when shaken again and again with even pure air tends to become normal carbonate ; for aught we know, the elimination of carbonic acid may stop as soon as the residual carbonate has come down to some composition

R"O(1 +z)CO2 (where *x* is less than 1), and *x* may be a function of temperature. Dittmar has attempted to determine the course of the function 1 *+ x=f(t)* in reference to natural sea water on the one hand and to pure air (air freed of its carbonic acid) and ordinary air on the other. One sample of sea water containing its surplus base as practically bicarbonate served for all the experiments. It was shaken again and again at a fixed temperature *t* with one or the other kind of air, until (after “ N ” shakings, always with renewed air) the stage of saturation appeared to have become con­stant. The investigation is not completed yet ; the following table (V. ) gives the results which have come out so far. The final carbonate was R2O.*n*CO2.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | t. | N. | Pure air. *n*0. | Ordinary air. *n*1*.* |  | N. | Pure air. Ordinary air. | |
| *n*0· 1 | »1· |
|  | 2“ C. | 200 | 190 |  | 15" | 200 | l'50 I |  |
|  | 2° | 200 | 2Ό4 |  | 20° | 200 | 1'42(7) |  |
|  | 2" | 52 |  | 2 06 | 25° | 52 | 1'53 |  |
|  | 10" | 200 | l∙70 |  | 32" | 52 | 1∙53 |  |
|  | 13\* | 50 |  | 1841 | 32" | 52 |  | 1'89 |
|  | 15\* | 100 | 1∙63 |  | I 32\* | 150 | \* \* I | 1'82 |

Hence we see that even at the highest temperature, and with air free from carbonic acid, the carbonate never came down below the state of sesquicarbonate, while with ordinary air, even at 32° C., it never fell below *n* = l·8. At 2° *nn* as well as n1 was =2, the value characteristic of bicarbonate. Now Buchanan reports a good number of cases where, even at lower temperatures, *n* was con­siderably less than 1,8 at any rate. Hence, if his numbers are correct, unless the atmosphere acts more powerfully than the air in Dittmar’s bottle, it would appear that deep-sea water is in general below even the stage of carbonic acid saturation which it could attain at the surface at high temperatures.

In any mixed solution of salts every base is combined with every acid; hence the “carbonate” of seawater is strictly speaking a complex plural. But as a matter of probability the carbonic acid has very little chance of uniting with any of the potash or soda, and the overwhelmingly large quantity of alkaline chloride would no doubt convert any carbonate of magnesia that was introduced into double chloride of magnesium and alkali metal ; hence it is fair to assume that oceanic carbonate is chiefly carbonate of lime. Now immense quantities of this compound are being constantly introduced into the ocean by rivers. Dumas once gave it as his opinion that this imported carbonate remains dissolved in the ocean as long as and wherever the carbonate there is at the bicarbonate stage ; but, as soon as part of the loose carbonic acid goes off into the air, the corresponding weight of normal carbonate separates out as an addition, ultimately, to the solids on the bottom. Dittmar has tried to test this notion synthetically, but without arriving at very definite results. According to his experiments sea water which contains free carbonic acid dissolves added solid carbonate of lime, and more largely carbonate of magnesia ; sea water which contains fully, or almost fully, saturated bicarbonate dissolves car­bonate of magnesia very appreciably, but would not appear to act on carbonate of lime at all. But, when carbonate of lime was produced in the water by successive additions of potential calcium carbonate in the form of dissolved sodium carbonate and its equivalent of calcium chloride, the original carbonate of lime could be increased very largely, with formation of solutions which remained clear during a long-continued period of observation. As a set-off against this a few of the many hundred samples of sea water which he received from the “ Challenger ” deposited in the course of a number of years crystalline crusts of carbonate of lime on the sides of the bottles; and the mother-liquor never contained more than the normal quantity of lime per 100 parts of chlorine. In discussing this question Dittmar gives an estimate, based on data furnished by Boguslawski’s work, of the total carbonate of lime introduced into the ocean annually by the thirteen principal rivers ; and by doubling the quantity he estimates the carbonate of lime intro­duced by all rivers as equal to about 1,34 × 109 tons. Now the sum total of carbonate of lime, CaCO3, in the ocean amounts to about 160×1012 tons; hence it would take 1190 years to increase the present stock of carbonate of lime in the ocean by one per cent. of its value.

*Absorbed Oxygen and Nitrogen in Ocean Water.—*As a matter of physical necessity these two gases must be present in the water of the ocean—and they may be presumed in general to pervade it to its greatest depth—because the whole of the surface of the sea is in constant contact with the atmosphere. Our knowledge regarding their distribution in the ocean may be said to date from 1872, when Jacobsen inquired into the matter in a most masterly manner in connexion with the German North Sea expedition. The work of his predecessors possesses no scientific value, because they em­ployed inadequate methods. Unlike them, Jacobsen did not attempt to analyse a sample of sea water air on board ship : he extracted the air from measured samples (by an excellent method of his own) and then sealed them up in glass tubes, to measure and analyse them after his return home. Buchanan, during the

@@@1 See Geology, vol. x. p. 222.