it will be seen that Moigno's mind was of a very practical cast, and that he was not immersed in the consideration of theories to the neglect of what is more useful.

THE COMPOSITION OF OCEAN WATER[1]

I.

ALTHOUGH ostensibly a report on the composition of ocean water, this memoir includes in its 250 large quarto pages the record of a far more extensive research than the title implies. It contains a detailed account of seventy-seven complete analyses of sea water, largely accomplished by the use of new and specially invented methods, the record of several independent researches into purely theoretical matters, and a number of exhaustive experimental criticisms of methods employed in similar work by other chemists. Taken altogether, the Report reads like the account of a life-work, and it is wonderful how the immense amount of work described in it could possibly be accomplished in the six years which have elapsed since the return of the Expedition. The rapid completion of the work is in great measure due to Prof. Dittmar's custom of having all the routine determinations made by assistants under his immediate supervision, while he devoted himself specially to the invention and trial of new methods and the repetition of doubtful experiments. The gentlemen who assisted in the research, and whose services Prof. Dittmar is scrupulously careful in acknowledging, are Messrs. John M'Arthur, Robert Lennox, Thomas Barbour, W. G. Johnston, James M. Bowie, James B. M'Arthur, G. A. Darling, and Moses T. Buchanan.

What first strikes a chemical reader on looking through the volume is the essentially mathematical treatment of the whole subject. The value of the statistical method in discussing experimental results has been gradually realised by chemists, but it is questionable if it has ever been applied more fully or with more satisfactory effect than here. The first care in every case, after taking all possible precautions to insure the utmost attainable accuracy, was to ascertain the limiting values of the probable error of the analytical method, and for this purpose there were never less than two and frequently more than four determinations made of each constituent. The utmost pains has been taken to represent the numerical results in as many aspects as possible, in tables, in mathematical formulæ, and by means of curves.

It is only possible here to indicate the principal contents of the six chapters into which the memoir is divided. The consideration of Chapter II. "On the Salinity of Ocean Water," may be conveniently reserved for a subsequent article, where it will be taken up along with Mr. Buchanan's report on the specific gravity of ocean water, which forms Part II. of the volume.

Although sea water had been subjected to many analyses in the earlier part of the present century, the only research of permanent importance until very recently was that of Forchhammer, who analysed a great number of surface waters from all parts of the ocean in 1864. Prof. Dittmar avowedly took this research as a guide, and intended his work to be merely supplementary to it; but from the circumstances of the two chemists the later work tends rather to supersede than to supplement the earlier. Forchhammer dealt with surface water only, collected and brought home in corked bottles by seafaring men who, however willing to do their best, could not be altogether trusted to observe requisite precautions, while Dittmar was supplied with water from all depths of the ocean collected at exactly known positions under the constant supervision of Mr. Buchanan, who secured each sample as it was drawn in a carefully stoppered bottle. We must take into account also the greater delicacy of the balances, and the more perfect analytical methods which are now available. The following table quoted from p. 203 of the Report, shows the most recent numbers assigned to the components of ocean-water salts compared with those given by Forchhammer:—

	Per 100 parts of total salts. Dittmar	Per 100 parts of halogen calculated as chlorine. Dittmar	Forchhammer
Chlorine	55·292	99·848	not determined
Bromine	0·1884	0·3402	,,
Sulphuric acid (SO_3)	6·410	11·576	11·88
Carbonic acid (CO_2)	0·152	0·2742	not determined
Lime (CaO)	1·676	3·026	2·93
Magnesia (MgO)	6·209	11·212	11·03
Potash (K_2O)	1·332	2·405	1·93
Soda (Na_2O)	41·234	74·462	not determined
(Basic oxygen equivalent to the halogens)	−12·493	—	—
Total salts	100·000	180·584	181·1

More than thirty elements are known to exist in solution in the ocean, but most of these are present in such minute quantity that it was hopeless to attempt to determine them in a number of small samples. Attention was accordingly confined to the chlorine, sulphuric acid, soda, potash, lime, and magnesia, which were estimated with very great accuracy and always by the same method, so that if more exact processes should be discovered at any future time the error of the method used may be calculated once for all, and applied as a correction to each analysis.

This rule of rigid adherence to one system was broken through in one case, that of the potash, where the ordinary process, which was first adopted, proved so unsatisfactory that it was worse than useless to continue to employ it, and the later analyses were conducted by a modification of Finkener's method that gave better results, through a curious balancing of the errors.

For the particular methods employed in each case it is necessary to refer to the memoir itself, where they are described with the utmost detail; but reference must be made to the great improvement which Prof. Dittmar has introduced in what was formerly called volumetric analysis, but which he now prefers to name *titrimetric*. It may be defined, somewhat paradoxically perhaps, as volumetric analysis by weight. The standard solutions are made up as usual by weighing the salt and measuring the water, but the whole solution is afterwards weighed, and its strength is thus determined with great accuracy. A balance combining strength and delicacy to an unusual degree is of course necessary for this purpose. By performing the titration in a weighed phial containing a weighed amount of liquid, and weighing it again after the reagent has been added to the proper amount, the burette error is obviated, except in those cases where the method of zig-zag titration is adopted, and then it only affects the measurements of the few drops of each reagent that are added in turn to produce and destroy the coloration which marks the end-point. All the chlorine determinations were made in this way by Volhard's method of precipitating the halogen by excess of silver nitrate, and estimating this excess by means of a standard solution of ammonium sulphocyanate in presence of iron alum.

The result of the seventy-seven complete analyses of ocean water, the description and discussion of which forms Chapter I., confirms Forchhammer's discovery that the percentage composition of the salts of sea water is the same in all parts of the ocean, and extends it to water from all *depths*. The application of the principle of constant composition to depth is subject to a slight but very important exception. The proportion of *lime* was found by Dittmar to be greater in very deep water than in that near the surface. Although the difference found exceeded

[1] "The Physics and Chemistry of the Voyage of H.M.S. *Challenger*. Vol. i. Part i. Report on the Composition of Ocean Water." By Prof. W. Dittmar, F.R.SS.L. and E.

the sum of all the probable errors of analysis, it was considered necessary to apply a more stringent test in order to make sure that the increase in lime was really in relation to the depth. For this purpose three mixtures were made, each of about seventy samples of water from all parts of the ocean, but the first consisting entirely of surface waters, the second of samples from between 300 and 1000 fathoms, and the third of waters from a greater depth. The exact analysis of these proved beyond question that the proportion of lime increases with the depth. The same bathymetrical mixtures were used for determining the bromine, as it, of all the minor components, is the one which might be supposed to vary most with the depth, owing to the fact of its being so largely absorbed by marine vegetation; but the proportion was found to be invariable within the limits of error. The details of this very difficult and interesting series of experiments occupy Chapter III.

The question of the amount of carbonic acid in sea water is one which cannot even yet be said to be definitely settled. The simple and elegant adaptation of Tornoe's modification of Berchert's and Classen's apparatus, which Prof. Dittmar made, and which is figured in the memoir, gets over the difficulty of determining the total carbonic acid in sea water; but unfortunately it had not been invented when the *Challenger* sailed. The daily determinations of carbonic acid in sea water which Mr. Buchanan made were performed by a method that only took account of what must be called, for lack of a better expression, the loosely-combined carbonic acid; that is, the portion of the gas existing in a state of absorption in the water, and the part combined with the normal carbonates to form bicarbonates. The immense number of determinations, made in the same way under exceptionally favourable conditions, form a valuable series for purposes of comparison, and Prof. Dittmar has not failed to utilise it. His critical experiments on Mr. Buchanan's method made with the view of ascertaining its limits of uncertainty were, he acknowledges, insufficient for the purpose. This is to be regretted, for an exhaustive series of carbonic acid determinations performed on the same water by the two forms of apparatus under favourable conditions might be expected to produce valuable results. Prof. Dittmar saw that it was useless to employ samples of *Challenger* water which had been kept for several years in order to estimate the total carbonic acid. But instead of giving up the research on this account he proceeded by an ingenious use of synthetic sea waters to study the behaviour of bicarbonates in solution. He says (p. 212):—

"I am aware that this part of my work lacks the degree of precision which would be desirable for my present train of reasoning. But I had not the time to embark in the far more elaborate investigation which would have been desirable. I have, however, quite lately resumed the matter on a new basis, and hope before long to be able to formulate the exact conditions of stability in sea-water bicarbonates as they exist when dissolved in real sea water, 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 sesquicarbonate. In the meantime we must reason on what data we have."

And reasoning on these data he produces a most interesting theoretical disquisition on the dissociation-tension of dissolved bicarbonates at various temperatures, and shows how the ocean acts as the great regulator of atmospheric carbonic acid. The three main results of the *Challenger* observations on this subject are given (p. 220) as:—

"1. Free carbonic acid in sea waters is the exception. As a rule the carbonic acid is less than the proportion corresponding to bicarbonate.

"2. In surface waters the proportion of carbonic acid increases when the temperature falls, and *vice versâ*.

"3. Within equal ranges of temperature it seems to be lower in the surface water of the Pacific than it is in the surface water of the Atlantic Ocean."

In relation to Mr. Murray's theory of coral-reef formation and of oceanic deposits generally, it would appear probable that bottom waters contained more carbonic acid than those near the surface, and that this carbonic acid was the agent which dissolved the calcium carbonate of shells at great depths. Prof. Dittmar thinks otherwise. In his opinion Mr. Buchanan's numbers prove bottom water to contain no more carbonic acid than surface waters, and he supposes that the solution is effected by prolonged contact with the sea water itself, for by experiment he found that it was capable of dissolving calcium carbonate, though very slowly. It is not quite plain that Mr. Buchanan's numbers do warrant this conclusion, and there seems to be room for further research in this direction.

Chapter V. treats of the alkalinity of ocean water. The seventy-seven complete analyses showed that in sea-water salts there is a distinct preponderance of base over fixed acid, the difference being presumably due to carbonates; and the direct determination of the extra base by standard hydrochloric acid at the boiling point, after the method devised by the chemists of the Norwegian North Atlantic Expedition, brought out precisely the same result. The alkalinity of bottom waters was found to be distinctly greater than that of those from the surface, and this increase was exactly proportional to the larger quantity of lime present in the former. The alkalinity determinations give the only satisfactory measure of the carbonate of lime which exists as such dissolved in sea water.

The last and longest chapter is by no means the least important. It deals in a very exhaustive manner with the whole question of the absorption of oxygen and nitrogen by pure water, as well as by sea water. Finding that all previous determinations of the coefficients of absorption of these gases were more or less unsatisfactory, Prof. Dittmar entered on an elaborate series of experiments, which is fully detailed in the memoir, having as an aim the determination of the desired coefficients at different temperatures for both pure water and the water of the ocean. The second part of the research consisted of the exact analysis of the samples of air which had been extracted from sea water on the cruise by Mr. Buchanan, using Jacobsen's ingenious apparatus, which he has since simplified and improved.

There is an element of uncertainty about the extraction of gases which Prof. Dittmar scarcely seems to emphasise sufficiently. The water in every case was collected in one vessel and then transferred to another in which the gases were boiled out. The danger of atmospheric gases being absorbed was obviated in great measure by the precautions used; but if highly aërated water were brought up from a great depth some of the absorbed gases would be certain to escape during transference. The only remedy would appear to be the collection of the water in the gas-extraction flask itself, and there is no method as yet by which this can be done.

Prof. Dittmar and Mr. Lennox constructed a modification of Doyère's apparatus for the analysis of gases, which was found to work well. It is described and figured in the memoir. The results of the analyses are discussed in the light of the coefficients of absorption found in the earlier part of the research. The amount of air which ought theoretically to be absorbed by sea water of the temperature and at the pressure at which each sample was collected was first calculated, and then, from the actual amount of nitrogen found, the quantity of oxygen which should be associated with it was arrived at. The quantities of air found in solution were usually in defect of calculation, as might be expected when it is recollected that the water of the ocean is always in motion, the temperature and pressure to which it is exposed being very

different at different places; and the fact that absorptiometric exchange had not gone far enough to reproduce equilibrium would account for the few cases in which the dissolved gases exceeded the amount calculated. The interpretation of his results seemed unsatisfactory to Prof. Dittmar. He says (p. 182):—

"I am sorry to have to confess that I have not been as successful as I should have wished in drawing general conclusions from my numbers, and if I here reproduce my endeavours in this direction, I do so chiefly in the hope that some other person, having more experience than I in dealing with statistics, may take up the problem after me, and perhaps be able to extract the latent propositions which are therein concealed. In the tables which I propose to give, he will find all the data arranged in the most convenient form, so that all he needs is at hand."

The problem of the dissolved gases is very difficult when deep waters are considered. The method pursued by Dittmar was to find the amount of nitrogen absorbed, and to calculate the temperature at which that quantity would be taken up by water at the surface; then to find the corresponding amount of oxygen, and compare that with what was found by experiment. It is evident that if the ocean were stagnant in any part the processes of oxidation always going on would tend to reduce the amount of absorbed oxygen finally to nothing, while the amount of dissolved nitrogen would be unaltered, unless it were slightly increased by the decomposition of animal matter. In many cases the oxygen deficit was found to assume very large dimensions, though oxygen was never wholly absent from the dissolved gases.

Part I. of the volume closes with a summary of the chemical work, a note by Mr. Buchanan on the determination of carbonic acid, and an appendix describing some analytical methods. The summary contains a number of valuable suggestions for future work. These are divided under two heads, the first comprising such observations of water density and rough volumetric determinations of the alkalinity as can be carried on by any intelligent seafaring man after a little instruction. The second head includes work requiring the services of a skilled chemist for its accomplishment. It embraces further researches on the composition of ocean salts by determining with the utmost precision the amounts of the principal constituents for one particular station in the ocean, water from which could be collected in large quantity at various seasons; then it could be compared with water taken at various seasons from a widely distant station, and thus the interesting question as to whether there is *any* difference in the proportion of the salts in different oceans could be settled. The minor constituents should also be estimated if possible, and very particular attention ought to be paid to alkalinity and carbonic acid determinations in freshly drawn samples. Prof. Dittmar concludes with this significant suggestion:—

"Meanwhile the best thing that could be done in regard to all the analytical problems referred to would be to work many times on samples of the same kind of water, with a view of improving on the methods and ascertaining the extent to which that one water fluctuates in its composition."

The only way in which this can be done properly is in a laboratory on shore situated within easy reach of an abundant supply of sea water, and the support of such laboratories ought to be a leading feature in the marine stations several of which, it is to be hoped, will soon be in working order on our coasts. A beginning has already been made at the Scottish Marine Station at Granton, where the special chemical problem under investigation is estuary water. The *Challenger* results may be regarded as final, for the present at least, for ocean water proper, and the results of the German and Norwegian North Atlantic Expeditions have put the waters of partially inclosed seas on a permanent basis; but the study of estuary water has been almost neglected. This is the more regrettable because of the practical importance of a correct knowledge of the conditions of the water of an estuary, on account of its bearing on the migration of fishes into firths and up tidal rivers.

There could be no better field than the estuaries of the British coast for carrying out Prof. Dittmar's suggestion of continuous work on one kind of sea water with a view to the perfecting of analytical methods; and the perfecting of analytical methods, important though it be, may safely be predicted to be one of the least valuable results of such researches.

HUGH ROBERT MILL

ORNITHOLOGICAL NOTES

SEVERAL new magazines have made their appearance during the present year, the most important of them being undoubtedly the *Auk*, which is the name proposed for the journal of the American Ornithologists' Union, and which is to represent in America our old friend the *Ibis* of this country. The *Auk* is in fact a continuation of the *Bulletin* of the Nuttall Ornithological Club, and the general style of the work is the same. The papers seem to be interesting enough, but what strikes us as being decidedly above the average is the quality of the reviewing, which is developing into an art with our American brethren. Mr. Cory describes some new species of birds from Santo Domingo, the plate which accompanies his paper being scarcely up to the level of American illustration. Mr. Barrows continues his useful papers on the birds of Uruguay, and Prof. Merriam criticises Dr. Coues' "Check List," calling forth a sharp rejoinder from the last-named author in an article called "Ornithophilologicalities." In No. 2 many of the above-named papers are further continued along with others by Dr. Stejneger, who advocates some startling changes in ornithological nomenclature, and who also writes a useful paper on the genus Acanthis. Altogether, although the American ornithologists have elected to name their quarterly journal after a bird whose powers of flight were small, the excellence of the two numbers which have appeared reminds us of the perfection of that bird's powers of swimming and diving, so that they have taken as their symbol a species of lusty prowess which argues well for a continuation of the life and enterprise which is visible in the new magazine. We do not forget also that the Auk was a species common to Great Britain and North America, and therefore the very title is suggestive of a bond of union between British and American ornithologists which is certain to be strengthened with each succeeding year.

We have also received No. 1 of the *Bulletin* of the Ridgway Ornithological Club, which has been started in Chicago, and is named after Mr. Robert Ridgway, the well-known Curator of the Ornithological Department in the United States National Museum. The secretary of the new club is Mr. H. K. Coale, who is well known as a zealous and painstaking ornithologist, and under whose auspices there is doubtless a useful future before the infant society which he represents. The first number of the *Bulletin* contains only a single paper by Messrs. W. W. Cook and Otto Widmann, entitled "Bird Migration in the Mississippi Valley."

Mr. J. H. Gurney has just issued a "List of the Diurnal Birds of Prey, with References and Annotations; also a Record of Specimens preserved in the Norfolk and Norwich Museum," consisting of 187 pages. The *raison d'être* of this most useful work consisted in the publication of the first volume of the "Catalogue of Birds in the British Museum," by Mr. R. Bowdler Sharpe. The Norwich Museum, as is well known, contains one of the finest series of birds of prey in the world, and it will always be an imperishable monument to that true and self-sacrificing naturalist, Mr. J. H.