

February 19, 1874.

JOSEPH DALTON HOOKER, C.B., President, in the Chair.

The Presents received were laid on the Table, and thanks ordered for them.

The following Papers were read:—

- I. "On the Absorption of Carbonic Acid by Saline Solutions."
By J. Y. BUCHANAN, Chemist on board H.M.S. 'Challenger.'
Communicated by Prof. WILLIAMSON, For. Sec. R.S. Received December 11, 1873.

(Abstract.)

Until lately it was believed that the atmospheric gases dissolved in sea-water could be extracted from it, as from fresh water, by boiling *in vacuo*. The merit of the discovery that such is not the case is due to Dr. Jacobsen, of Kiel, who found that, in order to drive out the whole of the carbonic acid, the water must be evaporated almost to dryness, and that no amount of boiling *in vacuo* will suffice to eliminate it. Being particularly interested in the matter, I immediately commenced a series of experiments to determine, if possible, the salt or salts to which sea-water owes this property.

Preliminary observations satisfied me, in the first place, that sea-water has this property, and, secondly, that solutions of the sulphates of magnesia and of lime possess the same property. In order to gain more precise information, two series of experiments were made, the one analytical, the other synthetical. The former consisted in saturating saline solutions with carbonic acid, and then distilling them, the carbonic acid passing in the various fractions being determined; the latter, in determining the absorption coefficients of two solutions, the one of sulphate of magnesia, the other of sulphate of lime.

First, the analytical series.—Before proceeding to saline solutions, distilled water was saturated with carbonic acid and distilled. The first eighth of the distillate contained abundance, the second a trace, and the remainder no carbonic acid. It may therefore be assumed, in the experiments which follow, that the carbonic acid held *simply in solution* by the water passes almost entirely in the first eighth of the distillate, and that whatever passes afterwards has been retained, in some way or other, by the salt in solution.

Experiments were made on solutions of sulphate of magnesia, of sulphate of magnesia and chloride of sodium, and of sulphate of lime, to which were added some on sea-water itself. In every experiment the quantity of solution operated on was 300 cub. centims., which was boiled in a flask connected by a doubly bored cork with a Liebig's condenser, which was fitted at its other end, air-tight, into a tubulated

receiver. To the tubulure was attached a bulbed U-tube, and, by means of an aspirator, air could be constantly sucked through. The carbonic acid coming off was retained by baryta-water of known strength distributed between the receiver and the U-tube; what remained unneutralized was determined by oxalic acid, the point of neutralization being indicated by rosolic acid. The oxalic acid was rather stronger than tenth normal; it contained 6·478 grammes $C_2H_2O_4 + 2H_2O$ in the litre. One litre baryta-water required 3235 cub. centims. oxalic acid for neutralization.

The method of conducting the operation was as follows:—Carbonic acid was passed through the solution until it could be assumed to be saturated. The object being to determine the carbonic acid retained by the salt, it was necessary to get rid, as much as possible, of the simply dissolved gas. This was effected by drawing six or seven litres of air through the solution cold, then heating it to boiling, and allowing it to boil for a couple of minutes in a current of air. The receiver, with the baryta solution, was then attached, and the distillation continued in a current of air, until the contents of the flask were nearly dry. The amount of carbonic acid was given by the remaining alkalinity of the baryta-water.

Experiments on sulphate-of-magnesia solution, containing 12·3 grammes crystallized salt per litre.—As all were conducted in precisely the same way, it will be sufficient to give the results in a tabular form. The first three experiments were made with one and the same solution; for the last two a fresh solution, prepared, to all appearance, in exactly the same way as the previous one, was used. The difference in the results shows the precarious nature of the combination.

Volume of solution used.	Volume of baryta-water.	Volume of oxalic acid.	Grammes carbonic acid in 300 cub. centims.	Grammes carbonic acid in one litre.
cub. centims.	cub. centims.	cub. centims.		
300	25	78·96	0·0043	0·0143
300	10	30·00	0·0053	0·0165
300	10	30·90	0·0033	0·0110
300	15	47·50	0·0023	0·0077
300	10	31·32	0·0023	0·0077

Two experiments were made with a solution prepared as follows:—The quantity of sulphuric acid necessary for the formation of 12·3 grammes crystallized sulphate of magnesia was diluted to a litre, and pulverized carbonate of magnesia suspended in it. Although the mixture was allowed to stand over night, shut off from the influence of the atmosphere, the solution was still very acid. It is well known that carbonate of magnesia is difficultly soluble in cold dilute acids. To have heated the solution would have frustrated the object of the experiment, which was, by bringing nascent sulphate of magnesia together with

nascent carbonic acid at ordinary temperatures, to give them the best opportunity of combining. Two experiments were made with a similarly prepared solution of sulphate of lime. In this case sulphuric acid was added to the water in quantity sufficient to form, with lime, more salt than would dissolve in the liquid. Here neutralization took place without difficulty; and, as might have been expected, the amount of carbonic acid found was considerably greater than in the case of the magnesia salt.

Two experiments were made with an ordinary sulphate-of-magnesia solution, containing 2·05 grammes crystallized salt per litre.

Two further experiments were made with a solution containing 2·05 grammes sulphate of magnesia and 20 grammes chloride of sodium per litre. All were conducted in the way described above, and the results are given in the following Table. The experiments with the carbonates of magnesia and of lime were made at a considerably later date than the others; the value of 10 cub. centims. baryta-water had in consequence become equivalent to 32·0 cub. centims. instead of 32·34 cub. centims. oxalic acid:—

Nature of solution.	Volume of solution.	Volume of baryta-water.	Volume of oxalic acid.	Grammes carbonic acid in 300 cub. centims.	Grammes carbonic acid in one litre.
	cub. centims.	cub. centims.	cub. centims.		
Mg CO ₃ , H ₂ SO ₄	300	10	30·6	0·0032	0·0107
	300	10	30·9	0·0025	0·0083
Ca CO ₃ , H ₂ SO ₄	300	10	27·5	0·1014	0·3380
	300	10	27·5	0·1014	0·3380
2·05 grms. Mg SO ₄ + 7H ₂ O per litre	300	10	31·2	0·0026	0·0087
	300	10	31·3	0·0023	0·0077
Mg SO ₄ 7H ₂ O + Na Cl	300	10	31·6	0·0016	0·0053
	300	10	31·4	0·0021	0·0070

Five experiments were made with sea-water taken at the end of Portobello Pier, on the Firth of Forth. In the first three it was submitted immediately to the same treatment as the saline solutions; in the last two carbonic acid was first passed through it for some time. As the results are identical, it is evident that, in its natural state, the water in question was practically saturated with carbonic acid in this peculiar state of combination.

Volume of sea-water.	Volume of baryta-water.	Volume of oxalic acid.	Grammes carbonic acid in 300 cub. centims.	Grammes carbonic acid in one litre.
cub. centims.	cub. centims.	cub. centims.		
300	15	39·75	0·0198	0·0660
300	10	23·00	0·0211	0·0703
330	10	23·15	0·0208	0·0693
300	10	23·34	0·0203	0·0677
300	10	23·34	0·0203	0·0677

From the large amount of organic matter poured into the Forth in the neighbourhood of Portobello, there must be an abundant production of carbonic acid in the water itself; and we have seen above the effect of bringing it together in the nascent state with sulphate of lime. Sea-water contains on an average about 8 parts sulphate of lime in 10,000. A saturated solution of the same salt in distilled water contains, at 15° C., 24 parts in 10,000. Under the most favourable circumstances, then, sea-water might be expected to bind about one third of the quantity retained by an equal volume of saturated gypsum solution. We have seen that a litre of this solution is capable of retaining 0.338 grm. CO_2 , while the same volume of sea-water contained at the most only 0.07 grm., or very little more than one fifth of that held by the sulphate of lime.

In ocean-water I have never yet found more than 0.064 grm. CO_2 per litre, including both *simply dissolved* and *half bound*. We have, then, in the sulphate of lime alone an agent capable of retaining much more carbonic acid than is usually found to exist in sea-water; and there is besides the sulphate of magnesia; so that whatever may be the function of the other salts, we do not, in order to find a *vera causa* for the phenomenon under consideration, require to go beyond the sulphates; and the practical lesson to be learned is that, if we get quit of the sulphates, the carbonic acid will be more easily disengaged by heat.

This is entirely borne out by experiment. In determining the carbonic acid in sea-water, I always add to it a sufficient quantity of a saturated solution of chloride of barium; and I find that, after about the first fifth of the distillate has passed, there is rarely a perceptible turbidity in fresh baryta-water.

The synthetical experiment consisted in determining directly the coefficients of absorption of a 1.23 per cent. solution of crystallized sulphate of magnesia and of a 0.205 per cent. solution of $\text{Ca SO}_4 + 2\text{H}_2\text{O}$. In Table I. the results of experiments on the magnesia solution are given, where the observations were made without loss of time. In Table II. the results of experiments on the same solution are given, only here the duration of the reaction was taken into account. The first reading was made at the highest pressure after the gas and solution had been together for nine days; the pressure was then successively reduced, and the other readings made at intervals of twenty-two, forty-one, and twenty-five hours from each other, the last of all being made only after the lapse of some days. Table III. gives the results of experiments on the gypsum solution, the readings in this case being made without allowing much time for the reaction to take place.

TABLE I.

Pressure in millims.	476.54	652.7	581.14	736.73
Temperature C.	12.0	11.5	11.9	11.9
Absorption coefficient of Mg SO_4 solution...	0.7095	0.9562	0.8496	1.0545
Absorption coefficient of water	0.6909	0.9631	0.8455	1.0718

TABLE II.

Pressure in millims.	832.7	695.3	551.5	498.1	468.6
Temperature C.	11.1	11.0	10.45	11.1	11.1
Absorption coefficient of Mg SO_4 solution	1.2467	0.9331	0.8823	0.8974	0.8221
Absorption coefficient of water	1.3052	1.0445	0.8461	0.7546	0.7014

TABLE III.

Pressure in millims.....	554.9	683.8	765.3	770.8	805.2	869.5
Temperature C.....	10.1	12.9	13.3	11.1	11.1	11.65
Absorption coefficient of Ca SO_4 solution	0.8845	0.9923	1.0651	1.1885	1.2191	1.2964
Absorption coefficient of water.....	0.8617	0.9618	1.0624	1.1534	1.2048	1.2757

The general result of these experiments is, that sulphate-of-lime solution absorbs a little more carbonic acid than water, but follows the same law of variation with temperature and pressure; sulphate-of-magnesia solution differs slightly from water when but little time is left for the reaction to complete itself. If, however, the gas and solution are left in contact for a considerable time, the difference between the coefficients of water and of the salt solution becomes very marked, that of the latter being less for high pressures and greater for low ones than that of water.

The details of these experiments will be found elsewhere in a more extended paper.

II. "On an Instrument for the Composition of two Harmonic Curves." By A. E. DONKIN, M.A., F.R.A.S., Fellow of Exeter College, Oxford. Communicated by W. SPOTTISWOODE, Treas. R.S. Received November 6, 1873.

The interest in such compound curves lies in the fact that as a simple harmonic curve may be considered to be the curve of pressure on the tympanic membrane when the ear is in the neighbourhood of a vibrating body producing a simple tone, so a curve compounded of two such simple harmonic curves will be the curve of pressure for the consonance of the two tones which they severally represent, and thus the effect on the ear of different consonances can be distinctly represented to the eye.

If the motion of a point be compounded of rectilinear harmonic vibrations and of uniform motion in a straight line at right angles to the direction of those vibrations, the point will describe a simple harmonic curve.

Thus a pencil-point performing such vibrations upon a sheet of paper moving uniformly at right angles to their direction would draw such a curve.

The same kind of curve would also be drawn by keeping the pencil fixed and by giving to the paper, in addition to its continuous transverse motion, a vibratory motion similar and parallel to that which the pencil had; and if the motion of the latter be now restored, a complicated curve will be produced whose form will depend on the ratio of the numbers of