

XLIV.—Note on the Distribution of Acids and Bases in a Solution containing Calcium, Magnesium, Carbonic acid, and Sulphuric acid, and on the Composition of Mineral Waters.

By C. H. BOTHAMLEY.

IN examining the mineral waters of Askern, it was observed that the precipitate formed when the free carbonic anhydride was expelled by heat, or by the prolonged passage of a current of hydrogen, was almost pure calcium carbonate, and contained the merest trace of magnesium, although this element was present in considerable quantity. It seemed of interest to investigate this matter further, with a view to obtain, if possible, some information as to the distribution of the acids and bases in a system containing calcium, magnesium, carbonic and sulphuric acid radicles, and water, and thus to throw some light on the constitution of mineral waters. Experiments on this subject were therefore made in the Chemical Laboratory of the Yorkshire College in the early part of 1891, with the assistance of Mr. H. H. Mann, Brown Scholar of Yorkshire College.

Solid Magnesium Carbonate and Calcium Sulphate Solution.

1.—0.5 gram of precipitated and well washed magnesium carbonate was mixed with 50 c.c. of water containing 0.0687 gram of calcium sulphate in solution, and the two were allowed to remain in contact for 24 hours at the ordinary temperature, with repeated agitation during the earlier part of the time. At the end of the experiment, the solution contained a very small quantity of calcium and a considerable quantity of magnesium, whilst the precipitate contained a considerable quantity of calcium carbonate.

2.—1.0 gram of magnesium carbonate and 50 c.c. of the calcium sulphate solution were allowed to remain in contact for 24 hours with occasional agitation. Only the merest trace of calcium remained in solution.

3.—0.5 gram of magnesium carbonate was treated in the same way with 50 c.c. of water containing twice the quantity (0.1377 gram) of calcium sulphate. At the end of 24 hours the solution contained only a trace of calcium.

4.—1.0 gram of magnesium carbonate and 50 c.c. of the stronger calcium sulphate solution. At the end of 24 hours only a trace of calcium remained in solution.

It may be pointed out that the fact that a trace of calcium remains in solution does not show that the reaction is incomplete, because calcium carbonate is distinctly, though very slightly, soluble in water. It follows that, in absence of free carbonic anhydride, calcium is completely precipitated from a solution of calcium sulphate by an excess of magnesium carbonate, magnesium sulphate going into solution.

Solid Calcium Carbonate and Magnesium Sulphate.

5.—1.0 gram of precipitated calcium carbonate and 50 c.c. of water containing 0.0525 gram of magnesium sulphate were agitated together at intervals during a day.

6.—0.5 gram of calcium carbonate and 50 c.c. of the magnesium sulphate solution were treated in the same way.

The result was the same in both cases. Although the calcium carbonate was present in large excess, only a mere trace of magnesium was found in the precipitate at the end of the experiment, and a mere trace of calcium in solution.

Magnesium Sulphate Solution and Calcium Carbonate Solution.

7.—50 c.c. of the magnesium sulphate solution used in the preceding experiments, and 50 c.c. of water containing 0.03790 gram of

calcium carbonate, together with sufficient free carbonic anhydride to keep it in solution, were mixed and boiled for half an hour in a flask fitted with a reflux condenser. The precipitate contained but a minute trace of magnesium.

8.—100 c.c. of the magnesium sulphate solution and 50 c.c. of the calcium carbonate solution were boiled together as in Exp. 7. The precipitate contained only a trace of magnesium.

These experiments, in which the solutions and the precipitate that is formed are subjected to the action of heat, are open to some objection, but the results distinctly confirm those obtained with the solid carbonates.

9.—50 c.c. of the magnesium sulphate solution and 50 c.c. of the calcium carbonate solution were mixed, and a current of hydrogen was passed through the liquid for some time. The precipitate contained no magnesium.

10.—10 c.c. of water containing 0.1094 gram of magnesium carbonate and sufficient free carbonic anhydride to keep it in solution was mixed with 100 c.c. of water containing 0.2754 gram of calcium sulphate, and a current of hydrogen was passed through the liquid. The precipitate that formed contained only a trace of magnesium, and consisted of calcium carbonate.

The complete precipitation of calcium by magnesium carbonate from a solution of calcium sulphate, and the absence of any distinct reverse action when calcium carbonate and magnesium sulphate solution are brought together, seems to indicate clearly that in presence of water the sulphuric acid radicle combines with magnesium in preference to combining with calcium. The experiments in which the carbonates were at first in solution in presence of carbonic anhydride, and more especially Exp. 9, lead to the same conclusion.

The heats of formation of the two sulphates in dilute solution are practically identical (CaSO_4 323.1 cal., and MgSO_4 322.6 cal.), although in the solid state the heat of formation of the calcium salt is distinctly the higher. The heats of formation of the two solid carbonates are: calcium carbonate 269.2 cal., and magnesium carbonate 267.6 cal., but there seem to be no determinations of the heats of formation of the two carbonates in solution and in presence of an excess of carbonic anhydride. It is clear, however, that the existing thermochemical data afford no explanation of the facts observed.

It follows from these results that, if we put aside any question of ionic dissociation in solution, and represent mineral waters and similar solutions of calcium, magnesium, and the sulphuric and carbonic acid radicles as containing salts as such, the sulphuric acid should be regarded as combining with magnesium in preference to

calcium, and not the reverse, as is generally supposed. In the case of the Askern waters, this view is supported by their therapeutic action.
