Theobromine Chlorotellurate, $(C_7H_8N_4O_2HCl)_2TeCl_4$.—On bringing together the acid solution of the alkaloid and tellurium tetrachloride, no precipitate appears as with the other substances, but, on standing, the light yellow salt separates.

Analysis.—Calculated: Cl, 30.44; Te, 18.25. Found: Cl, 30.59, 30.55; Te, 18.59.

Brucine Chlorotellurate, $(C_{23}H_{26}N_2O_4HCl)_2TeCl_4$.—This salt appears as light yellow crystals.

Analysis.—Calculated: Cl, 18.81.   Found: Cl, 18.36, 18.90.

With aconitine and atropine, non-crystalline bodies were first formed but quickly decomposed.

<div align="center">BROMIDES.</div>

Quinine Bromotellurate, $(C_{20}H_{24}N_2O_22HBr)TeBr_4$.—This salt forms bright red crystals and is easily decomposed by heat.

Analysis.—Calculated: Br, 51.32; Te, 13.67.   Found: Br, 51.27, 51.60; Te, 14.09.

Cocaine Bromotellurate, $(C_{17}H_{21}NO_4HBr)_2TeBr_4$.—The salt crystallizes readily in large carmine-red needles. It is quite readily decomposed by heat.

Analysis.—Calculated: Br, 39.47; Te, 10.48. Found: Br, 39.59, 39.14; Te, 11.18.

Brucine Bromotellurate, $(C_{23}H_{26}N_2O_4HBr)_2TeBr_4$.—This salt appears as brick-red crystals.

Analysis.—Calculated: Br, 34.26; Te, 9.12.   Found: Br, 34.21, 33.80; Te, 8.50.

Morphine Bromotellurate, $(C_{17}H_{19}NO_3HBr)_2TeBr_4$.—This salt appears as dark red crystals.

Analysis.—Calculated: Br, 40.70; Te, 10.81.   Found: Br, 40.42; Te, 10.70.

ON CERTAIN FACTORS INFLUENCING THE PRECIPITATION OF CALCIUM AND MAGNESIUM BY SODIUM CARBONATE.

By J. M. Stillman and Alvin J. Cox.

THE data contained in the following communication were obtained in an investigation undertaken primarily to determine some of the conditions which modify the results of the usual processes

for the purification of water for boiler-feed purposes.   In many of the waters of the more or less arid regions of this country the calcium and magnesium salts are present in large quantity, and experience has shown that the usual methods of purification by the use of lime and sodium carbonate give variable results.   To determine, if possible, some of the conditions affecting the problem, the experiments here described were undertaken.   The data obtained are but a contribution to the problem stated, but they have also application to other than the particular technical problem mentioned.

I.   INFLUENCE OF SALTS OF SODIUM UPON THE PRECIPITATION OF CALCIUM AND MAGNESIUM BY SODIUM CARBONATE.

Solutions of calcium chloride and of magnesium chloride were prepared of such concentration that 25 cc. of the calcium solution gave 0.3285 gram calcium oxide, and 25 cc. of the magnesium solution yielded 0.6410 gram magnesium pyrophosphate.

In each test 25 cc. of one of these solutions were placed in a 100 cc. flask, the desired quantity of sodium chloride or sodium sulphate added in the form of a standardized solution, sodium carbonate then added in solution, so that unless otherwise specified 1.2 molecules of sodium carbonate should be present for each molecule of calcium chloride or magnesium chloride present.   Larger excess was avoided as being foreign to the problem immediately under consideration.   Water was added to make the volume to 100 cc.   All conditions of manipulation were made as nearly equal as possible.

A. Influence of Sodium Chloride upon the Precipitation of Calcium.—Two series of tests were made with varying quantities of sodium chloride.   In each series, 0, 2, 4, 6, 8 molecules of sodium chloride were added for each molecule of calcium chloride, and then the slight excess of sodium carbonate was added and the flasks filled to 100 cc.   One series was then brought to the boiling-point and maintained there for three minutes; the other was not heated.   Both series were then allowed to stand at room temperature for seven days.

At the end of this time the contents of the flasks were filtered and the filtrate tested for calcium with ammonium oxalate.   No determinable amount of calcium was present, and it was therefore concluded that the presence of sodium chloride has no important

influence upon the precipitation of dilute calcium chloride solutions by sodium carbonate.

 B. Influence of Sodium Chloride and Sodium Sulphate upon the Precipitation of Magnesium.—Twenty-five cc. of the above-mentioned magnesium solution were treated in a similar manner with 1.2 molecules sodium carbonate after addition of 0, 2, 4, 6, 8, or 10 molecules of sodium chloride. Duplicate series were prepared as before and one boiled for three minutes, the other not. At the end of seven days' standing the solutions were filtered, the magnesium determined as pyrophosphate in 50 cc. of the filtrate, and the entire amount remaining in solution estimated. The following results were obtained:

	$Mg_2P_2O_7$ in sol. per 100 cc.	
Mols. NaCl for 1 mol. $MgCl_2$.	Boiled samples. Gram.	Not boiled. Gram.
0	0.3486	0.4350
2	0.4278	0.4766
4	0.4378	0.4988
6	0.4510	0.5150
8	0.4700	0.5356
10	0.4892	0.5590

Total amount magnesium as $Mg_2P_2O_7$ per 100 cc. before precipitation $= 0.6410$ gram. The influence of sodium chloride in diminishing the precipitation is here evident, and the brief heating increases the precipitation. It may be here stated that a preliminary experiment similar to the foregoing gave figures showing similar relations. In that test, however, the samples stood but four days, and equilibrium was not sufficiently attained.

With sodium sulphate the following data were obtained, the conditions of experiment being otherwise as with the preceding.

	$Mg_2P_2O_7$ in sol. per 100 cc.	
Mols. Na_2SO_4 for 1 mol. $MgCl_2$.	Boiled. Gram.	Not boiled. Gram.
0	0.3486	0.4350
2	0.4846	0.5568
4	0.5816	0.6218
6	0.5874	0.6412 no precipitate.
8	0.5874	0.6406 " "
10	......	...... " "

Total amount magnesium as $Mg_2P_2O_7$ per 100 cc. $= 0.6410$ gram.

The influence of the sodium sulphate is here again well marked, but seems to reach its maximum under the conditions of this experiment at about 6 molecules of sodium sulphate to 1 molecule mag-

nesium chloride, and here, as before, the short boiling influences the condition of equilibrium. The curves in Fig. 1 will illustrate
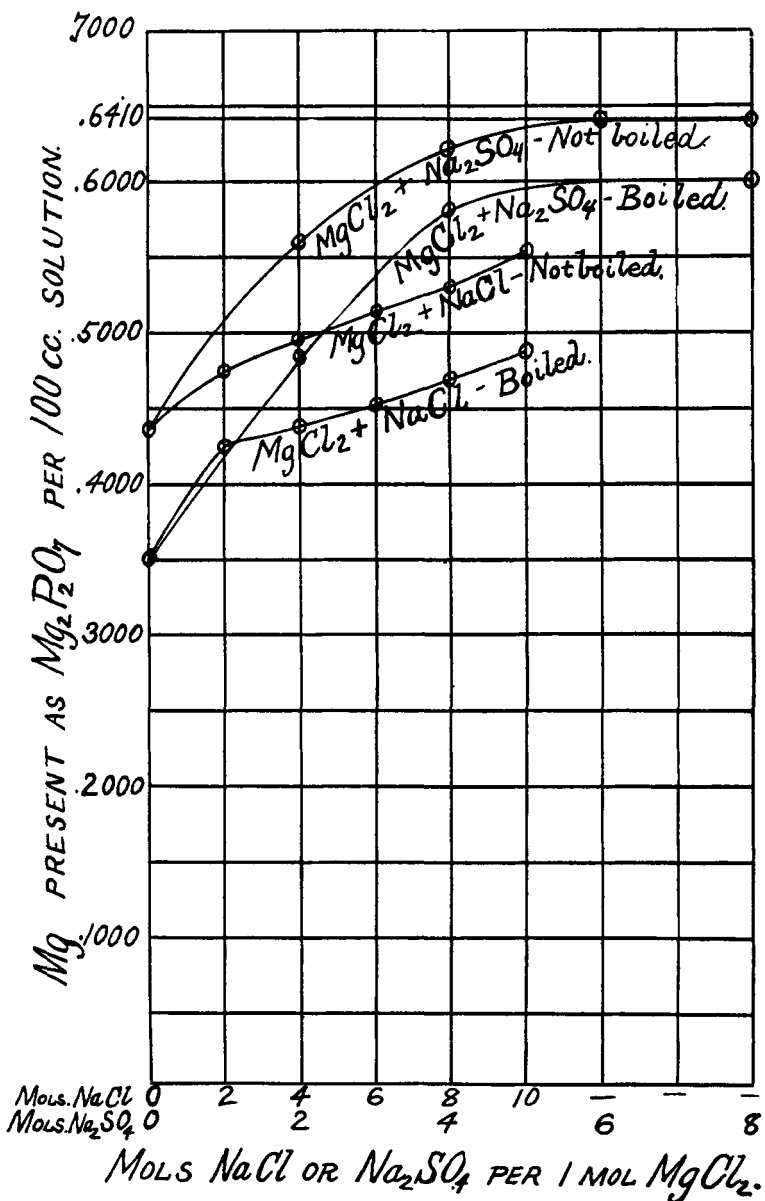

Fig. 1.

these relations. In order to bring out more clearly the relations, equivalent quantities of the two salts are coincident on the abscissas of the curves. It will be noticed that the sodium sulphate appears to exert a greater influence in preventing precipitation than the equivalent quantity of sodium chloride.

II. THE INFLUENCE OF TIME ON PRECIPITATION UNDER VARYING CONDITIONS.

This factor evidently has a direct bearing on the problem of water purification.

A magnesium solution was prepared containing magnesium equivalent to 0.6520 gram $Mg_2P_2O_7$ in 25 cc. The quantities of magnesium precipitated by sodium carbonate at different time intervals were determined under varying conditions.

First.—In solutions maintained at boiling temperature. For this purpose, the solutions were heated in pressure-bottles immersed in a boiling salt-water bath, the temperature of the bath being maintained at 102°-104° C. Three series were heated in this way.

(*a*) Twenty-five cc. of the magnesium solution (equivalent to 0.6520 gram magnesium pyrophosphate) were treated with 1.2 molecules sodium carbonate per 1 molecule magnesium chloride, and made up to 100 cc.

(*b*) Twenty-five cc. were treated as above, after addition of 4 molecules sodium sulphate to 1 molecule of magnesium chloride.

(*c*) Twenty-five cc. were treated as before, but with 10 molecules of sodium chloride instead of the sulphate. At intervals, the pressure bottles were removed from the bath, the contents thrown on a filter, and 50 cc. of the filtrate used for determination of magnesium. The data are calculated to a basis of 100 cc. of solution.

MAGNESIUM REMAINING IN SOLUTION AS $Mg_2P_2O_7$ PER 100 CC.

Hours.	Gram.	Hours.	Gram.	Hours.	Gram,
After $1/4$	0.1176	$1/4$	0.2246	$1/4$	0.1634
" $1/2$	0.1036	$1/2$	0.1946	$1/2$	0.1498
" 1	0.0740	1	0.0960	$3/4$	0.1322
" 2	0.0164	2	0.0832	1	0.0698
" 3	0.0108	3	0.0726	2	0.0522
"		4	0.0716	3	0.0420
"				$4 1/4$	0.0406

These data are shown graphically in Fig. 2.

Second.—The course of the reaction was studied in solutions maintained at room temperature without agitation.

For this purpose flasks containing 700 cc. of the various mix-

tures were immersed in a bath of running water, and the temperature thus kept within a narrow range of variation. At intervals, samples were removed by a pipette and filtered, and the magnesium remaining in solution was determined in 50 cc. of the filtrate.

The magnesium solution used was the same as last described, and the solution of calcium chloride used contained the equivalent of 0.3285 gram calcium oxide per 25 cc. The proportions employed in the different mixtures are given as per 100 cc. of the mixed solutions, though much larger quantities were made up.
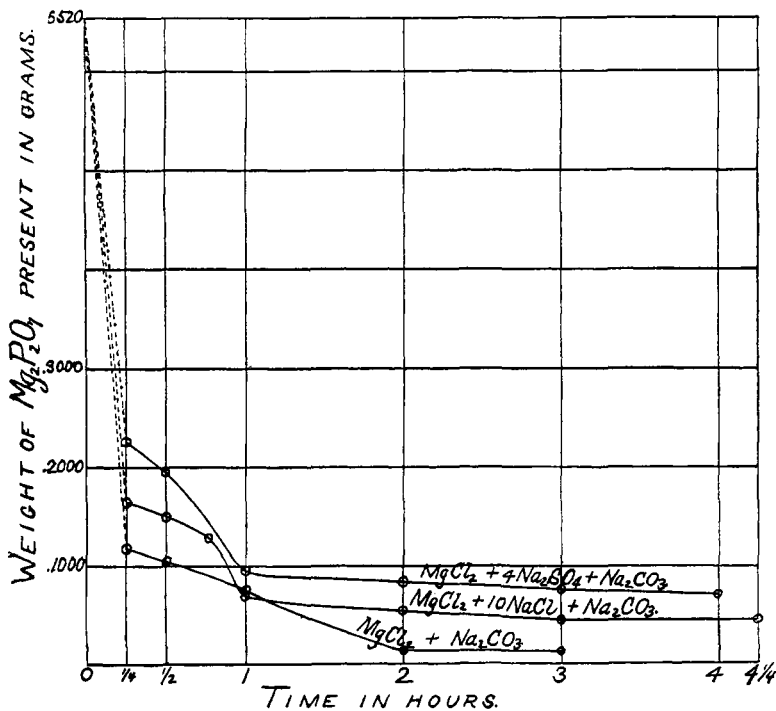
The following series of tests were made:

Fig. 2.

A.—Twenty-five cc. of the calcium solution were treated with 1.2 molecules of sodium carbonate and made up to 100 cc.

The calcium as calcium oxide remaining in solution after various time intervals was found as follows:

Of the total 0.3290 gram calcium oxide present, all but about 3 per cent. was precipitated in less than one-fourth hour.

Hours.	Calcium oxide. Gram.
After $1/_4$	0.0104
" $3/_4$	0.0104
" $1 \, 1/_4$	0.0100
" 2	0.0083
" 3	0.0076
" $4 \, 1/_4$	0 0062
" $6 \, 1/_4$	0.0044
" $8 \, 1/_4$	0.0032
" $20 \, 1/_4$	0.0000

B.—The magnesium chloride was treated under the following varying conditions:

(a) Twenty-five cc. with 1.2 molecules of sodium carbonate to 100 cc. solution.

(b) The same mixture with addition of 10 molecules of sodium chloride.

(c) The same with 4 molecules of sodium sulphate.

(d) The same with 10 molecules of sodium sulphate.

Magnesium remaining in solution at varying time intervals as $Mg_2P_2O_7$ per 100 cc. was determined as follows:

Total quantity as $Mg_2P_2O_7$ per 100 cc. of solution was 0.6520 gram.

Hours.	(a). Gram.	(b). Gram.	(c). Gram.	(d).
After 1	0.4152	0.5270	0.5982	No precipitate.
" 3	0.4084	0.5252	0.5832	" "
" $6 \, 1/_2$	0.4104	0.5216	0.5908	" "
" 12	0.3924	0.5072	0.5760	" "
" 22	0.3782	0.4880	0.5654	" "
" 32	0.3810	0.4882	0.5550	" "
" 46	0.3154	0.4484	0.5560	" "
" $60 \, 1/_2$	0.2358	0.3966	0.5542	" "
" $80 \, 1/_2$	0.1634	0.3094	0.5498	" "
" $107 \, 1/_2$	0.1278	0.2320	0.4824	" "
" $131 \, 1/_2$	0.1240	0.2204	0.3928	" "

These data are illustrated in the curves of Fig. 3. The variations in temperature are noted on the upper margin of the chart. It will be noticed that the temperature was not quite constant, and this fact may be partly responsible for the irregularities of the curves.

$Third$.—The influence of continuous agitation upon the course of the reaction.

For this purpose the bottles containing the mixtures were sub-

mitted at room temperature to violent agitation by means of a mechanical shaker operated by a motor. Three series were thus treated :

(*a*) A magnesium chloride solution containing the equivalent of 0.6871 gram magnesium pyrophosphate per 25 cc. was treated as before with sodium carbonate and diluted to 100 cc. for each 25 cc. of the magnesium solution.

(*b*) The same mixture after addition of 10 molecules of sodium chloride.

(*c*) The same mixture after addition of 4 molecules of sodium sulphate.

The shaking was interrupted at intervals for removing samples, and, as before, magnesium was determined in the filtered samples and the results calculated to a basis of 100 cc.

MAGNESIUM AS $Mg_2P_2O_7$ PER 100 CC. SOLUTION UNPRECIPITATED.

Hours.	(*a*). Gram.	(*b*). Gram.	(*c*). Gram.
After 3 $\frac{1}{4}$	0.4364	0.5288	0.6476
" 7 $\frac{1}{2}$	0.4216	.....	0.6384
" 13 $\frac{1}{4}$	0.1684	0.5084	0.6200
" 20 $\frac{3}{4}$	0.1464	0.4092	0.6224
" 34	0.1432	0.2360	0.4316
" 47	0.1364	0.2292	0.3380
" 61	0.1372	.....	0.3260
" 76	0.1368	0.2300	0.3200
" 99 $\frac{3}{4}$	0.1372	.....	0.3320

In the curves in Fig. 3 these data are plotted after recalculating to correspond to a total content before precipitation of 0.6520 gram instead of 0.6871 gram magnesium pyrophosphate per 100 cc., so that the curves may be better compared with the other data given on the chart.   On the same diagram are also reproduced for comparison the data of Fig. 2.   Comparison of these curves will show that in every case the influence of the presence of sodium chloride or sulphate is to diminish the precipitation of magnesium by sodium carbonate, and in these tests the sulphate exerts a greater influence in this direction than an equivalent quantity of the chloride.   It would be premature, however, to draw any sweeping quantitative generalizations from these few comparisons.   Even attempts to duplicate as exactly as possible the conditions of such a series as any one of the above, so far as our experience goes, do not give the same quantitative relations.   The reason for this is easily seen in the difficulty of equalizing all conditions to which the

establishment of equilibrium is sensitive. On the other hand, the general relations of the influence of the above-mentioned salts and of temperature and agitation upon the precipitation of magnesium by sodium carbonate seem to be quite clearly established.

It is well-known that for the separation of magnesium in water-purification, calcium hydroxide is a much more effective precipitant than sodium carbonate. In order to obtain an approximate notion of the relation of this reaction to such data as above obtained, a single series of experiments was executed.

A magnesium chloride solution was treated with a clear solution of calcium hydroxide (free from alkalies), with and without the presence of sodium chloride, and the same quantities of the same
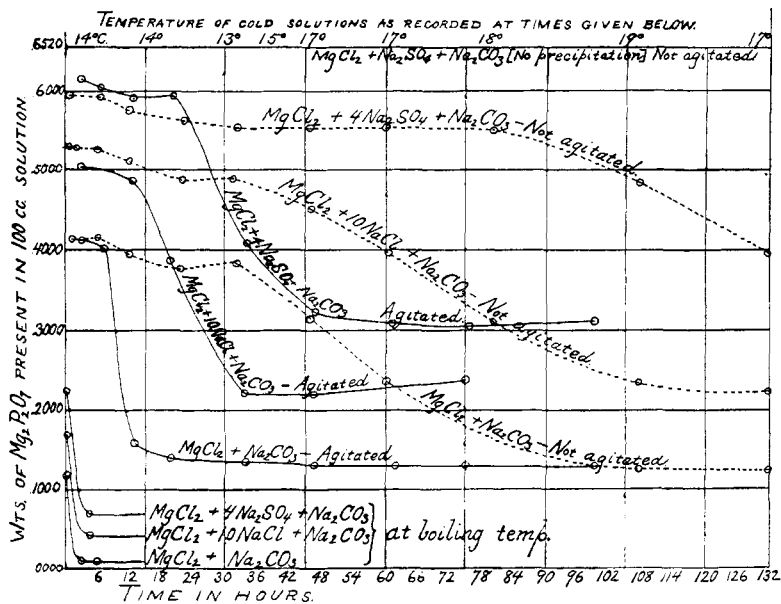

Fig. 3.

solution were treated under the same conditions with an equivalent quantity of sodium carbonate. Owing to the greater insolubility of calcium hydroxide, it was necessary to use a more dilute magnesium solution.

The magnesium solution contained 0.2063 gram as $Mg_2P_2O_7$ in 3.750 cc.

The calcium hydroxide solution contained 0.00144 gram as CaO per cubic centimeter.

Mixtures were made as follows:

(a).	(b).	(c).	(d).
3.75 cc. $MgCl_2$	3.75 cc. $MgCl_2$	3.75 cc. $MgCl_2$	3.75 cc. $MgCl_2$
77.75 cc. CaO(1.1 mol.)	do.	4.07 cc. Na_2CO_3 (1.1 mol.)	do.
			18.50 cc.
18.50 cc. H_2O	18.50 cc. NaCl (10 mol.)	92.18 cc. H_2O	(10 mol.) NaCl
			73.68 cc. H_2O
100.00	100.00	100.00	100.00

The data are here given per 100 cc., although larger quantities (400 cc.) were actually used. These solutions were kept agitated by the mechanical shaker at room temperature and sampled at intervals. The following quantities of magnesium pyrophosphate per 100 cc. were found in the filtered samples.

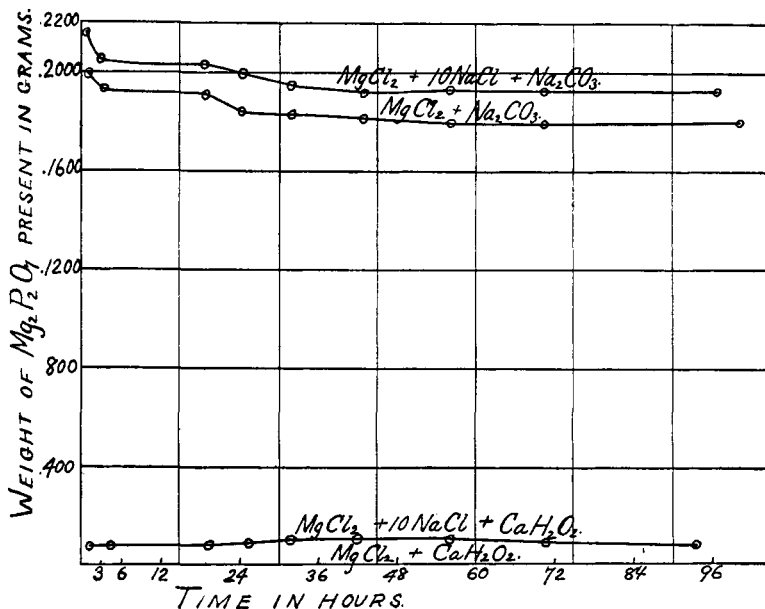Total amount of $Mg_2P_2O_7$ per 100 cc. is 0.2063 gram.

Fig. 4.

Hours.	(a). Gram.	(b). Gram.	(c). Gram.	(d). Gram.
After 1 $^1/_4$	....	....	0.1984	0.2124
" 1 $^1/_2$	....	0.0080	....	....
" 1 $^3/_4$	0.0000	....	....	...
" 4 $^3/_4$	0.0000	0.0076	0.1936	0.2048
" 19 $^1/_2$	0.0000	0.0072	0.1908	0.2028
" 25 $^1/_2$	0.0000	0.0080	0.1844	0.1996
" 31 $^3/_4$	0.0000	0.0100	0.1828	0.1956
" 43 $^1/_2$	0.0000	0.0096	0.1820	0.1928
" 56 $^1/_2$	0.0000	0.0084	0.1788	0.1928
" 71	0.0000	0.0080	0.1780	0.1928
" 93 $^3/_4$	0.0000	0.0080	....	0.1928
" 99 $^3/_4$	0.0000	....	0.1792	....

The foregoing data are produced graphically in Fig. 4. It will be noted that sodium chloride appears to have some influence on the precipitation of magnesium by calcium hydroxide, but that nevertheless the precipitation is quite complete. In the parallel tests with sodium carbonate, the amount of magnesium held in solution by sodium chloride is less in proportion to the entire amount present than was the case in the preceding experiments with solutions of somewhat greater concentration. In the more dilute solution, only about 6 per cent. of the magnesium present was held in solution, while in the less dilute about 15 per cent. was held in solution by 10 molecules of sodium chloride.

There is no intention to draw any generalizations from the single experiment with calcium hydroxide. Other experiments are in progress in this laboratory which may form the subject of a further communication on similar lines.

STANFORD UNIVERSITY, CAL.

THE DETERMINATION OF CARBONIC ACID IN DRINKING-WATER.

BY FRED B. FORBES AND GILBERT H. PRATT.

IN the course of an investigation of the action of the various public water supplies of Massachusetts upon metallic pipes, it became desirable to know the amount of free carbonic acid contained in these waters at different times, as the results of many experiments indicated that this substance was in a large measure responsible for the action of water upon pipes, especially those of lead.[1]

Carbonic acid, as is well known, may exist in natural waters in three forms: Fixed carbonic acid combined directly with the alkaline earth bases, calcium oxide and magnesium oxide, to form normal carbonates, half-combined carbonic acid, and free carbonic acid.

The actual existence of bicarbonates of calcium and magnesium in solution has never been absolutely proven, as these salts have never been isolated; but for all practical purposes these compounds may be assumed to exist, as the behavior of the normal carbonates in solution in the presence of an excess of carbonic acid leads strongly to this conclusion.

[1] Report of Massachusetts State Board of Health, 1898, 541 ; 1900, 487.