20. *The Chemical Nature of Precipitated Basic Magnesium Carbonate.*

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A study has been made of the chemical nature of precipitated basic magnesium carbonate, prepared by the addition of magnesium sulphate solutions to solutions of sodium carbonate. Precipitations carried out over a concentration range of 1M to 0·05M lead to the conclusion that the carbon dioxide content of the precipitate (which diminishes with decreasing initial concentration from a molecular ratio MgO/CO_2 of 0·888 to 0·626) is a continuous function of the carbon dioxide remaining in solution. It is therefore possible that freshly precipitated basic magnesium carbonate may be produced by the adsorption of HCO_3' ions by magnesium hydroxide. Commercial varieties of basic magnesium carbonate (*i.e.*, *magnesia alba*) appear to consist of mixtures of the crystalline so-called hydroxycarbonate, $Mg(OH)HCO_3$, and the amorphous product. The magnesium in solution after the precipitation is probably present in true solution, in the form of the hydroxy-carbonate.

THE author's investigation into the chemical nature of precipitated basic cupric carbonate (J., 1927, 2883) has now been extended to the basic carbonate of magnesium. Further work is in hand on the basic carbonates of zinc, cadmium, and mercury.

EXPERIMENTAL.

The experimental procedure closely followed that described in the earlier work (*loc. cit.*). The solutions of magnesium sulphate and of sodium carbonate employed were all prepared by dilution from standard 1M-solutions, and in every case the magnesium sulphate solution was added in a thin stream to the mechanically stirred solution of sodium carbonate.

Analysis.—Carbon dioxide was immediately estimated in the moist, freshly precipitated, basic carbonate by the author's method (*Analyst*, 1926, **51**, 622), in order to avoid any loss of carbon dioxide from the precipitate which might arise through air-drying following precipitation. The determination of carbon dioxide in solution presented difficulties, since none of the ordinary methods seemed readily applicable to this estimation. The author therefore developed a special method (see *J. Soc. Chem. Ind.*, 1939, **58**, 340), in which the dissolved carbon dioxide (both free and combined) is directly determined in a convenient volume of solution, 10, 25, or 50 c.c., according to the concentration.

Magnesium in solution was determined, either in the sulphuric acid solution resulting from the determination of dissolved carbon dioxide, or in a separate sample of the solution acidified with sulphuric acid. Both for precipitated and for dissolved magnesium, the 8-hydroxyquinoline (" oxine ") method was used.

It was intended, as in the investigation on basic cupric carbonate, to carry out determinations of adsorbed material in the precipitate (sulphate or sodium carbonate). Several tests, however, gave no indication of appreciable amounts of such adsorbed material, at any of the concentrations studied.

Results.—Results for the complete series of experiments (over a concentration range of 1M to 0·05M) are summarised in Table I, which gives in col. 5 the ratio MgO/CO_2 for the unwashed precipitate, freed as far as possible from adhering liquid by suction in the Buchner funnel. From these data, together with those in Tables II and III, the ratio MgO/CO_2 for the true precipitate, free from adhering mother-liquor, is calculated, allowance being made for the magnesium and carbon dioxide contained in the mother-liquor entrapped by the moist precipitate. These corrected figures are given in col. 6 of Table I.

TABLE I.

Initial concn. (mols./l.).	Unwashed moist precipitate.				Corrected value for true ppt.
	MgO (g.).	CO_2 (g.).	Molar ratio MgO/CO_2.	Mean value.	
1·00	0·05882	0·05796	1 : 0·903	1 : 0·916	1 : 0·888
,,	0·06586	0·06676	1 : 0·929		
0·50	0·05847	0·05312	1 : 0·833	1 : 0·850	1 : 0·833
,,	0·8063	0·7622	1 : 0·866		
0·25	0·03412	0·02970	1 : 0·797	1 : 0·798	1 : 0·783
,,	0·04457	0·03883	1 : 0·798		
0·10	0·03526	0·02772	1 : 0·721	1 : 0·721	1 : 0·703
,,	0·05549	0·04368	1 : 0·721		
0·05	0·04270	0·02831	1 : 0·608	1 : 0·626	1 : 0·626
,,	0·02902	0·02040	1 : 0·644		

TABLE II.

Initial concn. (mols./l.)	1·00	0·50	0·25	0·10	0·05	0·02
CO_2 remaining in solution after pptn. (g./l.)	9·615	5·512	3·406	1·795	0·924	0·330
Mg remaining in solution after pptn. (g./l.)	7·797	4·631	2·606	1·538	0·986	0·368

TABLE III.

Initial concn. (mols./l.).	Vol. of mixed solns. (c.c.).	Vol. of filtrate (c.c.).	Total Mg in filtrate (as MgO).	Mg, %, after precipitation	
				(*a*) in soln.	(*b*) pptd.
1·00	100	78·9	0·6152	30·52	69·48
0·50	200	183·0	0·8475	42·05	57·95
0·25	200	192·8	0·5024	49·86	50·14
0·10	500	498·3	0·7665	76·05	23·95
0·05	2000	1998	1·970	97·73	2·27

Table II gives the corresponding figures for the magnesium and carbon dioxide in solution after the precipitation. Determinations were also made of the percentage of the original magnesium remaining in solution. The volume of the filtrate was measured (to 0·1 c.c.), and the volume of the original solution, with allowance for drainings from the flask and beaker used during the precipitation. From these data, together with the figure for the concentration of magnesium remaining in solution, the percentages of the original magnesium precipitated and remaining in solution respectively were calculated. The results are in Table III.

The filtrates from precipitations at concentrations of 1M, 0·5M, and 0·25M all deposited colourless crystals after 12—24 hours, usually in a star-like clustered growth, adhering to the walls of the vessel. The filtrates from 0·1M- and 0·05M-solutions did not deposit such crystals until after a longer time, accompanied by free evaporation. The crystals separating from the 0·5M-filtrate were filtered, washed with cold water, dried in a desiccator, and analysed, with the following results.

Wt. of crystals (g.).	MgO (g.).	CO_2 (g.).	H_2O (by diff.) (g.).	Molar ratio, $MgO : CO_2 : H_2O$.
0·1234	0·03608	0·03850	0·04882	1 : 0·978 : 3·031
0·1292	0·03787	0·03950	0·05183	1 : 0·956 : 3·065

These figures indicate that the crystals consist of the so-called hydroxy-carbonate, $MgCO_3,3H_2O$ or $Mg(OH)HCO_3,2H_2O$ (Davis, *J. Soc. Chem. Ind.*, 1906, **25**, 788). It should be emphasised that, after deposition of crystals, the filtrate still contained an appreciable amount of dissolved magnesium, addition of alcohol to such a solution causing separation of further crystals of the hydroxy-carbonate.

When the filtrate from any precipitate was heated, precipitation began, below the boiling point, of the colloidal basic carbonate; in no case was the formation of crystals observed. In the more dilute solutions considerable frothing took place on boiling, and precipitation of the whole of the dissolved magnesium by boiling in this manner was a prolonged process, unlike that of the dissolved basic cupric carbonate, which was complete in a comparatively short time.

A microscopic study was also made of the changes occurring when the precipitated basic magnesium carbonate from 0·5M-solutions was kept in contact with the mother-liquor. The original precipitate was a gel and remained so for 12 hours. After 2 days, although a few crystals of the hydroxy-carbonate had been deposited from the solution in contact with the precipitate, in the manner described above, the bulk of the precipitate appeared to have been converted into small spherites (about 6μ in diameter), and some colloidal matter still remained. The rate of change of the precipitate from more dilute solutions was also studied, and the formation of spherites was also observed, after a larger time interval. No evidence was forthcoming of complete transformation of the precipitate into clearly visible crystals of the hydroxy-carbonate.

DISCUSSION.

A number of conflicting views on the chemical nature of basic magnesium carbonate occur in the literature. Rose (*Annalen*, 1851, **83**, 132, 417) regarded the basic carbonate, in common with other insoluble basic metallic carbonates, as the product of hydrolysis of the normal carbonate. On the other hand, several of the products, prepared in various ways, have been formulated by various authors as definite compounds, more than 15 being listed in standard textbooks. This tendency is clearly shown in the work of Anderson (J., 1905, **87**, 261), who made a series of analyses of commercial varieties of basic magnesium carbonate (*magnesia alba* of pharmacy). After pointing out that these show considerable variation in composition, the MgO/CO_2 ratio ranging from 1 : 0·80 to 1 : 0·50, Anderson concluded that these basic carbonates are substances of high molecular weight, and worked out complex formulæ for each, *e.g.*, $20MgCO_3,21Mg(OH)_2,62H_2O$.

Davis (*loc. cit.*), after giving a critical review of the literature, suggested that all the so-called basic carbonates of magnesium were mixtures in various proportions of the crystalline compound $Mg(OH)HCO_3,2H_2O$ and the hydroxide $Mg(OH)_2$. This view was partly based on microscopical examination, which revealed the presence in all varieties of *magnesia alba* of crystalline and of amorphous particles.

The effect upon the composition of the precipitate of systematic variation of the concentration of the reagents, now described, does not appear to have been previously studied. The results of the present investigation indicate that the precipitated basic magnesium carbonate is of variable composition, and that, under the particular experimental conditions employed, at any particular initial concentration the carbon dioxide content of the solid phase is a continuous exponential function of the total carbon dioxide in solution. In view of the well-known fact that such a relation is also characteristic of adsorption phenomena, it is therefore suggested that these substances may be the product of adsorption of the HCO_3' ion, which is known to be present in the solution, by the primarily formed colloidal magnesium hydroxide.

This view assumes that the precipitate, at any given initial concentration, is homogeneous, or at any rate that the final precipitate may be regarded as in equilibrium with the mother-liquor. It is not overlooked that the experimental method used, addition of successive portions of magnesium sulphate solution to the sodium carbonate solution, might give rise to a series of products, and that the earlier fractions might differ from the later ones in composition. No clear evidence that this is so has yet been obtained, and in view of the rapidity with which the precipitation is carried out, the question may not arise. It is, however, proposed to investigate this possibility more fully in further work on other basic carbonates, which may lend themselves more readily to such a study.

The Magnesium in Solution.—The results in Tables II and III show that a large proportion of the total magnesium remains in solution after each precipitation, this proportion increasing with decreasing initial concentration. A linear relationship is found to exist between the carbon dioxide in solution and the dissolved magnesium. It is of interest to compare these figures with those obtained by Treadwell and Reuter (*Z. anorg. Chem.*, 1898, **17**, 195) for the solubility of the crystalline " magnesium hydroxy-carbonate " in aqueous solutions of carbon dioxide. The comparison shows that the solubility of the crystalline hydroxy-carbonate is lower in every case than that of the precipitated basic carbonate; actually, a linear relationship is also shown by the figures of Treadwell and Reuter.

It is possible to conclude from these data that the freshly precipitated basic magnesium carbonate is in a very finely divided condition, since below a certain limit of particle size the solubility of such precipitates is known to increase with the degree of dispersity. The linear relationship shown also suggests that the precipitates obtained are of similar nature, despite the large variation observed in the carbon dioxide content, MgO/CO_2 varying from 0·888 to 0·626, and that they do not consist of the hydroxy-carbonate, as suggested by Davis. At the same time, the experimental evidence appears to support the view that a definite compound is present in solution, probably the hydroxy-carbonate.

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