

The dissociation of dolomite. II.

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IN this paper further evidence is put forward in support of a previous paper on the subject.¹ Very soon after the reading of that paper, A. E. Mitchell² read a paper before the Chemical Society on a closely related subject. Working quite independently, and employing other methods of investigation, Mitchell arrived at conclusions in close agreement with those detailed in the former paper. H. L. J. Bäckström³ has criticized Mitchell's paper, raising some objections 'against the experimental evidence produced and the . . . way of interpreting it'. Where Bäckström's objections touch on anything in Mitchell's paper which is incidentally akin to any of the work described in this or the earlier paper, they will be discussed herein. Thus, Bäckström states that Marc and Šimek⁴ found that, in the presence of water-vapour as a catalyst, magnesite suffered dissociation at a lower temperature than otherwise. In the method of experiment adopted by the present writer, the air which was constantly aspirated through the substance under examination was previously washed by being passed through a solution of potassium hydrate, and it would therefore contain much water-vapour. Bäckström, in support of his statement that 'It has been known for a number of years that the dissociation of dolomite takes place in two steps', merely cites K. Friedrich and L. G. Smith, and states that 'Grünberg⁵ showed that the amount of carbon dioxide given off in the first step corresponds exactly to the amount of magnesium present in the dolomite'.

N. V. S. Knibbs,⁶ however, cites the work of J. B. Shaw and G. A. Bole,⁷ who concluded that there are three different kinds of dolomite: one in which the dolomite dissociates as a whole; another in which the magnesium carbonate dissociates separately; and a third, a mixture of

¹ C. S. Garnett, *The dissociation of dolomite*. *Min. Mag.*, 1928, vol. 20, pp. 54-59.

² A. E. Mitchell, *Journ. Chem. Soc. London*, 1928, vol. 128, p. 1055.

³ H. L. J. Bäckström, *Journ. Chem. Soc. London*, 1924, vol. 125, p. 480.

⁴ R. Marc and A. Šimek, *Zeits. Anorg. Chem.*, 1918, vol. 82, p. 17.

⁵ K. Grünberg, *Zeits. Anorg. Chem.*, 1918, vol. 80, p. 887.

⁶ N. V. S. Knibbs, *Lime and magnesia*. London, 1924, p. 82.

⁷ J. B. Shaw & G. A. Bole, *Journ. Amer. Ceram. Soc.*, 1922, vol. 5, pp. 811, 817

the other two. C. H. Desch¹ states that dolomite ignited 'so as to decompose the magnesium carbonate while leaving the calcium carbonate unchanged, yields a product which sets with water'; also, that several patents have, from time to time, been taken out in many countries for the production of cements, artificial stones, &c., from dolomite by heating it so as to yield a mixture of magnesia (MgO) and calcium carbonate, which, after being mixed with water, will set hard.

Subsequent to the writing of the former paper, in which it was contended that the dissociation of dolomite does not proceed in two distinct stages, of which the first is represented by the equation $\text{CaCO}_3 \cdot \text{MgCO}_3 \rightarrow \text{CaCO}_3 + \text{MgO} + \text{CO}_2$, and in order to secure further evidence, the setting properties of such a mixture as the semi-burning was supposed to produce were tested. Magnesia and precipitated chalk ($\text{MgO} + \text{CaCO}_3$) in equal molecular proportions were mixed and made to a paste by the addition of water and allowed to stand at room temperatures; contrary to what might be expected from the cited statement of Desch and the patents, this did not set even in a small degree, and when the water had dried out there was not any cohesion between the particles.

Other mixtures were then tried, in order, if possible, to determine the true cause of the setting, and whether it is in agreement with the single-step dissociation theory. Magnesium carbonate ('magnesia alba') and dry slaked lime in equal molecular proportions, similarly treated, set decidedly and quickly. In this case, setting has resulted from a chemical reaction, and it will be noted that the mixture is the reverse of that which was supposed to set, but actually did not do so. Dry slaked lime was similarly tried with ground raw dolomite; also with calcite; and both these mixtures exhibited the ordinary and normal slow set of lime.

Magnesite gave the somewhat surprising result of behaving merely as the dolomite and calcite mixtures, and thus quite distinct from 'magnesia alba'. The marked difference between the dissociation temperatures of the native and prepared carbonates of magnesium was noted in the previous paper, and distinct difference in constitution now seems to be clearly indicated. It may be noted here that this observation is clearly quite neutral towards the question of the process of the dissociation of the dolomite molecule.

The peculiar setting properties of semi-burnt dolomite are lost when the material becomes stale, a condition which can be detected by the fact that no slaking and rise in temperature takes place on the addition of a suitable amount of water. This, again, would seem to indicate that

¹ C. H. Desch, *The chemistry and testing of cement*. London, 1911, p. 57.

the setting properties are connected with free lime in the intimately associated mixture of oxides, and, evidently, inert substance; and such is borne out by the fact that a similar setting mixture can be made by mixing, in suitable proportions, finely ground quicklime with dry slaked lime and a practically inert substance such as clean sand. Such a mixture, after being made to a paste with water, can be moulded and sets almost identically as the semi-burnt dolomite.

Thus, the setting properties of dolomite, calcined to the correct degree, appear to be due to hydration of free lime, and not to a mixture of magnesia and calcium carbonate. The single-step dissociation theory is thus in accordance with the facts of setting, but these are contrary to the two-step one.

During the investigations of the present author, a phenomenon has been noticed which, for some time, was perplexing. The process of formation of dolomite must undoubtedly be an exothermic reaction, yet under some conditions of dissociation a marked evolution of heat was noticed—accompanied by a bright incandescent glow in the rock, which is quite distinct from the ordinary red-heat glow of the same material after the reaction has passed. When dolomite was heated (as described in previous paper) in the iron vessel, and the gas adjusted, at the commencement of the heating, to raise the temperature to a little over 800°C . and the millivoltmeter watched, it was noticed that the needle would rise steadily and then, whilst the heating remained constant, the temperature would fall several degrees before it became stationary. This observation was made repeatedly; and, more recently, the writer has observed the phenomenon of the incandescent glow, accompanied by a rapid rise in temperature, which was not due to firing, in a mass of about two tons of rock which was being very carefully calcined in a commercial kiln.

The explanation offered is that whilst the temperature of the rock is rising at sufficient speed and the evolved carbon dioxide allowed to escape very freely, the dissociation proceeds smoothly as a single step, but when further dissociation becomes very slow or tends to cease, then a reaction takes place between free lime (CaO) present and the equilibrium proportion of magnesium carbonate remaining in the dolomite. From the setting tests it was found that lime and magnesium carbonate (when the latter was in suitable form) would react together in the presence of water at ordinary temperatures, and from the comparative affinities of lime and magnesia for carbon dioxide it is to be expected that such a reaction would take place at the noted temperatures. Moreover, the heat of formation of calcium carbonate is sufficiently in excess of that (or the

heat of dissociation) of magnesium carbonate, plus that of dolomite from the single carbonates, to account for the described phenomenon of heat evolution, the magnitude of which will be dependent on the temperature to which the rock is steadily raised and on the rate of heating; as, if it is done very slowly, the reaction between the lime and carbonate may be expected to accompany closely the dissociation. This reaction, in its most simple form, may be represented by: $\text{CaO} + \text{MgCO}_3 \rightarrow \text{CaCO}_3 + \text{MgO}$, but it is probably really $\text{CaO} + \text{CaCO}_3, \text{MgCO}_3 \rightarrow 2\text{CaCO}_3 + \text{MgO}$.

Thus, the composition of the residue from the heating of dolomite will not reveal the process of its dissociation, and Bäckström's contention that a pressure-composition curve would indicate the process of dissociation is clearly at fault; such a curve would be governed by the equilibrium products resulting from a reaction quite subsequent to actual dissociation of the original compound.

After the publication of the former paper, and during the course of the further work on the subject, a distinct improvement in the method of investigation (described in that paper) was evolved. It was realized that, although the results obtained led to conclusions which were being confirmed from other considerations (and were themselves subsequently found to be good), yet the procedure of heating the stone to a certain temperature and then determining the carbon dioxide content of the residue (as was done in the case of the higher temperatures) was not an entirely sound method. The vital part of the experiment, from the point of view of the question of the process of dissociation, was, however, free from the objection; but, in later work, the whole curve was substantially confirmed by conducting the entire range of dissociation in a fused silica flask and weighing the carbon dioxide evolved exactly as was done in the lower range of dissociation. By working on a small weight of rock, all the evolved carbon dioxide was easily absorbed and determined.

In view of the knowledge which we now possess of the course of the dissociation of dolomite, the author's method for its investigation would appear to be the most decisive for such an examination of similar substances. The principle of the method is the continuous thorough removal from the reaction vessel of the carbon dioxide as it is evolved during dissociation, and its accurate measurement at any and every desired moment. It may be noted that, as quite distinct from the behaviour of dolomite, when examined by this method, a mechanical mixture of magnesite and calcite is readily seen to be such, each dissociating in its own range and with a distinct break in the carbon dioxide evolution curve.