The dissociation of dolomite.

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THAT dolomite ($CaCO_3 . MgCO_3$) on being heated behaves as though it were a *mixture* of the two carbonates by dissociating in two distinct stages, appears to be the widely accepted opinion. Thus it is stated (Mem. Geol. Survey, Special Reports on Min. Resources, London, 1920, vol. 16, 'Refractory Minerals', p. 102): 'On calcination, dolomite undergoes a progressive dissociation which may be considered chemically as covering two distinct stages. The first effect of rising temperature is the expulsion of carbon dioxide from the magnesium carbonate contained in the dolomite and the formation of a mixture of magnesium oxide and calcium carbonate, accompanied by a considerable reduction in volume. . . . Complete calcination results in the expulsion of the remaining carbon dioxide, a still further reduction in volume, and the production of a dense crystalline aggregate of magnesium and calcium oxides.'

Also, Dr. C. H. Desch ('The Chemistry and Testing of Cement', 1911, p. 57): 'The double carbonate, dolomite if ignited at $300-400°$, so as to decompose the magnesium carbonate while leaving the calcium carbonate unchanged, yields a product which sets with water.'

And A. B. Searle ('Refractory Materials', 1917, p. 121): 'The effect of heat on dolomite is to form a mixture of calcium carbonate and magnesia with evolution of half the carbon dioxide of the dolomite, the calcium carbonate only being decomposed at a still higher temperature.'

During the course of some recent investigations, however, the present writer obtained results which do *not* confirm such statements.

K. Friedrich and L. Garrett Smith (Centralblatt für Mineralogie, 1912) describe experiments made for the study of the constitution and thermal dissociation of minerals by an adaptation of the method used in metallography (op. cit., p. 175) whereby the rate of rise in temperature of the material under examination is determined thermo-electrically. A thermo-couple was placed in the ground material contained in an open

platinum box within an electrically-heated, vertical 'oven' and the temperature of the material slowly raised. Numerous minerals were thus tested; the time-rate per unit rise in temperature was noted and the results depicted graphically. Among the minerals so examined were magnesite, calcite, and dolomite. The results obtained were plotted as heating-velocity curves and they show, in each case, a practically straight, vertical curve with one or more sharp and definite peaks, indicating uniform rise in temperature without differentiated heat absorption except at sharply defined points. With magnesite (op. cit., p. 653) the curve shows one very definite peak at 600° C.; with calcite (p. 654) a similar peak is shown at 910° C.; and with dolomite (pp. 655-6) two peaks were obtained, one at about 750° and the other at about 910° C. The slightly accelerated rise in temperature of the material after a prolonged arrest is, of course, a phenomenon resulting from the interruption.

Thus, if these curves are accepted as showing the progress of dissociation of the carbonates, in the cases of magnesite and of calcite such is represented as taking place suddenly at 600° and at 910° C. respectively; and in the case of dolomite, in two distinct stages, viz. at 750° and 910° C. The same authors, however (p. 184), quote a table showing that when calcite is subjected to gradually increasing temperature, dissociation is gradual and extends over a considerable range of temperature; the degree of dissociation, in this case, being measured by the pressure exerted by the liberated carbon dioxide. The results obtained by the heat-absorption measurement therefore do not seem to be capable of interpretation as indicating the process of dissociation.

In the experiments which are now to be described it was found that when dolomite is subjected to gradually increasing temperature, only traces of carbon dioxide are evolved in the range 300–400° C. (the lower range indicated by Desch) and that appreciable dissociation only begins to take place above about 625° C., up to which temperature the total amount of carbon dioxide evolved was only 1·23 %. Above 675° C., with small increments of further rise in temperature, dissociation becomes very vigorous, but the evolution of carbon dioxide is quite regular and shows no break or indication of separate stages. The magnesium carbonate of the double molecule certainly does not suffer dissociation in the range of temperature in which it does so when not combined with calcium carbonate.

Free lime (CaO) was detected in the residue after only a small amount of dissociation had taken place at the lowest temperatures; and from a consideration of this fact and that of the evolution of the carbon

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dioxide being continuous, it appears that 'half-burning' of dolomite does not produce $MgO + CaCO_3$.

These experiments were conducted at approximately atmospheric pressure and not in a closed vessel, but under open conditions; the liberated carbon dioxide being continuously removed from the dissociation chamber. The conditions were thus quite comparable with those of industrial practice, and it is certainly to such practice that Desch, Searle, and the Memoir of the Geological Survey refer.

Another fact revealed by the work is that dissociation is *not* accompanied by reduction in volume. There is no detectable shrinkage (except when using fine powder) even after all the carbon dioxide has been expelled, and a light, porous, amorphous mass of intimately mixed oxides of calcium and magnesium remains, retaining the shape and size of the original rock fragments. Shrinkage and the formation of a crystalline aggregate only take place at temperatures much higher than those of even complete dissociation.

Experimental Details.

The dolomite which was used in this work was a sample of almost white rock of a high degree of purity from Steetley near Worksop, and chosen after analysis of a number of picked samples from this and other localities. The analysis of this sample gave:

SiO_2	...	0·16%	...	...	⎫			
Al_2O_3	...	0·09	...	...	⎬	...	...	0·91%
FeO	...	0·41	≡ $FeCO_3$	0·66%	⎭			
CaO	...	30·4	≡ $CaCO_3$	54·2	⎫	$CaCO_3 \cdot MgCO_3$	98·4	
MgO	...	21·4	≡ $MgCO_3$	44·9	⎬	$CaCO_3$	0·7	
CO_2	...	47·6						
		————						
		100·06						

This material was quite porous and crystalline; it consisted of a loosely aggregated mass of crystals of dolomite with only 0·7 % excess calcium carbonate and 0·91 % other impurities. It was crushed and sieved, the portion used being that which passed 4 mm. holes but not 2 mm. After drying at 100° C., 100 grams were placed in a Jena-glass flask and very gradually heated. In order to ensure the uniform heating of the mineral, the flask was immersed in a bath of tin and lead, placed upon a large ring burner, and the whole encased in thick asbestos shields. The temperatures were measured thermo-electrically. using silver-constantan couples which were carefully calibrated, and one junction (protected) was placed in the metal bath, whilst another was placed in the midst of the dolomite within the flask. Air, freed

from carbon dioxide by washing with strong potassium hydrate solution and warmed, was drawn, by means of a pump, downwards through the rock, thence through calcium chloride drying tubes and weighed absorption tubes containing soda-lime and calcium chloride. The heating was performed slowly so that the maximum difference between the temperature of the metal bath and that of the centre of the flask did not exceed a few degrees centigrade. After each increment of rise in temperature, the removal from the flask of the liberated carbon dioxide being constantly maintained, the tubes were weighed.

Just before 700° C. was reached, the evolution of carbon dioxide became so rapid that its absorption by the weighed tubes was incomplete, and this was instantly indicated by the barium hydrate solution through which the gas was drawn after passing the absorption tubes. The air current was maintained, but the absorption tubes were removed and the temperature was raised to 760° C. After cooling, the amount of carbon dioxide still remaining in the rock was determined and that lost calculated back, remembering that the latter is not the difference between the percentage still remaining and the original content; but that during dissociation the bases are concentrated.

For the readings at the higher temperatures the metal bath and flask were discarded on account of the softness of the glass and the vigorous oxidation of the metal of the bath at such temperatures. The material was placed directly in an iron cup which was heated by the gas flame; one thermo-couple junction being placed in contact with the iron vessel, whilst the other was placed in the centre and near the surface of the dolomite. The whole was enclosed in a casing system of thick asbestos shields, and at these temperatures (805° C. and over) no difficulty was experienced in securing quite uniform heating. The carbon dioxide lost was calculated by determination of that remaining in the residue, and the following are the results obtained:

Temperature.	%CO_2 evolved.	Temperature.	%CO_2 evolved.
Up to 250° C.	Traces.	Up to 600° C.	0·81
,, 300	0·005	,, 625	1·23
,, 350	0·01	,, 650	2·21
,, 400	0·02	,, 675	3·73
,, 425	0·045	,, 760	19·6
,, 450	0·075	,, 805	33·1
,, 475	0·13	,, 830	44·8
,, 500	0·19	,, 850	46·6
,, 525	0·295	,, 870	47·3
,, 550	0·42	,, 898	47·6
,, 575	0·595		

In order to ascertain whether free lime (CaO) could be detected in rock which had suffered a small loss of carbon dioxide by being heated to the lower temperatures, a quantity of the rock fragments was placed in a flask and immersed in the metal bath. One such quantity was slowly raised to a temperature of 695° C. and another to 740° C. and then allowed to cool. That these temperatures were not exceeded locally within the flask is known by the temperature of the bath. A small quantity (about 15 to 20 grams) of each batch was separately taken, and distilled water added; 10 % sugar solution was added to another sim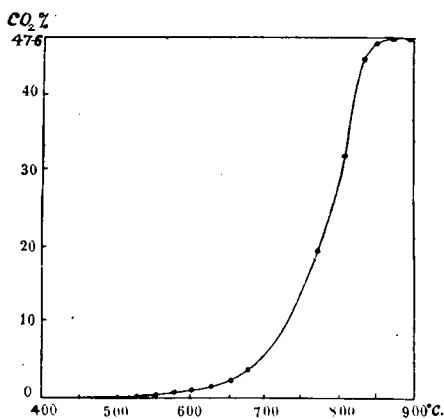ilar quantity of each batch separately, and after standing a few hours all were filtered. In each of the four extractions, lime was found in the filtrates by precipitating with ammonium oxalate in dilute ammoniacal solution containing ammonium chloride. The amount of free lime thus detected in the case of the lower temperature ignition was only small, but quite definite. The methods are unfortunately only reliable for qualitative tests.

Fig. 1.
Temperature-dissociation curve of dolomite.

On calcination at these temperatures (and up to about 1,000° C.) rock fragments retained their original size and shape, although finely ground powder showed a little diminution in volume.

In order to ascertain the temperature at which native magnesium carbonate suffers dissociation, a sample of pure Grecian magnesite ($MgCO_3$) was tested. It was found that appreciable dissociation did not take place below 500° C., up to this temperature only 0·84 % carbon dioxide being evolved; from 540° dissociation was very vigorous, and it was complete at below 650° C.

This range being so different from that indicated by Desch (as already quoted), chemically prepared magnesium carbonate ('magnesia alba') was tested. Up to 250° C. a total of 0·72 % of carbon dioxide had been liberated; dissociation was appreciable at 300° and at about 430° it was complete. Thus, this latter substance suffers dissociation within a range which closely agrees with that given by Desch for the

first half of dolomite dissociation, but it is quite different from that necessary to produce a commencement of that change in dolomite, or that required for magnesite.

From the foregoing it will be seen that dolomite does not dissociate in distinct stages as a mixture of the two carbonates (at least, under ordinary conditions of heating), and that dissociation is not accompanied by reduction in volume of rock fragments.