STUDIES ON THE DOLOMITE SYSTEM. PART I. 1055

# CXX.—Studies on the Dolomite System. Part I. The Nature of Dolomite.

By Allan Ernest Mitchell.

DOLOMITE has always been regarded by mineralogists as a compound of the composition  $CaCO_3$ ,  $MgCO_3$ , but some doubt as to the accuracy of this view has been expressed by Spangenberg (Z. Kryst. Min., 1914, 52, 529), who, from the results of his investig-0 O 2

ations on its synthesis, puts forward the idea that dolomite is not necessarily a compound, but is a solid solution of calcite and magnesite. He places the limits of miscibility between the proportions CaCO<sub>3</sub>,2MgCO<sub>3</sub> and MgCO<sub>3</sub>,2CaCO<sub>3</sub>, so that normal dolomite would be an equimolecular solid solution, and any naturally occurring dolomites departing appreciably from this proportion would be due to changes in the composition and not necessarily to admixture of accidental impurities. The substances prepared by him, however, have physical properties which do not correspond with normal dolomite and his results in general leave much doubt as to the actual nature of the products he obtained; it seems more than probable that his substances were mixtures of vaterite (modification of calcite plus immeshed aragonite) and magnesite, or aragonite and magnesite. It is necessary, therefore, that some investigation of the actual individuality of dolomite should be made.

If we consider the analyses of various samples of dolomite from different parts of the world (Doelter, "Handbuch der Mineralchemie," Bd. 1, 364, etc.), we shall readily see that so far as the natural product is concerned it does not depart appreciably from equimolecular proportions. Dolomite occurs in various parts of the world under different conditions, and it seems very hard to imagine that if the formation is one of solid solution the practically equimolecular mixture would occur in every case, unless the miscibility is only very limited, and certainly not as wide as that asserted by Spangenberg.

In order to get an idea as to the individuality of the substance, it became necessary first of all to determine its relative stability with respect to the other two members of the rhombohedral carbonates, calcite and magnesite, and since by the application of the Nernst heat theorem we are able to get a fairly accurate statement of the connexion between heat of formation, temperature, and dissociation pressure of a compound, the most fruitful line of attack seemed to be in a comparison of the thermal dissociation pressures of the three substances. In order, then, that these dissociation pressure relationships could be correlated, it was essential that we should have a knowledge of the specific heats and the heats of formation of all the reactants involved, and this necessitated the determination of the specific heats of magnesite and of the decomposition product of dolomite, and the heats of formation of dolomite and of its decomposition product.

Kallauner (Chem. Ztg., 1913, 37, 1317), who has made measurements of the thermal dissociation of dolomite, concludes that the substance is split into its components, calcium carbonate and magnesium carbonate, at 500°. The degree of this decomposition reaches a maximum at 700°, the liberated magnesium carbonate dissociating to give carbon dioxide. Dissociation of the residual calcium carbonate begins at  $875^{\circ}$  and reaches a maximum at  $900^{\circ}$ .

Johnston (J. Amer. Chem. Soc., 1910, 32, 933) has made measurements of the thermal dissociation of calcite, and has shown from his measurements that the relationship between dissociation pressure and temperature is represented by the equation

 $\log p = -9340/T + 1.1 \log T - 0.0012 T + 8.882,$ 

where p = pressure in atmospheres and T = absolute temperature.

### EXPERIMENTAL.

The materials required for these investigations offered some considerable difficulties owing to the necessity of employing natural magnesite and dolomite. Calcite can be easily prepared in the laboratory and the ordinary analytical reagent is sufficiently pure for the purpose. The supply of the other two is rendered difficult owing to natural conditions, since it is practically impossible to obtain natural minerals which are free of iron oxides and silica. After a search which necessitated an examination of samples from various parts of the world, two separate samples of dolomite were obtained which were of sufficient purity. These were respectively from Algeria and Binnental (Switzerland). Although they were not pure, they were the best that could be hoped for from a natural product. Their analyses are given below.

The only sufficiently pure magnesite obtainable was a sample of clear, colourless, rhombohedral mineral from the Greiner region of the Tyrol. Owing to the fact that it occurred in a chlorite schist it was very hard to get it free from iron oxide, but after careful hand-picking under a microscope a suitable sample was obtained.

	CaO.	MgO.	FeO.	SiO <sub>2</sub> .
Algerian dolomite	30.31	21.61	0.75	0.10
Binnental dolomite	30.89	21.21	trace	trace
Normal dolomite	30.45	21.72		
Greiner magnesite (hand-picked)	2.32	43.84	1.87	0.50

The samples for treatment were crushed to pass a 20-mesh sieve, and then hand-picked under a microscope until no fragments containing visible inclusions were left. The balance was crushed in an agate mortar until it passed a 120-mesh sieve.

Preliminary investigations were made in which the carbonate, enclosed in a platinum capsule, was heated in a transparent silica tube connected by stout rubber pressure tubing to a mercury manometer. The system was evacuated and the carbonate heated

by placing the silica tube in an electric furnace, but it was found to be impossible to obtain reproducible results. This was found to be due to (1) leakage through the rubber connecting tube. This was at the most very small and by no means so great as (2) leakage through the silica tube due to devitrification induced by the reaction of the silica and small traces of the carbonates which always escaped from the platinum no matter how carefully the tube was exhausted. The crystalline silicates formed on the surface of the silica glass by this reaction appear to have served as nuclei for the formation of quartz crystals, as was shown by microscopical examination of the tubes.

The apparatus ultimately employed is shown in Fig. 1. The



platinum tube P, 15 cm. long by 0.5 cm. internal diameter with thickness of wall 0.5 mm., was sealed directly to the glass manometer M, the joint Wcarrying a cooling coil to prevent cracking of the joint by heating from within the furnace. The tube was exhausted through the trap Y and the mercury allowed to rise from the lower bulb. Then, when A and B were closed, the mercury in the trap was so held that it could not be pushed round the bend when a pressure was developed. The substance to be heated was placed in the tube P, the open end of which was packed with asbestos dehydrated at about 800°, and the platinum tube then sealed on to the glass, and the electric furnace so arranged that the carbonate was well

within the zone of constant temperature. The tube was heated to about 200—300° in order to free the powder from adsorbed moisture and gases, and the exhaustion completed. The temperature, which was read by means of a carefully calibrated platinum-platinum-rhodium thermo-couple, was raised until an appreciable pressure was developed. On re-exhausting the tube at this temperature and then allowing the pressure to rise again, it was found that it did not return to its original value, but was always less. On repeating this process several times, a constant minimum pressure could be obtained for every temperature. The gas evolved under these conditions was collected, and analysis showed it to consist entirely of carbon dioxide. Micro-

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scopical examination of the decomposition product showed the existence of a small amount of needle-shaped crystals which were not present in the sample before heating. These were insoluble in alkalis or water, but gelatinised very readily with acids, giving microchemical tests for calcium and magnesium; these properties in conjunction with the optical properties identify the crystals as calcium and magnesium silicates formed by the interaction of the carbonates with the small traces of siliceous impurities, so that the initial high pressures of carbon dioxide must have been due to the reaction  $CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$ , etc. These reactions may be regarded as irreversible at the temperatures under discussion, and although it would be possible for further carbonate and silicate to react, giving further complex silicates, there will always be a time when the combination with silica comes to an end for every temperature, and the dissociation pressure of the carbonate will then be unaffected by the presence of the silica. The resultant constant minimum pressure for any temperature was therefore taken as the dissociation pressure of the carbonate for that temperature. The time taken for the establishment of the equilibria under these conditions was considerable in the case of the lower temperatures, but equilibrium was obtained much more rapidly the higher the temperature, and usually resulted within forty-eight hours of the initial evacuation at any temperature. Having established a method for obtaining reproducible results with rising temperature, it became necessary to test the reversibility of the process, and it was found that when equilibrium was attained at a higher temperature, which was then allowed to fall to a lower value, the equilibrium pressure for that temperature was not obtained, even after keeping the temperature constant for forty-eight hours. There was always some residual carbon dioxide which apparently would not recombine. This fact is referred to by Jolibois and Bouvier (Compt. rend., 1921, 172, 1182), who found that the reaction  $CaO + CO_2 \rightarrow CaCO_3$  was not reversible unless the calcium oxide used was previously mixed with some calcium carbonate, prepared by a precipitation method, when the reaction was completely reversible on cooling.

The procedure was then adopted in which the carbonates under treatment were mixed with their appropriate oxides, prepared by ignition of the precipitated hydroxides, or in the case of the dolomite by ignition of the moistened product of the decomposition. When this was done, it was found that with rising temperature the results obtained were the same as before, and that with falling temperature the reaction was completely reversible, the pressures checking to a fraction of a millimetre. It was found necessary,

however, to recharge the tubes frequently, since the reversibility would only hold for a few temperatures until further oxide was introduced. Thus it seems that we have an explanation of this phenomenon in the idea that a trace of moisture serves to catalyse the reaction. Carbonates and oxides prepared by precipitation methods will always contain small traces of moisture no matter how carefully they are afterwards ignited. This small trace of moisture would be easily sufficient to catalyse the reaction, but it will be slowly removed by the pumping off of the gas at each temperature, and would thus require renewal from time to time.

### TABLE I.

#### Calcite.

$T^{\circ}$ (abs.) Pressure (mm. of Hg) $T^{\circ}$ (abs.) Pressure (mm. of Hg) $T^{\circ}$ (abs.) Pressure (mm. of Hg)	$876^{\circ}$ 2·4 980^{\circ} 3·6 1084^{0} 10.0	890° 2·5 993° 3·9 1097° 1 13·0	$903^{\circ} \\ 2 \cdot 6 \\ 1006^{\circ} \\ 4 \cdot 2 \\ 1109^{\circ} 1 \\ 17 \cdot 8$	$915^{\circ} \\ 2 \cdot 7 \\ 1019^{\circ} \\ 4 \cdot 7 \\ 123^{\circ} 11 \\ 27 \qquad 4$	$929^{\circ} \\ 2 \cdot 9 \\ 1032^{\circ} \\ 5 \cdot 2 \\ 35^{\circ} 11 \\ 6 \cdot 5  10$	$942^{\circ} \\ 3 \cdot 0 \\ 1045^{\circ} \\ 5 \cdot 9 \\ 48^{\circ} 116 \\ 0 0 \cdot 0 316$	$954^{\circ} \\ 3 \cdot 2 \\ 1050^{\circ} \\ 6 \cdot 9 \\ 1^{\circ} 1166^{\circ} \\ \cdot 2 616 \cdot 6 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\$	$\begin{array}{c} 967^{\circ} \\ 3\cdot 4 \\ 1071^{\circ} \\ 8\cdot 1 \\ \circ 1169^{\circ} \\ 3 \cdot 761 \end{array}$		
Magnesite.										
$T^{\circ}$ (abs.) Pressure (mm. of Hg)	720° 10∙5	730° 11 810°	740° 11·6	$750^{\circ}$ $12 \cdot 2$ $820^{\circ}$	760° 12·9	770° 13·7	780° 14·6	790° 15∙5 870°		
Pressure (mm. of Hg) $T^{\circ}$ (abs.)	16·6 880°	18·1 910°	820 19∙5 950°	830 21·1 980°	23 1000°	25 1020°	27.5 1029°	31.3		
Pressure (mm. of Hg)	34.6	49·6	61·2	117	316.5	602.5	760			
		$D_0$	nomine	•						
$T^{\circ}$ (abs.) Pressure (mm. of Hg)	780° 7·5	785° 7•7	793° 8∙0	810° 8∙7	820° 9∙0	830° 9∙6	846° 10∙0	$875^{\circ}$ $12 \cdot 8$		
T° (abs.) Pressure (mm. of Hg)	896° 14∙6	910° 16∙5	920° 17∙8	936° 21·0	940° 22	960° 27·5	970° 29∙5	982° 32∙5		
$T^{\circ}$ (abs.) Pressure (mm. of Hg)	995° 43∙6	1010° 53∙0	1020° 66∙0	1030° 77	1042° 100∙0	1052° 121	1060° 150	1065° 193		
$T^{\circ}$ (abs.) Pressure (mm. of Hg)	$1070^\circ$ $212\cdot7$	1080° 275	1085° 352	1089° 368	1092° 468	1095° 505	1100° 603	1105° 695		

Determinations of the dissociation pressures of calcite, magnesite, and dolomite have been made by means of this method and the results are given in Table I. Fig. 2 shows the variation of pressure with temperature, and if these curves are tested by plotting  $1/\log p$ against T, it will be found that they express a definite linear relationship between the reciprocal of the logarithm of the pressure and the temperature.

## The Specific Heat of Magnesite.

This was determined in the following manner. As calorimeter, a small Dewar vessel of about 500 c.c. capacity and of very good

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insulation was employed. This was fitted with a Beckmann thermometer, stirrer, and small heating coil of carefully measured known resistance. The vessel was partly filled with carbon tetrachloride so that the thermometer was correctly situated. A steady known current, which was carefully checked by means of a silver coulometer in series, was passed for a definite time, the rise of temperature measured, and the corresponding amount of heat added was calculated from the ordinary expression  $Q = C^2 Rt \times 0.2349$ . Without changing the contents in any way, a known weight of dry magnesite was added and the same current passed for the



same time as before and the new rise in temperature determined. The amount of heat added, and the rise of temperature both with and without a known weight of the sample, being known, it is possible to calculate the amount of heat used up in heating the magnesite. In one experiment, which represents the smallest quantities employed, the following were the figures :

C = 0.085, R = 34.7, t = 600 secs., whence Q = 44.15 cals. Rise in temperature  $= 0.553^{\circ}$  (without magnesite) and  $0.548^{\circ}$  (with magnesite, 5.7114 grams).

Therefore heat for magnesite =  $44 \cdot 15 - 44 \cdot 15 \times 0.548/0.553 = 0.63$  cal., and its specific heat = 0.2013 cal.

Several determinations were made in this manner, employing 00\*

different amounts of liquid, solid, and current until the largest changes could be obtained. The results were fairly concordant and were sufficiently accurate to be used along with the other data employed in the approximate formula for the Nernst equation. The results obtained were: (1) 0.2013, (2) 0.1997, (3) 0.2007, (4) 0.1995; mean 0.2003 cal.

These determinations were made on a sample of Greiner magnesite which, although it was not absolutely pure, was sufficiently so for the purpose in view.

# The Specific Heat of CaO,MgO.\*

A sample of finely ground Binnental dolomite was heated in a vacuum at  $1000^{\circ}$  until its weight was constant and was then cooled in a desiccator over solid potassium hydroxide to prevent any reabsorption of carbon dioxide. The substance was not very reactive, however, and it was found possible to leave it exposed to the air for considerable periods when cold without any pronounced alteration taking place. The specific heat of this product, determined as above, was (1) 0.2100, (2) 0.2110, (3) 0.2093, (4) 0.2096, (5) 0.2106; mean 0.2101 cal.

# The Heat of Solution of Dolomite.

The heat of formation of this substance has never been determined either from its elements or in any other manner, and it became necessary to determine the value both for dolomite itself and for the decomposition product. When either dolomite or the decomposition product is dissolved in hydrochloric acid, the only possible products of the reaction are calcium and magnesium chlorides, water, and carbon dioxide. The heats of formation of these four substances have all been determined previously, and Berthelot has made careful determinations of the heat of dilution of hydrochloric acid over a fairly wide range, so that we have only one unknown in either equation for the reaction with acid.

The apparatus employed was similar to that used by Richards in his early measurements. The calorimeter consisted of a large Dewar vessel of about  $1\frac{1}{4}$  litres capacity and of very good insulation. This was closed at the top by a cork carrying a Beckmann thermometer, a stirrer, a large cylindrical vessel closed at the bottom by a large ground glass plug which could be withdrawn by means of a protruding rod at the top, and two tubes, into the lower ends of which were sealed the ends of the small platinum heating spiral, and the whole was placed in a large box packed with cotton wool

\* The formula CaO,MgO will be used for the sake of brevity to denote the decomposition product of dolomite.

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to provide further insulation. The bottom of the internal vessel was carefully sealed by liberal application of purified vaseline to the ground plug. In this vessel were placed 200 c.c. of pure 20 per cent. hydrochloric acid, prepared by distillation of ordinary hydrochloric acid. A known weight of dolomite less than that required to neutralise the acid completely was placed in the bottom of the calorimeter and the total volume of liquid made up to a litre with 800 c.c. of distilled water. The dolomite was kept in suspension by means of the stirrer, and the thermal capacity of the calorimeter and fittings determined both by the electrical method and the method of mixing, allowance being made for the thermal capacity of the dolomite. This determination was made both before and after the reaction and was found to be constant within the limits of error throughout. Then, when the plug of the internal vessel was withdrawn, the acid could be allowed to react with the carbonate and the rise in temperature determined. By making corrections for the heat of dilution of the acid and the amount of heat lost in the evolution of carbon dioxide (which amount was found in the end to be negligible, since at the concentrations employed most of the carbon dioxide remained in solution and very little was lost), the heat given out in the reaction

$$\begin{split} \text{MgCO}_3, \text{CaCO}_3 + 4\text{HCl aq.} &= (\text{MgCl}_2 + \text{CaCl}_2) \text{ aq.} + 2\text{H}_2\text{O} + \\ & 2\text{CO}_2 + Q \text{ cals.} \quad . \quad . \quad (i) \end{split}$$

can be calculated.

In the preliminary experiments, since it was anticipated that the loss of heat due to evolution of carbon dioxide would be considerable, two calorimeters were employed which were connected by a double-walled tube, silvered, and exhausted so as to form a Dewar jacket. This tube, which was bent twice at right angles, dipped under the surface of water in the second calorimeter, and thus by measuring the rise of temperature in the second calorimeter it was possible to obtain accurate measurement of the heat carried away by the issuing carbon dioxide. This amount of heat was in all cases negligible, never amounting to as much as 0.02 per cent. of the total amount developed, and it was soon apparent that attempts to increase the accuracy in this respect were largely counterbalanced by the inaccuracies introduced by the necessity of having to attend to two calorimeters and to read two Beckmann thermometers simultaneously. The only fault in this apparatus was that the size of the opening of the internal vessel could not be made sufficiently large owing to the presence of the other fittings. and consequently the mixing was not quite rapid enough. The Dewar vessel had very good insulation, however, and since the 0 0\* 2

radiation corrections could be reduced practically to zero this was not after all a serious defect in the working of the apparatus.

In an actual experiment the results were :

Weight of dolomite = 0.6766 gram; temperature rise =  $1.81^{\circ}$ ; total thermal capacity of calorimeter = 303 grams; acid diluted from 1.33:10.7 to 1.33:52.8 mols. For this range the heat of dilution is 1198 cals. (Berthelot, Landolt-Bornstein "Tabellen"). The total heat developed = 2353 cals. Therefore the heat of reaction = 1155 cals. for 0.6766 gram, that is, 31.42 Cals. for 1 gram-molecule.

Several determinations were made using different amounts of dolomite and acid, and the results, which are fairly concordant amongst themselves, are: (1) 31.52, (2) 31.32, (3) 31.26, (4) 32.02, (5) 31.68; mean 31.56 Cals., which is the value of Q in equation (i).

# The Heat of Solution of CaO, MgO in Hydrochloric Acid.

To determine the value of Q in the equation

CaO,MgO + 4HCl aq. = (CaCl<sub>2</sub> + MgCl<sub>2</sub>) aq. + 2H<sub>2</sub>O + Q (ii)

it was necessary to determine the heat of solution of this substance; from this value, by incorporating the known values for the heats of formation of the other reactants, it was possible to determine the heat of formation of the substance from its elements.

The apparatus employed was essentially the same as that already described, except that in this case, since we are dealing with a substance tending to undergo hydration on mixing with water, the oxide was placed in the internal vessel, which was made smaller, and the acid occupied the position of the water in the preceding determinations.

Several determinations of the heat of solution were made and the results are : (1) 62.82, (2) 62.75, (3) 62.90, (4) 63.15, (5) 62.53; mean 62.83 Cals., which is the value of Q in equation (ii).

### Discussion.

From equation (i) and the figures of Thomsen and Berthelot given in Landolt-Börnstein "Tabellen" we have

 $\begin{array}{l} Mg + Ca + 2C + 60 = MgCO_3, CaCO_3 + 545.98 \ Cals. \\ Mg + Ca + 20 = MgO, CaO + 320.79 \ Cals. \\ Mg + C + 30 = MgCO_3 + 266.6 \ Cals. \\ Ca + C + 30 = CaCO_3 \ (calcite) + 283.90 \ Cals. \\ \end{array}$ (1) whence, adding (1) and (2), we have,

 $Ca + Mg + 2C + 6O = (CaCO_3 + MgCO_3) + 550.5$  Cals., which leaves a balance of only 4.52 Cals. to account for the heat of formation of dolomite from calcite and magnesite.

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If we now consider the Nernst equation for a heterogeneous reaction in which only one gas is formed, we have

$$\log p = \frac{-Q_{T_1}}{2 \cdot 3RT} + \frac{3 \cdot 5}{R} \left(\log T + \frac{T_1}{2 \cdot 3T}\right) - \frac{\Sigma a}{2 \cdot 3 \times 2R} \left(T + \frac{T_1^2}{T}\right) + c.$$

Taking  $T_1 = 300^{\circ}$  abs., we have, according to Thomsen and De Forcrand (Landolt-Börnstein "Tabellen"),

 $\label{eq:CaO} {\rm CaO} + {\rm CO}_2 = {\rm CaCO}_3 + 42900 ~{\rm cals.}~{\rm (mean)} = Q_{T_1},$  also at 300° abs.,

 $c_{\text{CaCO}_{9}} - c_{\text{CaO}} - c_{\text{CO}_{9}} = 20 \cdot 2 - 10 \cdot 2 - 9 \cdot 0,$  $\Sigma a = 0.0153.$ 

whence

Substituting in the first equation, we have finally

$$\log p = -9160/T + 1.75 \log T - 0.0017T + 3.2,$$

where c = chemical constant for carbon dioxide = 3.2 (Nernst).

For  $T = 1000^{\circ}$  abs.,

 $\log p = -2.4 \text{ or } p = 0.004 \text{ atm.} = 3.0 \text{ mm.}$ 

Johnston (loc. cit.) obtained p = 44 mm.; in the present observations, we found p = 4.2 mm. at 1006° abs.

The equation given by Johnston departs very appreciably from the form derived directly from the Nernst equation, but the other values measured in this work agree much more closely with the Nernst expression, and when they are plotted do not depart appreciably from the calculated results, so that it seems unnecessary to modify the expression in order to make it fit the observed facts. The specific heat data are evidently quite accurate for this reaction. In the case of the magnesite and dolomite, the agreement between the observed results and those calculated from the Nernst equation is not so good, but the departure from the theoretical does not warrant the derivation of a special equation which would be of no physical significance. The curves are so decidedly logarithmic in form that it does not seem possible that they can represent any but the true state of affairs. The disagreements may possibly be due to the slight inaccuracies in the specific heat data or, what is more probable, they can be traced to the calcareous and ferruginous impurities in the samples used, which, it must be borne in mind, were natural products and not entirely free from impurity.

In dealing with the thermal dissociation of dolomite, we have to consider two possibilities, namely, that dolomite is either a compound or a solid solution. Assuming first that it is a compound, it is possible to conceive of the following as the products of its dissociation under the action of heat: (1) CaO,MgCO<sub>3</sub> + CO<sub>2</sub>, (2) CaCO<sub>3</sub>,MgO + CO<sub>2</sub>, (3) CaO, MgO + 2CO<sub>2</sub>, (4) CaCO<sub>3</sub> + MgO + CO<sub>2</sub>, (5) CaO + MgCO<sub>3</sub> + CO<sub>2</sub>, (6) CaO + MgO + 2CO<sub>2</sub>.

Now, in the experimental work described, it has been shown that magnesite, dolomite, and calcite all yield definite dissociation pressures,  $p_m, p_d, p_c$  such that  $p_m > p_d > p_c$ . These results at once rule out the possibility of such reactions as (5) and (6), since calcium oxide cannot exist as a solid phase at pressures of carbon dioxide greater than  $p_c$ , and also calcium oxide and magnesia cannot coexist at the same pressure of carbon dioxide.

On the assumption that dolomite has a second dissociation pressure, the reaction must be either (1) or (2), the latter being the more probable. Thus we should have a case somewhat similar to that of the ionisation of a dibasic acid or a diacidic base. Dolomite would show two definite and successive dissociation pressures,  $p_{d_1}$  and  $p_{d_2}$ , corresponding with the two successive reactions

and 
$$CaCO_3, MgCO_3 \longrightarrow CaCO_3, MgO + CO_2, \text{ giving } p_{d_1}$$
  
 $CaCO_3, MgO \longrightarrow CaO, MgO + CO_2, \text{ giving } p_{d_2}.$ 

It is to be noted that the second possibility could not be represented by  $CaCO_3$ , MgO  $\rightarrow CaO + MgO + CO_2$ , because it is impossible for calcium oxide and magnesia to coexist at the same pressure of carbon dioxide.

If the assumption of a second dissociation were correct, it would have been possible to isolate the basic carbonate and the double oxide. Dolomite, however, does not show a second dissociation pressure over the temperature range examined, and therefore reactions (1) and (2) are excluded.

If assumption (4) were correct, the curves showing the relationships between  $p_m$ ,  $p_d$ , and  $p_c$  would give us the energy changes of the reactions:

$$\begin{array}{c} \mathrm{CaCO_3} \longrightarrow \mathrm{CaO} + \mathrm{CO_2} + q_c \\ \mathrm{MgCO_3} \longrightarrow \mathrm{MgO} + \mathrm{CO_2} + q_m \\ \mathrm{CaCO_3, MgCO_3} \longrightarrow \mathrm{MgO} + \mathrm{CO_2} + \mathrm{CaCO_3} + q_d, \end{array}$$

from which it would follow that

$$egin{aligned} & ext{CaCO}_3, ext{MgCO}_3 \longrightarrow ext{CaCO}_3 + ext{MgCO}_3 + (q_m - q_d), \ & q_m - q_d = RT^2 \log rac{d}{dt} \log rac{p_m}{p_d}, \end{aligned}$$

where

although this value would in any case tend to be very small, even if it existed at all.

The corresponding diminution of free energy would be given by the expression

$$-F = F_d - (F_c + F_m) = RT \log \frac{p_d}{p_m},$$

but since from the observations at the temperature range at command we have  $p_m > p_d$ , then  $F_c + F_m > F_d$ , and therefore the

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reaction  $CaCO_3, MgCO_3 \longrightarrow CaCO_3 + MgCO_3$  should occur or, in other words, dolomite would be unstable with respect to the component simple carbonates and should not be capable of being formed from them. This result is indeed obvious, for if the condensed reaction  $CaCO_3, MgCO_3 \longrightarrow CaCO_3 + MgCO_3$  actually did occur, dolomite would show the same dissociation pressure as magnesite in its first dissociation phase, provided, of course, that no solid solutions whatsoever are formed during the process. Hence from the observed results the reaction cannot be (4), and we can only draw the conclusion that, if the substance be a compound, its mode of dissociation must be (3), for examination of the  $1/\log p$ curves for the temperature range shows conclusively that there is not a second dissociation phase.

If we now consider the second possibility that dolomite might be a singular point in a series of solid solutions, we should expect results analogous to those obtained. There would be a definite dissociation pressure curve and the resulting product would be an equimolecular solid solution of calcium oxide and magnesia. It has been shown by Rankin and Merwin (J. Amer. Chem. Soc., 1916, **38**, 568) that in fused mixtures of these two oxides no compounds or solid solutions are to be found. These results were all obtained at temperatures higher than  $2300^{\circ}$ , the melting point of the eutectic, but there does not seem any theoretical reason why it should not be possible for either solid solutions or compounds to exist at the temperatures at which the present measurements were made.

The very small value obtained for the heat of formation of dolomite from magnesite and calcite might possibly not be worthy of consideration, because it only involves the absorption of 4.52 kg.-cals. in the formation of one gram-molecule, or about 24.8 cals. per gram. The accuracy of the measurements involved and of the thermochemical data accepted would not allow of too much stress being laid upon this difference. It might be worth while considering, however, whether this amount of heat could represent merely the heat of solution of a gram-molecule of calcite in a gram-molecule of magnesite or whether the heat is actual heat of chemical combination. We know that when two substances of the type here considered unite to form a double compound its heat of formation is as a rule, although not always, only very slightly different from the sum of the heats of formation of the two combining molecules, and also that the heat of solution of similar substances one in the other is usually very small and can possibly be negative, so that it appears to be impossible from the evidence at hand to decide whether the substance is a solid solution or a compound. Experiments are in progress which it is hoped will enable us to decide the

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limits of possible miscibility of the two simple carbonates, and this information in conjunction with the results of investigations which the author hopes to make on the dissociation of some series of mixed crystals should ultimately allow us to come to a definite decision upon the matter. Most of the evidence adduced, however, points to the existence of a compound of the two carbonates, and it seems more useful, for the present at least, to regard the old and original idea of the constitution of dolomite as correct, unless we can come to a decision as to the essential difference between a definite chemical compound and an equally definite singular point in any series of solid solutions.

### Summary.

(1) Measurements of the dissociation pressures of calcite, magnesite, and dolomite have been made and it has been shown that the three substances yield three different and definite dissociation pressures  $p_c$ ,  $p_d$ ,  $p_m$  such that  $p_m > p_d > p_c$ . The possible modes of dissociation of dolomite have been considered on the ground that it is a compound and from the results it is concluded that the thermal dissociation of dolomite takes place according to the equation CaCO<sub>3</sub>, MgCO<sub>3</sub>  $\implies$  CaO, MgO + 2CO<sub>2</sub>.

(2) It has been shown that the thermal dissociation of calcite follows the Nernst equation, the agreement between the observed and calculated results being good, so that the necessity for the derivation of a particular equation to fit the case, as has been done by Johnston, has been proved unnecessary.

(3) A simple and fairly accurate apparatus for the determination of specific heats of solids has been described, and has been employed for the determination of the specific heats of magnesite and of the solid decomposition product of dolomite, which have been found to be 0.2003 and 0.2101 cal., respectively, for  $15-20^{\circ}$ .

(4) The heats of solution of dolomite and of its solid decomposition product in hydrochloric acid have been determined, and from these measurements the heats of formation of the two substances from their elements have been calculated.

(5) From these determinations, it has been deduced that the formation of dolomite from magnesite and calcite would involve the absorption of 4.52 kg-cals. per gram-molecule of dolomite. It has been pointed out that with our present knowledge it is impossible to decide definitely whether the substance is a singular point in a series of solid solutions, or whether it is a compound.

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