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High pressure differential analysis in the system $CaO–CO_2–H_2O$[1]

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Abstract

In the system $CaO–CO_2–H_2O$ the reaction $CaCO_3 + Ca(OH)_2 = L$ occurs at 632±2°C at 1 kbar and at 639±5°C at 9 kbar. These temperatures, which are calibrated against the high-low quartz transition, are 20°C lower than previously reported. The presence of 0.5 wt.% H_2O lowers the reaction temperature about 8°C. In the presence of excess H_2O the reaction $CaCO_3 + Ca(OH)_2 + V = L$ takes place at 614±2°C at 1 kbar and at 575±5°C at 9 kbar. The enthalpy of reaction is estimated at 38±8 kJ/mole. These data are useful for temperature calibrations of high pressure apparatus.

Introduction

The system $CaO–CO_2–H_2O$ has been repeatedly studied (Wyllie and Tuttle, 1960; Gittins and Tuttle, 1964, Harker, 1964; Wyllie and Raynor, 1965; Wyllie and Boettcher, 1969) because of its relevance to the understanding of the origin of carbonatites. It has been suggested that certain reactions in this system can be used for pressure and temperature calibrations in high-pressure apparatus (Wyllie and Boettcher, 1969). In this study the reactions $CaCO_3 + Ca(OH)_2 = L$ and $CaCO_3 + Ca(OH)_2 + V = L$ were studied using a new type of DTA apparatus.

Experimental method

The technique used has been described in detail elsewhere (Koster van Groos, 1979). Briefly, it consists of a copper DTA cell assemblage which accommodates two samples and a reference. The reference, usually powdered Al_2O_3 or TiO_2, and both samples are contained in gold capsules which may be either open or sealed. In this study only sealed capsules were used. They are approximately 5 mm long and weigh about 240 mg. The capsules have a re-entry well in which a thermocouple is placed, thus the temperatures are measured close to the center of the samples. The capsules are machined in quantity, which results in a highly uniform geometry. This is a considerable improvement over previous methods (*e.g.*, Wyllie and Raynor, 1965). The assembly is placed in an Internally Heated Pressure Vessel (IHPV) (*e.g.*, Holloway, 1971). The presence of two sample locations makes it possible to internally calibrate the system. Furthermore, the two DTA signals can be compared. Thus, if one is from the unknown and one from a substance with a known enthalpy of reaction, it becomes possible to make a reasonable estimate of the enthalpy of reaction of the unknown.

Starting materials were mechanical mixtures of fine grained, >200 mesh, $Ca(OH)_2$ and $CaCO_3$, the latter was obtained from Spex Industries. $Ca(OH)_2$ was prepared by decarbonizing $CaCO_3$ at 950°C for 5 hours, hydrating the resulting CaO in distilled water and drying it at 200°C for 4 hours under vacuum to prevent reaction with atmospheric CO_2. The starting material chosen, $44CaCO_3 \cdot 56Ca(OH)_2$ in weight, is close to the eutectic mixture (Wyllie and Tuttle, 1960). In one series of experiments the sample was dried inside the capsule for 10 minutes at 200°C just before sealing. In a second series of experiments 0.5 ± 0.2 wt.% H_2O was present. It was added by allowing the sample to adsorb the appropriate amount of water from a hydrous atmosphere. Finally, three series of experiments were carried out using samples with 5, 10, and 16 wt.% H_2O added. In all instances 25 ± 0.05 mg dry sample was present.

Pressures to 4 kbar were measured with a calibrated bourdon type high precision gauge, accurate to ±0.1%. Higher pressures were determined using a manganin cell, calibrated against the gauge. Over-

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all pressures are believed accurate to within 1%. Temperatures were determined using Pt–Pt90·Rh10 thermocouples, together with a recorder with a multispan 1 mV range. An icebath was used for the cold junction. Temperatures of the runs were calibrated in the following manner. First the thermocouples were calibrated against the melting point of NaC1, 801°C, using a potentiometer. Next the potentiometer was used to feed the same e.m.f. to the thermocouple connections of the IHPV, and the signal was read on the temperature recorder. It was found that the circuit subtracted 30 ± 10 μV, for which the initial data were corrected. After this correction, temperatures are believed to be accurate to ±2°C between the various series of experiments and to ±1°C within a run. The data are not corrected for pressure effects on the thermocouples (Getting and Kennedy, 1970).

Differential temperatures were measured with a dual channel high precision Kipp recorder, using its 20 and 50 μV range. Each series of experiments was carried out with one of the sample capsules containing quartz sand so that the high-low quartz transition could be used as an internal temperature calibrant. The quartz sand, cleaned and ground to pass 230 mesh, was derived from the St. Peter sandstone from the Ozark Dome, Missouri. In earlier experiments (Koster van Groos and ter Heege, 1973) it was found that the high-low quartz transition of such a composite quartz sample is very useful as a DTA standard due to the sharpness and the high reproducibility of the signal. Its only disadvantage is the low enthalpy of transition (0.474 kJ/mole, Robie *et al.*, 1978), which reduces its usefulness in piston cylinder apparatus. As the slope of this transition is about 25.8°C/kbar between 1 and 10 kbar (Koster van Groos and ter Heege, 1973), the pressure uncertainty of ±1% results in a temperature uncertainty of 2.6°C at 10 kbar for the temperature calibration curve. This means that the total temperature uncertainty for the reactions studied is within ±5°C at 10 kbar.

The DTA signal varied with pressure and composition, with the heating and cooling rates kept constant at 10°C/min. using a programmable controller. In general the signals, which are well developed, become somewhat smaller at higher pressures. This is most likely caused by the increase of heat transport by the argon pressure medium at higher pressures. The quartz peak is usually 0.2°C strong with a 1.6–1.8°C temperature range. The reactions studied generate peaks which are usually 3.5–4.5°C strong with a 15–25°C temperature range on heating, and about 4.5–5.5°C strong with a 10–15°C temperature range during cooling. Frequently a shoulder is present on the low-temperature side, on the high-temperature side, or sometimes on both sides of the peak of the heating curve. These shoulders sometimes separate into distinct but small peaks on the cooling curves. The interpretation of the additional signals is beyond the scope of this study. It does not seem likely that the starting mixture has the exact composition of the eutectic at all pressures investigated. Thus, it is possible that the signal on the high-temperature side represents the liquidus. The signal on the low-temperature side may represent a phase transition in $Ca(OH)_2$ (Wyllie and Boettcher, 1969). In future work on the system it may be possible to determine the exact causes of the additional signals.

In this study the intersection of the tangent to the steepest part of the low-temperature side of the peak with the extension of the base line is used as the temperature of the melting reaction. During cooling, the beginning of crystallization is usually indicated by a very sharp break in the curve, suggesting some degree of undercooling. As noted elsewhere (Wyllie and Raynor, 1965), the beginning of crystallization in the anhydrous join occurs at a higher temperature than the beginning of melting as defined above. The same was found in the system containing 0.5 wt.% H_2O. This temperature difference, usually 2–5°C, is probably caused by the fact that the starting composition does not have the exact eutectic composition so that the signal from the crystallization at the liquidus interferes with that of the solidus reaction. In the join containing the small amount of H_2O, the difference is easily explained by assuming a small melting interval due to the presence of H_2O. In the runs containing 5 wt.% or more H_2O the beginning of crystallization occurred usually 3–5°C below the beginning of melting. This suggests that in these runs melting does not occur over a temperature range at the pressures used in this study.

In all series of experiments the temperature range of each run extended from 400°C to about 100°C above the highest reaction temperature found in the run, whether it was a melting reaction or the high-low quartz transition. This was necessary in order to obtain a reasonably smooth base signal. All determinations were carried out at least three times; the temperatures of the reactions were within 1°C of each other. For each series of experiments only one set of capsules was used for all the runs at all the pressures investigated, so the composition was constant. After a series of experiments the capsules were checked for weight-loss. In case of a failure the results were discarded.

Results and discussion

The results of the experiments are shown in Figure 1 and listed in Table 1. Figure 1 shows the *P–T* curve of the high–low quartz transition as determined by Koster van Groos and ter Heege (1973). The crosses show the pressures and temperatures measured in the current study, after the correction of 30 μV. The results match the curve of the previous work rather well, being within 2°C of the results of the earlier work. The agreement between these determinations is rather striking, considering the difference in methods used; in the earlier work the measurements were made with the thermocouples in direct contact with quartz, without using capsules. Because the difference in the temperatures is within the error in the temperature measurements, as was discussed earlier, the data for the various melting reactions were not corrected, except for the addition of 30 μV.

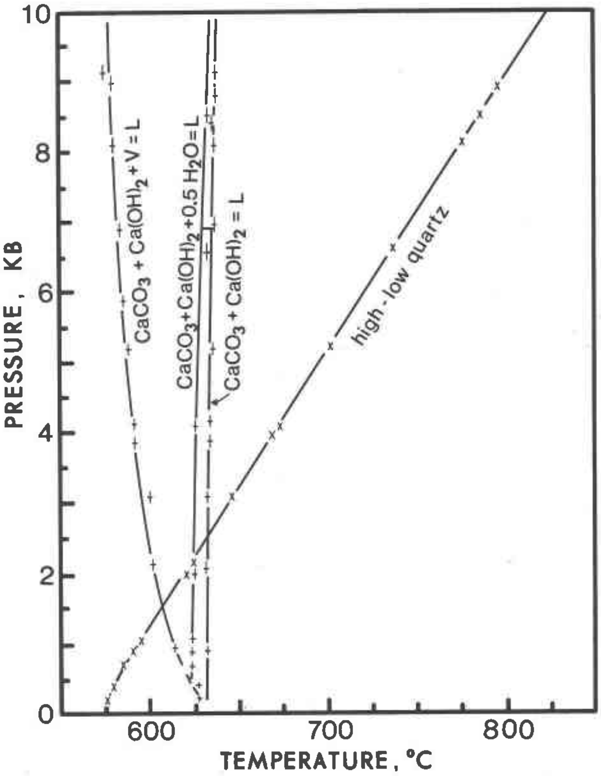

Fig. 1. *PT* projection for the univariant melting reactions $CaCO_3 + Ca(OH)_2 = L$ and $CaCO_3 + Ca(OH)_2 + V = L$. Also shown is the melting reaction with 0.5±0.2 wt.% H_2 present. The high–low quartz transition (Koster van Groos and ter Heege, 1973) is shown also. The crosses along this curve show the determination of this transition in the current study.

Table 1. DTA results for the melting reaction $CaCO_3+Ca(OH)_2+(V)=L$ using the composition $44CaCO_3 \cdot 56Ca(OH)_2 + H_2O$ in wt.%.

Pressure in bars	Reaction temperature in °C heating	cooling	peak
a. 0.0 percent H_2O:			
930	632	632	639
2070	632	634	640
3070	633	635	641
3880	635	638	643
4140	653	639	645
5170	637	639	646
6900	637	639	646
8070	638	640	645
8390	636	640	645
8690	639	640	647
9100	638	642	647
8480	634	629	641
b. 0.5 percent H_2O:			
210	628	630	939
345	627	629	639
680	623	626	633
880	623	625	632
1035	624	627	634
2140	624	629	632
4070	627	630	635
6570	634	635	640
c. 5.0 percent H_2O:			
3860	592	590	600
7725	580	579	589
8965	579	573	589
10000	579	757	588
d. 10.0 percent H_2O:			
4025	592	589	598
8900	575	572	583
9970	575	574	584
e. 16.0 percent H_2O			
930	614	607	620
2125	602	600	609
3070	600	595	608
4160	592	588	600
5180	590	588	599
5860	588	584	597
6950	585	583	592
8055	582	575	590
9110	575	574	586

The data show that the reaction $CaCO_3 + Ca(OH)_2 = L$ is very insensitive to pressure and, therefore, useful as a temperature calibrant as was suggested by Wyllie and Boettcher (1969). This reaction occurs at 632 ± 2°C at 1 kbar, and at 639 ± 5°C at 9 kbar. The slope of the reaction is 0.9°C/kbar. It is interesting to note that these values are approximately 20°C lower than those from Wyllie and Boettcher (1969). The difference may be explained by the efficacy of the DTA method over quench-type methods. Another possibility is that in cold seal vessels with a thermocouple well on the outside of the vessel the measured temperatures are about 20°C higher than the temperatures of the samples.

The results for the reaction $CaCO_3 + Ca(OH)_2 + V = L$ show the depression of the melting reaction in the presence of excess H_2O. In this series of experiments 5, 10, and 16 wt.% H_2O was present. Again the data are consistently 20°C lower than those determined by Wyllie and Boettcher (1969). They range from 614 ± 2°C at 1 kbar to 575 ± 5°C at 9 kbar. It is interesting to note that at 9 kbar the run containing 5 wt.% H_2O showed a reaction at 579°C while the run with 16 wt.% H_2O showed the melting reaction at 575°C. The difference may be explained by the inaccuracy of the pressure and temperature measurements. It is also possible that at a slightly lower pressure the solubility of H_2O in the melt reaches 5 wt.% so that at 9 kbar this melt is undersaturated with H_2O. The DTA signal was perhaps slightly broader at this pressure and at 10 kbar, suggesting the latter possibility. This would mean that the solubility of H_2O in the carbonate liquid is about 5 wt.% at 8 kbar.

The third *P–T* curve in this system was determined with samples containing 0.5 ± 0.2 wt.% H_2. The effect on the melting temperature was significant, lowering it by approximately 8°C. This clearly indicates the need to avoid adsorption of H_2O. Furthermore, the lowering of the melting reaction by 8°C with 0.5 wt.% H_2O present tends to support the possibility that at 8 kbar the H_2O solubility in the liquid is about 5 wt.%. However, more experiments with intermediate H_2O contents are necessary to establish its solubility in these liquids.

At low pressures the various reaction curves terminate in an invariant point where CaO becomes stable through the reaction $Ca(OH)_2 = CaO + H_2O$. In this study no attempt was made to investigate the *P–T* relations of this reaction; therefore it is not possible to determine the pressure and temperature of this invariant point.

As was mentioned above, it is possible to estimate the enthalpy of melting by comparing the peak area with that of the quartz transition. A direct comparison only yields a crude estimate, especially when the signal strength differs greatly . Even when the signals are similar it would be necessary to obtain signals at various heating rates for a reasonable estimate. Comparison of the average peak areas at the various pressures showed that the melting reaction generated a peak area approximately 80 times that of quartz. This ratio did not appear to be dependent on either H_2O content or pressure. Using a value of 0.474 kJ/mole (Robie *et al.*, 1978) for the quartz inversion, a value of 38±8 kJ/mole is obtained for the enthalpy of the melting reaction.

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