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DTA AND QUENCHING METHODS IN THE SYSTEM $CaO-CO_2-H_2O$[1]

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INTRODUCTION

Harker (1964) recently described a simple technique for differential thermal analysis in closed systems containing volatile components under pressure, which promises to be of great utility. He contrasted the reaction temperatures recorded in his preliminary studies with those reported in the same systems by quenching techniques, and he noted some rather large temperature discrepancies. This led him to conclude that the accuracy of the quenching technique in systems where the liquid phase cannot be quenched to a glass "is often somewhat low and sometimes quite misleading." However, if the melting temperature of portlandite recorded by Wyllie and Tuttle (1960) is corrected as shown by Gittins and Tuttle (1964), the results obtained by DTA and quenching techniques are almost identical, and Harker's concern for the validity of the quenching technique becomes unnecessary, in this system at any rate. This note contains revised values for melting reactions in the system $CaO-CO_2-H_2O$ measured by one of us (EJR) using the quench technique, and a discussion of this technique and DTA by the other (PJW).

REVISION OF THE SYSTEM $CaO-CO_2-H_2O$ (QUENCH TECHNIQUE)

Univariant curves for the reactions plotted in Fig. 1 were published originally by Wyllie and Tuttle (1960, Fig. 15). For a pressure of 1 kilobar, 685° C. was reported as the binary eutectic temperature between portlandite and calcite, and 675° C. for the same reaction in the presence of a vapor phase composed of almost pure H_2O. It was later discovered

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that these temperatures were too high by 30° C., and a brief note about the revised temperatures was presented by Gittins and Tuttle (1964) after their account of the system CaF_2-$Ca(OH)_2$-$CaCO_3$.

As a basis for the investigation of more complex systems, these reaction temperatures were re-measured in 1960, independently at Leeds University by Biggar (1962), and by E. J. Raynor; and at The Pennsylvania State University by J. Gittins, and by D. S. Coombs. In 1962, they were re-examined again at The Pennsylvania State University by J. L. Haas, D. H. Watkinson, and A. F. Koster van Groos. All of these investigators measured and confirmed the temperature of $655 \pm 5°$ C. for the binary eutectic temperature. The univariant reaction curves for the ternary system shown in Fig. 1 were measured by E. J. Raynor in order to correct and extend the melting curves reported by Wyllie and Tuttle (1960, Fig. 15). The liquid phase was present at 10 bars, the lowest pressure at which a run was made.

We have been unable to account for the temperature error incurred when the system CaO-CO_2-H_2O was first studied in 1958. Certainly, it had nothing to do with interpretation of the presence of a liquid phase,

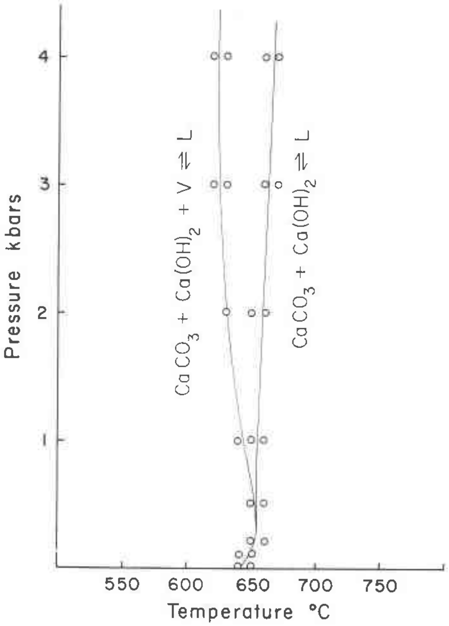

FIG. 1. Univariant melting curves in the system CaO-CO_2-H_2O, revised by E. J. Raynor. The curve for the beginning of melting was extended down to 10 bars pressure.

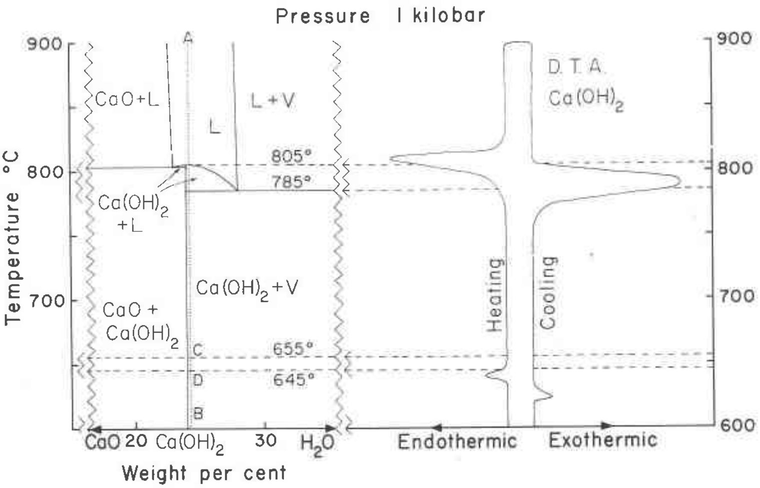

FIG. 2. The system CaO-H_2O at 1 kilobar pressure. The equilibrium diagram at the left is the corrected version of Wyllie and Tuttle (1960, Fig. 4) determined by the quenching technique. The DTA curves at the right for $Ca(OH)_2$ are from Harker (1964). The dotted line AB represents the bulk composition of the slightly impure sample used in the DTA experiments. The horizontal dashed lines at 645° C. and 655° C. represent the two ternary reactions of Fig. 1.

because the quenched liquid in the ternary system is very easily recognized. We have concluded, without satisfaction, that there was an instrument malfunction somewhere in the temperature-measuring circuit. A similar, smaller error was detected in 1962, during one of our periodic temperature calibrations. These calibrations have been made at more closely spaced intervals since the recognition of this earlier temperature error.

The melting temperature of portlandite itself has not been re-measured at any stage of the work outlined in this article, but there is evidence that the 30° C. correction is applicable. In several systems (*e.g.* CaF_2-$Ca(OH)_2$, Gittins and Tuttle, 1964, Fig. 2), the liquidus boundary for portlandite located within the system extends to a melting point of 805° C. for portlandite (compared to the original measurement of 835° C. recorded by Wyllie and Tuttle, 1960, Figs. 4 and 5). A portion of the equilibrium diagram for CaO-H_2O at 1 kilobar pressure, with the 30° C. correction applied, is illustrated at the left-hand side of Fig. 2 (compare Wyllie and Tuttle, 1960, Fig. 4). The revised melting temperature for portlandite is $805 \pm 5°$ C., with $785 \pm 5°$ C. for melting in the presence of water vapor. The horizontal dashed lines represent the corrected temperatures for the two ternary melting reactions illustrated in Fig. 1.

Comparison of Temperatures Obtained by DTA and Quenching Techniques

The right-hand side of fig. 2 shows the heating and cooling curves for portlandite, reproduced carefully from Harker's (1964) Figs. 4 and 5, and arranged so that the DTA temperature scale coincides with that for the phase diagram in the left-hand side of the figure. Because the DTA trace indicated a reaction below 650° C., Harker concluded that some $CaCO_3$ and H_2O was present as impurity in the portlandite. Indeed, it is extremely difficult to maintain a sample of $Ca(OH)_2$ free from adsorbed H_2O and CO_2. The H_2O content of the sample used for D.T.A. can therefore be represented by the position of the vertical dotted line AB in Fig. 2, and the $CaCO_3$ content is indicated by intersection of the dotted line with the ternary reaction lines at points C and D.

It will be noted immediately that the freezing temperature recorded by the DTA cooling curve corresponds precisely to the value of 805° C. in the corrected phase diagram. According to Harker (1964) the heating curve indicates a melting temperature of 770° C. However, the temperature for the beginning of the melting peak is not well defined; the peak is markedly asymmetrical, with a low-intensity extension of the low-temperature side of the peak. Although the peak for melting begins at a lower temperature than that for freezing, which is unusual (Harker, 1964), the maximum intensity of the peak lies at a higher temperature than the freezing temperature, as would be expected.

The heating curve shown in Fig. 2 indicates a small heat effect over a range of temperatures before the main part of the peak begins. This preliminary heat effect corresponds quite closely with the temperature interval between the two reactions for the melting of portlandite in the presence of excess H_2O, and the melting of dry portlandite. It is here interpreted as an effect caused by the fact that the bulk composition of the sample used was not pure $Ca(OH)_2$, with the result that the portlandite melts over a range of temperatures instead of at a single temperature. This effect was noted and taken into account in the interpretation of the runs using the quench technique in the systems $CaO\text{-}H_2O$ and $CaO\text{-}CO_2$. (Wyllie and Tuttle, 1960, p. 14, 17).

Using the phase diagram in Fig. 2 as a guide, one may consider the sequence of events if the sample of slightly impure $Ca(OH)_2$, represented by the vertical dotted line AB, is heated under equilibrium conditions from a temperature of 600° C. The sample contains a small quantity of $CaCO_3$ as well as H_2O, and therefore a trace of ternary liquid forms at 645° C. (Fig. 1, and D in Fig. 2); the DTA curve (Figure 2) shows a small endotherm beginning at 630° C. This liquid increases very slightly in quantity as the temperature is raised to 785° C., but in the temperature interval from 785° C. to 805° C. the amount of liquid increases from a fraction of a per cent to 100%; the quantity of liquid produced within a given temperature increment increases as 805° C. is approached. The major endotherm for the melting of portlandite begins at 770° C., but the differential heat effect remains small until the temperature exceeds 790° C., and the peak reaches its maximum temperature at 810° C.

Consider now cooling of the sample A from the liquid field. The phase diagram shows that crystallization begins at 805° C.; much crystallization occurs in a small temperature interval, and most of the sample is crystalline when the temperature reaches 785° C. The DTA cooling curve shows a very well-defined break starting precisely at 805° C. The trace of liquid remaining below 785° C. slowly decreases in amount as the charge is cooled, and it crystallizes completely at the ternary eutectic temperature 645° C., at D; the DTA trace shows a small exotherm beginning at 630° C.

DISCUSSION

The revised phase diagram for the system CaO-H_2O determined by quenching fits well with Harker's (1964) differential thermal analysis of portlandite. The small DTA peaks corresponding to a reaction about 15° C. below the temperature of beginning of melting in the ternary system CaO-CO_2-H_2O (Fig. 1, and D in Fig. 2) are related to this melting reaction, and further study is required to account for the discrepancy here. The discrepancy is small compared to Harker's (1964) interpretation of large discrepancies between the two techniques.

Each experimental technique, DTA and quenching, has its problems. With DTA methods, the main problems are kinetic and, for the more complex systems, in interpreting the heat effects observed in terms of specific reactions. With the quenching technique the problems include the attainment of equilibrium and the establishment of textural criteria for the recognition of quenched liquid. In many of the systems of the type under consideration, identification of a quenched liquid is very easy, *e.g.* in the system $CaCO_3$-$Ca(OH)_2$; in others it is more difficult, *e.g.* $Ca(OH)_2$ and $CaCO_3$ separately, and CaO-SiO_2-H_2O; and in others satisfactory distinction between primary crystals and quenched crystals has not been achieved, *e.g.* Na_2CO_3. Identification of the liquid phase in any mixture producing only a small amount of liquid may be very difficult. For the difficult materials, other physical methods may be employed for the recognition of melting, such as the use of platinum black mixed in the powdered sample (Boyd *et al.*, 1964, in their study of the melting curve for enstatite). In the more complex systems, the formation of a liquid in a multiphase reaction is accompanied by a change in the crystalline assemblage involved, so that additional phase criteria are available for recognizing a melting reaction. In all of these systems, the pressure DTA method described by Harker (1964) is an extremely useful way of locating phase transitions, but even in quite simple systems such as CaO-H_2O (Fig. 2), the interpretation of the reactions located by the dynamic method depends upon the correct identification of phase assemblages by the static quench method.

In view of the above discussion, Harker's (1964) statement with reference to the quenching method that "The accuracy of such methods is often somewhat low and sometimes quite misleading" should be restricted to the "difficult" systems. In very many systems the quenching method can yield results of high accuracy, given accurate temperature calibration and recording techniques. However, establishing the criteria for interpretation is not always easy. For many systems, an experimental study involving both techniques would appear to be desirable.

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