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EQUILIBRIUM DEHYDRATION OF DIASPORE AT LOW TEMPERATURES

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ABSTRACT. The equilibrium temperature of the reaction, diaspore = corundum + liquid water, has been located at 360 ± 7°C. The reaction was followed by measuring weight changes on a single crystal of corundum in the presence of diaspore and liquid water. The free energy of formation of diaspore at 25°C and one atmosphere is estimated to be –439 Kcal/mole.

INTRODUCTION

Among workers in the field of experimental petrology, there is a constant search for methods of obtaining reliable equilibrium conditions in systems where reaction rates are extremely slow. In some cases, it has been found necessary to work at extreme conditions of pressure and temperature to obtain information. These conditions are known to be far removed from those where the reactions occur under natural conditions, but thermodynamic devices may be used to extrapolate to regions of interest. For such extrapolation to be convincing, the high pressure-temperature studies must be of considerable precision, and it is in just this region that such precision becomes difficult to attain. Data from squeezers and even the rotating squeezer are difficult to evaluate on account of the known, large pressure gradients in such apparatus. It thus appears there is good reason to attempt to find methods that can be used in conventional hydrostatic fluid systems, at pressures and temperatures not too far removed from natural, crustal conditions.

In some reactions, nucleation of new phases is the slow step, and this can be overcome by appropriate seeding techniques and study of mixtures. In other reactions, growth or solution and transfer rates may be the slow steps, and where this is the case a more sensitive method of detection of a small amount of reaction is necessary. We have recently found in several systems (Weill, 1963; Evans, unpublished data on mica stability relations) that solubility methods can be valuable.

METHOD

The equilibrium conditions of the reaction:

$$Al_2O_3 \cdot H_2O \rightarrow Al_2O_3 + H_2O$$

$$\text{diaspore} \rightarrow \text{corundum} + \text{water}$$

have been studied by numerous workers with varying degrees of success (for a summary, see Fyfe and Godwin, 1962). Diaspore, like many refractory oxides, is insoluble in most normal calorimetric solvents, and standard thermodynamic data have not been obtained by these methods. If equilibrium can be obtained in direct studies, such data can be derived.

In this study, the direction of the above reaction was followed, by measuring weight changes on a large, synthetic, single crystal of corundum in the presence of diaspore and liquid water. Such an approach is simplified because corundum has negligible solubility in the small volumes of water used. Diaspore was hand picked from an excellent sample from Chester, Massachusetts. The only contaminating phase was a small amount of chlorite. This was selectively leached using hydrofluoric acid. The corundum crystal was placed in a small

stainless steel vessel, partially filled with 1.5 cm^3 of water and about 0.14 gm of diaspore. The pressure is always that of the vapor pressure of liquid water. Temperature control and variation were in the range $\pm$ 2°C. Charges were held at constant temperature for the desired time, and the direction of reaction found by following weight changes of the corundum crystal with a Mettler microbalance. Changes of less than 10 micrograms are of doubtful significance due to balance instability and weight changes occurring during handling and cleaning. Different corundum rods were used, but there was no consistent pattern between the size of a rod and its reactivity; probably a reflection of the distribution of a small number of dislocations where solution and growth are favored. The experimental results are shown in figure 1.

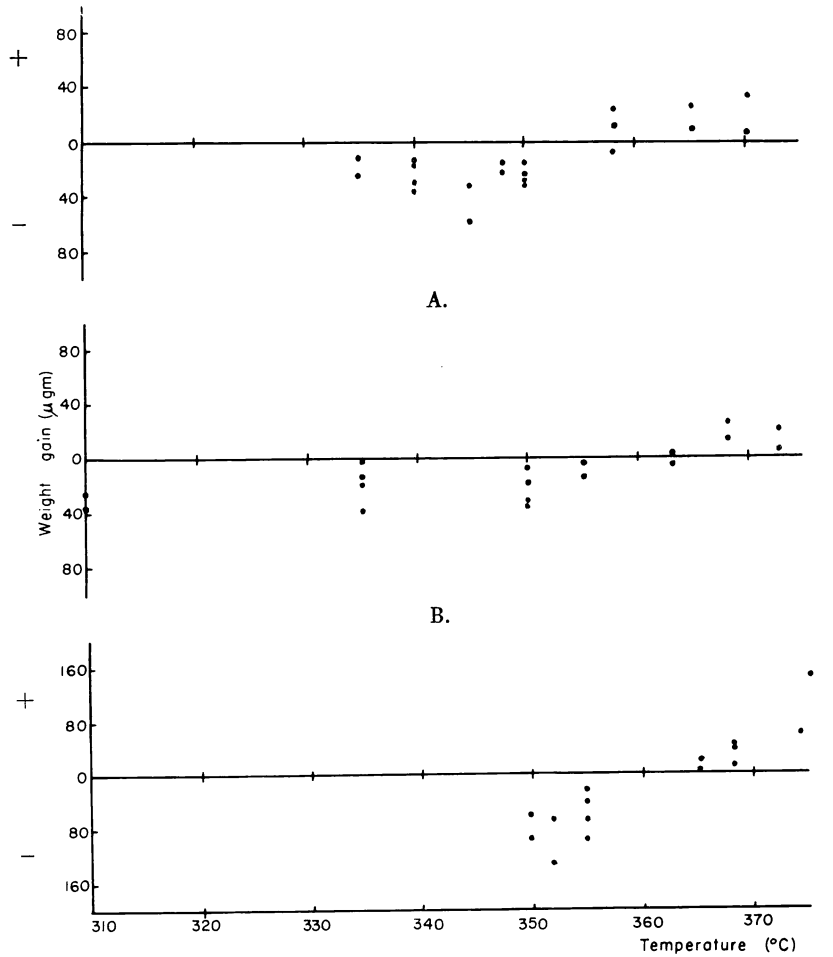

Fig. 1. Weight changes in micrograms observed on corundum rods in the presence of diaspore and liquid water: (A) one-week runs with 100 mesh diaspore; (B) one-week runs with 500 mesh diaspore; (C) two-week runs with 100 mesh diaspore.

DISCUSSION

Examination of the data in figure 1 indicates that the direction of reaction can be ascertained from the weight changes observed. No other reasonable explanation of the observations seems possible. Grain size, in the range studied, appears to have little effect. The region of zero weight change has been taken to represent the equilibrium temperature. From the two-week experiments that give the most sharp definition of the equilibrium region, the equilibrium temperature is taken to be 360 ± 7°C. All data taken into account, the mean figure is 358°C, and the three values range from 355 to 360°C. The value is only 20° below that found as a synthetic upper limit by Fyfe and Godwin (1962) and corresponds even more closely with extrapolation of the high pressure data of Kennedy (1959).

From the present data, the standard free energy of diaspore at 298°K may be estimated. The main uncertainty in this estimation is due to lack of entropy data for diaspore in the range 25 to 360°C. To estimate entropies of the reaction:

$$\text{diaspore} \rightarrow \text{corundum} + \text{water}_{\text{liquid}},$$

we have extrapolated the known value at 25°C along a parallel curve to those for the reactions:

$$\text{brucite} \rightarrow \text{periclase} + \text{water}$$

and

$$\text{boehmite} \rightarrow \text{corundum} + \text{water}$$

where high temperature data are available. Such an approach appears reasonable when additivity of entropies is considered (see Fyfe, Turner, and Verhoogen, 1958). For the diaspore reaction, ΔS at 25°C is 12.07 e.u., and at 360°C the extrapolated value found is 19.3 e.u.

Using estimated values for ΔS of reaction between 25 and 360°C and applying a small correction for the effect of pressure on the free energy of the reaction, ΔG° for diaspore is found to be −439 K cal. The corresponding calorimetric value for boehmite is −435 K cal. Errors in the estimated free energy arise from two parts: If we allow maximum uncertainty in the position of the boundary (±7°C), this implies an error in the free energy of ±135 cals. The other major source of error is in the extrapolated entropy of dehydration. This error, which could be removed with extended heat capacity studies, is hardly likely to exceed 1 e.u. and contributes an uncertainty of ± 300 cals to the free energy.

With the estimated free energies of formation and the known ΔS of the polymorphic reaction,

$$\text{diaspore} \rightarrow \text{boehmite (6.29 e.u.)}$$

it would be expected that boehmite would become stable relative to diaspore at around 500°C. But at this temperature both phases are less stable than the dehydration products. Thus, the present results provide additional confirmation that boehmite is a monotropic modification.

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