

## Enthalpies of formation of $\text{CaAl}_4\text{O}_7$ and $\text{CaAl}_{12}\text{O}_{19}$ (hibonite) by high temperature, alkali borate solution calorimetry

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**Abstract**—The enthalpies of formation of  $\text{CaAl}_4\text{O}_7$  and  $\text{CaAl}_{12}\text{O}_{19}$  (hibonite), by alkali borate solution calorimetry at 1063 K are:

$$\Delta H_{f,\text{CaAl}_4\text{O}_7}^0 (1063 \text{ K; from oxides}) = -[25.6 \pm 4.7] \text{ kJ/g.f.w.}$$

and

$$\Delta H_{f,\text{CaAl}_{12}\text{O}_{19}}^0 (1063 \text{ K; from oxides}) = -[33.0 \pm 9.7] \text{ kJ/g.f.w.}$$

Using experimental enthalpy data for  $\text{CaAl}_4\text{O}_7$  and estimated values for  $\text{CaAl}_{12}\text{O}_{19}$ , the standard enthalpies of formation of these compounds from the elements at 298 K are:

$$\Delta H_{f,\text{CaAl}_4\text{O}_7}^0 (298 \text{ K; from elements}) = -4,007 \pm 5.2 \text{ kJ/g.f.w.}$$

and

$$\Delta H_{f,\text{CaAl}_{12}\text{O}_{19}}^0 (298 \text{ K; from elements}) = -10,722 \pm 12 \text{ kJ/g.f.w.}$$

Comparison with high-temperature galvanic cell data for the Gibbs energy of formation of  $\text{CaAl}_{12}\text{O}_{19}$  allows a calculation of the standard entropy of hibonite,

$$S_{\text{hibonite}}^0 (1100 \text{ K}) = 1280.2 \text{ J/K g.f.w.}$$

This value is only about 2% larger than the oxide sum. Hence it is inferred that the standard entropy of hibonite at 298 K is probably only slightly larger than the oxide sum value of 343.7 J/K g.f.w.

The present data were used to extrapolate KUMAR and KAY's (1985) data for the Gibbs energies of formation of hibonite and  $\text{CaAl}_4\text{O}_7$  to the temperature range 1500–1700 K. These data were then used in equilibrium thermodynamic calculations of the condensation of a gas of solar composition. Contrary to calculations of KORNACKI and FEGLEY (1984), who used thermodynamic data of ALLIBERT *et al.* (1981) for calcium aluminates, our results show no stability field for  $\text{CaAl}_4\text{O}_7$  in a gas of solar composition at  $10^{-3}$  to  $10^{-5}$  atm total pressure. At  $10^{-3}$  atm pressure, hibonite forms by reaction of corundum with the gas at 1725 K, begins to react with the gas to form gehlenite at 1607 K and disappears completely in a reaction to form spinel at 1494 K. The absence of  $\text{CaAl}_4\text{O}_7$  from hibonite-, spinel-rich inclusions in carbonaceous chondrites cannot be used as an argument against a condensation origin for these objects.

### 1. INTRODUCTION

THE SYSTEM  $\text{CaO}-\text{Al}_2\text{O}_3$  contains a number of phases of interest to geochemists, mineralogists, and materials scientists. As many as seven intermediate phases have been found on this binary join, although there is some uncertainty whether they are all strictly binary compounds and if they are truly stable in a thermodynamic sense. Several calcium aluminate phases are important in the ceramics and cement industries. The very alumina-rich phases are of special interest to students of meteorites and cosmochemistry. Two of these phases are  $\text{CaAl}_{12}\text{O}_{19}$  ( $\text{CA}_6$ ; hibonite) and  $\text{CaAl}_4\text{O}_7$  ( $\text{CA}_2$ ). The latter does not as yet have a mineralogical name. The most aluminous phase, hibonite, has been reported from several terrestrial sites, where in at least one locality it contains abundant rare-earth elements (CURIEN *et al.*, 1956; MAASKANT *et al.*, 1980). Special interest in hibonite and in  $\text{CaAl}_4\text{O}_7$  has been

a result of their recent discovery in alumina-rich inclusions in ordinary and carbonaceous chondrites (FUCHS *et al.*, 1973; KEIL and FUCHS, 1971; GROSSMAN, 1980; CHRISTOPHE *et al.*, 1982). Meteoritic hibonite typically contains significant amounts of  $\text{TiO}_2$ ,  $\text{MgO}$ , and  $\text{FeO}$  (KEIL and FUCHS, 1971). The phase  $\text{CaAl}_4\text{O}_7$  is much less common than hibonite, with only three reports so far (CHRISTOPHE *et al.*, 1982; PAQUE, 1987; DAVIS *et al.*, 1987). Very little chemical information is available on its composition.

Both phases are important for cosmochemical reasons because they have been predicted from thermodynamic calculations to be very high-temperature condensates from the primitive solar nebula (GROSSMAN, 1972; BLANDER and FUCHS, 1975; KORNACKI and FEGLEY, 1984). If so, these meteoritic phases contain information regarding the physical conditions within the solar nebula at a very early time. For this reason, it is highly desirable to obtain accurate thermodynamic data for both phases; unfortunately, the existing data are fragmented or in gross disagreement. The adopted values influence in a dramatic way the condensation sequence

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which can be calculated theoretically. BLANDER and FUCHS (1975) calculated that both hibonite and  $\text{CaAl}_4\text{O}_7$  are stable, high-temperature phases in a solar gas, but also pointed out that their estimates of the free energies of these phases, based on melt activity data, are highly uncertain,  $\pm 12.6$  kJ/g.f.w. and  $\pm 8.4$  kJ/g.f.w., respectively. Using free energy data for hibonite and  $\text{CaAl}_4\text{O}_7$  from ALLIBERT *et al.* (1981), KORNACKI and FEGLEY (1984) calculated that hibonite would have reacted with the solar nebular gas to form  $\text{CaAl}_4\text{O}_7$  and that  $\text{CaAl}_4\text{O}_7$  would have reacted to form  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  as the gas temperature fell at a total nebular pressure of  $10^{-3}$  bars. MACPHERSON and GROSSMAN (1984) pointed out that if the data for  $\text{CaAl}_4\text{O}_7$  used by KORNACKI and FEGLEY (1984) were in error by as little as 6.1 kJ/mole, hibonite would have reacted to form  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  directly, without the appearance of  $\text{CaAl}_4\text{O}_7$ . The common occurrence of hibonite-bearing meteoritic inclusions that contain no  $\text{CaAl}_4\text{O}_7$  was interpreted by KORNACKI and FEGLEY (1984) to mean that these inclusions are not condensates at all, but formed by partial melting of nebular dust aggregates. On the other hand, MACPHERSON and GROSSMAN (1984) argued that the inclusions are condensates but that the thermodynamic data for  $\text{CaAl}_4\text{O}_7$  may be incorrect. A review of the literature on the standard thermodynamic properties of  $\text{CaAl}_4\text{O}_7$  and  $\text{CaAl}_{12}\text{O}_{19}$  reveals that differences larger than 6.1 kJ/mole exist in the reported data for  $\text{CaAl}_4\text{O}_7$ , whereas no direct calorimetric data exist for  $\text{CaAl}_{12}\text{O}_{19}$ . For these reasons, we initiated a thermochemical study of these phases in order to obtain their enthalpies of formation by oxide melt solution calorimetry.

#### (a) Previous studies

There are a number of studies of the thermodynamic properties of  $\text{CaAl}_4\text{O}_7$  ( $\text{CA}_2$ ), and there has been considerable discussion regarding the correct value of  $\Delta H_f^\circ$  for this phase. Its enthalpy of formation was first determined by KOEHLER *et al.* (1961) by HF solution calorimetry. Its third law entropy,  $S_f^\circ$ , was measured by KING (1955), while its high-temperature heat capacity is given in BONNICKSON (1955). HEMINGWAY (1982) advanced a revised value of  $\Delta H_f^\circ$ , because of errors associated with the Hess cycle data used by KOEHLER *et al.* (1961) to obtain  $\Delta H_f^\circ$ . He rejected a value proposed by ELIEZER *et al.* (1981). This discussion will not be repeated here. So far, no measurements based on high-temperature solution calorimetry have been attempted. Such measurements are highly desirable since it is well known that aluminous compounds do not dissolve readily in aqueous HF.

There is also a great deal of recent information on  $\Delta G_f^\circ$ , the free energy of formation, of  $\text{CaAl}_4\text{O}_7$  (POPOV *et al.*, 1979; SKOLIS *et al.*, 1981; ALLIBERT *et al.*, 1981; KUMAR and KAY, 1985). These studies make use of solid electrolyte galvanic cells to determine  $\Delta G_f^\circ$  over a temperature range of several hundred degrees at temperatures of 1000 K and higher.  $\Delta H_f^\circ$  can be calculated from these data; however, considerable caution must be exercised when the data are extrapolated to lower and higher temperatures.

The crystal structure of  $\text{CaAl}_4\text{O}_7$  was determined by LAGERQVIST *et al.* (1937) and confirmed by BOYKO and WISNYI (1958). Although the X-ray data were of poor quality, they proposed that this compound is essentially isostructural with  $\text{SrAl}_4\text{O}_7$ . The  $\text{Al}^{3+}$  ions occur only in tetrahedral coordination, but in two crystallographically distinct sites (LAGERQVIST *et al.*, 1937). A more recent structure refinement of  $\text{Nd}^{3+}$ -doped  $\text{CaAl}_4\text{O}_7$  confirms this proposal and yields more accurate cell dimensions and atomic positions (GOODWIN and LINDOP, 1970).

There are no calorimetric data for  $\text{CaAl}_{12}\text{O}_{19}$  ( $\text{CA}_6$ ), hibonite. Estimates of  $\Delta H_f^\circ$  have been derived from electrochemical measurements at high temperatures (POPOV *et al.*, 1979; SKOLIS *et al.*, 1981; ALLIBERT *et al.*, 1981; KUMAR and KAY, 1985) and from phase equilibrium studies and thermodynamic studies of the systematics

of thermochemical data for the other calcium aluminates (ELIEZER *et al.*, 1981; HEMINGWAY, 1982).

The crystal chemistry of hibonite was reviewed by BURNS and BURNS (1984). In natural hibonite, extensive substitution of other elements such as  $\text{Mg}^{2+}$ ,  $\text{Ti}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  may occur. These cations substitute for  $\text{Al}^{3+}$ , which is found in three different coordination sites, including three separate and independent octahedral sites, one tetrahedral site, and one five-fold trigonal bipyramidal site.

The alumina-rich portion of the  $\text{CaO} - \text{Al}_2\text{O}_3$  phase diagram is shown in Fig. 1. It will be noted that both  $\text{CaAl}_4\text{O}_7$  and  $\text{CaAl}_{12}\text{O}_{19}$  have very high melting points. While hibonite melts incongruently at 2181 K to corundum and a liquid richer in  $\text{CaO}$ ,  $\text{CaAl}_4\text{O}_7$  melts congruently at about 2065 K.

## 2. EXPERIMENTAL

### (a) Preparation and characterization of materials

**CaO.** A pressed pellet of  $\text{CaO}$  was prepared from Ultrex-grade  $\text{CaCO}_3$  (Baker). This pellet was fired at  $1400^\circ\text{C}$  for 72 hours. The sintered product had medium crystallinity; X-ray scans revealed only peaks indicative of  $\text{CaO}$ .

**$\text{Al}_2\text{O}_3$ .** The alumina was from two sources. The first sample was prepared by firing a pellet of  $\text{Al}_2\text{O}_3$  (Fisher-Certified) at  $1300^\circ\text{C}$  for 48 hours. It was the same material previously used by CHATILLON-COLINET *et al.* (1983). The second sample of  $\text{Al}_2\text{O}_3$  (Baker-Ultrex) was prepared by sintering a pellet at  $1400^\circ\text{C}$  for 48 hours. Despite the high sintering temperature, this second sample was somewhat finer-grained than the first sample. There was no discernible difference in the heats of solution of the two samples.

**$\text{CaAl}_4\text{O}_7$  and  $\text{CaAl}_{12}\text{O}_{19}$ .** Considerable effort was devoted to the synthesis of hibonite and  $\text{CaAl}_4\text{O}_7$ ; the synthesis was carried out at the Geophysical Laboratory in Washington, D.C.

The initial attempts at synthesis were carried out at high temperature and high pressure in a piston-cylinder device. Stoichiometric mixtures of  $\text{CaCO}_3$  and  $\text{Al}_2\text{O}_3$ , on the  $\text{CA}_6$  and  $\text{CA}_2$  compositions, were sealed in Pt capsules and run at 15 kbars and  $1450^\circ\text{C}$  for 20 hours. In each case the reaction product contained a great deal of unreacted corundum. Another attempt at high-pressure synthesis of  $\text{CA}_2$  was carried out hydrothermally at  $1450^\circ\text{C}$  and 15 kbar for 135 hours. Examination of the run product with a scanning electron microscope (SEM) showed substantial amounts of unreacted corundum again. Apparently,  $\text{CaO} + \text{Al}_2\text{O}_3$  is the stable high-pressure phase assemblage, rather than  $\text{CA}_6$  and  $\text{CA}_2$ . Hence, high pressure techniques were abandoned in favor of repeated cycles of grinding and 1 bar sinterings to synthesize the two phases.

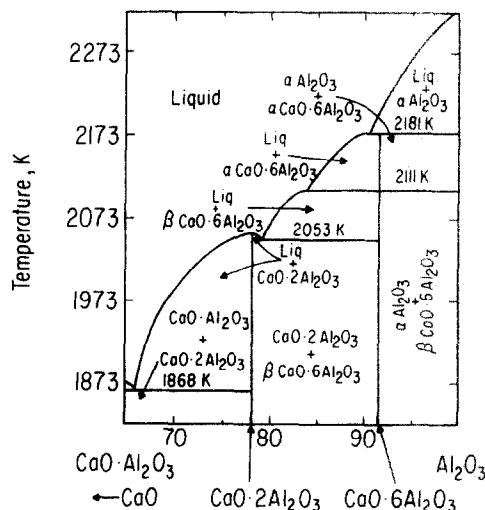


FIG. 1. The phase diagram of the  $\text{CaO} + \text{Al}_2\text{O}_3$  system in the alumina-rich region (after ROLIN and THANH, 1965).

A starting mixture on the composition  $\text{CaAl}_4\text{O}_7$  was prepared by heating an intimate mixture of  $\text{CaCO}_3$  and  $\text{Al}_2\text{O}_3$  at  $1250^\circ\text{C}$  overnight. This mixture was then subjected to a number of cycles of high-temperature sintering and intermediate grinding operations as follows: five cycles of 4 to 6 hours at  $1650^\circ\text{C}$ , three 15-hour sinterings at  $1600$ – $1650^\circ\text{C}$ , one 24-hour sinter at  $1550^\circ\text{C}$  and then again for 72 hours, with a final heating for 240 hours at  $1400^\circ\text{C}$ .

Two samples of  $\text{CaAl}_{12}\text{O}_{19}$  were synthesized. The first, labelled here hibonite-A, received nine cycles of sintering between  $1500^\circ\text{C}$  and  $1625^\circ\text{C}$ , interrupted by grindings in between. The total heating period for all cycles was about 400 hours. The second sample, hibonite-B, was made similarly.

All synthesis products were characterized by X-ray diffraction, optical microscopy and microbeam analysis, the latter by means of an SEM equipped with an energy-dispersive, X-ray detector. The samples were difficult to characterize by optical examination due to their fine grain size and the optical similarity between hibonite and corundum, which are both hexagonal.

X-ray powder diffraction scans revealed no peaks other than those of  $\text{Ca}_2$  in the sample of that composition. In both hibonite samples, however, the three most intense reflections of  $\alpha\text{-Al}_2\text{O}_3$  were present at low intensities, in addition to those of  $\text{Ca}_6$ . Relative peak heights suggest that  $\text{Al}_2\text{O}_3$  is only a minor constituent (<10%) in the hibonite. Unit-cell dimensions of both hibonite samples and  $\text{CaAl}_4\text{O}_7$  were determined by slow X-ray scans using  $\text{CuK}_\alpha$  radiation at a scanning rate of  $1/8^\circ (2\theta)$  per minute in the range  $10^\circ$ – $70^\circ$ ; this was followed by least-squares refinement of the data. An internal standard of synthetic spinel,  $\text{MgAl}_2\text{O}_4$ , was used in the scans. All reflections were assignable based upon comparisons with standard X-ray patterns available in the JCPDS compilation. Unit-cell parameters and molar volumes are given in Table 1. Between 15 and 20 reflections were used in the refinements. Cell constants obtained are in reasonable agreement with those listed in the JCPDS files.

Powders from the hibonite-A, hibonite-B and  $\text{Ca}_2$  synthesis products were set in epoxy on glass slides which were polished, carbon-coated and studied with the SEM. In agreement with the X-ray diffraction results, back-scattered electron images revealed the presence of a second phase in both hibonite-A and hibonite-B which was found by energy-dispersive analysis to be corundum. This material may be from the corundum mortar used for grinding. Additional phases, such as  $\text{CaO}$  and other calcium aluminates, were searched for carefully, but not detected. In the case of the  $\text{Ca}_2$  run product, however, impurity phases were found by SEM examination which were undetected by X-ray diffraction. These are hibonite and tiny grains of a calcium silicate phase (Fig. 2). The latter are smaller than the electron beam spot size, preventing analysis of the pure phase without

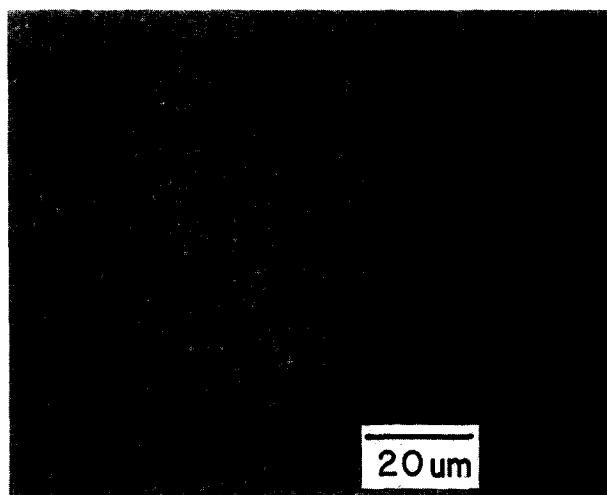


FIG. 2. Backscattered electron photomicrograph, showing a typical sample of synthetic  $\text{CaAl}_4\text{O}_7$ . Light gray matrix is  $\text{CaAl}_4\text{O}_7$ . Dark, angular crystals, some with hexagonal outline, are hibonite. Tiny, bright specks are an unidentified, Ca-bearing silicate, and rounded, black areas are cavities.

contamination by surrounding  $\text{CaAl}_4\text{O}_7$ . The phase has a Ca/Si atomic ratio of  $\sim 0.75$  and may or may not contain alumina. The source of the  $\text{SiO}_2$  in this phase is probably the agate mortar in which the grinding steps occurred. Because this phase has a higher Ca/Al ratio than the bulk sample, a phase with a lower Ca/Al ratio had to form, resulting in the hibonite.

Modal abundances of all phases present in all run products were determined by point-counting SEM back-scattered electron photos taken at a magnification of 1000 $\times$ . In the case of  $\text{Ca}_2$ , 39,000 points were counted in an area of  $40,600 \mu\text{m}^2$ , yielding  $90.84 \pm 0.48\%$   $\text{CaAl}_4\text{O}_7$ ,  $7.03 \pm 0.13\%$   $\text{CaAl}_{12}\text{O}_{19}$  and  $2.13 \pm 0.07\%$  silicate by volume. Assuming the silicate to have a density midway between that of  $\text{CaSiO}_3$  and  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ,  $\rho = 2.97$ , yields  $89.00 \pm 0.47\%$   $\text{CaAl}_4\text{O}_7$ ,  $8.86 \pm 0.16\%$   $\text{CaAl}_{12}\text{O}_{19}$  and  $2.14 \pm 0.07\%$  silicate by weight. A total of 28,500 points were counted in  $58,300 \mu\text{m}^2$  of the hibonite-A and hibonite-B samples, yielding  $91.48 \pm 0.57\%$   $\text{CaAl}_{12}\text{O}_{19}$  and  $8.52 \pm 0.18\%$  corundum by weight. These data were used to correct the heat of solution values of our synthetic run products for the presence of impurities. The silicate impurity in the synthetic  $\text{CaAl}_4\text{O}_7$  was considered to be  $\text{CaSiO}_3$  and the final correction to the heat of formation was made using the heat of solution values for  $\text{CaO}$  and  $\text{SiO}_2$  (BROUSSE *et al.*, 1984) and the heat of formation of  $\text{CaSiO}_3$  (ROBIE *et al.*, 1979). This correction has a very minor effect on the final corrected heat of solution value for  $\text{CaAl}_4\text{O}_7$ .

The method of synthesis of calcium aluminates used here, multiple cycles of heating and grinding stoichiometric mixtures of decarbonated  $\text{CaCO}_3$  and  $\text{Al}_2\text{O}_3$ , is similar to that employed in other recent studies of the thermodynamic properties of these materials (POPOV *et al.*, 1979; SKOLIS *et al.*, 1981; ALLIBERT *et al.*, 1981; KUMAR and KAY, 1985). In the latter studies, the purity of the run products was assessed by X-ray diffraction. We have found that formation of pure  $\text{CaAl}_{12}\text{O}_{19}$  and pure  $\text{CaAl}_4\text{O}_7$  is very difficult by this technique, despite our use of far longer total heating times, far longer heating times above  $1500^\circ\text{C}$ , more intermediate grinding steps and usually higher maximum temperature than in the earlier studies. Furthermore, our SEM studies of  $\text{CaAl}_4\text{O}_7$  run products revealed the presence of significant amounts of impurities that were undetected by X-ray diffraction, suggesting that the latter technique is insufficient to establish the purity of these materials.

#### (b) Calorimetric methods

The technique of high-temperature oxide melt solution calorimetry has been used extensively to determine the enthalpies of formation

Table 1. Unit-cell constants of  $\text{CaAl}_4\text{O}_7$  and  $\text{CaAl}_{12}\text{O}_{19}$ . (Numbers in parentheses are uncertainties in last significant figures.)

Phase	a (Å)	b (Å)	c (Å)	$\beta$ (Deg)	V (Å <sup>3</sup> )
$\text{CaAl}_4\text{O}_7$	12.882(5)	8.879(3)	5.451(2)	107.04(3)	598.07(42)
This study					
$\text{CaAl}_4\text{O}_7$	12.888(1)	8.888(1)	5.443(1)	106.93(1)	598.5
BALDOCK <i>et al.</i> (1970)					
$\text{CaAl}_{12}\text{O}_{19}$	5.5580(3)		21.897(1)		585.81(06)
This study-A					
$\text{CaAl}_{12}\text{O}_{19}$	5.5594(10)		21.895(5)		586.02(19)
This study-B					
$\text{CaAl}_{12}\text{O}_{19}$	5.561		21.880		---
JCPDS					
$\text{CaAl}_{12}\text{O}_{19}$	5.80		22.08		---
IHINGER and STOLPER (1986)					
$\text{CaAl}_{12}\text{O}_{19}$ *					
Madagascar	5.597(2)		22.20(1)		---
Leoville	5.57(1)		22.01(3)		---
KEIL and FUCHS (1971)					

\*All samples are synthetic, except the Madagascar hibonite which has been described by CURIEN *et al.* (1958) and Leoville hibonite which is from a meteorite and has been described by KEIL and FUCHS (1971).

of various silicate and oxide compounds (KLEPPA, 1972; NAVROTSKY, 1979). The procedures used in the present study were similar to those of GEIGER (1986). The calorimetric measurements were performed at  $1063 \pm 10$  K in a Ni-block, Calvet-type, twin calorimeter (KLEPPA, 1972; KLEPPA, 1976). The solvent was a eutectic mixture of  $(\text{Li, Na})_2\text{B}_2\text{O}_4$  which was stored in a desiccator to minimize water absorption. The procedure for making this solvent has been described by CHATILLON-COLINET *et al.* (1983). The same master batch of solvent was used in all experiments in order to eliminate any variations in the melt which might influence the magnitude of the heats of solution. For each experiment, about 40 mg of powdered sample was dissolved in a 10 g batch of alkali borate melt. Five or six dissolutions were made in each batch of solvent. Fairly vigorous stirring ensured good dissolution. After each series of experiments, the melt was quenched on a large silver plate. The melt was clear and transparent and did not contain any unreacted material.

The temperature sensitive elements of the two calorimeters were two 48-couple Pt-Pt13Rh thermopiles connected in series but bucked against each other. The heat effects generated a d.c. signal which was recorded electronically and displayed visually with a Leeds and Northrup Azar recorder. The signal was integrated digitally using a small computer. The total integrated area under the temperature-time curve is proportional to the heat effect. A typical dissolution experiment lasted about 40 minutes. The heat effect due to stirring was subtracted from the heat effect resulting from dissolution. Experiments with longer dissolution times or giving rise to a shift in base line were rejected. The observed heat effects were of the order of 10–12 joules. The calorimeter was calibrated frequently by dropping small pieces of 1 mm diameter gold wire from room temperature into the calorimeter. Around six or seven drops were made for each calibration, which was calculated on the basis of the enthalpy equations for gold given by KELLEY (1960).

### 3. RESULTS AND DISCUSSION

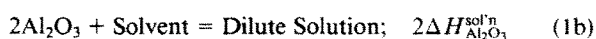
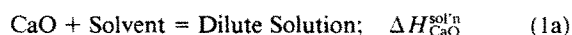
The possibility that errors might arise in solution calorimetry if rigorous stoichiometry is not maintained in the reaction scheme has been discussed by HEMINGWAY and ROBIE (1973) and CHARLU *et al.* (1978). As noted by CHARLU *et al.* (1978), this problem is particularly important if the enthalpies of solution are numerically large as they frequently are in HF solution calorimetry. On the other hand, this problem is not quite as severe in oxide melt calorimetry where the heats of solution are much smaller in magnitude.

A basic tenet underlying the methods used in the present work is that the solution experiments are carried out under conditions that approach those that apply at infinite dilution. Under these conditions there will be no solute-solute interaction in the melt, and the enthalpy of formation can be calculated from the observed enthalpies of solution of the individual constituents in the same solvent. The following example illustrates the scheme:

Formation reaction:



Dissolution reactions:



If solute-solute interactions are neglected, we have:

$$\begin{aligned} \Delta H_{f, \text{CaAl}_4\text{O}_7}^0 (1063 \text{ K, from oxides}) \\ = \Delta H_{\text{CaO}}^{\text{sol'n}} + 2\Delta H_{\text{Al}_2\text{O}_3}^{\text{sol'n}} - \Delta H_{\text{CaAl}_4\text{O}_7}^{\text{sol'n}} \quad (1d) \end{aligned}$$

The calculated heat of formation,  $\Delta H_f$ , will not depend on the amounts of solute dissolved in the solvent as long as the condition of very dilute solution is maintained. That this is in fact the case is demonstrated by the results of successive heat of solution measurements in the same batch of solvent. Within our experimental error of about  $\pm 2\%$ , we were unable to detect any systematic changes in the observed enthalpies of solution for five or six consecutive dissolutions. Moreover, this was the case both for successive dissolutions of  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$ , and for alternating dissolutions of these two oxides. It also held for runs with  $\text{CaAl}_4\text{O}_7$  and with  $\text{CaAl}_{12}\text{O}_{19}$ . In other words, no systematic changes in the enthalpies of solution were observed, regardless of the solutes used or the order in which they were dissolved. This observation is consistent with past experience in this laboratory.

Table 2 summarizes the observed average enthalpies of solution of the phases studied in the course of the present investigation. Also given are the numbers of experiments averaged in parentheses and the calculated standard deviations. For  $\text{CaAl}_4\text{O}_7$  and  $\text{CaAl}_{12}\text{O}_{19}$ , we also give corrected enthalpies of solution, taking into account corrections for impurities based on analytical information given above.

#### (a) Standard enthalpy of formation of $\text{CaAl}_4\text{O}_7$

From the data in Table 2, we calculate the standard enthalpy of formation of  $\text{CaAl}_4\text{O}_7$  from the oxides at 1063 K to be:

$$\begin{aligned} \Delta H_{f, \text{CaAl}_4\text{O}_7}^0 (1063 \text{ K, oxides}) \\ = -(25.6 \pm 4.7) \text{ kJ/g.f.w.} \quad (2) \end{aligned}$$

This value can be referred to 298 K using the heat capacity equations for  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  given by ROBIE *et al.* (1979) and the corresponding equation for  $\text{CaAl}_4\text{O}_7$  of BONNICKSON (1955). We get

$$\Delta H_{f, \text{CaAl}_4\text{O}_7}^0 (298 \text{ K, oxides}) = -20.9 \text{ kJ/g.f.w.} \quad (3)$$

The error in this value is at least  $\pm 4.7$  kJ/g.f.w. Using the standard enthalpies of formation of  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  at 298 K given by ROBIE *et al.* (1979), this result yields for the standard enthalpy of formation from the elements

$$\Delta H_{f, \text{CaAl}_4\text{O}_7}^0 (298 \text{ K, elements}) = -4.007 \text{ kJ/g.f.w.} \quad (4)$$

Neglecting the unknown uncertainty which arises from the

Table 2. Average enthalpies of solution of listed phases at  $1063 \pm 10$  K in a eutectic mixture of  $\text{NaBO}_2$ - $\text{LiBO}_2$  solvent. (Number in parentheses are the numbers of experiments performed. The error limits represent one standard deviation.)

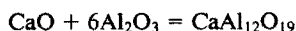
Phase	$\Delta H^{\text{sol'n}}$ , kJ/g.f.w.	
	Measured	Corrected
$\text{Al}_2\text{O}_3$	$52.59 \pm 1.13$ (10)	
$\text{CaO}$	$-23.39 \pm 0.88$ (7)	
$\text{CaAl}_4\text{O}_7$	$109.33 \pm 2.97$ (4)	$107.4 \pm 4.3$
$\text{CaAl}_{12}\text{O}_{19}$	$326.27 \pm 9.00$ (11)	$325.2 \pm 9.2$

heat capacity equations, but including the error limits given by ROBIE *et al.* (1979) for the enthalpies of formation of  $\text{Al}_2\text{O}_3$  ( $\pm 1.3$  kJ) and  $\text{CaO}$  ( $\pm 0.88$  kJ), we find the probable error in this value to be  $\pm 5.2$  kJ/g.f.w. Our new value for  $\Delta H_f^\circ$  (298, elements) is compared with other recently published estimates in Table 3.

Note that our value is in excellent agreement with that calculated by SKOLIS *et al.* (1981) from high-temperature electrochemical measurements extrapolated to lower temperatures. However, our value is more exothermic than that advanced by ELIEZER *et al.* (1981, 1982), and much less exothermic than that recommended by GLUSHKO (1979). It is also considerably less exothermic than the value advanced by HEMINGWAY (1982). This latter value was derived and corrected from the early HF solution calorimetry of KOEHLER *et al.* (1961). The difference of about 17 kJ/g.f.w. is far outside the sum of the errors estimated in both studies. ELIEZER *et al.* (1982), in a reply to HEMINGWAY (1982), reject his revised value of  $\Delta H_f^\circ$  (298 K) as untenable because it would make  $\text{CaAl}_4\text{O}_7$  too stable with a melting point too high. The present authors do not accept this argument because the observed  $\text{CaO} - \text{Al}_2\text{O}_3$  phase diagram, in large measure, reflects the free energy differences between the solid and liquid phases which are in equilibrium, rather than the properties of the solid phase alone. (There are no reliable thermodynamic data on the liquid mixtures of  $\text{CaO} + \text{Al}_2\text{O}_3$ .)

(b) Standard enthalpy of formation of  $\text{CaAl}_{12}\text{O}_{19}$  ( $\text{CA}_6$ ), hibonite

From the data in Table 2, we find for the reaction



$$\Delta H_{f,\text{CaAl}_{12}\text{O}_{19}}^\circ (1063 \text{ K, oxides}) = -(33.0 \pm 9.7) \text{ kJ/g.f.w.} \quad (5)$$

Since high-temperature heat capacity data for hibonite are not available, this value cannot be referred to 298 K in any rigorous manner. However, if we make the plausible assumption that  $\Delta C_p(T, P) \cong 0$  for the formation reactions between 1063 K and 298 K, the value given in Eqn. (5) should also apply to a reasonable approximation at 298 K.

If we combine this value with the enthalpies of formation of  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  from the elements (with their uncertainties (ROBIE *et al.*, 1979)), we obtain for the standard enthalpy of formation of  $\text{CaAl}_{12}\text{O}_{19}$  from the elements at 298 K

$$\begin{aligned} \Delta H_{f,\text{CaAl}_{12}\text{O}_{19}}^\circ (298 \text{ K; from elements}) \\ = -10,722 \pm 12 \text{ kJ/g.f.w.} \quad (6) \end{aligned}$$

Table 3. Standard enthalpy of formation of  $\text{CaAl}_4\text{O}_7$  from the elements at 298 K and 1 bar according to different sources.

Reference	$\Delta H_f^\circ$ (298 K; from elements) kJ/g.f.w.
SKOLIS <i>et al.</i> (1981)	$-4,011.2 \pm 7.5$
GLUSHKO (1979)	$-4,029.6 \pm 6.3$
ELIEZER <i>et al.</i> (1982)	$-3,995.3 \pm 3.0$
HEMINGWAY (1982)	$-4,023.6 \pm 4.6$
Present study	$-4,007 \pm 5.2$ (est.)

Table 4. Standard enthalpy of formation of  $\text{CaAl}_{12}\text{O}_{19}$  at 298 K and 1 bar according to different sources.

Reference	$\Delta H_f^\circ$ (298 K; from elements) kJ/g.f.w.
GLUSHKO (1979)	$-10,742.8 \pm 12.9$
ELIEZER <i>et al.</i> (1982)	$-10,605.2 \pm 10$
HEMINGWAY (1982)	$-10,813 \pm 20$
Present study	$-10,722 \pm 12$ (est.)

In Table 4 we give a summary of values of this quantity taken from recent sources compared with our own result.

Note that our experimentally determined result is *much more* exothermic than that calculated by ELIEZER *et al.* (1981) from phase diagram analysis. In fact, ELIEZER *et al.* argue that  $\text{CA}_6$  is endothermic from the oxides and hence entropy stabilized. As was also the case for  $\text{CaAl}_4\text{O}_7$ , our new value is *much less* exothermic than the estimated value advanced by HEMINGWAY (1982) on the basis of a corresponding states argument,  $-10813.0 \pm 20$  kJ. On the other hand, our result is in plausible agreement with that given by GLUSHKO (1979).

(c) Comparison with enthalpy data for other mixed oxide phases in the system  $\text{CaO} - \text{Al}_2\text{O}_3$

Although many questions regarding the details of the  $\text{CaO} - \text{Al}_2\text{O}_3$  binary phase diagram remain unanswered, there seems to be general agreement that the principal intermediate phases in this system, apart from  $\text{CA}_2$  and  $\text{CA}_6$ , are  $\text{CA}(\text{CaAl}_2\text{O}_4)$ ,  $\text{C}_{12}\text{A}_7(\text{Ca}_{12}\text{Al}_{14}\text{O}_{33})$ , and  $\text{C}_3\text{A}(\text{Ca}_3\text{Al}_2\text{O}_6)$ . In the discussion above, we compared our new enthalpy data for  $\text{CA}_2$  and  $\text{CA}_6$  with values for these phases advanced in earlier studies. It remains to compare our new results with earlier calorimetric data for  $\text{C}_3\text{A}$ ,  $\text{C}_{12}\text{A}_7$ , and  $\text{CA}$ .

The enthalpies of formation of these three compounds, from metallic aluminum and calcium oxide, were determined by hydrochloric acid calorimetry by COUGHLIN (1956). Referred to  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$ , Coughlin reported the following values:

$$\begin{aligned} \Delta H_{f,\text{Ca}_3\text{Al}_2\text{O}_6}^\circ (298 \text{ K; from oxides}) \\ = -(6.56 \pm 1.38) \text{ kJ/g.f.w.} \end{aligned}$$

$$\begin{aligned} \Delta H_{f,\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}}^\circ (298 \text{ K; from oxides}) \\ = -(79.37 \pm 11.13) \text{ kJ/g.f.w.} \end{aligned}$$

$$\begin{aligned} \Delta H_{f,\text{CaAl}_2\text{O}_4}^\circ (298 \text{ K; from oxides}) \\ = -(15.43 \pm 1.46) \text{ kJ/g.f.w.} \end{aligned}$$

A more recently determined value for  $\text{CaAl}_2\text{O}_4$  is available from the oxide melt solution calorimetry work of NAVROTSKY *et al.* (1982) and WESTRICH and NAVROTSKY (1981):

$$\Delta H_{f,\text{CaAl}_2\text{O}_4}^\circ (298 \text{ K; from oxides}) = -(12.9 \pm 2) \text{ kJ/g.f.w.}$$

This value is in reasonable agreement with that of COUGHLIN (1956).

In order to compare our results for  $\text{CA}_2$  and  $\text{CA}_6$  with these earlier values, which apply for mixed oxides with other stoichiometries, all the enthalpies of formation [from the oxides, referred to one mole of  $(\text{CaO} + \text{Al}_2\text{O}_3)$ ] are plotted against the mole fraction of  $\text{Al}_2\text{O}_3$  in Fig. 3. This comparison shows that our enthalpy of formation for  $\frac{1}{3}\text{CA}_2$  is somewhat more exothermic than, but comparable in magnitude to the two literature values for  $\frac{1}{2}\text{CA}$ ; this is consistent with the general appearance of the  $\text{CaO} - \text{Al}_2\text{O}_3$  phase diagram. Note also that this figure shows that the enthalpy of formation of  $\frac{1}{7}\text{CA}_6$  is more negative than the equivalent mixture of  $(\frac{1}{3}\text{CA}_2 + \text{Al}_2\text{O}_3)$ . Hence, it is not necessary to invoke entropy stabilization for  $\text{CA}_6$  in order to understand the phase diagram as was done by ELIEZER *et al.* (1981). On the other hand, when COUGHLIN's (1956) values of  $\frac{1}{4}\text{C}_3\text{A}$  and  $\frac{1}{19}\text{C}_{12}\text{A}_7$  are compared with  $(\text{CaO} + \frac{1}{2}\text{CA})$ , the possibility of entropy stabilization for  $\text{C}_3\text{A}$  and  $\text{C}_{12}\text{A}_7$  at high temperatures clearly must be considered as a possibility.

(d) Standard entropy of hibonite

There are no low-temperature heat capacity data for hibonite that would allow a calculation of its third law entropy. However, there are a number of high-temperature electrochemical studies that provide information on its Gibbs energy of formation. When these data are compared with our new calorimetric results, calculations of the entropy of formation of hibonite and of its standard entropy,  $S_f^\circ$ , are possible.

KUMAR and KAY (1985) give the following equation for the standard Gibbs energy of formation of  $\text{CaAl}_{12}\text{O}_{19}$  from the oxides valid between 1100 K and 1500 K:

$$\Delta G_f^\circ(\text{CaAl}_{12}\text{O}_{19}, \text{from oxides}) = -[17,869 + 39.3T \pm 840] \text{ J/g.f.w.} \quad (7)$$

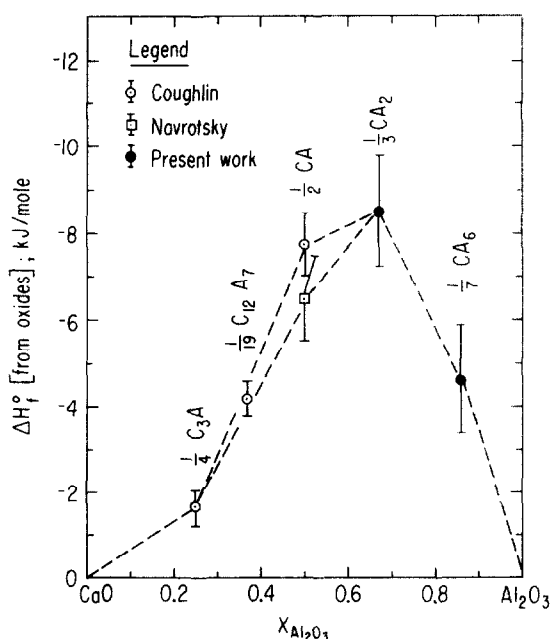


FIG. 3. Standard enthalpies of formation, from  $\text{CaO} + \text{Al}_2\text{O}_3$ , to form indicated intermediate phases. All data refer to the formation of one mole of  $(\text{CaO} + \text{Al}_2\text{O}_3)$ .

ALLIBERT *et al.* (1981) give:

$$\Delta G_f^\circ(\text{CaAl}_{12}\text{O}_{19}, \text{from oxides}) = -[17,430 + 37.2T \pm 1500] \text{ J/g.f.w.} \quad (8)$$

At 1100 K, we get:

$$\Delta G_f^\circ(7) = -[61,099 \pm 840] \text{ J/g.f.w.} \quad (9a)$$

and

$$\Delta G_f^\circ(8) = -[58,350 \pm 1500] \text{ J/g.f.w.} \quad (9b)$$

The average of these values is  $-59,725 \text{ J/g.f.w.}$  This value may be compared with our own result for  $\Delta H_f^\circ$  at 1063 K (which applies with equal confidence also at 1100 K) to yield

$$\begin{aligned} \Delta S_f^\circ(1100 \text{ K}; \text{from oxides}) &= \frac{\Delta H_f^\circ - \Delta G_f^\circ}{1100} \\ &= +24.3 \text{ J/K g.f.w.} \quad (10) \end{aligned}$$

Taking the values of  $S^\circ(1100 \text{ K})$  for  $\text{Al}_2\text{O}_3$  (192.17 J/K g.f.w.) and  $\text{CaO}$  (102.85 J/K g.f.w.) from ROBIE *et al.* (1979), we obtain  $S_{\text{hibonite}}^\circ(1100 \text{ K}) = 1280.2 \text{ J/K g.f.w.}$  Note that this value is only about 2% larger than the oxide sum value. Hence, it may be inferred that the standard entropy of hibonite at 298 K probably is only slightly larger than the oxide sum value of 343.7 J/K g.f.w. HEMINGWAY's (1982) entropy estimate of  $432 \pm 10 \text{ J/K g.f.w.}$  clearly is way out of line. The GLUSHKO (1979) suggestion of  $S^\circ(298) = 376.6 \pm 20.9 \text{ J/K g.f.w.}$  undoubtedly is also too large. A third law determination of the entropy of hibonite would be very desirable.

(e) Effect of new data on condensation calculations

Condensation calculations performed by KORNACKI and FEGLEY (1984) for a gas of solar composition predict the appearance of  $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$  and  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  in the temperature range 1600–1750 K on the basis of Gibbs energy of formation data for the two phases from the electrochemical study of ALLIBERT *et al.* (1981). Since the latter data were obtained over the temperature range 900–1200 K, a relatively long extrapolation is needed to reach the temperature of interest. For our purposes, Gibbs energy of formation data from the electrochemical study of KUMAR and KAY (1985) are preferred, as the quoted uncertainties are a factor of two smaller than in ALLIBERT *et al.* (1981) and the temperature range of the measurements extends to 1500 K, much closer to the temperature of interest than the data of ALLIBERT *et al.* (1981).

From Eqn. (7), we obtain  $\Delta G_f^\circ(1300 \text{ K}; \text{from oxides}) = -69.00 \pm 0.84 \text{ kJ/g.f.w.}$  for hibonite at the middle of the temperature range investigated experimentally by KUMAR and KAY (1985). Without heat capacity data for this phase, we assume  $\Delta H_f^\circ(1300 \text{ K}; \text{from oxides}) = -33.0 \pm 9.7 \text{ kJ/g.f.w.}$ , the same as the experimental value obtained herein at 1063 K. An entropy of formation,  $\Delta S_f^\circ(1300 \text{ K}; \text{from oxides}) = 27.7 \text{ J/K g.f.w.}$ , is obtained as in Eqn. (10). When linear equations are used to describe the variation of  $\Delta G_f^\circ$  over a range of temperature, the slopes should be equivalent to  $-\Delta S_f^\circ$  for that temperature range. Our value for  $\Delta S_f^\circ(1300 \text{ K}; \text{from oxides})$  of hibonite derived from our calorimetric determination of  $\Delta H_f^\circ(1063; \text{from oxides})$  and  $\Delta G_f^\circ(1300;$

from oxides) obtained from Eqn. (7) is lower than that taken from the slope of Eqn. (7) by 30%, suggesting that this equation cannot be used to extrapolate  $\Delta G_f^\circ$  data beyond the temperature range of the experiments of KUMAR and KAY (1985). When Eqn. (8) is used, the discrepancy in  $\Delta S_f^\circ$  values is 39%, suggesting that the ALLIBERT *et al.* (1981) equation cannot be used for temperature extrapolation either. For temperatures greater than 1300 K, we use our calculated value of  $\Delta S_f^\circ$  (1300 K; from oxides) to determine the Gibbs energy of formation from the oxides *via*:

$$\begin{aligned}\Delta G_f^\circ(T > 1300 \text{ K}) &= \Delta G_f^\circ(1300 \text{ K}) \\ &\quad - (T - 1300)\Delta S_f^\circ(1300 \text{ K}) \\ &= -69.00 - .0277(T - 1300) \text{ kJ/g.f.w.} \quad (11)\end{aligned}$$

Our value for the Gibbs energy of formation of hibonite at 1600 K is 0.36 kJ/g.f.w. more negative than that obtained by extrapolating the ALLIBERT *et al.* (1981) equation shown as Eqn. (8), above.

For  $\text{CaAl}_4\text{O}_7$ , we obtain  $\Delta G_f^\circ$  (1300 K; from oxides) =  $-47.67 \pm 1.26$  kJ/g.f.w., again at the middle of the temperature range investigated by KUMAR and KAY (1985). Using heat capacity data for  $\text{CaAl}_4\text{O}_7$  from BONNICKSON (1955) and for  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  from ROBIE *et al.* (1979), we obtain  $\Delta H_f^\circ$  (1300 K; from oxides) =  $-28.78 \pm 5.15$  kJ/g.f.w. from  $\Delta H_f^\circ$  (1063 K; from oxides) measured herein. The entropy of formation,  $\Delta S_f^\circ$  (1300 K; from oxides) = 14.5 J/K g.f.w., is again obtained as in Eqn. (10). As was the case for hibonite, our calculated value of  $\Delta S_f^\circ$  (1300; from oxides) for  $\text{CaAl}_4\text{O}_7$  is substantially lower than estimates obtained from the slopes of the linear fits to electrochemical data for  $\Delta G_f^\circ$  (from oxides) *versus* temperature, by 54% compared to the KUMAR and KAY (1985) results and 51% compared to the ALLIBERT *et al.* (1981) results. For temperatures greater than 1300 K, we again use our calculated value for  $\Delta S_f^\circ$  (1300 K; from oxides) to obtain the Gibbs energy of formation of  $\text{CaAl}_4\text{O}_7$  *via* Eqn. (11) which, in this case, becomes:

$$\begin{aligned}\Delta G_f^\circ(T > 1300 \text{ K; from oxides}) \\ &= -47.67 - .0145(T - 1300) \text{ kJ/g.f.w.} \quad (12)\end{aligned}$$

Our value for the Gibbs energy of formation of  $\text{CaAl}_4\text{O}_7$  at 1600 K is 7.25 kJ/g.f.w. more positive than that obtained by extrapolating the ALLIBERT *et al.* (1981) equation.

LATTIMER and GROSSMAN (1978) presented results of full equilibrium, solar nebular condensation calculations. We have used the same technique as in that paper and an updated set of thermodynamic data, including free energies of hibonite and  $\text{CaAl}_4\text{O}_7$  obtained from Eqn. (11) and Eqn. (12) herein, respectively. In a gas of solar composition at  $10^{-3}$  atm total pressure, we find that corundum condenses first at 1749 K and disappears at 1725 K where it reacts with gaseous Ca to form hibonite. Perovskite condenses at 1675 K. Hibonite begins to react with gaseous Ca and Si to form gehlenite at 1607 K and the hibonite in excess of this reaction reacts totally to form spinel at 1494 K. The sequence of reactions is the same at  $10^{-4}$  and  $10^{-5}$  atm total pressure. Thus,  $\text{CaAl}_4\text{O}_7$  does not form over the entire pressure range investigated.

Considering the uncertainties in the free energies of hibonite and  $\text{CaAl}_4\text{O}_7$ , a dialuminate field does not appear in the condensation sequence at  $10^{-3}$  atm if that phase is as unstable as its error bars permit whether hibonite is made as stable or as unstable as hibonite's error bars permit. Only in the cases where the dialuminate is made as stable as its error bars permit, when hibonite is made as stable or as unstable as hibonite's error bars permit, would the dialuminate have a small stability field. In these cases, hibonite forms by reaction of corundum first and then the dialuminate would form by partial reaction of hibonite with the gas at around 1610 K. Even in these cases, however, the stability field of the dialuminate would be very narrow, as this phase would be completely consumed by reaction with gaseous Si to form either melilite or melilite + hibonite, between 6 and 22° after it formed.

As suspected by MACPHERSON and GROSSMAN (1984),  $\text{CaAl}_4\text{O}_7$  probably has no stability field in a gas of solar composition. This is contrary to the findings of KORNACKI and FEGLEY (1984) who used the calcium aluminate data of ALLIBERT *et al.* (1981). On the basis of their calculations that predicted that  $\text{CaAl}_4\text{O}_7$  is a high-temperature condensate from a solar gas, KORNACKI and FEGLEY (1984) argued that spinel-, hibonite-rich inclusions in C2 chondrites did not form by condensation, since they do not contain  $\text{CaAl}_4\text{O}_7$ . The data in the present paper effectively dismiss this argument. As noted above,  $\text{CaAl}_4\text{O}_7$  has been found in only three inclusions. If this phase has no stability field in a gas of solar composition, the origin of these three  $\text{CaAl}_4\text{O}_7$ -bearing assemblages requires comment. The petrographic and chemical characteristics of these occurrences have been described in too little detail so far to provide clues to their origin. It should be noted, however, that the stability field of  $\text{CaAl}_4\text{O}_7$  lies close enough to solar nebular conditions that  $\text{CaAl}_4\text{O}_7$  occasionally might have been able to form metastably during condensation, particularly if the reaction of hibonite with the gas to form melilite were delayed below the equilibrium temperature for that reaction.

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