

STABILITY OF HIBONITE AND CaAl_4O_7 IN THE SOLAR NEBULA; L. Grossman¹, C.A. Geiger¹, O.J. Kleppa¹, B.O. Mysen², and J.M. Lattimer³. ¹Dept. of the Geophysical Sciences, University of Chicago, Chicago, IL 60637. ²Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20008. ³Dept. of Earth & Space Sciences, SUNY, Stony Brook, NY 11794.

Many calcium aluminates are known, but only two are found in meteorites. Hibonite, $\text{CaAl}_{12}\text{O}_{19}$, has been found in many refractory inclusions in C2 and C3 chondrites (1,2). CaAl_4O_7 , in contrast, has been reported from only 3 refractory inclusions (3,4,5). Equilibrium thermodynamic calculations of the sequence of condensation of phases from a cooling gas of solar composition did not consider calcium aluminates until after free energy data for these compounds were reported by Allibert et al. (6). Fegley (7), Davis et al. (8) and Kornacki & Fegley (9) computed that, at 10^{-3} atm total pressure, corundum condenses first at ~ 1740 K and reacts with gaseous Ca to form hibonite $10\text{--}20^\circ$ lower in temperature. Calculations in (7) and (9) show that, at a still lower temperature, hibonite reacts with the gas to form CaAl_4O_7 . Kornacki & Fegley (9), as a result, used the absence of CaAl_4O_7 from hibonite-bearing inclusions as an argument that the latter are not high-temperature condensates but, instead, formed by partial melting and distillation of dust aggregates. MacPherson & Grossman (10) pointed out, however, that CaAl_4O_7 would disappear completely from the condensation sequence if its free energy were only 6.1 kJ/mole less stable than the value in (6) and suggested that the absence of CaAl_4O_7 from condensate assemblages may be due to incorrect thermodynamic data for this phase. Since differences larger than 6.1 kJ/mole exist in the reported data for CaAl_4O_7 and since no direct calorimetric data exist for hibonite, we determined the enthalpies of formation of CaAl_4O_7 and hibonite by oxide melt solution calorimetry.

Synthetic CaAl_4O_7 and $\text{CaAl}_{12}\text{O}_{19}$ were prepared by heating intimate, stoichiometric mixtures of CaCO_3 and Al_2O_3 at 1250°C overnight. These mixtures were then subjected to a number of cycles of high-temperature sintering and intermediate grinding operations. This is the same synthesis technique used to prepare these compounds in all previous studies of their thermodynamic properties (6,11,12,13), except that care was taken here to use more intermediate grinding steps, far longer total heating times, far longer heating times above 1500°C and usually higher maximum temperatures than in all previous work. For CaAl_4O_7 , 11 cycles were used, ranging from 1 cycle of 240 hr at 1400°C to 5 cycles of 4–6 hr each at 1650°C . For $\text{CaAl}_{12}\text{O}_{19}$, 9 cycles between 1500 and 1625°C were used, totalling 400 hr of heating. In all previous thermodynamic studies, synthetic calcium aluminates were found to be pure by X-ray powder diffraction. X-ray study showed no impurities in our synthetic CaAl_4O_7 but minor amounts of $\alpha\text{-Al}_2\text{O}_3$ in the hibonite. SEM study of our powders, however, revealed hibonite and a calcium silicate in the synthetic CaAl_4O_7 , and corundum in the synthetic hibonite. Excess Al_2O_3 in the hibonite sample and SiO_2 in the CaAl_4O_7 were probably introduced during grinding in Al_2O_3 and agate mortars, respectively. SEM study of CaAl_4O_7 run products thus revealed significant impurities undetected by X-ray diffraction, suggesting that the latter technique may have been insufficient to establish the purity of calcium aluminates prepared for earlier thermodynamic studies (6,11,12,13). From point-count modes of SEM photos, we determined that the heat of solution value obtained for the hibonite sample had to be corrected for the presence of 8.5 wt.% corundum and the value for the CaAl_4O_7 sample had to be corrected for 8.9 wt.% hibonite and 2.1% silicate, assumed to be wollastonite.

Using a Ni-block, Calvet-type, twin calorimeter (14,15), 40 mg samples of powdered CaO , Al_2O_3 , CaAl_4O_7 and $\text{CaAl}_{12}\text{O}_{19}$ were dissolved in 10 g of a eutectic mixture of molten $(\text{Li,Na})_2\text{B}_2\text{O}_4$ as in (16) at $1063 \pm 10^\circ\text{K}$. The heat effect in each dissolution experiment was determined by digital integration of the temperature-time curve generated by two 48-couple Pt-Pt13Rh thermopiles. Frequent calibration was done by dropping small pieces of gold into the calorimeter and measuring the heat effect as the gold rose from room temperature to calorimeter temperature. After correction for impurities, the heat of formation of each of the calcium aluminates from its oxides at 1063 K , $\Delta H_f^\circ(1063)$, was calculated by subtracting its heat of solution from those of its constituent oxides in stoichiometric proportion. $\Delta H_f^\circ(1063) = -25.6 \pm 4.7$ kJ/gfw for CaAl_4O_7 and -33.0 ± 9.7 kJ/gfw for $\text{CaAl}_{12}\text{O}_{19}$.

Kornacki & Fegley (9) used free energy data for CaAl_4O_7 and $\text{CaAl}_{12}\text{O}_{19}$ from the electrochemical study of Allibert et al. (6) in their condensation calculations. Those data were obtained in the temperature range $900\text{--}1200\text{ K}$ and had to be extrapolated to $1600\text{--}1750\text{ K}$, the range of condensation temperatures. Gibbs free energy data for these 2 phases have since become available from the later electrochemical study of Kumar & Kay (13) over the temperature range $1100\text{--}1500\text{ K}$. These data are preferred over those in (6) as the uncertainties are a factor of 2 smaller and the extrapolation to condensation temperatures 250° less than in those of (6). Using the equations given in (13) for the temperature variation of the free energies of formation from the oxides, $\Delta G_f^\circ = -69.00 \pm 0.84$ kJ/gfw for hibonite and -47.67 ± 1.26 kJ/gfw for CaAl_4O_7 at 1300 K , the midpoint of the temperature range investigated experimentally in (13).

Using heat capacity data from (17) and (18), we make the small temperature correction to our measured $\Delta H_f^\circ(1063)$ to yield $\Delta H_f^\circ(1300) = -28.78 \pm 5.15$ kJ/gfw for CaAl_4O_7 from the oxides. Using this value and the above $\Delta G_f^\circ(1300)$ from (13), we calculate $\Delta S_f^\circ(1300) = [\Delta H_f^\circ(1300) - \Delta G_f^\circ(1300)]/1300 = 14.5\text{ J/K gfw}$. Assuming $\Delta G_f^\circ(1300)$ from (13) is correct, our calorimetrically determined $\Delta H_f^\circ(1063)$ results in $\Delta H_f^\circ(1300)$ and $\Delta S_f^\circ(1300)$ which differ by more than a factor of 2 from the intercept and slope, respectively, of the ΔG_f° vs. T equation for CaAl_4O_7 in (13). Thus, the equation in (13) cannot be used for temperature extrapolation. We calculate $\Delta G_f^\circ(1600) = -52.03 \pm 1.95$ kJ/gfw for CaAl_4O_7 from $\Delta G_f^\circ(1300)$ from (13) and our calculated value of $\Delta S_f^\circ(1300)$.

Without heat capacity data for hibonite, we assume $\Delta H_f^\circ(1300) \sim \Delta H_f^\circ(1063)$ determined experi-

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mentally above and calculate $\Delta S_f^\circ(1300) = 27.7 \text{ J/K gfw}$ as above. Again, $\Delta H_f^\circ(1300)$ and $\Delta S_f^\circ(1300)$ determined here are greatly different from the intercept and slope of the equation for hibonite in (13). For hibonite, we calculate $\Delta G_f^\circ(1600) = -77.31 \pm 2.46 \text{ kJ/gfw}$ from $\Delta G_f^\circ(1300)$ from (13) and our value for $\Delta S_f^\circ(1300)$.

Using the same technique as in Lattimer & Grossman (19) but with an updated set of thermodynamic data including free energies for hibonite and CaAl_4O_7 determined herein, we calculated the sequence of condensation of phases from a cooling gas of solar composition. At 10^{-3} atm total pressure, corundum condenses first at 1749 K and disappears at 1725 K where it reacts with gaseous Ca to form hibonite, as shown in Fig. 1. Perovskite condenses at 1675 K. Hibonite begins to react with gaseous Ca and Si to form gehlenite at 1607 K. 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, use of the new thermodynamic data yields no stability field for CaAl_4O_7 in a solar gas over the pressure range 10^{-3} - 10^{-5} atm. Fig. 2 shows the maximum possible stability field of CaAl_4O_7 in a solar gas at 10^{-3} atm, obtained by making CaAl_4O_7 as stable and hibonite as unstable as the error bars on their free energies permit. In this case, hibonite first appears by reaction of corundum with gaseous Ca at 1715 K. Hibonite begins to react with gaseous Ca to form CaAl_4O_7 at 1616 K and disappears at 1605 K. CaAl_4O_7 begins to react with gaseous Ca and Si to form melilite at 1600 K and the CaAl_4O_7 in excess of this reaction is completely converted back to hibonite at 1593 K. After this, hibonite gradually reacts with the gas to form gehlenite, finally disappearing at 1495 K. Thus, even in this extreme case, the stability field of CaAl_4O_7 is only 23° wide. It is unlikely that CaAl_4O_7 has a stability field in a gas of solar composition. Certainly, its absence from refractory inclusions cannot be used as an argument that the latter are not high-temperature condensate assemblages, as was done by Fegley (7) and Kornacki & Fegley (9). The three known occurrences of CaAl_4O_7 in refractory inclusions may be the result of metastable condensation. As the stability field of CaAl_4O_7 lies close to solar nebular conditions, it might have been able to form occasionally if the reaction of hibonite with the gas to form melilite were delayed below its equilibrium temperature.

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Figure 1

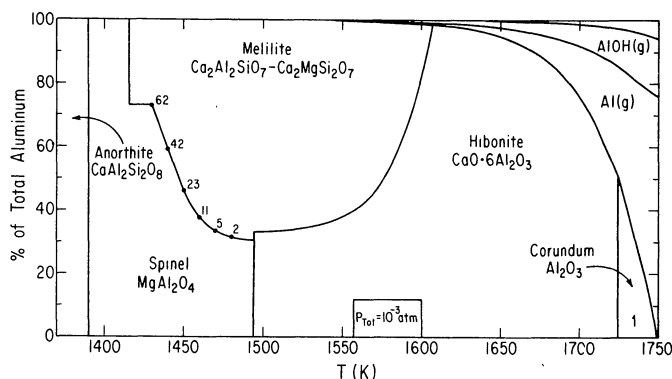


Figure 2

