Enthalpies of formation of CaAl_4O_7 and CaAl_12O_19 (hibonite) by high temperature, alkali borate solution calorimetry

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Abstract—The enthalpies of formation of CaAl_4O_7 and CaAl_12O_19 (hibonite), by alkali borate solution calorimetry at 1063 K are:

\[ \Delta H^\text{f,CaAl_4O_7} (1063 \text{ K}, \text{from oxides}) = -25.6 \pm 4.7 \text{ kJ/g.f.w.} \]

and

\[ \Delta H^\text{f,CA12O_19} (1063 \text{ K}, \text{from oxides}) = -33.0 \pm 9.7 \text{ kJ/g.f.w.} \]

Using experimental enthalpy data for CaAl_4O_7 and estimated values for CaAl_12O_19, the standard enthalpies of formation of these compounds from the elements at 298 K are:

\[ \Delta H^\text{f,CaAl_4O_7} (298 \text{ K, from elements}) = -4.007 \pm 5.2 \text{ kJ/g.f.w.} \]

and

\[ \Delta H^\text{f,CA12O_19} (298 \text{ K, from elements}) = -10.722 \pm 12 \text{ kJ/g.f.w.} \]

Comparison with high-temperature galvanic cell data for the Gibbs energy of formation of CaAl_12O_19 allows a calculation of the standard entropy of hibonite,

\[ S^\text{f,hibonite} (1100 \text{ K}) = 1280.2 \text{ J/K g.f.w.} \]

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 CaAl_4O_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 CaAl_4O_7 in a gas at composition at 10^{-2} to 10^{-3} 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 CaAl_4O_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 CaO-Al_2O_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 CaAl_12O_19 (CA_6; hibonite) and CaAl_4O_7 (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 (CURIE et al., 1956; MAASKANT et al., 1980). Special interest in hibonite and in CaAl_4O_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 TiO_2, MgO, and FeO (KEIL and FUCHS, 1971). The phase CaAl_4O_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...
which can be calculated theoretically. BLANDER and FUCHS (1975) calculated that both hibonite and CaAlO$_3$ 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/mol and $\pm 6.4$ kJ/mol, respectively. Using free energy data for hibonite and CaAlO$_3$ from ALLIBERT et al. (1981), KORNACKI and FEGLEY (1984) calculated that hibonite would have reacted with the solar nebular gas to form CaAlO$_3$ and that CaAlO$_3$ would have reacted to form Ca$_2$Al$_2$SiO$_6$ 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 CaAlO$_3$ used by KORNACKI and FEGLEY (1984) were in error by as little as 6.1 kJ/mol, hibonite would have reacted to form Ca$_2$Al$_2$SiO$_6$ directly, without the appearance of CaAlO$_3$. The common occurrence of hibonite-bearing meteoric inclusions that contain no CaAlO$_3$ 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 CaAlO$_3$ may be incorrect. A review of the literature on the standard thermodynamic properties of CaAlO$_3$ and Ca$_2$Al$_2$O$_6$ reveals that differences larger than 6.1 kJ/mol exist in the reported data for CaAlO$_3$, whereas no direct calorimetric data exist for Ca$_2$Al$_2$O$_6$. 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 CaAlO$_3$ (Ca$_2$), and there has been considerable discussion regarding the correct value of $\Delta H$ for this phase. Its enthalpy of formation was first determined by KOEHLER, et al. (1981) by HF solution calorimetry. Its third law entropy, $S$, was measured by KING (1955), while its high-temperature heat capacity is given in STODDART (1975). HEMINGWAY (1982) advanced a revised value of $\Delta H$, because of errors associated with the Hess cycle data used by KOEHLER et al. (1981) to obtain $\Delta H$. 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 they are well known that aluminous compounds do not dissolve readily in aqueous HF.

There is also a great deal of recent information on $\Delta G$, the free energy of formation, of CaAlO$_3$ (POPOV et al., 1979; SKOLIS et al., 1981; ALLIBERT et al., 1981; KUMAR and KAY, 1985). These studies make use of solid electrolytic galvanic cells to determine $\Delta G$ over a temperature range of several hundred degrees at temperatures of 1000 K and higher. $\Delta H$ 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 CaAlO$_3$ was determined by LAGERQVIST et al. (1933) and confirmed by BOYKO and WISSNY (1958). Although the X-ray data were of poor quality, they proposed that this compound is essentially isosstructural with SrAlO$_3$. The Al$^{3+}$ ions occur in more than one coordination, but in two crystallographically distinct sites (LAGERQVIST et al., 1937). A more recent study of the structure of CaAlO$_3$ confirmed this proposal and yields more accurate cell dimensions and atomic positions (GOODWIN and LINDORF, 1970).

There are no calorimetric data for CaAlO$_3$ (Ca$_2$). Hibonite. Estimates of $\Delta H$ 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 thermodosimetric 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 Mg$^{2+}$, Ti$^{3+}$, Ti$^{4+}$, Fe$^{2+}$, and Fe$^{3+}$ may occur. These cations substitute for 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 CaO - Al$_2$O$_3$ phase diagram is shown in Fig. 1. It will be noted that both CaAlO$_3$ and Ca$_2$Al$_2$O$_6$ have very high melting points. While hibonite melts incongruently at 2181 K to corundum and a liquid richer in CaO, Ca$_2$Al$_2$O$_6$ melts congruently at about 2085 K.

2. EXPERIMENTAL

(a) Preparation and characterization of materials

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

Al$_2$O$_3$. The alumina was from two sources. The first sample was prepared by firing a pellet of Al$_2$O$_3$ (Fisher-Certified) at 1300°C for 48 hours. It was the same material previously used by CHATILLON-COLINET et al. (1983). The second sample of Al$_2$O$_3$ (Baker-Ultrex) was prepared by sintering a pellet at 1400°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.

CaAlO$_3$ and Ca$_2$Al$_2$O$_6$. Considerable effort was devoted to the synthesis of hibonite and CaAlO$_3$; 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 CaCO$_3$ and Al$_2$O$_3$, on the Ca$_2$ and Ca$_4$ compositions, were sealed in Pt capsules and run at 15 kbars and 1450°C for 20 hours. In each case the reaction product contained a great deal of unreacted corundum. Another attempt at high pressure synthesis of Ca$_2$ was carried out hydrothermally at 1450°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, CaO + Al$_2$O$_3$ is the stable high-pressure phase assemblage, rather than Ca$_2$ and Ca$_4$. 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 CaO - Al$_2$O$_3$ system in the alumina-rich region (after ROLIN and THANH, 1965).](image)
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°C, three 15-hour sintering at 1600-1650°C, one 24-hour sinter at 1550°C and then again for 72 hours, with a final heating for 240 hours at 1400°C.

Two samples of CaAl2O4 were synthesized. The first, labelled here hibonite-A, received nine cycles of sintering between 1500°C and 1625°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 CA2 in the sample of that composition. In both hibonite samples, however, the three most intense reflections of α-Al2O3 were present at low intensities, in addition to those of CA2. Relative peak heights suggest that Al2O3 is only a minor constituent (<10%) in the hibonite. Unit-cell dimensions of both hibonite samples and CaAl2O4 were determined by slow X-ray scans using CuKα radiation at a scanning rate of 6°(2θ) per minute in the range 10°-70°; this was followed by least-squares refinement of the data. An internal standard of synthetic spinel, MgAl2O4, 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 CA2 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 CaO and other calcium aluminates, were searched for carefully, but not detected. In the case of the CA2 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 contamination by surrounding CaAl2O4. The phase has a Ca/Al atomic ratio of ~0.75 and may or may not contain alumina. The source of the SiO2 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 toution, forming 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×. In the case of CA2, 39,000 points were counted in an area of 40,600 μm², yielding 90.84 ± 0.48% CaAl2O4, 7.03 ± 0.13% CaAl12O19 and 2.13 ± 0.07% silicate by volume. Assuming the silicate to have a density midway between that of CaSiO3 and Ca3Al2Si2O8, p = 2.97, yields 89.00 ± 0.47% CaAl2O4, 8.86 ± 0.16% CaAl12O19 and 2.14 ± 0.07% silicate by weight. A total of 28,500 points were counted in 58,300 μm² of the hibonite-A and hibonite-B samples, yielding 91.48 ± 0.57% CaAl2O4 and 8.52 ± 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 CaAl2O4 was considered to be CaSiO3 and the final correction to the heat of formation was made using the heat of solution values for CaO and SiO2 (BROUSSO et al., 1984) and the heat of formation of CaSiO3 (ROBB et al., 1979). This correction has a very minor effect on the final corrected heat of solution value for CaAl2O4.

The method of synthesis of calcium aluminates used here, multiple cycles of heating and grinding stoichiometric mixtures of decarbonated CaCO3 and Al2O3, 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 CaAl2O4 and pure CaAl12O19 is very difficult by this technique, despite our use of far longer total heating times, far longer heating times above 1500°C, more intermediate grinding steps and usually higher maximum temperature than in the earlier studies. Furthermore, our SEM studies of CaAl2O4 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

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Table 1. Unit-cell constants of CaAl2O4 and CaAl12O19. (Numbers in parentheses are uncertainties in last significant figures.)

<table>
<thead>
<tr>
<th>Phase</th>
<th>a   (Å)</th>
<th>b   (Å)</th>
<th>c   (Å)</th>
<th>β   (°)</th>
<th>V   (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaAl2O4</td>
<td>5.805(1)</td>
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<td>5.805(1)</td>
<td>90.5(1)</td>
<td>469.4(1)</td>
</tr>
<tr>
<td>CaAl12O19</td>
<td>5.581(1)</td>
<td>21.880(1)</td>
<td>3.613(1)</td>
<td>90.5(1)</td>
<td>892.4(1)</td>
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</table>

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*All samples are synthetic, except the Madagascar hibonite which has been described by CURRIE et al. (1955) and Leoville hibonite which is from a meteorite and has been described by KELL and FUCHS (1971).
of various silicate and oxide compounds (Kleppl, 1972; Navrot, 1979). The procedure used in the present study was similar to those of Geiger (1986). The calorimetric measurements were performed at 1063 ± 10 K in a Na-block Calvet-type twin calorimeter (Kleppl, 1972; Kleppl, 1976). The solvent was a eutectic mixture of (Li, Na)_2B_4O_7 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 248-couple Pt-Pt3Rh 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 6 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 Chari 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:**

\[
\text{CaO} + 2\text{Al}_2\text{O}_3 = \text{CaAl}_2\text{O}_7
\]  

(1)

**Dissolution reactions:**

\[
\begin{align*}
\text{CaO} + \text{Solvent} &= \text{Dilute Solution} \quad \Delta H_{\text{CaO}}^{\text{soln}} \quad (\text{la}) \\
2\text{Al}_2\text{O}_3 + \text{Solvent} &= \text{Dilute Solution} \quad 2\Delta H_{\text{Al}_2\text{O}_3}^{\text{soln}} \quad (\text{lb}) \\
\text{CaAl}_2\text{O}_7 + \text{Solvent} &= \text{Dilute Solution} \quad \Delta H_{\text{CaAl}_2\text{O}_7}^{\text{soln}} \quad (\text{lc})
\end{align*}
\]

If solute-solute interactions are neglected, we have:

\[
\Delta H_{\text{CaAl}_2\text{O}_7}^{\text{soln}} = \Delta H_{\text{CaO}}^{\text{soln}} + 2\Delta H_{\text{Al}_2\text{O}_3}^{\text{soln}} - \Delta H_{\text{CaAl}_2\text{O}_7}^{\text{soln}} \quad (1d)
\]

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 ±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 \Al_2\text{O}_3 and \text{CaO}, and for alternating dissolutions of these two oxides. It also held for runs with \CaAl_2\text{O}_4 and with \CaAl_2\text{O}_7. 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 \CaAl_2\text{O}_4 and \CaAl_2\text{O}_7, 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 \CaAl_2\text{O}_7:**

From the data in Table 2, we calculate the standard enthalpy of formation of \CaAl_2\text{O}_7 from the oxides at 1063 K to be:

\[
\Delta H_f^{\text{CaAl}_2\text{O}_7} (1063 \text{ K, oxides}) = -(25.6 \pm 4.7) \text{ kJ/g.f.w.} \quad (2)
\]

This value can be referred to 298 K using the heat capacity equations for \CaO and \Al_2\text{O}_3 given by Robie et al. (1979) and the corresponding equation for \CaAl_2\text{O}_7 of Bonnickson (1955). We get

\[
\Delta H_f^{\text{CaAl}_2\text{O}_7} (298 \text{ K, oxides}) = -20.9 \text{ kJ/g.f.w.} \quad (3)
\]

The error in this value is at least ±2.7 kJ/g.f.w. Using the standard enthalpies of formation of \Al_2\text{O}_3 and \CaO at 298 K given by Robie et al. (1979), this result yields for the standard enthalpy of formation from the elements

\[
\Delta H_f^{\text{CaAl}_2\text{O}_7} (298 \text{ K, elements}) = -4.007 \text{ kJ/g.f.w.} \quad (4)
\]

Neglecting the unknown uncertainty which arises from the

<table>
<thead>
<tr>
<th>Phase</th>
<th>(\Delta H_f^{\text{soln}}), kJ/g.f.w.</th>
</tr>
</thead>
<tbody>
<tr>
<td>\Al_2\text{O}_3</td>
<td>52.59 ± 1.15 (10)</td>
</tr>
<tr>
<td>\CaO</td>
<td>-29 ± 6 (11)</td>
</tr>
<tr>
<td>\CaAl_2\text{O}_7</td>
<td>109.23 ± 2.97 (4)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>\CaAl_2\text{O}_4</td>
<td>326.27 ± 9.00 (11)</td>
</tr>
</tbody>
</table>

Table 2: Averaged enthalpies of solution of listed phases at 1063 ± 10 K in a eutectic mixture of \NaBO_3-LiBO_2 solvent. (Numbers in parentheses are the numbers of experiments performed. The error limits represent one standard deviation.)
heat capacity equations, but including the error limits given by Robie et al. (1979) for the enthalpies of formation of \( \text{Al}_2\text{O}_3 \) (±1.3 kJ) and \( \text{CaO} \) (±0.88 kJ), we find the probable error in this value to be ±5.2 kJ/g.f.w. Our new value for \( \Delta H_f^0 \) (298, elements) is compared with other recently published estimates in Table 3.

Note that our value is in excellent agreement with that calculated by Skolik 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 Kohler (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 \( \Delta H_f^0 \) (298 K) as untenable because it would make \( \text{CaAl}_2\text{O}_4 \) 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 \( \text{CaAl}_2\text{O}_4 \) (CA6), hibonite

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

\[
\text{CaO} + 6\text{Al}_2\text{O}_3 = \text{CaAl}_2\text{O}_4
\]

\[
\Delta H_f^0(\text{CaAl}_2\text{O}_4) = -(33.0 \pm 9.7) \text{ kJ/g.f.w.}
\]  

(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 \( \Delta C_P(T, P) \approx 0 \) 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 \( \text{CaAl}_2\text{O}_4 \) from the elements at 298 K

\[
\Delta H_f^0(\text{CaAl}_2\text{O}_4) = -(10.722 \pm 12) \text{ kJ/g.f.w.}
\]  

(6)

Table 3. Standard enthalpy of formation of \( \text{CaAl}_2\text{O}_4 \) from the elements at 298 K and 1 bar according to different sources.

<table>
<thead>
<tr>
<th>Reference</th>
<th>( \Delta H_f^0 ) (298 K; from elements)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SKOLIS et al. (1981)</td>
<td>-4.011.2 ± 7.3</td>
</tr>
<tr>
<td>GLUSHKO (1979)</td>
<td>-4.028.6 ± 6.3</td>
</tr>
<tr>
<td>ELIEZER et al. (1982)</td>
<td>4.005.5 ± 1.0</td>
</tr>
<tr>
<td>HEMINGWAY (1982)</td>
<td>-4.023.8 ± 4.6</td>
</tr>
<tr>
<td>Present study</td>
<td>-4.007 ± 5.2 (est.)</td>
</tr>
</tbody>
</table>

(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 \( \text{CA}(\text{CaAl}_2\text{O}_4) \), \( \text{C}_12\text{A}_7(\text{Ca}_{12}\text{Al}_{13}\text{O}_{42}) \), and \( \text{C}_3\text{A}(\text{Ca}_3\text{Al}_2\text{O}_6) \).

In this discussion, 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:

\[
\Delta H_f^0(\text{Ca}_3\text{Al}_2\text{O}_6) = -(6.56 ± 1.38) \text{ kJ/g.f.w.}
\]

\[
\Delta H_f^0(\text{Ca}_{12}\text{Al}_{13}\text{O}_{42}) = -(79.37 ± 11.13) \text{ kJ/g.f.w.}
\]

\[
\Delta H_f^0(\text{Ca}_3\text{Al}_2\text{O}_6) = -(15.43 ± 1.46) \text{ kJ/g.f.w.}
\]

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):

\[
\Delta H_f^0(\text{CaAl}_2\text{O}_4) = -(12.9 ± 2) \text{ kJ/g.f.w.}
\]

This value is in reasonable agreement with that of Coughlin (1956).
In order to compare our results for CA$_2$ and CA$_6$ with these earlier values, which apply for mixed oxides with other stoichiometries, all the enthalpies of formation \([\text{from the oxides, referred to one mole of (CaO + Al}_2\text{O}_3\text{)]}\) are plotted against the mole fraction of Al$_2$O$_3$ in Fig. 3. This comparison shows that our enthalpy of formation for \(\frac{1}{3}\)CA$_2$ is somewhat more exothermic than, but comparable in magnitude to the general appearance of the CaO - Al$_2$O$_3$ phase diagram. Note also that this figure shows that the enthalpy of formation of \(\frac{1}{3}\)CA$_2$ is more negative than the equivalent mixture of \((\frac{1}{3}\)CA$_2$ + Al$_2$O$_3\)\). Hence, it is not necessary to invoke entropy stabilization for CA$_2$ 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 \(\frac{1}{3}\)C$_3$A and \(\frac{1}{6}\)C$_4$;A$_7$ are compared with (CaO + \(\frac{1}{3}\)CA), the possibility of entropy stabilization for C$_3$A and C$_4$;A$_7$ at high temperatures clearly must be considered as a possibility.

\section{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 own calorimetric results, calculations of the entropy of formation of hibonite and of its standard entropy, \(S^\circ\), are possible.

KUMAR and KAY (1985) give the following equation for the standard Gibbs energy of formation of CaAl$_2$O$_9$ from the oxides valid between 1100 K and 1500 K:

\[\Delta G^\circ_{CaAl_2O_9} \text{ (from oxides)} = -[17,869 + 39.3T \pm 840] \text{ J/g.f.w.} \text{ (7)}\]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{Standard enthalpies of formation, from CaO + Al$_2$O$_3$, to form indicated intermediate phases. All data refer to the formation of one mole of (CaO + Al$_2$O$_3$).}
\end{figure}

ALLIBERT et al. (1981) give:

\[\Delta G^\circ_{CaAl_2O_9} \text{ (from oxides)} = -[17,430 + 37.2T \pm 1500] \text{ J/g.f.w.} \text{ (8)}\]

At 1100 K, we get:

\[\Delta G^\circ_{CaAl_2O_9} = -[61,099 \pm 840] \text{ J/g.f.w.} \text{ (9a)}\]

and

\[\Delta G^\circ_{CaAl_2O_9} = -[38,950 \pm 1500] \text{ J/g.f.w.} \text{ (9b)}\]

The average of these values is \(-59,725 \text{ J/g.f.w.}\). This value may be compared with our own result for \(\Delta H^\circ_{\text{CaAl}_2\text{O}_9}\) at 1063 K (which applies with equal confidence also at 1100 K) to yield

\[\Delta S^\circ_{1100 \text{ K; from oxides}} = \frac{\Delta H^\circ_{1100 \text{ K; from oxides}} - \Delta G^\circ_{1100 \text{ K; from oxides}}}{1100} \text{ (10)}\]

Taking the values of \(S^\circ\) (1100 K) for Al$_2$O$_3$ (192.17 J/K g.f.w.) and CaO (102.85 J/K g.f.w.) from ROBIE et al. (1979), we obtain \(S^\circ_{\text{hibonite}} (1100 \text{ K}) = 1280.2 \text{ J/K g.f.w.}\). 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 J/K g.f.w. clearly is 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.

\section{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 CaO - 6Al$_2$O$_3$ and CaO - 2Al$_2$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 \(\Delta G^\circ_{CaAl_2O_9} (1300 \text{ K; from oxides}) = -69.00 \pm 0.84 \text{ kJ/g.f.w.}\), 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 \(\Delta H^\circ_{\text{CaAl}_2\text{O}_9} (1300\text{ K; from oxides}) = -33.0 \pm 9.7 \text{kJ/g.f.w.}\), the same as the experimental value obtained herein at 1063 K. An entropy of formation, \(S^\circ (1300 \text{ K; from oxides}) = -27.7 \text{ J/K g.f.w.}\), is obtained as in Eqn. (10). When linear equations are used to describe the variation of \(\Delta G^\circ\) over a range of temperature, the slopes should be equivalent to \(-\Delta S^\circ\) for that temperature range. Our value for \(\Delta S^\circ (1300 \text{ K; from oxides})\) of hibonite derived from our calorimetric determination of \(\Delta H^\circ (1063 \text{ K; from oxides})\) and \(\Delta G^\circ (1300 \text{ K; from oxides})\).
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 \( \Delta G^f \) data beyond the temperature range of the experiments of Kumar and KAY (1985). When Eqn. (8) is used, the discrepancy in \( \Delta S^f \) 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 \( \Delta S^f (1300 \text{ K}; \text{from oxides}) \) to determine the Gibbs energy of formation from the oxides via:

\[
\Delta G^f (T > 1300 \text{ K}) = \Delta G^f (1300 \text{ K}) - (T - 1300) \Delta S^f (1300 \text{ K}) = -69.00 - 0.0277(T - 1300) \text{kJ/g.f.w.} \tag{11}
\]

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 CaAlO\(_4\), we obtain \( \Delta G^f (1300 \text{ K}; \text{from oxides}) = -47.67 \pm 1.26 \text{kJ/g.f.w.} \), again at the middle of the temperature range investigated by Kumar and Kay (1985). Using heat capacity data for CaAlO\(_4\) from BONNICKSON (1955) and for Al\(_2\)O\(_3\) and CaO from Bobie et al. (1979), we obtain \( \Delta H^f (1300 \text{ K}; \text{from oxides}) = -28.78 \pm 5.15 \text{kJ/g.f.w.} \) for \( \Delta H^f (1063 \text{ K}; \text{from oxides}) \) measured herein. The entropy of formation, \( \Delta S^f (1300 \text{ K}; \text{from oxides}) = 14.5 J/K \text{g.f.w., is again obtained as in Eqn. (10).} \) As was the case for hibonite, our calculated value of \( \Delta S^f (1300 \text{ K}; \text{from oxides}) \) for CaAlO\(_4\) is substantially lower than estimates obtained from the slopes of the linear fits to electrochemical data for \( \Delta G^f \) (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 \( \Delta S^f (1300 \text{ K}; \text{from oxides}) \) to obtain the Gibbs energy of formation of CaAlO\(_4\) via Eqn. (11) which, in this case, becomes:

\[
\Delta G^f (T > 1300 \text{ K}; \text{from oxides}) = -47.67 - 0.0145(T - 1300) \text{kJ/g.f.w.} \tag{12}
\]

Our value for the Gibbs energy of formation of CaAlO\(_4\) 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 CaAlO\(_4\) 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, CaAlO\(_4\) does not form over the entire pressure range investigated.

Considering the uncertainties in the free energies of hibonite and CaAlO\(_4\), 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 melilitite or melilitite + hibonite. between 6 and 22° after it formed.

As suggested by MacPherson and Grossman (1984), CaAlO\(_4\) 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 CaAlO\(_4\) 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 CaAlO\(_4\). The data in the present paper effectively dismiss this argument. As noted above, CaAlO\(_4\) 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 CaAlO\(_4\)-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 CaAlO\(_4\) lies close enough to solar nebular conditions that CaAlO\(_4\) occasionally might have been able to form metastably during condensation, particularly if the reaction of hibonite with the gas to form melilitite were delayed below the equilibrium temperature for that reaction.

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