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High-Temperature Calorimetry in Liquid Oxide Systems

V. The Enthalpy of Formation of Be_2SiO_4, $BeAl_2O_4$, $BeAl_6O_{10}$

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The enthalpies of formation of Be_2SiO_4 (phenacite), $BeAl_2O_4$ (chrysoberyl) and $BeAl_6O_{10}$ have been determined by oxide melt calorimetry at 695 ± 2°C.

The following results were obtained:

$2BeO + SiO_2 = Be_2SiO_4$; $\Delta H_{968} = -4.7 \pm 0.3$ kcal/mole
$BeO + Al_2O_3 = BeAl_2O_4$; $\Delta H_{968} = -4.0 \pm 0.3$ kcal/mole
$BeO + 3Al_2O_3 = BeAl_6O_{10}$; $\Delta H_{968} = +2.9 \pm 0.45$ kcal/mole

The results are compared with information derived from recent equilibrium and heat capacity studies. The positive enthalpy of formation for $BeAl_6O_{10}$ indicates that this compound is stabilized at high temperatures by a significant positive entropy of formation. It is suggested that there may be a certain amount of Be–Al disorder in the (unknown) structure of this compound.

In the post-war years there has been a greatly increased interest in the chemistry of beryllium compounds. Through this work it was shown that beryllium oxide at high temperatures reacts with water vapor to form a volatile compound believed to be $Be(OH)_2$.[1] This discovery provided an approach to the thermodynamic properties of solid beryllium-oxygen compounds through the measurement of high-temperature heterogeneous equilibria. Using this approach Young [2] studied the following equilibria near 1400°C:

$$BeO(s) + H_2O(g) = Be(OH)_2(g) \quad (1)$$
$$BeAl_6O_{10}(s) + H_2O(g) = 3Al_2O_3(s) + Be(OH)_2(g) \quad (2)$$
$$3/2\ BeAl_2O_4(s) + H_2O(g) = 1/2\ BeAl_3O_{10}(s) + Be(OH)_2(g) \quad (3)$$

Both before and after the work of Young other investigators have carried out less extensive equilibrium studies in this field.[3–5] We shall in the present work restrict our attention to the data of Young.[2]

In the area of calorimetry investigators at the National Bureau of Standards recently have reported both low-temperature and high-temperature heat capacity data for these substances.[6–8] However, so far there has been no

calorimetric data on their enthalpies of formation. This is due to the low rates of solution of these compounds in aqueous HF and other room temperature calorimetric solvents.

In the present work we present the first calorimetric information on the heats of formation, from the oxides, of three simple beryllium-oxygen compounds: Be_2SiO_4 (phenacite), $BeAl_2O_4$ (chrysoberyl) and $BeAl_6O_{10}$ ($BeO{\cdot}3Al_2O_3$). The new data have been obtained by the use of oxide melt solution calorimetry, as developed by Yokokawa and Kleppa.[9,10] In this approach the compound and its component oxides are dissolved in a lead-cadmium-borate melt in a calorimeter operated near 700°C. The heat of formation of the compound is calculated from the observed heats of solution.

EXPERIMENTAL AND MATERIALS

The calorimeter used in the present work and the experimental procedures were similar to those of Yokokawa and Kleppa.[9,10] All experiments were performed at 695 ± 2°C. Calibration was by the gold-drop method, based on the heat content equation for pure gold as given by Kelley.[11] The solvent was prepared from reagent grade lead(II) oxide, cadmium(II) oxide, and boric acid in the ratio $9PbO{\cdot}3CdO{\cdot}4B_2O_3$. This melt is a good solvent for a variety of different oxides of basic, amphoteric, and acid character. In each solution experiment a small sample (about 1 mmole BeO, 0.5 mmole Be_2SiO_4, $BeAl_2O_4$ and 0.25 mmole $BeO{\cdot}3Al_2O_3$) was dissolved in 40 g of melt (250 mmoles of oxides). The solvent was renewed after each experiment. The beryllium oxide was a Berylco Beryllium Oxide Powder, Grade V, from Beryllium Corporation, Penn. U.S.A.

The two beryllium aluminates were furnished by Dr. George Furukawa of the National Bureau of Standards. The compounds had been prepared by arc fusion of stoichiometric amounts of high purity BeO and Al_2O_3 powder. Analyses of these compounds were reported by Furukawa and Saba.[6,7] Before they were put into the calorimeter the powdered samples were preheated at 700°C for several hours to remove traces of graphite introduced through the arc fusion process.

The phenacite samples (Be_2SiO_4) were prepared from handpicked, water-clear crystals from two mineralogical specimens from S. Miguel di Piraci Caba Minas Geraes, Brazil, found at the Field Museum, Chicago, Illinois (M# 12901 and M# 12902). The crystals were crushed in a mortar and the calorimetric samples drawn from the fraction −250 + 325 mesh. A microprobe analysis for the trace elements in these minerals showed about 0.05 % K, and less than 0.01 % of other expected impurities.

The solution experiments involving beryllium oxide were associated with some special difficulties. Because of the small grain size and low density of this material there was a tendency for the powder to float on the surface of the oxide melt, thus giving incomplete solution. To counteract this effect the beryllium oxide was heated repeatedly for 12 h periods at 1150°C. After two heating periods constant heats of solution within the experimental uncertainty were observed. However, even so it was necessary to stir more frequently and more vigorously than usual in order to achieve complete solution. Since each stirring operation was associated with a heat effect of the order of 0.0025 cal, the corrections due to stirring in this case were larger and correspondingly more uncertain than for the other compounds.

RESULTS AND DISCUSSION

The heat of solution ($\Delta H/n_{\text{solute}}$) of α-Al_2O_3 (corundum) in the lead-cadmium-borate melt was determined by Yokokawa and Kleppa,[10] whose value was later confirmed by Navrotsky and Kleppa.[12] Their value, 7.60 ± 0.10 kcal/mole has been adopted in the present work. Similarly we have adopted

the heat of solution of quartz previously reported by Holm and Kleppa,[13] -3.64 ± 0.07 kcal/mole.

In the course of the present investigation we carried out experiments on the heats of solution of BeO in the solvent melt, and separately in melts containing about one mmole of Al_2O_3 or SiO_2. We could find no difference in these values within our experimental error, indicating little interaction between Be^{2+} and Al^{3+}, and between Be^{2+} and Si^{4+} at the low concentrations used. Our results for the heat of solution of BeO in the pure melt were 3.4, 3.4, 3.4_5, 3.5, and 3.5_5 kcal/mole for a mean of 3.4_5 kcal/mole. In view of the considerations discussed above we estimate that the uncertainty in this figure may be as large as 6 % * ($\pm$ 0.2 kcal/mole).

The following values were obtained for the heat of solution of $BeAl_2O_4$: 14.91, 15.04, 15.05, 15.11, and 15.12 kcal/mole for a mean of 15.05 kcal/mole. We estimate the uncertainty in this figure to be about 1 %, or $\pm$ 0.15 kcal/mole.

In the case of $BeO{\cdot}3Al_2O_3$ we carried out 4 separate experiments, which gave the heats of solution 23.25, 23.28, 23.37, and 23.44 kcal/mole, respectively. The mean is 23.35 kcal/mole, and the error estimated at 1 % ($\pm$ 0.23 kcal/mole).

Finally, we performed six experiments with Be_2SiO_4. These gave the following values

# M 12901	7.92,	7.93,	7.93 kcal/mole
# M 12902	7.87,	7.93,	8.10 kcal/mole.

The overall mean is 7.95 ± 0.15 kcal/mole ($\pm$ 2 %).

In Table 1 is presented a summary of the enthalpy changes associated with the various solid-solid reactions considered in the present work. The experimental data all are referred to the temperature of the solution experiments, 968°K. Also given in this table are corresponding values at 298°K, calculated by the use of JANAF Thermochemical Tables [14] and the recent heat content values for $BeAl_2O_4$ and $BeAl_6O_{10}$ given by Ditmars and Douglas.[8]

Table 1. Enthalpy changes associated with indicated solid-solid reactions. Data in kcal/mole.

Process	ΔH_{968}	ΔH_{298}
$2BeO + SiO_2 = Be_2SiO_4$	-4.7 ± 0.3	—
$BeO + Al_2O_3 = BeAl_2O_4$	-4.0 ± 0.3	-4.0
$BeO + 3Al_2O_3 = BeAl_6O_{10}$	$+2.9 \pm 0.45$	$+2.8$
$BeAl_2O_4 + 2Al_2O_3 = BeAl_6O_{10}$	$+6.9 \pm 0.35$	$+6.8$

* Throughout the present section it will be noted that we quote experimental uncertainties which are larger than the indicated random error. This is due to the possibility of systematic errors for small heat effects. These errors arise from uncertainties associated with the completion of the reaction period in the presence of small drifts in the calorimetric system.

It will be noted that where data are available the temperature dependence of the quoted heat data is very small. This point was noted and demonstrated by Ditmars and Douglas,[8] who for these compounds found the deviations from the Kopp-Neumann rule above room temperature to be of the order of 1 % or less.

By linear combination of his equilibrium data for reactions (1), (2), (3) Young [2] calculated the Gibbs free energies of formation for the compounds $BeAl_2O_4$ and $BeAl_6O_{10}$ from BeO and Al_2O_3 at 1673°K. Similarly, from the dependence of these equilibrium constants on temperature he derived approximate values for the heats and entropies of the formation reactions. Appropriate data obtained from Young's work are given in Table 2.

Table 2. Thermodynamic data for solid-solid reactions involving the beryllium aluminates.

Process	Young		Present work + Young + Douglas + JANAF		Furukawa and JANAF	
	ΔG_{1673} kcal/mole	ΔH_{1673} kcal/mole	ΔH_{1673} kcal/mole	ΔS_{1673} cal/deg mole	ΔS_{298} cal/deg mole	ΔS_{1673} cal/deg mole
$BeO + Al_2O_3 = BeAl_2O_4$	-3.2 ± 1.4	-4.9	-4.3	-0.65 ± 0.85	$+0.29$	$+0.13$
$BeO + 3Al_2O_3 = BeAl_6O_{10}$	$-3.7 + 2.2$	-0.8	$+3.9$	$+4.55 \pm 1.3$	$+2.06$	$+2.96$
$BeAl_2O_4 + 2Al_2O_3 = BeAl_6O_{10}$	-0.5 ± 2.6	$+4.1$	$+8.2$	$+5.2 \pm 1.6$	$+1.77$	$+2.83$

In considering the data in Table 2 it should be kept in mind that from equilibrium investigations, such as that of Young,[2] one generally may derive fairly reliable information on the free energies of reaction. However, on the whole one should attach less weight to calculated enthalpy and entropy data, which are obtained from the temperature dependence of the equilibrium constants. For this reason we consider the apparent agreement between the values of ΔH for the reaction $BeO + Al_2O_3 = BeAl_2O_4$ in Table 2 to be entirely fortuitous. Similarly, we consider the apparent disagreement in the case of the reaction $BeO + 3Al_2O_3 = BeAl_6O_{10}$ to be of little significance.

On the other hand, from a combination of the free energy data of Young and our own enthalpy values, we should be able to obtain fairly reliable information on the entropies of reaction. These entropies may in turn be compared with the values derived from low temperature heat capacity work, which are included in the last columns in Table 2. This comparison shows that for chrysoberyl ($BeAl_2O_4$) there is approximate agreement between the entropy values given in Table 2. In view of the uncertainty in the 2nd law value, that of Furukawa and Saba clearly must be preferred. In the case of $BeAl_6O_{10}$ the discrepancy is even larger, the two values differing by more than the estimated error in our calculated value. We propose that this discrepancy may arise from Be—Al disorder in this compound. Unfortunately, the

crystal structure of $BeAl_6O_{10}$ has not been determined. However, enough is known about the crystal chemical properties of the Be^{2+} and Al^{3+} ions to make this suggestion entirely plausible. For example, while it is known that Al^{3+} prefers octahedral coordination with respect to oxygen, the ability of Al^{3+} to assume tetrahedral coordination in certain structures is well known. On the other hand, Be^{2+} has a strong preference for tetrahedral coordination, as demonstrated by the wurzite structure of BeO. On the basis of the calculated entropy data one may speculate that the structure of $BeAl_6O_{10}$ is such that it allows disorder among Be^{2+} and one mole of Al^{3+} ions. In the random mixing approximation this would yield an extra entropy contribution of + 2.76 cal/deg mole. This is somewhat more than the discrepancy between the two entropy values listed in Table 2 for this compound.

It finally should be mentioned that Young [2] noted that the compound $BeAl_6O_{10}$, after heating for two weeks at 1150°C (1423°K), showed some disproportionation into chrysoberyl and alumina. This is consistent with the small negative value of ΔG_{1673} for the reverse reaction in Table 2. In view of the fairly large positive enthalpy of formation of $BeAl_6O_{10}$ determined in the present work, this compound clearly is stabilized at higher temperatures by a significant positive entropy of formation.

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