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The Enthalpy of Formation of Kyanite (Al_2SiO_5)

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Received November 17, 1965

During the past year Yokokawa and Kleppa[1,2] have reported the development of new solution–calorimetric methods at high temperature. This approach permits determination of the heats of formation of many previously inaccessible compounds. Among the substances investigated up to the present we mention in particular the magnesium–aluminum spinel.[3] In the present communication we report the extension of these studies to the thermochemistry of the silicates.

In order to illustrate the potential of the new method we have selected for attention the mineral kyanite (Al_2SiO_5). This is one of the several aluminum silicates which all have defied repeated attack by the HF-solution technique.[4] We report in the present work a new value for the enthalpy of formation of kyanite, as formed from the component oxides at 695°. Work is in progress on the other polymorphs of Al_2SiO_5 (andalusite and sillimanite) and on mullite ($3Al_2O_3 \cdot 2SiO_2$). The results of these studies and a more general discussion of the significance of our results will be given in a future communication. Extension of these investigations to other silicate minerals is planned.

Experimental Section

The calorimeter used in the present work and the experimental procedures adopted were similar to those of Yokokawa and Kleppa.[2] All experiments were performed at 695 ± 2°. The solvent was prepared from reagent grade lead(II) oxide, cadmium(II) oxide, and boric acid in the ratio $9PbO:3CdO:4B_2O_3$. About 40 g was used in each experiment.

The kyanite sample was furnished by Dr. E. K. King of the Bureau of Mines Experiment Station, Berkeley, Calif. This mineral was available as a fine, purified powdered sample with a large part of the powder finer than 400 mesh. Our samples were drawn from the fraction −300 to +400 mesh.

The kyanite had previously been used by Todd[5] in an investigation of the low-temperature heat capacity of the Al_2SiO_5 polymorphs. According to Todd this sample contains 63.20% Al_2O_3 (theoretical 62.93%), 36.90% SiO_2, 0.10% Fe_2O_3, and 0.05% CaO, for an oxide sum of 100.25%. No attempt was made to correct for the impurities present or for the slight deviation from the theoretical composition. The powder was dried at 400° before use.

The sample of quartz was provided by Dr. D. R. Waldbaum of Harvard University. It was a powder (−200 to +325 mesh) of crystalline quartz from Brazil of the type used in the oscillator plate industry. According to a semiquantitative spectrographic analysis furnished by the donor it contains less than 0.003% B and less than 0.001% of all other detected impurities (Al, Ca, Ba, Cu). This sample was used as received after appropriate drying at 400°.

Results and Discussion

Yokokawa and Kleppa[2] reported the enthalpy of solution of α-Al_2O_3 (corundum) in the solvent melt at 705° to be 7.6 ± 0.2 kcal/mole. This value was confirmed by Navrotsky and Kleppa,[3] who found 7.60 ± 0.10 kcal/mole at 697°. In view of the agreement between these earlier investigations the heat of solution of alumina in the lead–cadmium–borate melt was not redetermined.

In the course of the present investigation four separate determinations of the heat of solution of quartz in a melt containing 0.9 mmole of Al_2O_3 were carried out at 695°. These measurements gave the results −3.64, −3.63, −3.66, and −3.62 kcal/mole for a mean of −3.64 kcal/mole. The uncertainty in this figure is believed to be about ±0.07 kcal/mole (2%).

We similarly carried out four separate determinations of the heat of solution of our kyanite sample in the pure lead–cadmium–borate melt at 695°. The results were +6.34, +6.36, +6.29, and +6.31 kcal/mole, with a mean of 6.33 kcal/mole. We again estimate the uncertainty to be ±0.07 kcal/mole.

On the basis of these observations we obtain for the process

$$Al_2O_3(\text{corundum}) + SiO_2(\text{high quartz}) = Al_2SiO_5(\text{kyanite})$$

$$\Delta H_{968°K} = -2.37 \pm 0.15 \text{ kcal/mole.}$$

The compilation of thermodynamic data by Rossini, *et al.*,[6] refers to an investigation of the aluminum silicates by Neumann,[7] who measured the various heats of solution in aqueous HF. From these data the enthalpies of formation of these silicates from the compound oxides were estimated to be of the order of −40 to −45 kcal/mole. However, these values have been questioned by many investigators and numerous attempts to repeat the measurements of Neumann have failed.[4] On the other hand, more recent consideration of the pressure–temperature stability relations of the Al_2SiO_5 polymorphs as well as other equilibrium information seem to indicate that these are stable with respect to the oxides by 5 kcal/mole or less. A survey of the literature and of the arguments involved is given by Waldbaum.[4] It will be noted that our new experimental value for the enthalpy of formation of kyanite is entirely consistent with these recent considerations.

Acknowledgments.—The authors are indebted to Drs. E. G. King and D. R. Waldbaum for the gift of the mineral samples and to Miss A. Navrotsky for counsel and assistance in the early stages of this investigation. This work has been supported by the Office of Naval Research and by the Army Research Office, Durham. General support of the Institute for the Study of Metals provided by ARPA also is acknowledged.

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