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High-Temperature Calorimetry in Liquid Oxide Systems. III. The Enthalpy of Formation of Magnesium-Aluminum Spinel

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The heats of solution in a lead–cadmium–borate melt at 697° of α-alumina, magnesium oxide, and of several synthesized samples of magnesium–aluminum spinel have been determined. From the heats of solution the enthalpy of formation of $MgAl_2O_4$, from the component oxides at 697°, was found to be -8.7 ± 0.3 kcal./mole.

In recent communications[1-3] we have reported the development of new techniques and solvents for solution calorimetry in oxide systems at elevated temperatures. These techniques were used for a determination of the enthalpies of transformation of several metastable forms of alumina to the stable corundum (α-Al_2O_3) modification.[2] In the present work these investigations have been extended to a study of the heats of formation of spinels.

The thermodynamic properties of the spinels is a problem of considerable scientific and technological interest. It is recalled here that the spinel structure is a remarkably simple one. It consists in the main of a nearly cubic close-packed arrangement of the oxygen ions, with one-eighth of the tetrahedral and one-half of the octahedral interstices filled by a variety of different cations. Both the distribution of the cations among octahedral and tetrahedral sites and the degree of order within each sublattice may vary with composition and with temperature.

Because of their slow rate of solution in conventional solvents, the spinels are not readily studied by solution calorimetry at or near room temperature. Therefore, most of the available enthalpy values have been derived from the temperature dependence of equilibrium or e.m.f. data. In many cases these values are of doubtful significance.

In the present work we report a new value for the heat of formation of magnesium–aluminum spinel, as formed from the component oxides at 700°. This compound, which is found in nature as the mineral spinel, has given its name to the spinel group. Investigations of the enthalpies of formation of other spinels are in progress and will be reported in future communications.

Experimental Section

The solvent used in the present work was prepared from reagent grade lead(II) oxide, cadmium(II) oxide, and boric acid in the ratio $9PbO:3CdO:4B_2O_3$, as reported by Yokokawa and Kleppa.[2] It was found to be convenient to melt down a few pounds of this mixture and to store the resulting nonhygroscopic glass in the form of small pellets.

The aluminum and magnesium oxide starting materials were Baker analyzed reagents. A semiquantitative spectrographic check of these oxides showed the following impurities. MgO, Si, 0.05%; Zn, 0.03%; Al, 0.01%; Ca, 0.005%; Fe, Ni, Cu, Ag: 0.001%. Al_2O_3: Si, Fe, 0.01%; Mg, Mn, Ni, Cu, Ag, 0.001%.

Ignition of the oxides and preparation of the spinels was carried out in a closed platinum crucible in a Marshall furnace wound with Pt-40Rh wire and suitable for work up to about 1500°. The magnesium–aluminum spinel was prepared by sintering pellets of intimately mixed −250 mesh MgO + α-Al_2O_3 mixtures in air at 1450°. Completeness of reaction was checked by the absence of MgO and Al_2O_3 lines in the X-ray powder diagram and by the fact that further ignition of the reground and repelletized samples did not change the heat of solution. In carrying out the ignition of oxides and spinel the samples were introduced into the furnace at 800°, brought to 1450°, maintained at this temperature for the desired period of time, furnace cooled to 800°, and then air cooled to room temperature.

The calorimeter and experimental procedures were similar to those used by Yokokawa and Kleppa in their work on alumina.[2] All experiments were performed at 697 ± 1°. As before, calibration was by the gold-drop method.

In each solution experiment a small oxide or spinel sample (0.5–1.0 mmole) was dissolved in 40 g. of mixture (about 250 mmoles of oxides). The solvent was renewed after each two consecutive experiments. In the concentration range used, *i.e.*, below about 1 mole % solute oxide, the heat of solution showed no detectable dependence on concentration. Similarly, within our experimental precision, we were unable to detect any dependence of the heat of solution of one oxide on the presence in the melt of a comparable amount of the other oxide. Thus we may consider the sum of the molar enthalpies of solution of pure MgO and of pure α-Al_2O_3 to be equal to the molar enthalpy of solution of an equimolar mixture of the two unreacted oxides. The difference between this quantity and the enthalpy of solution of $MgAl_2O_4$ gives the enthalpy of formation of the spinel at the temperature of the calorimetric experiments.

Results and Discussion

Table I gives a summary of all significant calorimetric measurements carried out on MgO, α-Al_2O_3, and $MgAl_2O_4$ in the course of the present investigation.

In the case of α-Al_2O_3 we carried out a total of nine experiments. These experiments yielded a mean heat of solution of $+7.60 \pm 0.10$ kcal./mole, in excellent agreement with the value reported by Yokokawa and Kleppa[2] for alumina samples ignited at somewhat lower temperatures.

For MgO, Table I gives the results of two series of measurements on samples of magnesium oxide of widely different origin. On the one hand, we ignited a sample of Baker's analyzed MgO for 24 hr. at 1450°. This sample gave a mean value of the enthalpy of solution of -2.19 ± 0.16 kcal./mole. On the other hand,

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[1] T. Yokokawa and O. J. Kleppa, *Inorg. Chem.*, **3**, 954 (1964).

[2] T. Yokokawa and O. J. Kleppa, *J. Phys. Chem.*, **68**, 3246 (1964).

[3] T. Yokokawa and O. J. Kleppa, *Inorg. Chem.*, **4**, 1806 (1965).

TABLE I

MOLAR ENTHALPIES OF SOLUTION OF MgO, α-Al_2O_3, AND $MgAl_2O_4$ IN $9PbO:3CdO:4B_2O_3$ AT 697 ± 1°[a]

Sample no.	Heat treatment Hr.	Heat treatment Temp., °C.	No. of experiments	$\Delta H^m_{soln}/N_{solute}$, kcal./mole
		MgO		
1	24	1450	9	-2.19 ± 0.16
2[b]	3	130	3	-2.13 ± 0.15
		α-Al_2O_3		
1	16	1400	9	7.60 ± 0.10
		$MgAl_2O_4$		
1a[c]	24	1450	3	14.06 ± 0.12
1b	48	1450	4	13.99 ± 0.07
2a	36	1450	6	14.24 ± 0.27
2b	60	1450	5	14.24 ± 0.30
3a	36	1450	5	14.10 ± 0.18
3b	60	1450	5	14.11 ± 0.13
Over-all av. of 28 expts.				14.13 ± 0.22

[a] Quoted uncertainties are standard deviations. [b] −250 mesh powder from single crystals from the Norton Company. [c] a and b refer to successive heat treatment of the same sample.

we ground a small sample of MgO single crystals obtained from the Norton Company to a powder of −250 mesh. This gave a mean enthalpy of solution of −2.13 ± 0.15 kcal./mole. However, this sample dissolved rather slowly in the lead–cadmium–borate melt, and we consider the result to be somewhat less accurate than the value obtained by dissolution of the polycrystalline samples.

The original Baker MgO is a very finely divided powder, presumably obtained by thermal decomposition of a magnesium carbonate at temperatures of the order of 500–600°. This powder, at 700°, gave a net endothermic heat of solution. However, the over-all solution process clearly involved two different steps: a fast exothermic step followed by a slower endothermic one. The endothermic step was not affected by prolonged ignition at 800°, but disappeared completely after ignition at 1450°.

This behavior of the magnesium oxide is in agreement with the earlier sintering experiments of Livey, *et al.*[4] It is probably caused by traces of water and/or carbonate adsorbed on the highly developed surface of the oxide powder. In the case of MgO this behavior persists until the sample is ignited above 900°. At this point it should be noted that most acid solution calorimetry of refractory oxides of necessity involves the use of very finely powdered samples. Giauque[5] has already pointed out that the heat of solution in acids of finely divided MgO samples may differ by as much as 1 kcal./mole from that of single crystals. It may be useful to keep this point in mind when viewing calorimetric data involving refractory oxides in general.

For the spinel samples we give in Table I the results of six series of experiments, the principal variable being the total ignition time of the sample. It will be noted from the quoted data that within our experimental precision there is no dependence of the heat of solution on the length of the period of ignition. In fact, it appears that reaction between −250 mesh MgO and Al_2O_3 is essentially complete after 24 hr. at 1450°. The over-all average of 28 solution experiments on $MgAl_2O_4$ gave a molar heat of solution in the lead–cadmium–borate melt of +14.12 ± 0.22 kcal./mole.

From the data quoted above on the heats of solution of MgO, α-Al_2O_3, and $MgAl_2O_4$ we calculate for the formation of the spinel $MgO(s) + Al_2O_3(\alpha,s) = MgAl_2O_4(s)$ that $\Delta H_{971} = -8.7 \pm 0.3$ kcal./mole.

This value is in reasonable agreement with the enthalpy of formation estimated by Altman[6] on the basis of his own equilibrium data and those of Grjotheim, *et al.*[7] However, it is numerically somewhat closer to Altman's value of the Gibbs free energy of formation (−8.4 kcal./mole). Recently, a new value of the Gibbs free energy of formation near 1400° of −8.4 ± 0.3 kcal./mole has been obtained by Muan, *et al.*,[8] from equilibrium work. In either case the Gibbs free energy appears to be comparable in magnitude to the enthalpy of formation, indicating that the entropy of formation is small. This is entirely consistent with the work of Kelley and King,[9] who calculated for $MgAl_2O_4$ a standard entropy of formation at 298°K. of +0.5 ± 0.2 cal./mole deg. from low-temperature heat capacity data.

Finally it should be mentioned that according to the observations of Hafner and Laves[10] naturally occurring spinels seem to undergo what appears to be an irreversible transformation near 800°. This transformation is believed to be due to the partial *inversion* of the natural spinel, *i.e.*, the transfer of Mg^{+2} ions from their normal tetrahedral sites to the octahedral sublattice and the transfer of Al^{+3} ions in the opposite direction. This transformation should have noticeable influence on the thermodynamic properties of the spinel. Presumably the synthetic spinels prepared in the course of the present work are also in a partially inverted state. We plan to give this problem further attention in future work.

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