Enthalpies of Solution of CaF_2 and MgF_2 in Molten Cryolite

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Enthalpies of solution of MgF_2 and CaF_2 in molten cryolite have recently been measured by Nicollin, Mme Lenoir and Eyrand.[1] They obtained the following results: $L_{MgF_2(s)} = 90 \pm 18$ kcal/mole and $L_{CaF_2(s)} = 40 \pm 18$ kcal/mole. The heats of fusion of the two compounds at their melting points are 13.9 kcal/mole and 7.1 kcal/mole, respectively.[2] On the basis of these values, the results given above seem far too high.

Experimental. The chemicals used in the present work were MgF_2, analytical reagent grade, Rare & Fine Chemicals, K & K Laboratories Inc., USA, and CaF_2, analytical reagent grade, Mallinckrodt Chemical Works, USA. Both chemicals were dried at 150° before use.

The calorimetric experiments were performed at 1014 ± 1°C in a single-unit microcalorimeter for work up to 1100°C. The calorimeter has a termopile consisting of 54 Pt/Pt-13 Rh couples connected in series. The thermopile is placed inside a Nichrome block. The liquid cryolite melt, about 12–13 g, was contained in a platinum crucible of about 76 mm height and 17 mm in diameter. The fluoride to be dissolved, 0.1–0.3 g, was contained in a very shallow platinum cup of about 10 mm diameter. This cup was attached by means of three platinum wires to a graphite holder which could be manipulated from outside the furnace system. The solution reaction was initiated by lowering the platinum cup into the melt. Stirring was achieved by moving the cup up and down in the crucible. All experiments were performed in a purified N_2-atmosphere. Calibration of the calorimeter was by the platinum drop method based on the heat content equation of pure platinum given by Kelley.[2] A correction of 4 % was applied for the heat pick-up of the 2 grams platinum pieces during the drop into the calorimeter.

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Results and discussion. The results are presented in Table 1. For MgF_2 a mean of 13.2 ± 0.2 kcal/mole, and for CaF_2 a mean of 9.7 ± 0.3 kcal/mole is obtained.

Table 1. Enthalpies of solution of MgF_2 and CaF_2 in molten cryolite at 1014 ± 1°C.

	Mole fraction MF_2	L, kcal/mole
MgF_2	0.0291	13.04
	0.0692	13.16
	0.0881	13.37
CaF_2	0.0252	9.48
	0.0392	9.77
	0.0649	9.96

The heats of fusion of MgF_2 and CaF_2 at 1014°C are according to available thermodynamic data (Kelley [2]) $\Delta H_{f,MgF_2} = 13.4$ kcal/mole and $\Delta H_{f,CaF_2} = 8.9$ kcal/mole, respectively. The obtained enthalpies of solution are in good agreement with these values.

According to the results given above, the enthalpy of mixing of molten magnesium fluoride and cryolite should be negative, while the enthalpy of mixing of molten calcium fluoride and cryolite should be positive. This is in excellent agreement with recent phase diagram calculations by Holm.[3]

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