The Enthalpy of Fusion of Magnesium Chloride

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The enthalpy of fusion of $MgCl_2$ has been redetermined by means of a high precision drop calorimeter with adiabatic shields.

The drop experiments were carried out by using the same method and technique as described by Grønvold[1] and used for the enthalpy of fusion determinations on the alkali magnesium chlorides, K_2MgCl_4, Rb_2MgCl_4, Cs_2MgCl_4, $KMgCl_3$, $RbMgCl_3$, and $CsMgCl_3$, by Holm, Jenssen Holm, Rinnan, and Grønvold.[2]

Anhydrous magnesium chloride was prepared by the same method as described before.[2] Chemical analysis showed the purified product to contain 99.5 mol % $MgCl_2$.

The results from the drop experiments are given in Table 1 and plotted in Fig. 1.

Table 1. Enthalpy increments for solid and liquid $MgCl_2$ ($cal_{th} = 4.1847$).

T/K	$\frac{H_T - H_{298.15}}{cal_{th} mol^{-1}}$ exp	calc
906.1	11586	11553
918.0	11853	11802
922.6	11951	11898
929.3	11903	12038
942.2	12236	12308
948.3	12493	12436
953.6	12450	12547
964.8	12891	12781
997.7	19638	—
1002.2	23035	23061
1004.6	23077	23115
1015.5	23292	23356
1019.0	23478	23434
1024.2	23518	23549
1027.9	23718	23631
1035.1	23861	23791
1040.4	23951	23908
1048.1	24100	24079
1056.9	24200	24274
1072.0	24578	24609

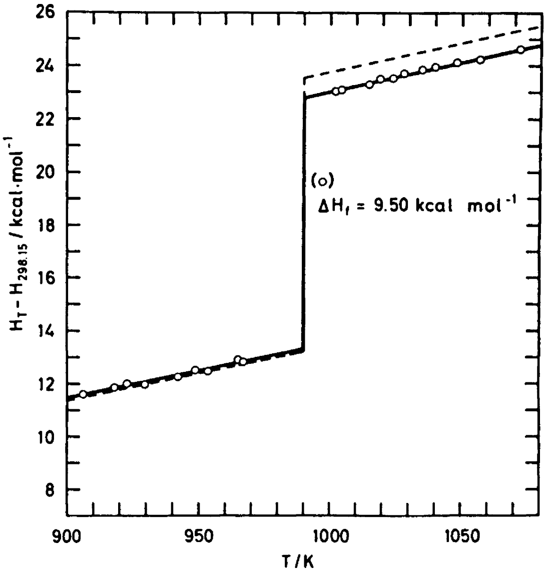

Fig. 1. Enthalpy curve, $H_T - H_{298.15}$ for $MgCl_2$. Results from this work, O; from literature (Ref. 3) — — —.

The data were fitted by a least squares treatment to equations of the type

$$H_{\mathrm{T}} - H_{298.15} = \mathrm{a} + \mathrm{b} \times T$$

where b corresponds to the assumed constant heat capacity of the solid or the liquid over the limited temperature ranges in question; (*cf.* Table 1). The following equations were obtained:

solid $\mathrm{MgCl_2}$: $H_{\mathrm{T}} - H_{298.15} = 7407 + 20.92T$ $\mathrm{cal_{th}mol^{-1}}$ ($\sigma = 96$)
liquid $\mathrm{MgCl_2}$: $H_{\mathrm{T}} - H_{298.15} = +837 + 22.18T$ $\mathrm{cal_{th}mol^{-1}}$ ($\sigma = 58$) corresponding to

$$\Delta H_{\mathrm{f}}(\mathrm{MgCl_2}) = 8244 + 1.26T\mathrm{cal_{th}mol^{-1}}$$

At the melting point 980 K this corresponds to an enthalpy of fusion

$$\Delta H_{\mathrm{f}}(\mathrm{MgCl_2}) = 9500\mathrm{cal_{th}mol^{-1}}$$

with an estimated uncertainty of 200 $\mathrm{cal_{th}mol^{-1}}$. This value should be compared with the value given by Moore [3] and adopted by Kelley,[4] $\Delta H_{\mathrm{f}} = 10\ 300$ $\mathrm{cal_{th}mol^{-1}}$.

The agreement between the literature values and ours are excellent for solid $\mathrm{MgCl_2}$,[3,4], while our data are about 4 % lower than those given for liquid $\mathrm{MgCl_2}$.

Our heat capacity value for liquid $\mathrm{MgCl_2}$, 22.17 $\mathrm{cal_{th}K^{-1}}$ $\mathrm{mol^{-1}}$ is, however, in good agreement with the value reported in literature,[4] 22.1 $\mathrm{cal_{th}K^{-1}}$ $\mathrm{mol^{-1}}$.

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1. Grønvold, F. *Acta Chem. Scand.* **26** (1972) 2216.
2. Holm, J. L., Jenssen Holm, B., Rinnan, B. and Grønvold, F. *J. Chem. Thermodynamics* **5** (1973) 97.
3. Moore, G. E., *J. Am. Chem. Soc.* **65** (1943) 1700.
4. Kelley, K. K, *Contributions to the Data on Theoretical Metallurgy*, XIII, Bull. 584, U.S. Bur. Mines 1960.

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The Structure of Molten Sodium Tetrafluoro Aluminate, $\mathrm{NaAlF_4}$

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The use of the term "complex" in ionic molten salt mixtures has been questioned on several occasions. Critic has been raised mainly because formation of complexes has been postulated in several molten salt solutions without reference to properties like the symmetry of the complex, its life time, *etc.* Despite these objections it has generally been accepted that complex ions may be formed in binary charge unsymmetrical mixtures like $\mathrm{AX\text{-}BX_2}$, $\mathrm{AX\text{-}CX_3}$ *etc.* The strong negative deviation from ideality which has often been found in certain concentration ranges in ionic mixtures of, for instance, $\mathrm{KF\text{-}BeF_2}$, $\mathrm{RbF\text{-}BeF_2}$,[1] and in certain $\mathrm{AlkCl\text{-}MgCl_2}$ mixtures,[2] may very well justify the use of the term complex, despite the fact that important structural properties are not known. The term "complex" does not always mean the same thermodynamically as it does spectroscopically. This is because in spectroscopy one looks for interactions between the atoms in the complex, while the thermodynamical stability of the complex depends on the surroundings as well. This is particularly the case when dealing with ionic liquids or molten salts with a "lattice-like" structure.

In this paper the thermodynamic stability of the rather controversial $\mathrm{AlF_4^-}$-ion will be discussed. This ion has for some time been assumed to be a stable complex ion in mixtures of molten sodium fluoride and aluminium fluoride.[3] The present author has shown [4,5] how the degree of dissociation, or stability, of ionic complex ions can be calculated using enthalpy of mixing data. The equation.

$$\Delta H_{\mathrm{C}}^{\mathrm{M}} = \Delta H^{\mathrm{Diss}} N_0(\alpha_1 - \alpha_0) \qquad (1)$$

where ΔH^{Diss} is the enthalpy of dissociation of the pure complex, N_0 is the weighed-in mol fraction of the complex, and α_0 and α_1 are the degrees of dissociations in the pure complex and in the mixture, respectively, was used to calculate the dissociation of cryolite, $\mathrm{Na_3AlF_6}$, in molten $\mathrm{NaF\text{-}Na_3AlF_6}$ mixtures.