calorimetric measurements. The JANAF value for ΔH_f of BeF_2—based on measurements of Kolesov, Popov, and Skuratov[26] of heats of solution of BeO and BeF_2 in aqueous HF—includes the JANAF value for ΔH_f of BeO. If the present value for BeO is introduced, the effect is to reduce the discrepancy between the present values for BeF_2 and that given by JANAF to less than their combined uncertainties.

Reference Electrodes.—Both electrode half-cells used in the present investigation performed acceptably for use as reference electrodes, both being stable and reproducible.

The $Be^{2+}|Be^0$ electrode should work well in any melt containing beryllium ions, provided no reducible cations are constituents of the solution. Potential fluctuations due to this electrode were masked in the present study by the fluctuations due to the $HF-H_2$ electrode but should be less than ± 0.1 mV. Beryllium electrodes were fabricated from three different batches of beryllium metal and no discrepancies in potentials were noted when the electrodes were interchanged. Therefore, the electrode response does not appear to be a function of a particular batch of beryllium metal.

The beryllium electrode does not appear to be suitable for small cell compartments since mass transfer causes the electrode to become enlarged owing to spongy deposition of the beryllium metal, and eventually electrical shorts develop between the electrode and the cell compartment wall.

The Pt, HF, $H_2|F^-$ electrode should be a suitable reference electrode in any fluoride-containing melt in which solution constituents undergo no oxidation by HF or reduction by H_2. The solubility of HF in $LiF-BeF_2$ is low[27] (about 0.0003 mol fraction for the partial pressures of HF used in this study), and no significant solubility of hydrogen is expected in this system. Potential fluctuations due to this electrode appear to be a function of the melt viscosity. Fluctuations were about ± 0.1 mV in melts with a viscosity of 1 P or less.

The precision of this electrode was limited somewhat in the present study by the method of HF delivery, as previously mentioned. In future experiments it is planned to prepare the H_2-HF mixture by passing hydrogen through a thermostated $NaHF_2$ bed. It is hoped that this will be a more precise method of producing mixtures of HF and H_2 of constant composition.

(26) V. P. Kolesov, M. M. Popov, and S. M. Skuratov, *Russ. J. Inorg. Chem.*, **4**, 557 (1959).

(27) P. E. Field and J. H. Shaffer, *J. Phys. Chem.*, **71**, 3320 (1967).

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Enthalpies of Mixing in Liquid Beryllium Fluoride–Alkali Fluoride Mixtures

By J. L. HOLM and O. J. KLEPPA

The integral enthalpies of mixing of the liquid mixtures of beryllium fluoride with lithium fluoride, potassium fluoride, and rubidium fluoride have been determined calorimetrically at 862°. The beryllium fluoride–lithium fluoride system has an S-shaped enthalpy curve with positive values in the high lithium fluoride range. The beryllium fluoride–potassium fluoride system is exothermic at all compositions, but the curvature of the enthalpy of mixing curve is positive at high beryllium fluoride contents. The strong, energetic asymmetry of the considered systems is attributed to the energy associated with the breakdown of the network structure of liquid BeF_2. The data also indicate the existence of the complex anionic species BeF_4^{2-}, particularly in the concentration range 0–50 mol % BeF_2 in mixtures with KF and RbF. For the system BeF_2-LiF the partial excess enthalpies of BeF_2 have been derived from our data for comparison with corresponding excess free energies available in the literature. The comparison shows that the partial excess entropies of BeF_2 in this system are positive, rising from zero at $N_{BeF_2} = 1$ to values of the order of 3.0 cal/deg mol at about 30% BeF_2. The partial excess entropies of BeF_2 at high to intermediate contents of BeF_2 are to some extent consistent with a model proposed by Førland, based on a random distribution of bridging and nonbridging fluoride ions.

Introduction

Mixtures of molten fluorides constitute an important and interesting group of solutions, both from a theoretical point of view and because of their technological applications. However, unlike most other halides, they cannot be handled in fused silica containers, and require special techniques and special container materials. Thus, they cannot be investigated by the "break-off" technique which we have used extensively in calorimetric studies of mixed nitrates and halides.[1,2]

During the past year we have developed techniques and methods which allow the study of molten fluoride mixtures by means of high-temperature reaction calorimetry. The first report on this work is given in the recent paper by Holm and Kleppa[3] on binary

(1) O. J. Kleppa and L. S. Hersh, *J. Chem. Phys.*, **34**, 351 (1961).
(2) L. S. Hersh and O. J. Kleppa, *ibid.*, **42**, 1309 (1965).
(3) J. L. Holm and O. J. Kleppa, *ibid.*, **49**, 2425 (1968).

mixtures formed by the alkali fluorides. In the present communication we report an extension of this work to the mixtures of beryllium fluoride with lithium, potassium, and rubidium fluorides. These are examples of charge-unsymmetrical molten-salt mixtures, of the types previously studied calorimetrically by McCarty and Kleppa.[4,5]

It has been recognized since the work of Goldschmidt that the ionic fluorides may be considered to represent "weakened models" of the oxides.[6] This is due to the fact that the size of the fluoride ion ($r_{F^-} = 1.36$ Å) is very nearly the same as that of the oxygen ion ($r_{O^{2-}} = 1.40$ Å), while the charge is reduced by a factor of 2. The following pairs of compounds serve as examples: $LiF-MgO$, $NaF-CaO$, BeF_2-SiO_2, and MgF_2-TiO_2. While, with few exceptions, the liquid oxides are at present inaccessible to direct calorimetric measurements, the molten fluorides can be studied.

From the point of view of the present investigation, it is of particular interest that beryllium fluoride represents a weakened model of silica. These two compounds are both well-known glass formers, which in the liquid state assume random network structures.[7] However, while silica (cristobalite) melts at 1713°, the melting point of beryllium fluoride is 555°.

Experimental Section and Materials

All experiments were performed in the single-unit microcalorimeter for work up to 1100° which we used in our work on the binary alkali fluorides. The temperature-sensing element of this calorimeter is a 54 + 54 junction Pt—Pt-13% Rh thermopile, which measures the outside wall temperature of the calorimeter with respect to the inside wall of a surrounding nichrome jacket. The experimental arrangements were similar to those described in greater detail by Holm and Kleppa.[3] All experiments were carried out under an atmosphere of dry, purified nitrogen (~99.99% N_2), which was passed through the outside silica envelope ("liner") at a rate of about 50 cm³/min.

The chemicals used were: (a) lithium fluoride, Fisher Certified reagent, analytical reagent grade; (b) potassium fluoride, Baker and Adamson Anhydrous Granular reagent, analytical reagent grade; (c) rubidium fluoride, Kawecki Chemical Co., Rare Metals Division, high purity [semiquantitative spectrographic analysis of this salt showed the presence of the following impurities (per cent): Na, 0.001; K, 0.01; Ca, 0.001; Cs, 0.1]; (d) beryllium fluoride, for which two different samples were used: (1) BeF_2 from the Brush Beryllium Co., high purity [according to the manufacturer the salt contains 99.5% BeF_2, with the following known impurities (per cent): Al, 0.026; Fe, 0.017; Cr, 0.0001; N, 0.002; Mn, 0.035]; (2) distilled BeF_2 which was provided by Dr. S. Cantor, Oak Ridge National Laboratory.

Near its melting point pure beryllium fluoride is an exceedingly viscous liquid. All calorimetric experiments reported in the present work were carried out at 862 ± 2°, at which temperature its viscosity is very much lower, but still quite high compared to that of "normal" liquids. However, we had no difficulties in achieving complete mixing of the two constituents, presumably owing to the very strong dependence of viscosity on composition.

According to Greenbaum, et al.,[8] the vapor pressure of pure

beryllium fluoride at 850° is about 10^{-2} atm. Thus it is so large that it may cause some loss of BeF_2 by evaporation. In order to minimize the influence of this effect, which is not large compared to other sources of error (*e.g.*, stirring corrections, see below), all calorimetric experiments were initiated as soon as possible after the charged liner was introduced into the calorimeter. In most cases the elapsed time at temperature prior to mixing was 2–2.5 hr.

Before their use in the calorimetric experiments the alkali fluorides were premelted in purified nitrogen in a platinum (KF, RbF) or graphite crucible (LiF). Clear crystals were selected from the solidified material for use in the calorimetric work. The premelted potassium and rubidium fluorides were analyzed by an ion-exchange method and were found to contain 99.12 ± 0.10% KF and 99.74 ± 0.1% RbF, respectively. Potassium, rubidium, and beryllium fluorides were weighed out in a nitrogen-filled drybox.

The calibration of the calorimeter was by the platinum drop method, based on the heat content equation for pure platinum given by Kelley.[9] Small pieces of 2-mm diameter Pt wire (reference grade) of total weight 1–2 g were dropped from room temperature into the calorimeter at 862°. A correction of 2% was applied for the small heat pickup of the wire pieces during their drop into the calorimeter. Corrections were made also for the heat effect associated with the introduction of the platinum cup into the melt and the displacement of liquid levels resulting from the mixing experiment. Through blank experiments this effect was determined to be 0.4–0.5 cal per stirring operation.

Results and Discussion

Enthalpies of Mixing.—In the course of the present work we carried out 17 successful experiments in the system $LiF-BeF_2$, 20 in $KF-BeF_2$, and 3 in $RbF-BeF_2$. While the first two mentioned systems were studied essentially over the complete range of liquid compositions, the three experiments involving rubidium fluoride were carried out on mixtures which contained about 33 mol % BeF_2.

For $LiF-BeF_2$ the experimental results were (N_{BeF_2}, H^M (cal/mol)): 0.0503, −247; 0.0924, −503; 0.1252, −680; 0.1552, −882; 0.1901, −1011; 0.2172, −1031; 0.2903, −1070; 0.3554, −1048; 0.4033, −860; 0.4513, −630; 0.4988, −280; 0.5489; +9; 0.6034, +295; 0.6460, +484; 0.6994, +631; 0.7969, +654; 0.8989, +522.

For $KF-BeF_2$ the results were (N_{BeF_2}, H^M (kcal/mol)): 0.0508, −1.377; 0.0984, −2.676; 0.1039, −2.719; 0.1488, −4.498; 0.1906, −5.710; 0.2444, −6.952; 0.2486, −7.139; 0.2899, −7.687; 0.3296, −8.173; 0.3497, −8.337; 0.3890, −8.105; 0.4948, −6.652; 0.5784, −5.637; 0.6490, −4.807; 0.7234, −3.529; 0.8100, −2.273; 0.8384, −1.700; 0.8960, −1.012; 0.9443, −0.337; 0.9720, −0.081.

For $RbF-BeF_2$ the results were (N_{BeF_2}, H^M (kcal/mol)): 0.3270, −9.264; 0.3300, −9.096; 0.3316, −9.200.

These results are presented in graphical form in Figures 1 and 2. In Figure 1 we give the molar enthalpy of mixing plotted against mole fraction, while Figure 2 shows the same data in a plot of the interaction parameter, $\lambda = H^M/N_1N_2$, *vs.* N. Since the interaction parameter varies relatively slowly with

(4) F. G. McCarty and O. J. Kleppa, *J. Phys. Chem.*, **68**, 3846 (1964).

(5) O. J. Kleppa and F. G. McCarty, *ibid.*, **70**, 1249 (1966).

(6) V. M. Goldschmidt, "Geochemische Verteilungsgesetze. VIII," *Skrifter Norske Videnskaps-Akad. Oslo, I: Mat. Naturv. Kl.* (1926).

(7) W. H. Zachariasen, *J. Am. Chem. Soc.*, **54**, 3841 (1932).

(8) M. A. Greenbaum, J. N. Foster, M. L. Arin, and M. Farber, *J. Phys. Chem.*, **67**, 36 (1963).

(9) K. K. Kelley, Bureau of Mines Bulletin 584, U. S. Government Printing Office, Washington, D. C., 1960.
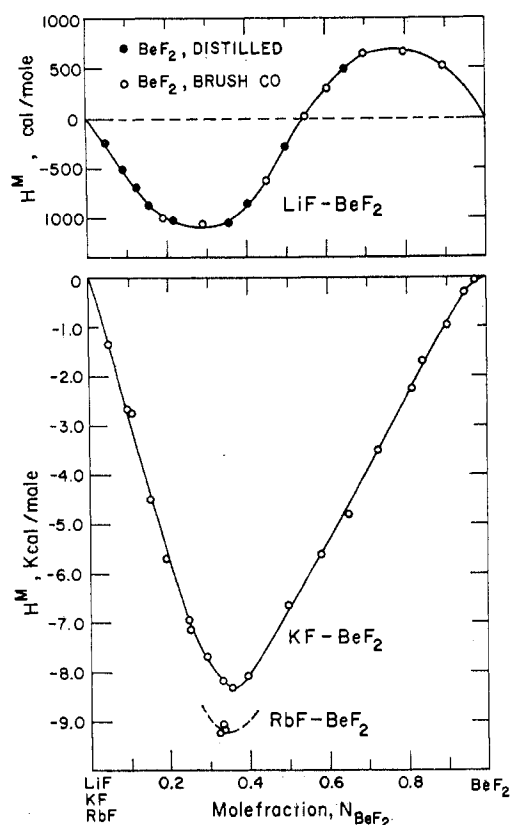
Figure 1.—Integral enthalpies of mixing in liquid mixtures of beryllium fluoride with lithium fluoride, potassium fluoride, and rubidium fluoride at 862°.
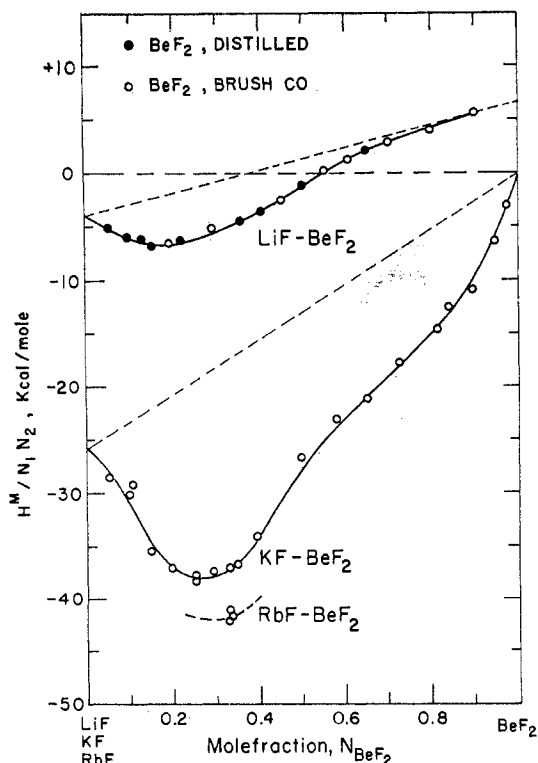

Figure 2.—Enthalpy of mixing interaction parameters (H^M/N_1N_2) in liquid mixtures of beryllium fluoride with lithium fluoride, potassium fluoride, and rubidium fluoride.

composition, this last graph is useful in illustrating the experimental precision achieved. It also is of value in demonstrating energetic asymmetry, *i.e.*, the deviation of the enthalpy of mixing from the simple, symmetrical, parabolic curve predicted by the first-approximation solution theories.

In the case of LiF–BeF₂ we see that the integral enthalpy of mixing is positive in the high BeF₂ range and negative in the high LiF range. The actual value of the interaction parameter changes from about +6.5 kcal/mol in pure BeF₂ to about −4 kcal/mol in pure LiF. The difference between these two values represents a convenient quantitative measure of the energetic asymmetry, which in this case is about 10.5 kcal/mol. For KF–BeF₂ the energetic asymmetry is even larger with the interaction parameter having a value near zero in pure BeF₂ and about −26 kcal in pure KF. It is important to note that for both systems the interaction parameter is more positive in the BeF₂-rich melts.

Energetic asymmetry of the magnitude shown by these solution systems is largely unknown among the simple fused-salt mixtures which we have studied in the past. Among these only the mixtures of MgCl₂ with CaCl₂, SrCl₂, and BaCl₂, recently investigated by Papatheodorou and Kleppa,[10] show somewhat similar, although much less extreme, behavior. These authors found that MgCl₂–CaCl₂ has positive enthalpies of mixing at all compositions, MgCl₂–BaCl₂ has negative values, while MgCl₂–SrCl₂ is intermediate in character and has positive values in the high MgCl₂ range and negative values in the high SrCl₂ range. All three systems show much more positive values of the interaction parameter in the high MgCl₂ range than in the CaCl₂, SrCl₂, and BaCl₂ range.

Papatheodorou and Kleppa suggested that this behavior of the MgCl₂-containing systems may reflect a certain tendency of pure MgCl₂ to polymerize, *i.e.*, to form Mg–Cl–Mg bridges. Then, if MgCl₂ is mixed with other salts, some energy is expended in breaking down these bridges, which in turn gives rise to a positive contribution to the enthalpy of mixing.

Since the tendency of MgCl₂ to polymerize is relatively weak, its electrical conductivity and viscosity near the melting point fall in the normal range for simple, unassociated ionic melts (viscosity $\sim 10^{-2}$ P; specific conductivity ~ 1 ohm⁻¹ cm⁻¹). On the other hand, according to Mackenzie,[11] the viscosity of pure BeF₂ near its melting point is about 10⁶ P, while its specific conductivity is of the order of 10⁻⁸ ohm⁻¹ cm⁻¹. These numbers provide strong evidence for a highly developed network structure. When alkali fluorides are added to liquid BeF₂, there is a drastic reduction in its viscosity and a corresponding increase in the electrical conductivity, presumably due to the breaking down of the network structure. We suggest

(10) G. N. Papatheodorou and O. J. Kleppa, *J. Chem. Phys.*, **47**, 2014 (1967).

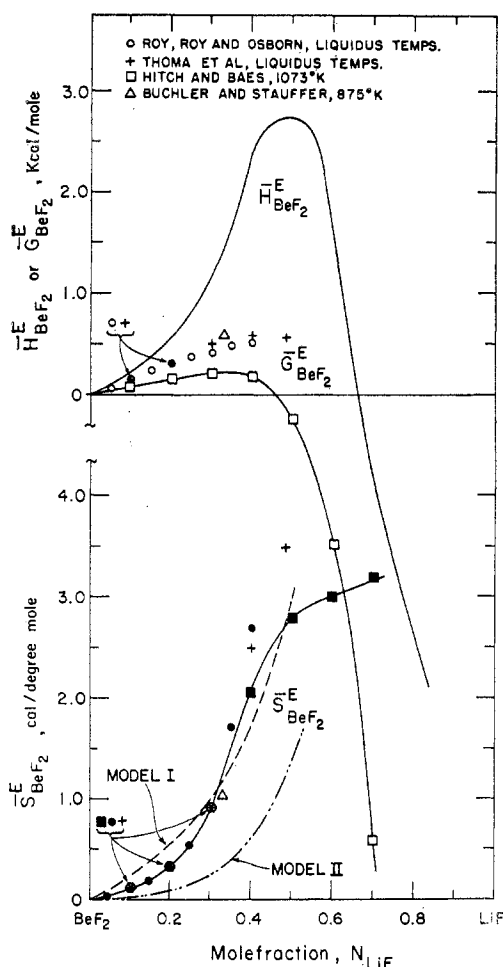(11) J. D. Mackenzie, *ibid.*, **32**, 1150 (1960).

Figure 3.—Partial excess enthalpies, excess free energies, and excess entropies of beryllium fluoride in liquid mixtures of beryllium fluoride with lithium fluoride. The excess entropy values are compared with values derived from models proposed by Førland.[19]

that this also accounts for the positive enthalpies of mixing in the high BeF_2 range of the LiF–BeF_2 system and for the positive curvature of the enthalpy of mixing curve in the high BeF_2 region in the KF–BeF_2 system. Related behavior may be predicted for the liquid mixtures of BeF_2 with the alkaline earth fluorides.

Before we leave the present discussion of the enthalpy of mixing, we wish to return briefly to Figure 2, which shows the dependence of the interaction parameter on the composition of the binary mixtures. We note that both for LiF–BeF_2 and for KF–BeF_2 the plot of the interaction parameter against composition shows significant negative deviations from the straight line which connects the two terminal values of λ. In our earlier work such deviations of λ from linearity were attributed to nonrandom mixing of the cations and/or to the presence in the liquid mixture of anionic configurations of special stability. For example, in the mixtures of $MgCl_2$ with KCl, $RbCl$, and $CsCl$ the relatively sharp dip in λ in the vicinity of $N_{MgCl_2} = 0.33$ was attributed to the special stability of the anionic configuration $MgCl_4{}^{2-}$. If we compare the curves in Figure 2 with the corresponding curves for the alkali chloride–$MgCl_2$ systems we find obvious similarities.

Thus KF–BeF_2 may be compared with KCl–$MgCl_2$ and LiF–BeF_2 with $LiCl$–$MgCl_2$, and perhaps also with $NaCl$–$MgCl_2$. In each case the maximum deviation of λ from linearity occurs in the vicinity of $N_{BeF_2} = 0.3$. This suggests that $BeF_4{}^{2-}$ is an important anionic species in these mixed systems, particularly in KF–BeF_2 (and presumably also in RbF–BeF_2). To a lesser extent this species may be formed also in the system LiF–BeF_2. It is of interest to note that the phase diagrams for the systems KF–BeF_2 and RbF–BeF_2 show the presence of stable, congruently melting compounds at $N_{BeF_2} = 0.33$, with compositions K_2BeF_4 and Rb_2BeF_4.[12] These compounds are isostructural with the alkali metal sulfates such as K_2SO_4. On the other hand, Li_2BeF_4, which does not melt congruently, is isostructural with Be_2SiO_4 (phenacite).

Entropies of Mixing.—It is well known that the use of integral enthalpy data to derive the corresponding partial values may be associated with some uncertainty. Even so, we have applied our new data for the liquid system BeF_2–LiF to determine the relative partial enthalpies of BeF_2 ($\bar{H}^E{}_{BeF_2}$) at 862°. These values are given as a solid line in Figure 3. As expected, this curve starts out with positive partial enthalpies of BeF_2 at low concentrations of LiF, rises to a maximum of the order of 2.7 kcal/mol at about 50% LiF, and falls sharply at higher LiF contents, passing through zero near 65% LiF.

Figure 3 also contains excess partial free energy values for BeF_2 in mixtures with LiF obtained from four different sources. The open squares in this figure represent excess free energy values valid at 800° taken from the recent emf fork of Hitch and Baes.[13] According to the authors, these values are to be preferred to those of Mathews and Baes,[14] who reported comparable data from a study of the heterogeneous equilibrium in the system LiF–BeF_2(l), BeO(s), H_2O(g), HF(g) at 500–700°. Figure 3 also contains a single experimental value of $\bar{G}^E{}_{BeF_2}$ (for $N_{BeF_2} = 0.67$ at 602°) obtained from the mass spectrometric vaporization study of Büchler and Stauffer.[15] Finally, the figure gives a series of excess free energies of BeF_2 calculated from the phase diagrams of Roy, Roy, and Osborn[16] and of Thoma, *et al.*[17] While Thoma, *et al.*, used a purer preparation of BeF_2, with a correspondingly higher melting point of the pure compound (555° compared to 548°), the freezing point depressions ($T - T_f$) are quite comparable for the two studies.

In calculating excess free energies from the phase diagram we have made use of the well-known relation

$$\bar{G}^E{}_{BeF_2} = \Delta S_f(T - T_f) - RT \ln N_{BeF_2} \qquad (1)$$

Here ΔS_f is the entropy of fusion of BeF_2. This is

(12) E. M. Levin, C. R. Robbins, and H. F. McMurdie, "Phase Diagrams for Ceramists," The American Ceramic Society, Columbus, Ohio, 1964.

(13) B. F. Hitch and C. F. Baes, Jr., *Inorg. Chem.*, **8**, 201 (1969).

(14) A. L. Mathews and C. F. Baes, Jr., *ibid.*, **7**, 373 (1968).

(15) A. Büchler and J. L. Stauffer in "Proceedings of the Symposium on Thermodynamics," International Atomic Energy Agency, Vienna, 1966.

(16) D. M. Roy, R. Roy, and E. F. Osborn, *J. Am. Ceram. Soc.*, **33**, 85 (1950).

(17) R. E. Thoma, *et al.*, submitted for publication.

assumed to be independent of temperature between the melting point, T_f, and the liquidus temperature for mole fraction N_{BeF_2}, T. The formula further assumes that there is no solid solubility of the solute in solid BeF_2.

Quite recently a calorimetric value of the heat of fusion of BeF_2 was reported in the literature. Based on room-temperature heat of solution calorimetry on glassy and crystalline BeF_2, Taylor and Gardner[18] gave $\Delta H_f = 1.13 \pm 0.02$ kcal/mol at 25°. Since this value differs widely from that calculated by Førland,[19] from the cryoscopic data of Roy, *et al.* (9.7 kcal/mol), we considered it desirable to obtain an independent check on the calorimetric result. Such a check was provided by Melnichak,[20] who carried out a new determination of the enthalpy difference between glassy and crystalline BeF_2, prepared by annealing the glass for 20 hr at 500°. His result, which was obtained by transposed temperature-drop calorimetry, was 1.1 ± 0.2 kcal/mol at 25°, in excellent agreement with the value of Taylor and Gardner.

It is stressed that these values of the enthalpy of fusion apply at room temperature. Since we have no reliable data on the heat capacity of the glass between room temperature and the melting point, we have made the simplifying assumption that ΔC_p is zero for the process of fusion. On this basis we obtain for BeF_2 an entropy of fusion, ΔS_f, of 1.37 cal/deg mol. Because the heat capacity of the liquid tends to be somewhat larger than that of the corresponding solid, we believe this entropy value may be somewhat low. Even so, the resulting uncertainties in the values of $\bar{G}^E{}_{BeF_2}$ calculated from the cryoscopic data are estimated to be of the order of about 10% only. This is due to the fact that at most compositions of interest the second term on the right-hand side of eq 1 tends to dominate compared to the first term.

From Figure 3 we see that the four quoted equilibrium studies agree in showing positive excess free energies for BeF_2 at high BeF_2 contents. All of the values fall significantly below the corresponding curve for the partial enthalpy. Accordingly, the partial excess entropies are positive. In order to make numerical calculations of the excess entropies, we shall make the additional assumption that the enthalpies of mixing in the considered mixtures are independent of temperature between 862° and the temperature of the free energy measurement. While this assumption is a reasonable one in the light of what we now know about the temperature dependence of the enthalpy of mixing in simple fused-salt systems, it does introduce some additional uncertainty into the entropy values. The calculated partial excess entropies are plotted in the lower part of Figure 3. It is encouraging that the values derived from the four independent free energy determinations agree reasonably well, particularly at

mole fractions of LiF below about 0.35. While this is no proof that our excess entropy curve actually is "correct," it does give us some confidence in the significance of the results.

Figure 3 shows that the excess partial entropy of BeF_2 rises sharply (see below) as N_{LiF} is increased from 0 to 0.5, but seems to level off at values of the order of 3 cal/deg mol at higher LiF contents. It is suggested that the sign and magnitude of this "limiting" value of the excess entropy is in a simple way related to the fact that the entropy of fusion of BeF_2 is unusually low compared to more typical AX_2 compounds. At low BeF_2 contents the observed excess entropy of BeF_2 may be considered to represent the sum of two terms: (1) the entropy change associated with transforming BeF_2 from the network-type structure actually observed to a hypothetical, normal, and unassociated form of liquid BeF_2; (2) the nonconfigurational partial entropy change associated with diluting this hypothetical form of BeF_2 to the considered liquid composition. If entropy data for other simple fused-salt mixtures may serve as a guide, the latter contribution should be relatively small, probably of the order of ± 1 cal/deg mol or less. Thus the major part of the observed positive partial excess entropy at lower BeF_2 concentrations presumably is due to the former term.

Particular interest is attached to the partial entropy of BeF_2 at low and intermediate concentrations of LiF. It was suggested by Førland[19] that in this concentration range the entropy of mixing may be calculated from a statistical model different from that of Temkin.[21] Specifically, he assumed that a mixture of BeF_2 and alkali fluoride contains two types of fluoride ions—those which are attached to a single beryllium ion (–F) and those which are attached to two beryllium ions forming one of the fluoride bridges in the network structure (–F–). If bridging and nonbridging fluoride ions are randomly distributed, we would have the following expression for the partial entropy of beryllium fluoride[19]

$$\Delta \bar{S}_{BeF_2} = -2R \ln [(1 - {}^3/_2 N_{AF})/(1 - {}^1/_2 N_{AF})] \quad (2)$$

We shall refer to this as model I. From this model we obtain the excess entropy curve given as a broken line in Figure 3.

It was also suggested by Førland that it is possible that the mixture of bridging and nonbridging fluoride ions is not random but that the nonbridging fluoride ions actually will occur in pairs, presumably associated with alkali metal cations. If the model melt is considered to contain a random mixture of bridging and paired fluoride ions (model II), the partial entropy of beryllium fluoride will be[19]

$$\Delta \bar{S}_{BeF_2} = -2R \ln [(1 - {}^3/_2 N_{AF})/(1 - N_{AF})] \quad (3)$$

The corresponding excess entropy curve is also included in Figure 3. For solutions of LiF, NaF, and

(18) A. R. Taylor and T. E. Gardner, Bureau of Mines Report RI-6644, Mines Bureau, Pittsburgh, Pa., 1965.

(19) T. Førland in "Fused Salts," B. R. Sundheim, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964.

(20) M. E. Melnichak, private communication, Aug 1968.

(21) M. Temkin, *Acta Physicochim. URSS*, **20**, 411 (1945).

RbF in BeF_2 Førland[19] attempted to test these two models on the basis of the quoted cryoscopic data of Roy, Roy, and Osborn.[16] Owing to the absence of reliable, independent information on the enthalpy of fusion and on the partial enthalpy of BeF_2, these attempts were not successful. More recently the same problem was considered by Mathews and Baes[14] on the basis of their heterogeneous equilibrium data. However, this work does not allow a reliable separation of the partial free energy data for BeF_2 into the appropriate enthalpy and entropy terms.

Figure 3 gives a comparison of the two "theoretical" excess entropy curves for models I and II with the experimental values. While the experimental uncertainties do not allow us to make a clear-cut choice between the two models at very low contents of LiF, the data show reasonable agreement with model I at intermediate contents of lithium fluoride, say between $N_{LiF} = 0.25$ and $N_{LiF} = 0.5$. In this range model II yields much too low values of the excess entropy.

The FCl₂⁺ Cation

By KARL O. CHRISTE and WOLFGANG SAWODNY

The FCl_2^+ cation, a new oxidizing species based on chlorine fluorides, has been prepared in the form of its AsF_6^- and BF_4^- salts. Chlorine monofluoride reacts with AsF_5 or BF_3 in a 2:1 mole ratio to form the FCl_2^+-containing salts. No evidence has been found for the existence of the Cl^+-containing 1:1 adducts reported previously for both the ClF–BF_3 and the ClF–AsF_5 systems. The results of the present investigation indicate that the actual 2:1 adducts may previously have been mistaken for 1:1 adducts. The $FCl_2^+AsF_6^-$ complex, a white crystalline solid, is stable at $-78°$ and is completely dissociated in the gas phase at $25°$. A pressure–temperature curve gives a heat of reaction, 32.83 kcal mol^{-1}, for the dissociation process: $FCl_2^+AsF_6^-(s) = 2ClF(g) + AsF_5(g)$. Reaction of solid $FCl_2^+AsF_6^-$ with NO_2F results in the quantitative displacement of 2 mol of ClF/mol of NO_2F and in the formation of a solid residue, $NO_2^+AsF_6^-$. Low-temperature infrared measurements on both salts, $FCl_2^+AsF_6^-$ and $FCl_2^+BF_4^-$, prove their ionic nature in the solid state. For FCl_2^+ all three fundamentals have been observed. They are split into several components by crystal field and ^{35}Cl–^{37}Cl isotope effects. Force constants based on a modified valence force field have been calculated for various structural models, bond angles, and assignments. From these data it is concluded that the most probable structure for FCl_2^+ is that of a symmetric, bent ion of symmetry C_{2v}. This ion has fluorine as a central atom and is isoelectronic with OCl_2. The FCl_2^+ cation can be considered as the first example of a polymeric halogen fluoride cation.

Introduction

Owing to their amphoteric nature, halogen fluorides can form (by combining with strong Lewis acids and bases) cations and anions containing one F^- ion less or more than the parent molecule. This group of compounds offers a unique chance to study the influence of the number of free electron pairs, of coordination number, and of a positive or negative charge at the central atom on the structure and bonding.[1] Recently, we have investigated the structure of ClF_2^-.[2-4]

ClF_2^+,[5,6] ClF_4^-,[7,8] IF_4^+,[9] IF_6^-,[10] and IF_6^+.[11] The existence of the Cl^+ cation, derived from ClF by combination with strong Lewis acids, such as AsF_5 or BF_3, has been reported in 1963 by Schmeisser[12]

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(12) M. Schmeisser, paper presented at the Symposium on Inorganic Fluorine Chemistry, Argonne, Ill., Sept 1963. For summary see *Science*, **143**, 1058 (1964).