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# An Electromotive Force Study of Molten Lithium Fluoride–Beryllium Fluoride Solutions[1,2]

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The potential of the cell

$$\mathrm{Be^0|BeF_2, LiF|HF, H_2, Pt}$$

was measured over a composition range of 0.30–0.90 mol fraction of BeF$_2$ and a temperature range of 500–900°. Since the cell potential was related to the activity of BeF$_2$ in the solutions by

$$E = E° - \frac{RT}{2F} \ln (P_{\mathrm{H_2}}a_{\mathrm{BeF_2}}/P_{\mathrm{HF}}{}^2)$$

activity coefficients could be derived for BeF$_2$ (and by a Gibbs–Duhem integration for LiF). Usefully accurate measurements could not be made with pure BeF$_2$ in the cell; hence values of $E°$ were calculated using values for $a_{\mathrm{BeF_2}}$ derived from the phase diagram and a previously reported heat of fusion (1.13 kcal/mol) giving $E° = 2.4430 - 0.0007952T$ V. This comparison of the emf data with the LiF–BeF$_2$ phase diagram also indicated that the heat of fusion for BeF$_2$ is <2.0 kcal/mol. A power series in $x_{\mathrm{LiF}}$ was assumed for log $\gamma_{\mathrm{BeF_2}}$ and the coefficients were determined by a least-squares fit to the data. This gave

$$\log \gamma_{\mathrm{BeF_2}} = \left(3.878 - \frac{2354}{T}\right)x_{\mathrm{LiF}}{}^2 + \left(-40.738 + \frac{36293}{T}\right)x_{\mathrm{LiF}}{}^3 + \left(94.400 - \frac{84871}{T}\right)x_{\mathrm{LiF}}{}^4 + \left(-67.418 + \frac{52924}{T}\right)x_{\mathrm{LiF}}{}^5$$

Formation free energies and heats for BeF$_2$ and BeO were also calculated by combining the results of the present study with available thermochemical data. The Be$^{2+}$|Be$^0$ and HF, H$_2$|F$^-$ electrodes performed acceptably for use as reference electrodes, both being stable and reproducible.

## I. Introduction

Precise emf measurements in molten fluoride solutions have been difficult to achieve in the past because of the lack of reliable electrodes, container materials, and insulators. In connection with the development of the molten salt reactor experiment (MSRE) at this laboratory,[3] techniques have been developed for purifying and containing molten fluoride melts—principally LiF–BeF$_2$ mixtures. Dirian, Romberger, and Baes[4] used these techniques in a study of the cell

$$\mathrm{Be^0|0.33\ BeF_2, 0.67\ LiF|HF, H_2, Pd}$$

They found from polarization measurements that the Be$^{2+}$|Be$^0$ and the H$_2$, HF|F$^-$ electrodes were reversible. The purposes of the present investigation were (1) to examine further the suitability of these electrodes as reference electrodes in such melts and (2) to use this cell, with the assumed cell reaction

$$\mathrm{Be^0(s) + 2HF(g) \rightleftharpoons BeF_2(soln) + H_2(g)} \qquad (1)$$

to extend and improve the thermodynamics of the important and interesting LiF–BeF$_2$ system.

Thus far, activity data for the LiF–BeF$_2$ system have been obtained from mass spectroscopic studies of the vapor,[5,6] from the phase diagram,[7,8] from emf measurments,[9] and from transpiration measurements of gaseous HF–H$_2$O mixtures equilibrated with the molten fluoride mixture.[10] The values derived from the phase data, besides being nonisothermal, have been limited in accuracy because the BeF$_2$ liquidus has been difficult to determine. In addition, various estimates[7,8,10–12] for the heat of fusion for BeF$_2$ are not in agreement. Mass spectroscopic and emf values of the activity were determined for only a limited number of compositions and temperatures. Probably the best activity values are those determined by Mathews and Baes[10] using a transpiration method to equilibrate gaseous HF–H$_2$O mixtures with molten LiF–BeF$_2$ mixtures. However, activities derived from these heterogeneous equilibria were of somewhat limited precision (±6%) and the equilibrium quotients

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(1) B. F. Hitch and C. F. Baes, Jr., USAEC Report ORNL-4257, July 1968.

(2) Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corp.

(3) W. R. Grimes, USAEC Report ORNL-3708, July 31, 1964, p 230.

(4) G. Dirian, K. A. Romberger, and C. F. Baes, Jr., USAEC Report ORNL-3789, Jan 1965, pp 76–79.

(5) J. Berkowitz and W. A. Chupka, *Ann. N. Y. Acad. Sci.*, **79**, 1073 (1960).

(6) A. Büchler and J. L. Stauffer in "Thermodynamics," Vol. 1, IAEA, Vienna, 1966, p 271.

(7) T. Førland in "Fused Salts," B. R. Sundheim, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 156.

(8) J. Lumsden, "Thermodynamics of Molten Salt Mixtures," Academic Press, London, 1966, p 227.

(9) A. Büchler, "Study of High Temperature Thermodynamics of Light Metal Compounds," Progress Report No. 9, Contract DA-19-020-ORD-5584, Army Research Office, Durham, N. C., Sept 30, 1963.

(10) A. L. Mathews and C. F. Baes, Jr., *Inorg. Chem.*, **7**, 373 (1968).

(11) J. A. Blauer, *et al.*, *J. Phys. Chem.*, **69**, 1069 (1965).

(12) A. R. Taylor and T. E. Gardner, "Some Thermal Properties of Beryllium Fluoride from 8 to 1200°K," U. S. Bureau of Mines, Report of Investigations, No. 6644, Mines Bureau, Pittsburgh, Pa., 1965.

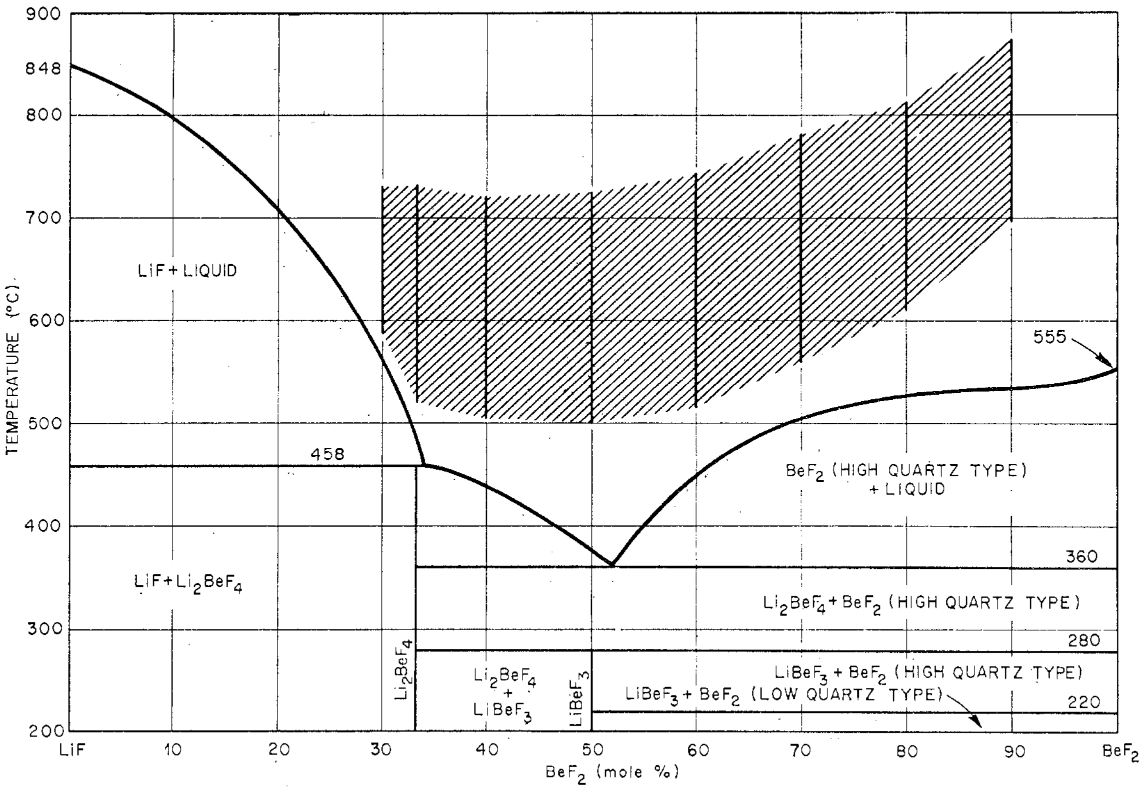

Figure 1.—Phase diagram of the LiF–BeF$_2$ system. Shaded portion represents composition and temperature range of emf measurements.

were measured in the presence of BeO as a saturating solid which might have influenced the activity values.

In the present investigation emf measurements were made over a composition range of 0.30–0.90 mol fraction of BeF$_2$ and a temperature range of 500–900° (Figure 1). An attempt was made to make measurements in pure BeF$_2$, but results of useful accuracy could not be obtained presumably because of its high viscosity and/or high electrical resistivity. Even at 900°, pure BeF$_2$ is very viscous (about 180 P[13]). The nickel cell vessel was not heated above 900° because of the tendency of the metal to soften at such elevated temperatures. The melting points of mixtures below 0.33 BeF$_2$ increase rapidly as the concentration approaches pure LiF as shown in the LiF–BeF$_2$ phase diagram[14] in Figure 1. The lower BeF$_2$ concentrations (below 0.30 BeF$_2$) were not investigated, therefore, since the accessible temperature range was so limited.

According to the assumed cell reaction (eq 1), the cell potential should be dependent on the activity of BeF$_2$, the activity of beryllium metal, and the partial pressures of HF and H$_2$

$$E = E^\circ - \frac{RT}{2F} \ln \frac{P_{H_2} a_{BeF_2}}{P_{HF}^2 a_{Be^0}} \qquad (2)$$

Previous measurements[4] with the HF–H$_2$ electrode, as well as the present ones, indicate the gases to be sufficiently ideal at the elevated temperatures and low-pressure levels involved to allow the use of partial pressures in place of fugacities in this Nernst expression.

In this study, mixtures of HF–H$_2$ were bubbled through molten LiF–BeF$_2$ and the partial pressures of the gases were determined by alkalimetric titration and gas volume measurements. The measured cell potential ($E$) was then corrected for the effect of the gas pressure quotient

$$E_c = E + \frac{RT}{2F} \ln \frac{P_{H_2}}{P_{HF^2}} \qquad (3)$$

The corrected potential $E_c$ is related to the activity of BeF$_2$ by

$$E_c = E^\circ - \frac{RT}{2F} \ln a_{BeF_2} \qquad (4)$$

assuming the activity of Be$^0$ to be unity.

## Notation

| | |
|---|---|
| 0.00 BeF$_2$ | The number preceding "BeF$_2$" denotes mole fraction |
| $P_T$, $P_{HF}$, $P_{H_2}$, $V$, $T$ | Total pressure (atm), partial pressures (atm), volume (l.) per unit time, and temperature (°K) in the region where gas enters the melt |
| $P^0_T$, $P^0_{H_2}$, $V^0$, $T^0$ | Corresponding measurements at the Bubble-O-Meter |
| $P_B$, $P^0_{H_2O}$ | Barometric pressure and vapor pressure of H$_2$O at $T^0$ |
| $P^0_{HF}$ | The approximate partial pressure of HF at the titrator (see below) |
| $\Delta P$ | Pressure drop required to maintain gas flow through the melt |

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(13) C. T. Moynihan and S. Cantor, USAEC Report ORNL-4076, Dec 1966, p 25.

(14) R. E. Thoma, *et al.*, *J. Nucl. Mater.*, **27**, No. 2, 176 (1968).

| | |
|---|---|
| $E$ | Cell potential measured experimentally for a fixed BeF$_2$ concentration and temperature |
| $E_0$ | The observed cell potential corrected to a gas pressure quotient of unity (eq 3) |
| $E°$ | The standard cell potential with pure BeF$_2$ as the standard state |

## II. Experimental Section

**Chemicals.**—Commercial hydrogen and helium were purified by passage through magnesium perchlorate and liquid nitrogen traps. Anhydrous hydrogen fluoride (99.9%) was used without further purification. Lithium fluoride (99.5%) was obtained from American Potash and Chemical Corp. Beryllium fluoride (from Brush Beryllium Corp. and from K & K Laboratories, Inc.) was vacuum distilled at 850° to remove reducible impurities which "poisoned" the electrodes (see below).

**Apparatus.**—The electrode vessel, constructed of 2.5-in. schedule 40 nickel pipe, 10 in. long, was separated into two compartments by a nickel sheet which extended to within 0.5 in. of the bottom and was so welded in place that the only salt contact between the two compartments was through this lower opening. Each compartment was equipped with a Swagelok fitting through which melt components could be added or an electrode inserted, a gas exit tube, and a thermocouple well. The Swageloks, which were water cooled, were equipped with Teflon insulator seals when the electrodes were inserted. The reaction vessel was located inside an upright tube furnace, the temperature of which was controlled by an L & N Series 60 DAT control unit.

The HF manifold pressure was controlled by regulating the temperature of the HF supply cylinder. The HF flow was controlled by a mass spectrometer leak valve.[15] A pressure relief valve was used to obtain a constant hydrogen manifold pressure and the flow was controlled by a needle valve.

**Electrodes.**—The H$_2$–HF–Pd electrode used by Dirian, *et al.*,[4] consisted of an open-ended palladium tube through which the gas mixture was bubbled. We found that while this arrangement produced stable potentials, it was somewhat noisy (±1 mV). Much less noisy electrodes ((±0.1 mV) were prepared by forming an egg-shaped bag of platinum gauze around the end of a nickel tube, tying it securely in place with small-diameter nickel wire, and crimping the free end so that the HF–H$_2$ mixture passing through the nickel tubing was forced through the gauze.

The beryllium electrode consisted of a cylinder of beryllium metal held in place 0.5 in. from the end of a nickel tube by crimping the tube slightly above and below it. Helium gas was passed through the tube to mix the salt. When the beryllium was placed too close to the tip of the nickel tube, the effect of helium bubbling was to make the electrode noisy. This was probably due to gas bubbles temporarily insulating the beryllium from the melt.

**Measurements.**—Four series of measurements were made, each beginning with a freshly prepared melt—either 0.33 BeF$_2$ or pure BeF$_2$ to which LiF or BeF$_2$ was added in increments to change the melt composition. At each composition the cell potential was measured as a function of temperature. The noise level of the potential varied from ±0.2 mV to as high as ±1.0 mV for the high-viscosity melts, but it did not show any drift toward a higher or lower potential. The temperature of the melt was determined by a calibrated chromel–alumel thermocouple positioned carefully to the exact depth of the electrode to reduce any error in temperature readings caused by thermal gradients in the melt. The partial pressures $P_{H_2}$ and $P_{HF}$ required to correct the observed cell potentials (eq 3) were determined as follows. The moles of HF ($n_{HF}$) found by alkalimetric titration to be present in a measured volume of gas ($V^0$) was used first to determine an approximate partial pressure $P^0_{HF}$

$$P^0_{HF} = n_{HF}RT^0/V^0$$

The following more exact expression[1] for the partial pressure of HF ($P_{HF}$) at the electrode includes the effect of the barometric pressure $P_B$, the pressure drop ($\Delta P$) caused by the pressure required to maintain bubbling through the melt and the titrator, and the saturation of the hydrogen stream with water (giving a partial pressure $P_{H_2O}$) prior to measuring the flow rate

$$P_{HF} = P^0_{HF}\left[\frac{P_B + \Delta P}{P_B - P_{H_2O} + P^0_{HF}}\right] \qquad (5)$$

The value of $P_{H_2}$ is then given by

$$P_{H_2} = P_B + \Delta P - P_{HF} \qquad (6)$$

**Errors.**—The HF–H$_2$ mixtures were analyzed before and after entering the HF–H$_2$ electrode compartment, and no discrepancy between the two could be detected. These analyses were performed periodically on all compositions up to 0.60 BeF$_2$ and temperatures up to 700°. (Melts of higher BeF$_2$ concentrations were not checked in this manner because difficulty was encountered in keeping the flow rate constant through these high-viscosity melts when the split-flow technique was attempted.) This indicates either (1) that no appreciable loss of HF occurred by diffusion to and reaction with the beryllium electrode and that no significant hydrogen loss occurred by diffusion through the walls of the nickel vessel, or (2) that if these effects were appreciable, they approximately cancelled one another. To test the possibility that H$_2$ and HF might tend to separate along the thermal gradient in the reaction vessel or that the electrodes were cooled significantly by the gas flowing to them, we varied the gas flow rate from 23 to 160 ml/min. This increase resulted in about a 1-mV increase in cell potential. Over the range of flow rates employed in the measurements, this corresponds to less than a 0.3-mV change in cell potential.

Early in the experimental work it was found that impurities present in commercial BeF$_2$ (*e.g.*, 1000 ppm total of Fe, Cr, Co, and Ni) were reduced at and poisoned both electrodes, causing reductions of the cell potential by as much as 0.5 V. With distilled BeF$_2$, containing only trace amounts of impurities, poisoning was not noted and this material was used for all measurements in this investigation. Since HF–H$_2$ sparging is a standard purification procedure for removing oxides from fluoride melts,[16] the use of HF–H$_2$ as one of the electrode materials in the present study undoubtedly kept the oxide concentration small. Typically, beryllium metal contains about 1000–4000 ppm of oxygen.[17] Using the larger value, the maximum concentration of oxide contributed by the beryllium electrode would have been $10^{-3}$ mol/kg, which is about one order of magnitude below the solubility of BeO.[18] Therefore, no significant error is expected owing to oxide contamination of the melt.

A composition error was discovered at the end of one run, caused apparently by distillation losses from pure BeF$_2$ during a prolonged period above 800°, where the vapor pressure is appreciable.[19] After subsequent additions of LiF, a thermal analysis[20] indicated the amount of the composition error.

The random errors in the measured quantities were estimated to be ±0.5 mV for the cell potential, ±0.5° for the temperature, and 0.001 atm for $P_{HF}$. These errors were predicted to produce, typically, a standard deviation of about 2 mV for the corrected cell potential, consistent with observed scatter of about 1–3 mV. The major source of this uncertainty was the ±0.001-atm uncertainty in $P_{HF}$ which in turn was caused by the limited precision of the HF flow rate.

## III. Results and Discussion

The corrected cell potentials (Table I) were least-

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(15) Diaphragm-type adjustable-leak valve (Reference No. C-I 24492A) obtained from ORGDP, Oak Ridge, Tenn.

(16) J. H. Shaffer, USAEC Report ORNL-3078, July 1964, p 288.

(17) G. E. Darwin and J. H. Buddery, "Beryllium," Butterworth and Co. Ltd., London, 1960, p 85.

(18) B. F. Hitch and C. F. Baes, Jr., USAEC Report ORNL-4076, Dec 1966, p 19.

(19) S. Cantor, *et al.*, USAEC Report ORNL-3913, Dec 1965, p 27.

(20) Temperature–composition values used here for the BeF$_2$ liquidus were supplied by S. Cantor of this laboratory.

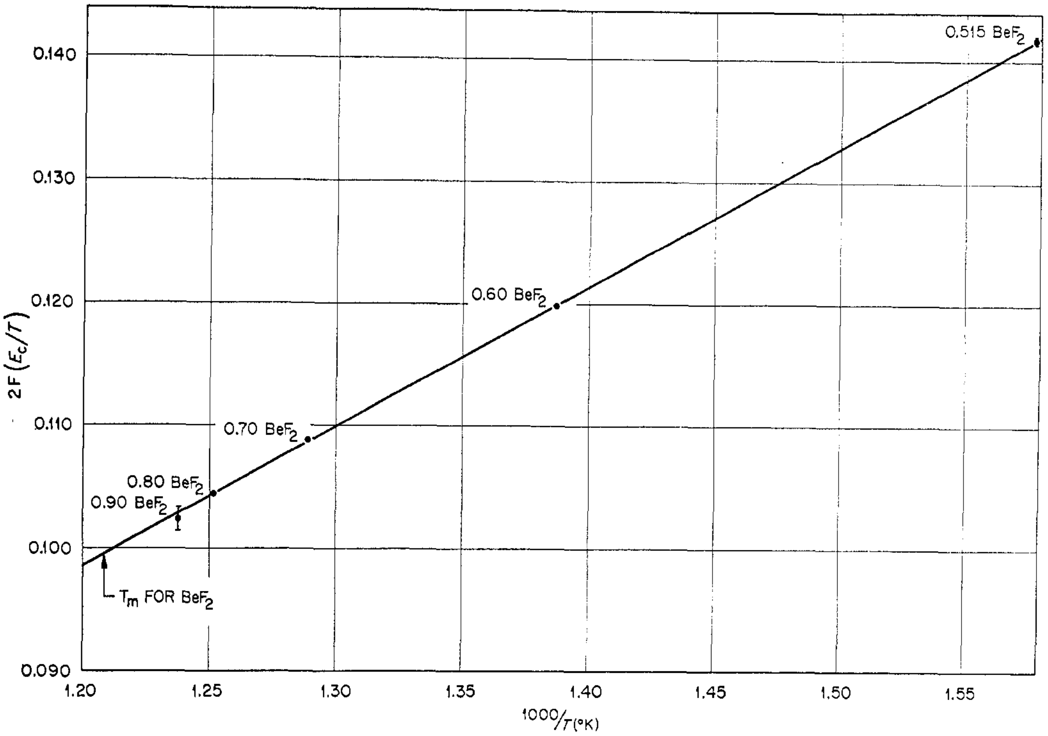

Figure 2.—Correlation of $E_c$ with BeF$_2$ liquidus data according to eq 9.

TABLE I

PRESSURE-CORRECTED CELL POTENTIALS ($E_c$) OBTAINED FROM MEASUREMENTS IN MOLTEN LiF–BeF$_2$

| $X_{BeF_2}$ | Temp. (°C) | $E_c$ (volts) | $X_{BeF_2}$ | Temp. (°C) | $E_c$ (volts) | $X_{BeF_2}$ | Temp. (°C) | $E_c$ (volts) |
|---|---|---|---|---|---|---|---|---|
| 0.30 | 585.1 | 1.8864 | 0.50 | 617.3 | 1.7629 | 0.80 | 800.4 | 1.6027 |
| 0.30 | 646.0 | 1.8447 | 0.50 | 568.3 | 1.7991 | 0.80 | 751.0 | 1.6335 |
| 0.30 | 696.2 | 1.8126 | 0.50 | 546.6 | 1.8127 | 0.80 | 656.5 | 1.7132 |
| 0.30 | 732.0 | 1.7882 | 0.50 | 503.3 | 1.8467 | 0.80 | 632.5 | 1.7252 |
| 0.30 | 609.2 | 1.8680 | 0.50 | 511.8 | 1.8387 | 0.80 | 704.9 | 1.6725 |
| 0.30 | 681.0 | 1.8213 | 0.50 | 608.5 | 1.7671 | 0.80 | 754.0 | 1.6321 |
| 0.33 | 562.9 | 1.8812 | 0.50 | 613.1 | 1.7648 | 0.80 | 681.0 | 1.6907 |
| 0.33 | 514.0 | 1.9152 | 0.50 | 685.2 | 1.7116 | 0.80 | 633.5 | 1.7205 |
| 0.33 | 601.0 | 1.8561 | 0.50 | 681.0 | 1.7163 | 0.80 | 611.5 | 1.7484 |
| 0.33 | 649.5 | 1.8230 | 0.50 | 632.8 | 1.7516 | 0.80 | 639.7 | 1.7206 |
| 0.33 | 698.0 | 1.7891 | 0.50 | 561.5 | 1.8022 | 0.79 | 887.5 | 1.5304 |
| 0.33 | 624.1 | 1.8397 | 0.50 | 728.0 | 1.6765 | 0.79 | 810.0 | 1.5967 |
| 0.33 | 565.0 | 1.8757 | 0.50 | 707.0 | 1.6972 | 0.79 | 735.4 | 1.6482 |
| 0.33 | 720.8 | 1.7653 | 0.50 | 658.0 | 1.7340 | 0.79 | 663.0 | 1.7051 |
| 0.33 | 529.0 | 1.9035 | 0.60 | 637.0 | 1.7263 | 0.79 | 616.0 | 1.7387 |
| 0.33 | 617.2 | 1.8436 | 0.60 | 566.5 | 1.7856 | 0.79 | 814.1 | 1.5909 |
| 0.33 | 617.2 | 1.8396 | 0.60 | 735.0 | 1.6555 | 0.90 | 804.1 | 1.5819 |
| 0.33 | 550.0 | 1.8857 | 0.60 | 637.0 | 1.7283 | 0.90 | 866.0 | 1.5307 |
| 0.33 | 624.5 | 1.8356 | 0.60 | 591.1 | 1.7656 | 0.90 | 754.8 | 1.6208 |
| 0.33 | 671.0 | 1.8016 | 0.60 | 521.0 | 1.8160 | 0.90 | 706.2 | 1.6613 |
| 0.33 | 812.0 | 1.7081 | 0.60 | 591.0 | 1.7672 | 0.90 | 778.0 | 1.5996 |
| 0.40 | 597.5 | 1.8069 | 0.60 | 591.0 | 1.7667 | 0.90 | 876.5 | 1.5277 |
| 0.40 | 609.5 | 1.8000 | 0.60 | 521.2 | 1.8170 | 0.90 | 802.5 | 1.5905 |
| 0.40 | 609.5 | 1.7991 | 0.60 | 710.0 | 1.6760 | 0.90 | 702.0 | 1.6620 |
| 0.40 | 661.2 | 1.7623 | 0.60 | 709.0 | 1.6771 | | | |
| 0.40 | 686.6 | 1.7430 | 0.60 | 662.0 | 1.7128 | | | |
| 0.40 | 685.8 | 1.7478 | 0.69 | 760.0 | 1.6310 | | | |
| 0.40 | 528.2 | 1.8578 | 0.69 | 706.5 | 1.6736 | | | |
| 0.40 | 528.2 | 1.8578 | 0.69 | 609.6 | 1.7477 | | | |
| 0.40 | 536.5 | 1.8540 | 0.69 | 562.0 | 1.7844 | | | |
| 0.40 | 535.0 | 1.8522 | 0.69 | 663.0 | 1.7085 | | | |
| 0.40 | 706.0 | 1.7337 | 0.69 | 794.9 | 1.6079 | | | |
| 0.40 | 706.0 | 1.7316 | | | | | | |

squared to the expression $E_c = A + BT$ at each composition. The values of $A$ and $B$ obtained are listed in Table II.

**Thermodynamics of LiF–BeF$_2$.**—The activity of BeF$_2$ may be calculated from eq 4 using the emf data ($E_c$) obtained in this study if the appropriate values for the standard cell potential ($E°$) are known. As mentioned previously, several attempts were made to determine $E°$ experimentally, but values of useful accuracy could not be obtained because of the high viscosity and possibly because of the high electrical resistivity of pure BeF$_2$.

The values of $E_c$ obtained for various BeF$_2$ compositions do not lend themselves to direct extrapolation to $E°$. However, the standard cell potential may be calculated by relating data in this study with the BeF$_2$ liquidus data in the following manner. If the assumption is made that the standard cell potential ($E°$) varies linearly with temperature ($E° = A° + B°T$),[21] then eq 4 may be written

$$E_c = A° + B°T - \frac{RT}{2F} \ln a_{BeF_2}$$

$$\ln a_{BeF_2} = \frac{2F(A° + B°T - E_c)}{RT} \qquad (7)$$

It is then possible to equate eq 7 to

$$\ln a_{BeF_2}\,(\text{BeF}_2 \text{ satn}) = -\frac{\Delta H_f}{R}\left(\frac{1}{T} - \frac{1}{T_f}\right) \qquad (8)$$

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[21] Using the heat capacity data in the JANAF tables, the $\Delta C_p$ effect over a temperature range of 450–900° was evaluated and found to produce a negligible deviation from a linear dependence of $E°$ on temperature. The $\Delta C_p$ correction also produces negligible changes in the plot in Figure 2.

Table II

Parameters in the Expression $E = A + BT$ (Volts)

| $X_{\mathrm{BeF_2}}$ | $A$ | $\sigma_A$ | $10^3B$ | $10^3\sigma_B$ | $\sigma E_0$, mV |
|---|---|---|---|---|---|
| 0.30 | 2.4521 | 0.0053 | −0.6607 | 0.0080 | 0.98 |
| 0.33 | 2.4602 | 0.0048 | −0.6944 | 0.0077 | 2.28 |
| 0.40 | 2.4258 | 0.0040 | −0.7091 | 0.0065 | 1.56 |
| 0.50 | 2.4179 | 0.0041 | −0.7369 | 0.0065 | 1.68 |
| 0.60 | 2.4162 | 0.0054 | −0.7537 | 0.0061 | 1.98 |
| 0.70 | 2.4226 | 0.0049 | −0.7643 | 0.0071 | 1.42 |
| 0.80 | 2.4149 | 0.0072 | −0.7595 | 0.0101 | 3.28 |
| 0.90 | 2.4296 | 0.0162 | −0.7861 | 0.0205 | 3.54 |

(where $\Delta H_f$ is the heat of fusion of BeF$_2$ and $T_f$ is the melting point of pure BeF$_2$) to obtain at the BeF$_2$ liquidus temperatures and compositions a relationship between $A°$, $B°$, $\Delta H_f$, and $E_c$. Combining eq 7 and 8

$$\frac{2F(A° + B°T - E_c)}{RT} = -\frac{\Delta H_f}{R}\left(\frac{1}{T} - \frac{1}{T_f}\right)$$

which may be rearranged to

$$\frac{2FE_c}{T} = 2FB° - \frac{\Delta H_f}{T_f} + (2FA° + \Delta H_f)\frac{1}{T} \qquad (9)$$

This relationship permits correlation of the data ($E_c$) obtained in the present investigation with the phase diagram data[14] since a plot of $2FE_c/T$ *vs.* $1/T$ should be linear. Using the least-squares parameters for each composition (Table II), values for $E_c$ were calculated for the liquidus temperatures at 0.515, 0.60, 0.70, 0.80, and 0.90 BeF$_2$ and then plotted according to eq 9, Figure 2.[21] The resulting points follow the predicted linear relationship within their estimated uncertainties. Parameters for the least-squared line in Figure 2 are

$$\text{intercept} = -0.03805 \pm 0.0034\ \text{(kcal/deg)} = 2FB° - \frac{\Delta H_f}{T_f} \qquad (10)$$

$$\text{slope} = 113.84 \pm 2.48\ \text{(kcal)} = 2FA° + \Delta H_f \qquad (11)$$

The point at 0.90 BeF$_2$ was not used because the uncertainty in $E_c$ is relatively large.

When values for $A°$ and $B°$ were calculated using various literature values for the heat of fusion of BeF$_2$ and a melting point of 555° for pure BeF$_2$, it was found that a heat of fusion >2.0 kcal/mol yields values of $E°$ which are greater than corresponding values of $E_c$ at the higher BeF$_2$ concentrations (Figure 3). This creates an impossible situation in which the activity of BeF$_2$ in the mixture is greater than the activity of pure liquid BeF$_2$. Thus the results of this study clearly support the lower values for the heat of fusion for BeF$_2$.[11,12]

The emf data ($E_c$) obtained in the present study were fitted by least squares to the empirical eq III in Table III, using the calorimetric value (1.13 kcal/mol) of Taylor and Gardner[12] for the heat of fusion of BeF$_2$. The resulting smoothed lines for $E_c$ at various BeF$_2$ concentrations are shown in Figure 4. The average deviation of the measured $E_c$ values from these smoothed values was approximately ±2.5 mV or 1.41 standard deviations.

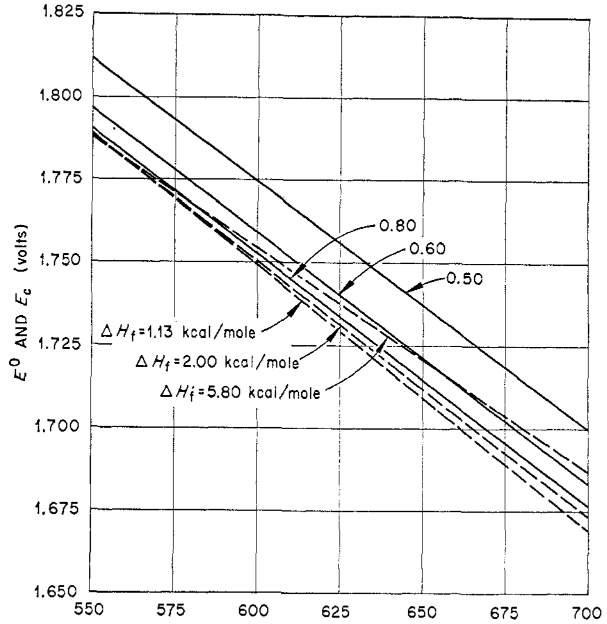

Figure 3.—Effect of the heat of fusion of BeF$_2$ in determining $E°$ (dashed lines). The solid lines represent $E_c$ for various mole fractions of BeF$_2$.

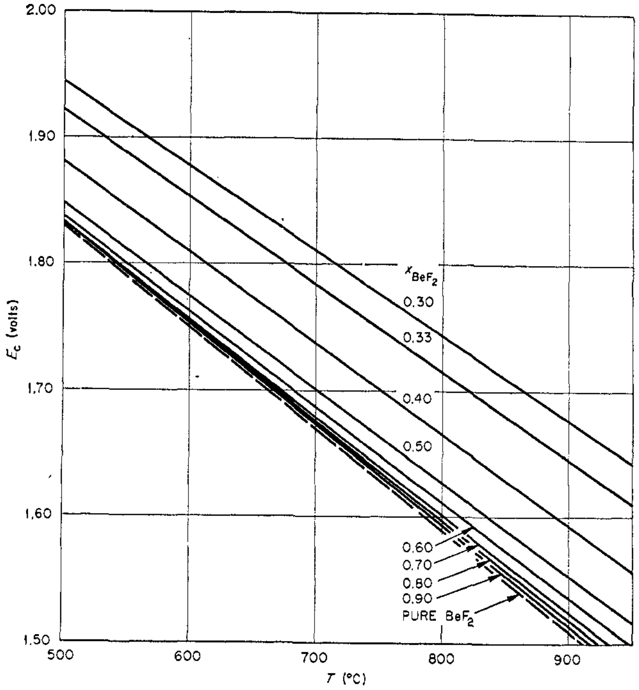

Figure 4.—Pressure-corrected cell potentials ($E_c$) as a function of temperature based on equations in Table IV.

A Gibbs–Duhem integration for the expression for $\gamma_{\mathrm{BeF_2}}$ (eq III, Table III) was carried out to give the corresponding expression for $\gamma_{\mathrm{LiF}}$ (eq IV, Table III). The integration constant for eq IV was determined by comparison with $\gamma_{\mathrm{LiF}}$ values derived from the liquidus data[14] with a heat of fusion of 6.47 kcal/mol[22] for LiF. A more accurate evaluation of the integration constant

[22] T. B. Douglas and J. L. Dever, *J. Am. Chem. Soc.*, **76**, 4826 (1954).

TABLE III

EXPRESSIONS FOR CELL POTENTIALS AND ACTIVITY COEFFICIENTS IN THE $LiF-BeF_2$ SYSTEM

| Eq No. | |
|---|---|
| I | $E_0 = E° - \frac{2.3RT}{2F} \log x_{BeF_2} - \frac{2.3RT}{2F} \log \gamma_{BeF_2}$ |
| II | $E° = 2.4430 - 0.0007962T^a$ |
| III | $\log \gamma_{BeF_2} = \left(3.878 - \frac{2354}{T}\right)x_{LiF}^2 + \left(-40.738 + \frac{36293}{T}\right)x_{LiF}^3 + \left(94.400 - \frac{84871}{T}\right)x_{LiF}^4 + \left(-67.418 + \frac{52924}{T}\right)x_{LiF}^5$ |
| IV | $\log \gamma_{LiF} = 0.938 - \frac{232}{T} + \left(-36.973 + \frac{14653}{T}\right)x_{BeF_2}^2 + \left(126.095 - \frac{74589}{T}\right)x_{BeF_2}^3 + \left(-158.417 + \frac{113592}{T}\right)x_{BeF_2}^4 + \left(67.418 - \frac{52924}{T}\right)x_{BeF_2}^5$ |

[a] Calculated from eq 10 and 11 using a heat of fusion for $BeF_2$ of 1.13 kcal/mol.

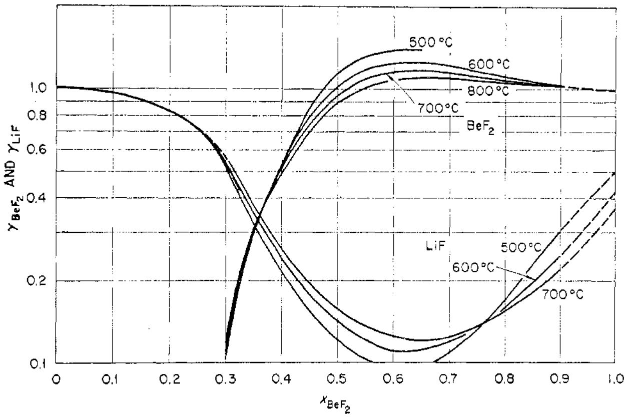

Figure 5.—Activity coefficients in molten $LiF-BeF_2$ mixtures based on eq III and IV of Table III.

should be possible when the heat of mixing measurements of Holm and Kleppa[23] become available for the $LiF-BeF_2$ system.

Smoothed values of $\gamma_{BeF_2}$ are shown as a function of composition at several temperatures in Figure 5. These results are consistent with those obtained by Mathews and Baes[10] over a composition range 0.30–0.60 $BeF_2$. However at $x_{BeF_2} > 0.60$ the two sets of results diverge. The values obtained in the present study are thought to be the more reliable since they are consistent both with the phase data and with a low heat of fusion for $BeF_2$. The previous measurements at compositions >0.60 $BeF_2$ might have been affected by difficulties in mixing LiF and $BeF_2$ at high $BeF_2$ concentrations and by BeO saturation. In the present study it was found that at 0.90 $BeF_2$, a well-mixed melt was not obtained until the temperature was raised above 850°. This procedure was followed at all high $BeF_2$ concentrations to ensure proper mixing of the $LiF-BeF_2$. The effect of the presence of BeO as a saturating solid should have been inappreciable for compositions up to 0.50 $BeF_2$ since the solubility of BeO was known to be low (<0.1 mol %[18]); however, if its solubility increases with further increases in $BeF_2$ content, this might have appreciably affected the results of Mathews and Baes.

The free energy and heat of the cell reaction (eq I) were calculated and combined with the available thermochemical values for HF[24] to derive the free energy and heat of formation for liquid $BeF_2$ (Table IV). Mathews and Baes[10] measured the equilibrium quotient for the reaction

$$H_2O(g) + BeF_2(soln) \rightleftharpoons 2HF(g) + BeO(s) \qquad (12)$$

If eq 12 is combined with the reaction in eq 1, the result is

$$H_2O(g) + Be(s) \rightleftharpoons BeO(s) + H_2(g) \qquad (13)$$

The free energy and heat of this last reaction thus could be obtained by combining the two sets of measurements at each composition (<0.60 $BeF_2$) where they are consistent, and, since the thermochemical data for $H_2O$ are accurately known, improved free energy and heats of formation for BeO could be calculated (Table IV). These calculations were made for a temperature of 900°K and values were generated at other temperatures using the heat capacity data in the JANAF tables.[24] From the $\Delta G_f$ values thus obtained at 298°K, $\Delta H_f$ values were also calculated using third-law $\Delta S_f$ values derived from the JANAF tables.

The JANAF value for $\Delta H_f$ of BeO—an oxygen-bomb calorimeter measurement of Cosgrove and Snyder[25]—differs from the present one by much more (>2 kcal) than its reported uncertainty (±0.1 kcal). Since the discrepancy also is considerably greater than the estimated error in the present values, we can only suggest that an unsuspected error was present in the

TABLE IV

FORMATION HEATS AND FREE ENERGIES OF $BeF_2$ AND BeO

| Temp, °K | State | $\Delta H_f$, kcal/mol | $\Delta G_f$, kcal/mol |
|---|---|---|---|
| | | $BeF_2$ | |
| | | −246.0 | −234.4 |
| 298 | c | (−245.7)[a] | |
| | | (−242.3 ± 2)[b] | (−231.0 ± 2)[b] |
| 800 | c | −244.8 | −215.5 |
| 900 | l | −243.1 ± 1 | −211.9 ± 1 |
| 1000 | l | −242.5 | −208.5 |
| | | BeO | |
| | | −145.9 | −138.4 |
| 298 | c | (−145.3)[a] | |
| | | (−143.1 ± 0.1)[b] | (−136.1 ± 1)[b] |
| 800 | c | −145.7 | −125.7 |
| 900 | c | −145.6 | −123.2 ± 0.5 |
| 1000 | c | −145.5 | −120.7 |

[a] $\Delta H_f$ values derived from present $\Delta G_f$ values at 298°K and third-law entropies from JANAF tables. [b] See ref 24.

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calorimetric measurements. The JANAF value for $\Delta H_f$ 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 $\Delta H_f$ 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.

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# Enthalpies of Mixing in Liquid Beryllium Fluoride–Alkali Fluoride Mixtures

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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

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