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AN EMF STUDY OF $LiF-BeF_2$ SOLUTIONS

B. F. Hitch
C. F. Baes, Jr.

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
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ABSTRACT

The potential of the cell

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

with the assumed cell reaction

$$Be(s) + 2HF(g) \rightleftarrows BeF_2(d) + H_2(g)$$

was measured over a composition range of 0.30 to 0.90 mole fraction BeF_2 and a temperature range of 500 to 900°C. Since this cell potential is related to the activity of BeF_2 in the solutions by

$$E = E^{o} - \frac{RT}{2F} \ell n \frac{P_{H_2}\ a_{BeF_2}}{P_{HF}^2}$$

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^{o} were calculated using values for a_{BeF_2} derived from the phase diagram and previously reported heat of fusion (1.13 kcal/mole) giving

$$E^{o} = 2.4430 - 0.0007952T$$

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/mole. A power series in x_{LiF} was assumed for $\log \gamma_{BeF_2}$ and the coefficients determined by a least squares fit to the data. This gave

$$\log \gamma_{BeF_2} = (3.8780 - \frac{2353.5}{T})x_{LiF}^2 + (-40.7375 + \frac{36292.8}{T})x_{LiF}^3 + (94.3997 - \frac{84870.9}{T})x_{LiF}^4 + (-67.4178 + \frac{52923.5}{T})x_{LiF}^5$$

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 $Be^{2+}|Be^{o}$ and $HF,H_2|F^-$ electrodes performed acceptably for use as reference electrodes, both being stable and reproducible.

I. INTRODUCTION

Molten fluoride mixtures of LiF and BeF_2 are of considerable interest at this Laboratory since they are the principal constituents in the molten-salt reactor (MSRE) fuel and coolant salts.[1] Although the molten LiF-BeF_2 system has received considerable attention, only a limited number of emf investigations have been attempted. The development of reference electrode half-cells for molten fluorides in general would facilitate the determination of electrode potentials for various fluoride constituents and the detection of certain impurities contained in these mixtures.

The purpose of this investigation was to study the cell reaction

$$Be^{o}(s) + 2HF(g) \rightleftarrows BeF_2(d) + H_2(g) \qquad (1)$$

in the molten LiF-BeF_2 system using $Be^{2+}|Be^{o}$ and $HF,H_2|F^-$ electrodes. Emf data obtained in this study would hopefully extend and improve the thermodynamics of this molten fluoride system. At the same time emf measurements should demonstrate useful electrodes which may serve as reference electrodes in future emf studies in this important molten salt solvent system.

Thus far activity data for the LiF-BeF_2 systems has been obtained from mass spectroscopic studies of the vapor,[2,3] from the phase diagram,[4,5] from emf measurements,[6] and from transpiration data where gaseous HF-H_2O mixtures were equilibrated with the molten fluoride mixture.[7] The values derived from the phase data, besides being non-isothermal, have been limited in accuracy because the BeF_2 liquidus has been difficult to determine. In addition, the reported values[4,5,7,8,9] 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[7] using a transpiration method to equilibrate gaseous $HF-H_2O$ mixtures with molten $LiF-BeF_2$ mixtures. However, activities derived from these heterogeneous equilibria are somewhat limited in accuracy (± 6%) and the equilibrium quotients were measured in the presence of BeO as a saturating solid which might have influenced the activity values.

Direct determination of the activity of BeF_2 by emf measurements should yield more accurate values over a greater composition range than any of the methods previously mentioned. Dirian, Romberger and Baes[10] measured the potential of the following cell as a function of temperature.

$$Be^{o}|0.33\ BeF_2 - 0.67\ LiF|HF,H_2,Pd$$

The cell reaction is that shown in eq. (1). The two electrodes - $Be^{2+}|Be^{o}$ and $HF,H_2|F^-$ - were judged by Dirian et al, to be reversible from polarization measurements.

In the present investigation these two electrodes were used to determine the cell potential over a composition range of 0.30 to 0.90 mole fraction BeF_2 and a temperature range of 500 to 900°C (Fig. 1). An attempt was made to obtain 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°C, pure BeF_2 is very viscous (about 180 poise[11]). The reaction vessel was not heated above 900°C because of the tendency of nickel 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[12] in Fig. 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.

$$E = E^o - \frac{RT}{2F} \ln \frac{P_{H_2} \quad a_{BeF_2}}{P^2_{HF} \quad a_{Be^o}} \tag{2}$$

Previous measurements[10] 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 determined by alkalimetric titration and gas volume measurements. The measured cell potential (E) was then corrected for the effect of the gas pressure quotient.

$$E_c = E + \frac{RT}{2F} \ln \frac{P_{H_2}}{P^2_{HF}} \tag{3}$$

The corrected potential E_c is related to the activity of BeF_2 by

$$E_c = E^o - \frac{RT}{2F} \ln a_{BeF_2} \tag{4}$$

assuming the activity of Be^o to be unity.

Notation

The following notation will be used:

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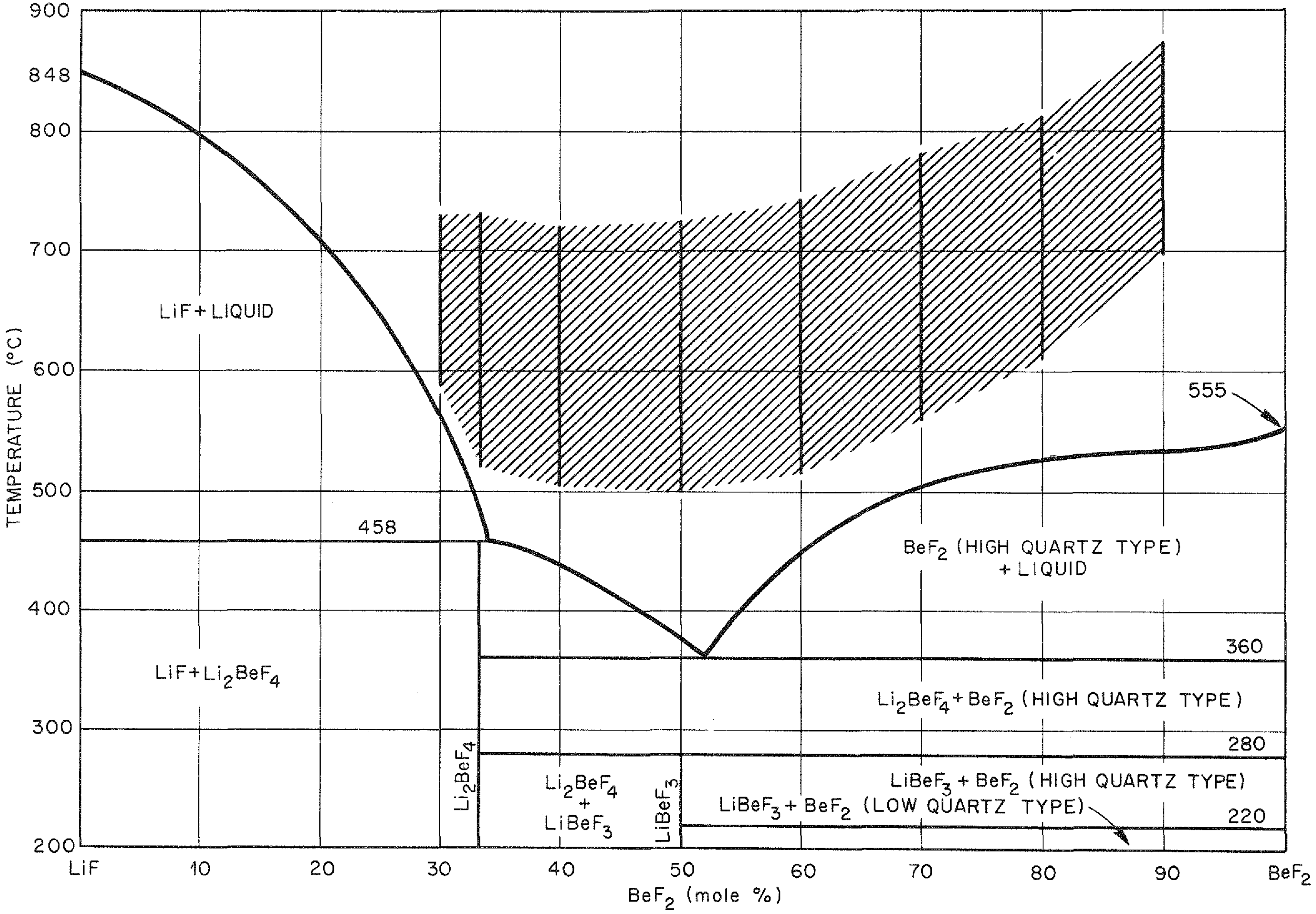

Fig. 1. Phase Diagram of the LiF-BeF_2 System.

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.
$P^o_T, P^o_{H_2}, V^o, T^o$	Corresponding measurements at the Bubble-O-Meter.
$P_B, P^o_{H_2O}$	Barometric pressure and vapor pressure of H_2O at T°.
P^o_{HF}	The approximate partial pressure of HF at the titrator. (see Calculations section below.)
ΔP	Pressure drop required to maintain gas flow through the melt.
E	Cell potential measured experimentally for a fixed BeF_2 concentration and temperature.
E_c	The observed cell potential corrected to a gas pressure quotient of unity (eq. 3).
E^o	The standard cell potential with pure BeF_2 as the standard state.

II. EXPERIMENTAL

Chemicals

Gases

Commercial H_2 was purified by passage through a deoxo unit, a magnesium perchlorate drying tube and, finally, a liquid N_2 trap. Anhydrous HF (99.9%) was used without further purification. Commercial He was purified by passage through an ascarite trap, a magnesium perchlorate trap and, finally, a liquid N_2 trap.

Melt Components

Lithium fluoride (99.5%) was obtained from American Potash and Chemical Corporation. Beryllium fluoride was from three sources:

Brush Beryllium Corporation, K and K Laboratories, Inc., and commercial BeF_2 distilled by the Reactor Chemistry Division at Oak Ridge National Laboratory. Most of the commercial BeF_2 contained impurities which "poisoned" the electrodes (see p. 20). With the exception of one composition, the distilled BeF_2 was used throughout this investigation since the purity was such that no electrode "poisoning" was encountered.

Reagents

Reagent grade 1N NaOH from Fisher Chemical Company was standardized with potassium acid phthalate.

Apparatus

Experiments were carried out in the apparatus shown in Fig. 2.

Cell Design

A sketch of the nickel reaction vessel used to contain the LiF-BeF_2 mixtures is shown in Fig. 3. This vessel was constructed of 2-1/2-in. schedule 40 nickel pipe and was separated into two compartments by a 1/16-in. nickel sheet which extended to within 1/2-in. of the vessel bottom. The nickel sheet was welded so that the only contact between the two compartments was through the 1/2-in. opening at the bottom. The vessel was 10-in. long.

Each compartment was equipped with the following: a 3/4-in. Swagelok fitting through which melt components could be added or an electrode inserted, a 1/4-in. gas exit tube, and a thermocouple well. The Swageloks were equipped with Teflon seals when the electrodes were inserted. This provided an electrical insulator as well as a leak-tight fitting for the 1/8-in. nickel tubing. Cooling coils were wrapped around each Swagelok to provide cooling when the reaction vessel

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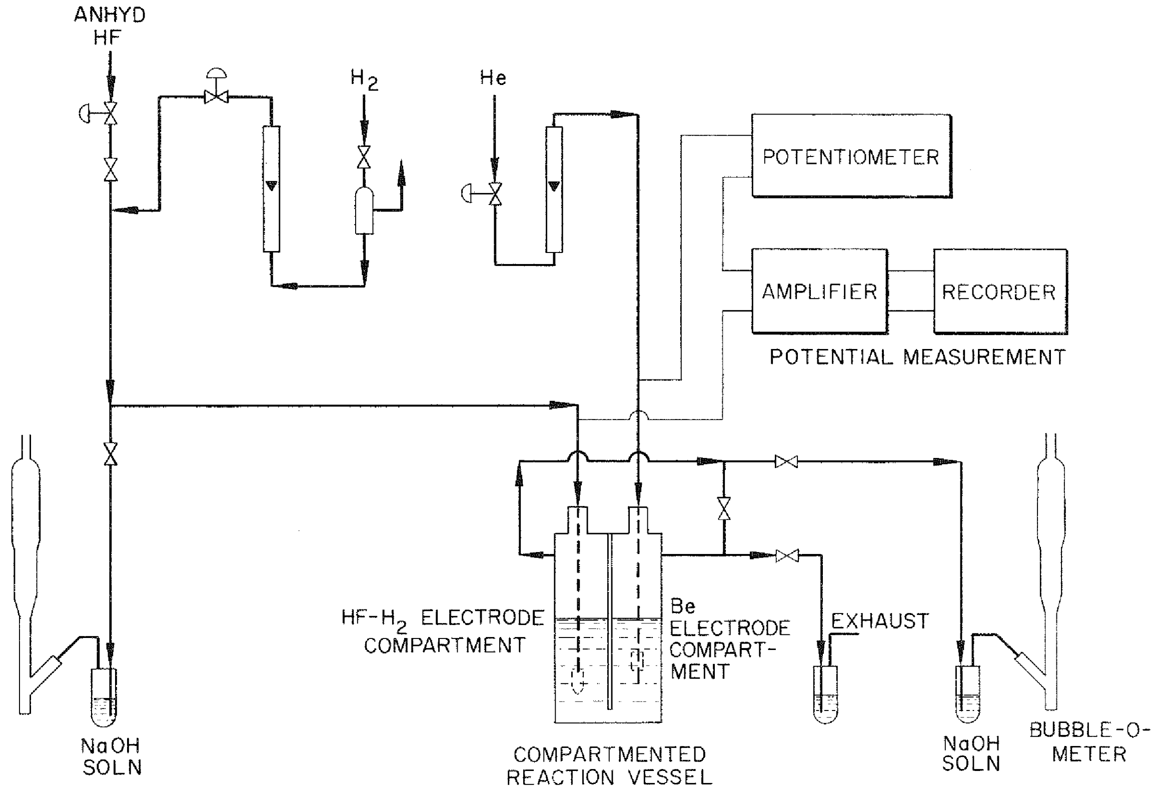

Fig. 2. Schematic Diagram of Apparatus Used to Measure Cell Potentials in Molten LiF-BeF$_2$ Mixtures.

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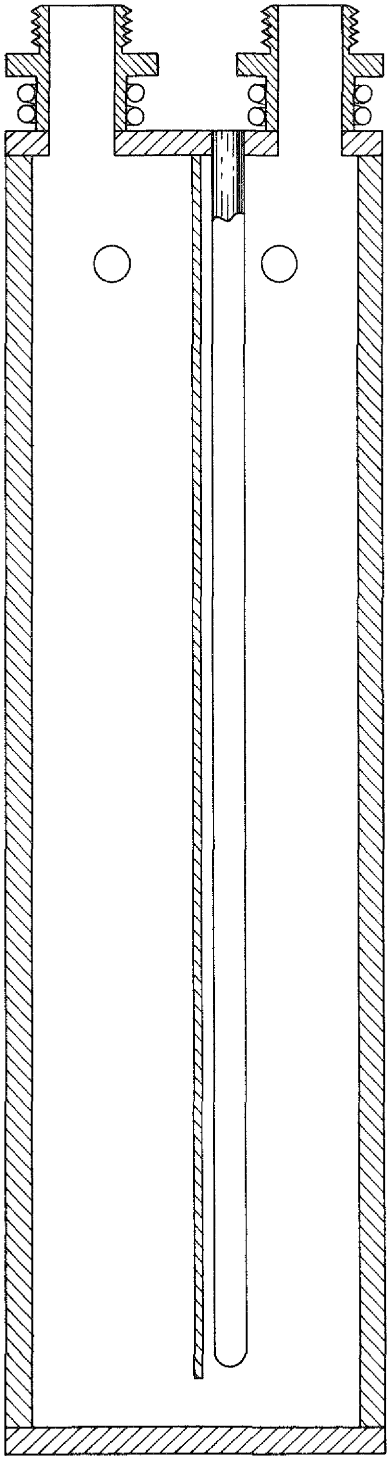

Fig. 3. Compartmented Cell Used to Contain Molten LiF-BeF$_2$ Mixtures.

was at elevated temperatures.

The reaction vessel was located inside an upright tube furnace, the temperature was controlled by an L & N Series 60 D.A.T. Control Unit. The temperature of the reaction vessel was checked with a calibrated Chromel-Alumel thermocouple and an L & N K-3 potentiometer.

A 4-in. diameter vessel, fitted with 1/2-in. diameter electrode compartments, was used for preliminary measurements. Electrodes used in the cylindrical compartments were insulated from the compartment walls with boron nitride spacers, but even then accidental electrical shorts were a problem. The large compartments of the reaction vessel used in the present investigation eliminated the need for insulating spacers except the Teflon seal at the top of the compartment, and no problems from electrical shorting were encountered.

$HF-H_2$ Electrode

An H_2,HF,Pd electrode of the type used by Dirian and Romberger[10] was used in some of the preliminary measurements. This electrode produced stable potentials but was quite noisy (± 1 mv). Platinum gauze was substituted for the palladium and was found to be just as responsive and capable of very low noise levels (0.1 mv). The platinum gauze type (Fig. 4) was used for all measurements in this investigation. Electrodes were prepared by forming an egg-shaped bag with th- gauze and slipping the open end over 1/8-in. nickel tubing and tying it securely with small diameter nickel wire. The other end of the bag was crimped together so that the $HF-H_2$ mixture, passing down through the nickel tubing had to pass through the gauze. The 1/8-in. nickel tubing transmitted the $HF-H_2$ mixture and provided electrical contact.

Beryllium Electrode

These electrodes (Fig. 4) were constructed by slipping a beryllium metal cylinder (3/8-in. O.D., 1/8-in. I.D., and 1/2-in. length) over a 1/8-in. nickel tube and crimping the nickel tube slightly on each side of the beryllium cylinder to hold it securely. The cylinder was positioned about 1/2-in. from the tip of the nickel tube. Lowering the beryllium metal closer to the tip of the nickel tube caused an increase in the potential noise. This was probably due to helium bubbles temporarily insulating the beryllium from the melt. The 1/8-in. nickel tube was used to bubble helium into the compartment and to provide electrical contact.

Flow Control of Gases

Hydrogen Fluoride.-- The HF manifold pressure was controlled by regulating the temperature of the HF supply cylinder. The flow of HF was controlled by a mass spectrometer leak valve.[13] The gas flowed to a monel tee where it mixed with H_2. The mixed gases were passed either directly to the $HF-H_2$ electrode or a portion was split off for influent gas analysis.

Hydrogen.-- A pressure relief valve (Moore Products Company, differential type flow controller, Model 63 BD, modified form) was used to reduce the hydrogen manifold pressure to a constant value of 3.0 lb. gauge. The flow was then controlled by a brass needle valve obtained from Nuclear Products Company. The H_2 was then mixed with the HF as described above.

Helium.-- Helium flow was controlled with the same type needle valve used for the H_2; no attempt was made to control the manifold

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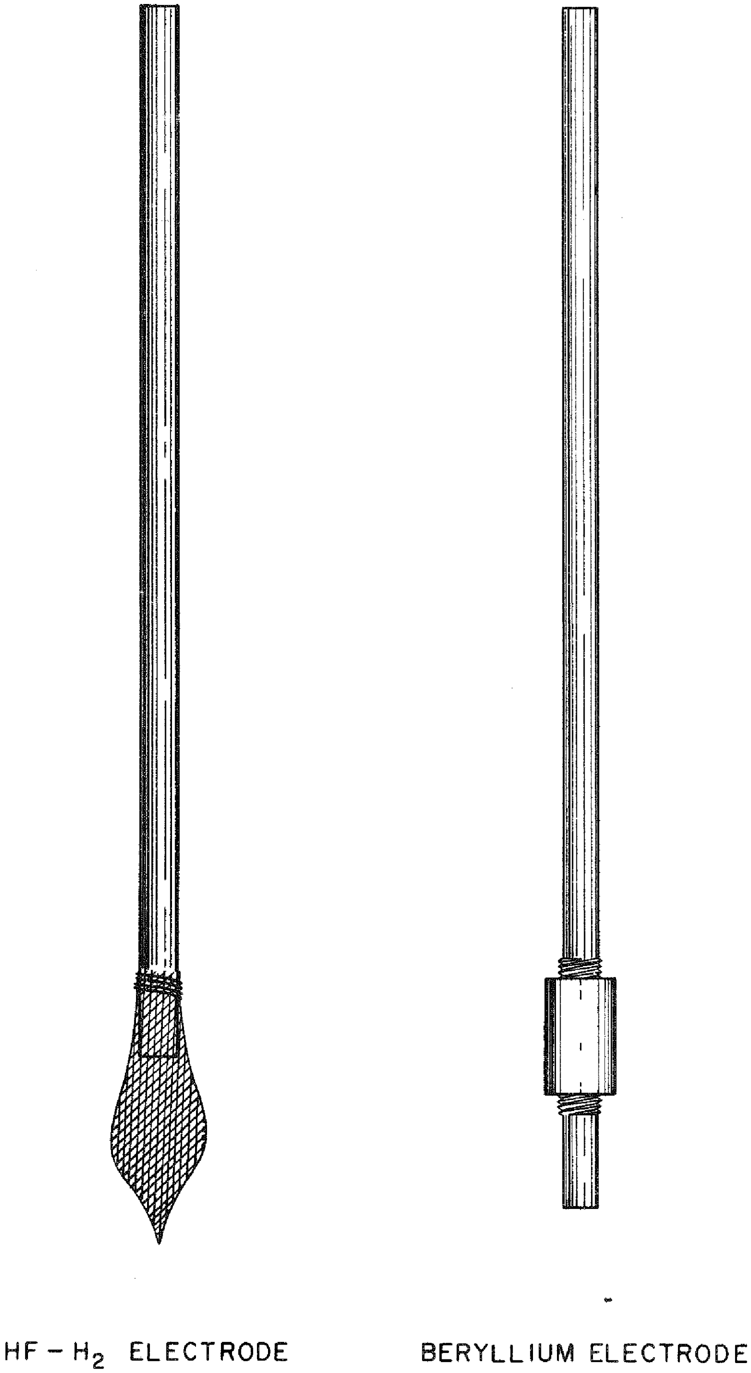

Fig. 4. HF-H_2 and Beryllium Electrodes.

pressure since a constant flow through the beryllium electrode was unnecessary.

Titration Assembly

The NaOH titration vessel was a 200-ml test tube. A rubber stopper was inserted into the test tube and was equipped with the following: Teflon (1/4-in. dia.) entrance and exit tubes for gas, a 5-ml Lab-Crest microburet, and Beckman No. 39166 (glass, Ag-AgCl) electrodes. A Beckman Zeromatic II pH meter was used to determine the endpoint. The pH was maintained on the alkaline side of the endpoint to avoid glass attack. Duplicate titration assemblies were used to measure influent and effluent HF concentrations.

Electronic Equipment

An L & N K-3 potentiometer, calibrated with a standard cell from Eppley Laboratory, Inc., was used to buck out most of the cell voltage. When the cell voltage exceeded the range of the potentiometer, a mercury battery (Mallory Duracell No. RM 42R) was connected in series to extend the bucking voltage range. The voltage of the battery was checked daily with the potentiometer, and it proved to be an extremely stable voltage source ($\pm$ 0.02 mv/day). The remainder of the cell voltage ($<$ 100 mv) was coupled, through a Philbrick Model MP solid state operational manifold equipped with P65 AU amplifiers, to a Honeywell Brown Electronik recorder.

Procedure

Measurements

The data obtained for each cell measurement were cell potential, cell temperature, and partial pressures of HF and H_2.

Cell Potential.-- Cell potential measurements were always preceded by standardization of the potentiometer against a standard cell and a check of the amplifier zero on the recorder. During measurements of the cell potential, most of the voltage was bucked out by the potentiometer (or potentiometer plus mercury battery), and the remainder read off the recorder. The noise level of the potential varied from ± 0.2 mv to as high as ± 1.0 mv for the high viscosity melts. Although the potential fluctuated as indicated, it did not show any drift toward a higher or lower potential.

H_2 and HF Partial Pressures.-- The determination of partial pressures was made as follows:

(1) A measured volume of standardized NaOH was added to the titration vessel.

(2) The time required for the HF to neutralize the base was determined.

(3) H_2 flow rates were determined by the use of a Bubble-O-Meter.

(4) Influent partial pressures were checked simultaneously in experiments up to .60 BeF_2.

(5) Partial pressure determinations were never begun until the cell potential had been steady for at least 30 minutes.

(6) Six to ten successive titrations were carried out.

(7) The barometric pressure, temperature of the titration assembly, and pressure drop across the system were recorded.

(8) Helium flowed through the beryllium electrode at a rate of 30 to 75 ml/min. This flow rate provided adequate sparging for this compartment and decreased the thermal gradients. Helium also protected the electrode from any HF which might

have entered the compartment.

Melt Temperature.-- The temperature of the melt was determined by a calibrated Chromel-Alumel thermocouple positioned carefully to the exact depth of the electrode. Positioning was carried out as accurately as possible to reduce any error in temperature readings caused by thermal gradients in the melt.

Calculations.-- The required calculations to evaluate P_{HF}, P_{H_2} and E_c were carried out as follows:

(1) The titration times were averaged for a series of titrations of a fixed increment of standard base. The gas volume passed was then calculated by (time of titration)/(time per 100 ml of gas) x 100 = ml of gas.

(2) The number of millimoles of HF removed from the H_2 stream by the titration was calculated by

(ml NaOH)(conc. of NaOH) = millimoles HF.

(3) It was found convenient first to define an approximate partial pressure of HF (P^o_{HF}) by introducing these measured quantities into the following simple gas law expression

$$P^o_{HF} = \frac{\text{(mmoles HF)(0.08206)(abs.temp. of Bubble-O-Meter)}}{\text{ml of } H_2 \text{ passed}}$$

$$= n_{HF} \frac{RT^o}{V^o}$$

The exact expression for the partial pressure of HF (P_{HF}) at the electrode includes the effect of the pressure drop (ΔP) caused by the pressure required to maintain bubbling through the melt and subsequent titrator, and the saturation of the H_2 stream with water prior to measuring the flow rate. The relationship (eq. 11) between P^o_{HF} and

P_{HF} which is required was developed as follows:

(3.1) The system may be visualized as consisting of three regions - the cell vessel (at P_T,T), the titration assembly, and the Bubble-O-Meter (at P^o_T, T^o).

(3.2) Assuming that the number of moles of HF passing through the cell assembly and into the titrator is the same for a given time interval, then

$$n_{HF} = \frac{P^o_{HF}\ V^o}{RT^o}$$

and

$$n_{HF} = \frac{P_{HF}\ V}{RT}$$

(Note that the first expression is merely a rearranged form of the previous equation which defines P^o_{HF}).

Combining these two equations,

$$\frac{P^o_{HF}\ V^o}{RT^o} = \frac{P_{HF}\ V}{RT}$$

$$P_{HF} = P^o_{HF}\ \frac{V^o\ T}{V\ T^o}\ . \tag{5}$$

(3.3) Moles of H_2 passing through the cell and through the Bubble-O-Meter may be treated in a like manner

$$n_{H_2} = \frac{P_{H_2}\ V}{RT} = \frac{P^o_{H_2}\ V^o}{RT^o}$$

$$\frac{V^o\ T}{V\ T^o} = \frac{P_{H_2}}{P^o_{H_2}}\ . \tag{6}$$

(3.4) Combining equations (5) and (6)

$$P_{HF} = P^o_{HF}\ \frac{P_{H_2}}{P^o_{H_2}} \tag{7}$$

(3.5) The total pressure at the HF-H_2 electrode is

$$P_T = P_B + \Delta P = P_{HF} + P_{H_2}$$

$$\therefore \quad P_{H_2} = P_B + \Delta P - P_{HF} \qquad (8)$$

and the total pressure of the gas at the Bubble-O-Meter is

$$P^o_T = P_B = P^o_{H_2} + P^o_{H_2O}$$

$$\therefore \quad P^o_{H_2} = P_B - P^o_{H_2O} . \qquad (9)$$

(3.6) Substituting (8) and (9) into equation (7)

$$P_{HF} = P^o_{HF} \left[\frac{P_B + \Delta P - P_{HF}}{P_B - P_{H_2O}} \right] \qquad (10)$$

and solving equation (10) for P_{HF} gives

$$P_{HF} = P^o_{HF} \left[\frac{P_B + \Delta P}{P_B - P_{H_2O} + P^o_{HF}} \right] . \qquad (11)$$

P_{HF} can be evaluated since all the other quantities are known. The values for P_{HF} then can be substituted into equation (8) and the P_{H_2} determined.

(4) Using the measured cell potential (E) and the partial pressures of HF (P_{HF}) and H_2 (P_{H_2}) the corrected cell potential was then calculated by

$$E_c = E + \frac{RT}{2F} \ln \frac{P_{H_2}}{P^2_{HF}} . \qquad (12)$$

The cell potential E was recorded after gas equilibration with the melt was accomplished, and the melt temperature was constant.

Systematic Errors

The preceding method of calculating partial pressures does not include corrections for the diffusion of H_2 through the walls of the nickel reaction vessel, nor does it consider the effect of thermal diffusion. Melt purity and composition should also be considered as sources of systematic errors.

Hydrogen Diffusion.-- According to published diffusion coefficients,[14] the diffusion of H_2 out of the nickel reaction vessel could be a few milliliters per minute at elevated temperatures. The rate of H_2 diffusion was measured experimentally by Mathews and Baes[7] in a vessel similar to the one used in the present experiment. They obtained the following rates: 700°C, 0.035 ml/sec; 650°C, 0.025 ml/sec; 600°C, 0.015 ml/sec. Extrapolation of these measurements to 800°C and 900°C yields diffusion rates of 0.055 ml/sec and 0.075 ml/sec, respectively. Typically emf experiments were conducted with a H_2 flow rate of 2.5 ml/sec. This means that the measured volume of H_2 would be in error by 0.6% at 600°C, 1.40% at 700°C, 2.20% at 800°C, and 3.00% at 900°C. These errors in partial pressures would cause the calculated potential to be about 1.0 mV lower at 700°C, 1.5 mV lower at 800°C, and 2.0 mV at 900°C. As mentioned previously, 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 .60 BeF_2 and temperatures up to 700°C. 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.

Since the H_2 diffusion effect was not observed at temperatures up to 700°C, the errors calculated above seem to be somewhat high.

Thermal Diffusion.-- Recognizing the possibility that H_2 and HF might tend to separate along the thermal gradient in the reaction vessel, we carried out an experiment to see if this effect was significant.

The total flow of HF-H_2 passing through the HF-H_2 electrode was varied between 23 ml/min and 160 ml/min. The cell potential increased by about one millivolt over this range; the increase in cell potential over the range of flow rates where potential measurements were actually made (100-160 ml/min) was less than 0.3 millivolt. This is thought to be sufficient evidence that the thermal diffusion effect was not significant.

Gas Cooling Effect on Electrodes.-- The experiment mentioned above also indicates that cooling of the electrodes by gas flow could not have caused more than a one millivolt error in the potential measurements. It was felt that although the possibility of a small error in potential might result from flow rates of 100-160 ml/min, vigorous agitation of the melt was necessary to reduce the effect of thermal gradients in the melt.

Melt Composition.-- A composition error which was discovered at the end of run No. 4 was apparently caused by distillation of BeF_2 to cooler regions of the apparatus. In this particular run, many attempts were made to measure the cell potential of pure BeF_2 over a temperature range of 800°C to 900°C. At these elevated temperatures the vapor pressure of BeF_2 is appreciable.[15] Evidently loss of BeF_2 occurred during the periods at high temperatures. Subsequent additions of LiF were made to bring the BeF_2 composition down to 0.90 BeF_2, 0.80 BeF_2, 0.70 BeF_2, and finally to 0.33 BeF_2. The error was discovered at 0.33 BeF_2 since the potentials did not correspond to previous measurements. At this point enough BeF_2 was added to bring the composition up to a book value of 0.40 BeF_2 permitting thermal analysis of the liquidus temperature. Thermal analysis was carried out and compared with the LiF-BeF_2 liquidus data.[16] Results indicated that the true composition was 0.388 BeF_2. Assuming that all or most of the BeF_2 was lost before the LiF additions were begun, the compositions at 0.90, 0.80, and 0.70 BeF_2 were reduced to 0.896, 0.791, and 0.686 BeF_2, respectively. Changes in E_c in the 0.60 BeF_2 to 0.80 BeF_2 regions are small; thus, the composition error at these concentrations should not be significant. However, the values obtained for 0.33 BeF_2 in this run were more seriously affected by the uncertainty in composition and were not used.

Melt Impurities.-- Early in the experimental work it was found that commercial BeF_2 which contained about 1000-2000 ppm sulfur and 1000 ppm total of Fe, Cr, Cu, and Ni caused "poisoning" of both electrodes. The cell potential would decay as much as 0.5 volts. Spectrographic examination of the Be electrode showed that Fe, Cr, and Ni had been reduced on the surface of the electrode; also metallic impurities originally in the beryllium metal were much higher in concentration on the electrode surface after exposure to the melt. These included Al, Mn, and Ti, the most abundant one being aluminum.

The platinum gauze on the $HF-H_2$ electrode was darkened by exposure to these contaminated melts. This effect was not pursued since it was already evident that BeF_2 with the impurities mentioned above was not suitable for use with the beryllium electrode.

Distilled BeF_2, containing only trace amounts of impurities, was tested; and none of the problems mentioned above were encountered. This material was used for all measurements in this investigation.

Oxide Contamination of Melt.-- The oxide chemistry of $LiF-BeF_2$ mixtures must be considered since the raw materials contain small amounts of moisture, and since beryllium oxide is an impurity in beryllium metal. Moisture contamination of the melt was kept to a minimum by freezing the mixtures prior to additions of raw materials. Beryllium fluoride was stored in a dry box prior to use.

A standard purification procedure for removing oxides[17] from fluoride mixture is $HF-H_2$ sparging. This procedure was used throughout the present investigation to remove oxide impurities from the melts. Continuous use of $HF-H_2$ as one of the electrode materials undoubtedly kept the oxide concentration small. Typically, beryllium metal contains about 1000 to 4000 ppm oxygen.[18] Using the larger value for oxide contamination, the maximum concentration of oxide contributed by the beryllium electrode would have been 1×10^{-3} moles/kg, which is about one order of magnitude below the solubility of BeO.[19] Therefore, no significant error is expected due to oxide contamination of the melt by addition of raw materials or from the metal electrode.

Summary.-- The only known systematic errors that might be significant are those attributed to H_2 diffusion and gas cooling of the electrodes. These are opposite in effect, and both are expected to be within the experimental scatter of the data.

Random Errors

In order to obtain a satisfactory estimate of the expected precision of the experimental measurements, the various random errors and their probable magnitude were considered.

Precision of Potential Measurements.-- Typically short term potential fluctuations were about ± 0.2 mV for mixtures up to 0.60 BeF_2. These fluctuations increased to about ± 1.0 mV for 0.90 BeF_2 mixtures. However, even at the higher BeF_2 concentrations, the average value of the potential did not change more than ± 1.0 mV over a period of one to two hours.

Melt Temperature.-- The temperature of the melt was controlled to ± 0.2°C. The temperature gradient in the melt varied from about 2°C in melts up to 0.60 BeF_2, to a maximum of 9°C in 0.90 BeF_2. However, care was taken during each potential measurement to position the thermocouple in the melt so that it coincided within ± 1/8-in. of the electrode depths. This should have reduced the temperature uncertainty to no more than ± 0.5°C, which corresponds to an uncertainty of ± 0.4 mV in the potential.

Melt Composition.-- The LiF-BeF_2 mixtures were prepared by adding weighed amounts of the components to the reaction vessel. The precision of weighing and transferring materials to the vessel was about ± 0.2%.

Titer Precision.-- Commercial 1N NaOH in one quart bottles was standardized with potassium acid phthalate. Agreement of the standardization values was about ± 0.1% of the average value. The uncertainty in burette readings during HF titrations was about ± 0.5%.

Temperature of Bubble-0-Meter.-- The Bubble-0-Meter temperature, which was the temperature of the gas as its volume was being measured, varied no more than ± 0.1°C during a given experiment. The same temperature variation applies to the titration vessel where the H_2 was saturated with water.

Flow Rate Determination.-- The precision in the timing of H_2 flow rates was 0.1 sec per 100 ml. For a typical value of 50 seconds per 100 ml, this would amount to 0.2%.

Endpoint Precision.-- The precision in timing of the endpoints was about ± 0.3% of the measured value.

H_2 and HF Flow Rates.-- The H_2 flow rate was constant at ± 0.1% of the measured value. Successive HF titrations varied as much as ± 1.0% from the average value. This was apparently due to irregular flow rates of HF. The variation was random and no bias was noted. The error involved in HF flow rate is much greater than any of the other errors associated with the calculation of P_{HF}; therefore the others will be considered negligible.

Statistical Error Analysis

The probable error to be expected in the calculated cell potential, E_c was determined from the estimated magnitude of random errors in various quantities which appear in eq. 3. If the contribution of each observable is related to a calculated function Q and expressed as

$$Q = f\,(a,b,c----),$$

the contribution of such errors can be calculated. If the errors follow a normal distribution, it can be shown[20] that the following equation allows for partial cancellation of errors of opposite sign:

$$\sigma Q^2 = \left(\frac{\partial Q}{\partial a}\right)^2 \sigma a^2 + \left(\frac{\partial Q}{\partial b}\right)^2 \sigma b^2 + \left(\frac{\partial Q}{\partial c}\right)^2 \sigma c^2 + \ldots\ .$$

Applying this relation to

$$E_c = E + \frac{RT}{nF}\,\ell n \frac{P_{H_2}}{P_{HF}^2}$$

gives

$$\sigma^2_{E_c} = \left(\frac{\partial E_c}{\partial E}\right)^2 \sigma^2_E + \left(\frac{\partial E_c}{\partial T}\right)^2 \sigma^2_T + \left(\frac{\partial E_c}{\partial P_{H_2}}\right)^2 \sigma P^2_{H_2} + \left(\frac{\partial E_c}{\partial P_{HF}}\right)^2 \sigma P^2_{HF}\ . \qquad (13)$$

Differentiation of the above quantities may be carried out to obtain

$$\frac{\partial E_c}{\partial E} = 1\ , \qquad \frac{\partial E_c}{\partial T} = \frac{\partial E}{\partial T} + \frac{R}{2F}\,\ell n \frac{P_{H_2}}{P^2_{HF}}\ ,$$

and

$$\frac{\partial E_c}{\partial P_{HF}} = \frac{RT}{2F}\left[\frac{\partial\left(\ell n \dfrac{P_B - P_{HF}}{P^2_{HF}}\right)}{\partial P_{HF}}\right] = -\ \frac{RT}{F}\left[\frac{2P_B - P_{HF}}{2P_{HF}\,(P_B - P_{HF})}\right]$$

(It may be recalled that $P_{H_2} = P_B + \Delta P - P_{HF}$. For the present analysis ΔP may be neglected, thus, $P_{H_2} \cong P_B - P_{HF}$).

The expected uncertainty of E_c can now be calculated by

$$\sigma_{E_c}^2 = \sigma_E^{\ 2} + \left[\frac{\partial E}{\partial T} + \frac{R}{2F}\,\ell n\,\frac{P_{H_2}}{P_{HF}^2}\right]^2 \sigma_T^2 + \left[-\frac{RT}{F}\left(\frac{2P_B - P_{HF}}{2P_{HF}(P_B - P_{HF})}\right)\right]^2 \sigma_{P_{HF}}^2 . \quad (14)$$

Evaluating the above equation numerically for the uncertainty in the calculated potential, using typical partial pressures of HF and H_2 at a temperature of 1000°K and using the estimated uncertainties of ± 0.5 mV, ± 0.5°C, ± 0.001 atm respectively in E, T, and P_{HF}, one obtains

$$\sigma_{E_c}^2 = (5 \times 10^{-4})^2 + (8.95 \times 10^{-4})^2 (5 \times 10^{-1})^2 + (2.103)^2 (1 \times 10^{-3})^2$$

$$\sigma_{E_c}^2 = (2.50 \times 10^{-7}) + (2.00 \times 10^{-7}) + 4.42 \times 10^{-6})$$

$$\sigma_{E_c}^2 = 4.87 \times 10^{-6}$$

$$\sigma_{E_c} = \pm .0022 \text{ volts.}$$

The calculated standard deviation of ± 2.2 mV is slightly larger than the standard deviation obtained from least squaring the actual data. The range of the standard deviation for the actual data was about 1.0 mV to 2.0 mV. The major uncertainty is in the P_{HF} term and is due to the limited precision of HF flow.

III. RESULTS

Tabulation

Table 1 contains the data obtained from each experiment, arranged according to melt composition.

Experiments

Four separate series of experiments were conducted during this investigation. The cell potential of each melt composition was determined for a range of temperatures. In the first series the reaction vessel was initially loaded with 0.33 BeF_2. Subsequent additions of BeF_2 were made to bring the concentrations up to 0.40 BeF_2, 0.50 BeF_2, and to 0.60 BeF_2.

In the second series the reaction vessel was initially loaded with pure BeF_2, enough LiF was then added to give 0.90 BeF_2, 0.80 BeF_2, 0.70 BeF_2, 0.60 BeF_2, 0.50 BeF_2, 0.40 BeF_2, and finally 0.33 BeF_2. Only one or two determinations were made for 0.60 BeF_2 and lower BeF_2 compositions since these were checks of previous measurements.

Pure BeF_2 was also the initial composition for the third series of measurements. Subsequent additions of LiF were made to give 0.90, 0.80, 0.70, 0.60, and 0.33 BeF_2. As previously mentioned the data for 0.33 BeF_2 was considered to be in error and was not used.

In the last series of measurements the reaction vessel was loaded initially with 0.33 BeF_2. Enough LiF was added to give 0.30 BeF_2; then BeF_2 was added to bring the composition back to 0.33 BeF_2.

Corrected Cell Potentials

The corrected cell potentials (E_c) for various compositions are plotted as a function of temperature and shown in Fig. 5. E_c is assumed to be a linear function of temperature, $E_c = A+BT$, over the temperature range investigated. The data points for each composition were least squared, and the calculated lines are also shown in Fig. 5. The parameters from the least squaring treatment are listed in Table 2.

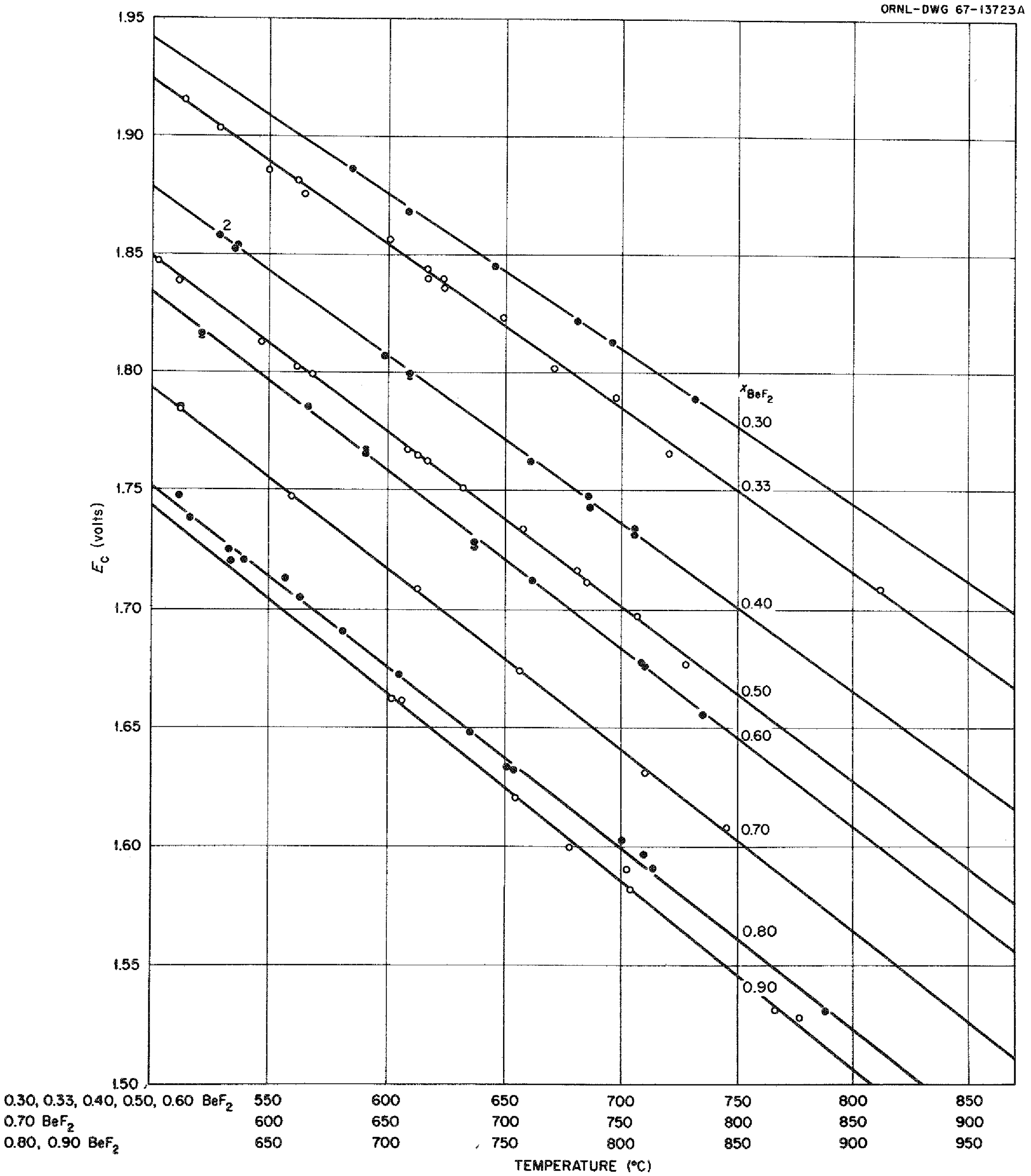

Fig. 5. Correlation of Pressure Corrected Cell Potentials for Various Compositions as a Function of Temperature.

Table 1. Pressure Corrected Cell Potentials (E_c) Obtained from Measurements in Molten LiF-BeF_2

X_{BeF_2}	Temp. (°C)	E_c (volts)
0.30	585.1	1.8864
0.30	646.0	1.8447
0.30	696.2	1.8126
0.30	732.0	1.7882
0.30	609.2	1.8680
0.30	681.0	1.8213
0.33	562.9	1.8812
0.33	514.0	1.9152
0.33	601.0	1.8561
0.33	649.5	1.8230
0.33	698.0	1.7891
0.33	624.1	1.8397
0.33	565.0	1.8757
0.33	720.8	1.7653
0.33	529.0	1.9035
0.33	617.2	1.8436
0.33	617.2	1.8396
0.33	550.0	1.8857
0.33	624.5	1.8356
0.33	671.0	1.8016
0.33	812.0	1.7081
0.40	597.5	1.8069
0.40	609.5	1.8000
0.40	609.5	1.7991
0.40	661.2	1.7623
0.40	686.6	1.7430
0.40	685.8	1.7478
0.40	528.2	1.8578
0.40	528.2	1.8578
0.40	536.5	1.8540
0.40	535.0	1.8522
0.40	706.0	1.7337
0.40	706.0	1.7316
0.50	632.8	1.7516
0.50	561.5	1.8022
0.50	728.0	1.6765
0.50	707.0	1.6972
0.50	658.0	1.7340
0.50	617.3	1.7629
0.50	568.3	1.7991
0.50	546.6	1.8127
0.50	503.3	1.8467
0.50	511.8	1.8387
0.50	608.5	1.7671
0.50	613.1	1.7648
0.50	685.2	1.7116
0.50	681.0	1.7163
0.60	637.0	1.7263
0.60	566.5	1.7856
0.60	735.0	1.6555
0.60	637.0	1.7283
0.60	591.1	1.7656
0.60	521.0	1.8160
0.60	591.0	1.7672
0.60	591.0	1.7667
0.60	521.2	1.8170
0.60	710.0	1.6760
0.60	709.0	1.6771
0.60	662.0	1.7128
0.70	760.0	1.6310
0.70	706.5	1.6736
0.70	609.6	1.7477
0.70	562.0	1.7844
0.70	663.0	1.7085
0.70	794.9	1.6079
0.80	800.4	1.6027
0.80	751.0	1.6335
0.80	656.5	1.7132
0.80	632.5	1.7252
0.80	704.9	1.6725
0.80	754.0	1.6321
0.80	681.0	1.6907
0.80	633.5	1.7205
0.80	611.5	1.7484
0.80	639.7	1.7206
0.80	887.5	1.5304
0.80	810.0	1.5967
0.80	735.4	1.6482
0.80	663.0	1.7051
0.80	616.0	1.7387
0.80	814.1	1.5909
0.90	804.1	1.5819
0.90	866.0	1.5307
0.90	754.8	1.6208
0.90	706.2	1.6613
0.90	778.0	1.5996
0.90	876.5	1.5277
0.90	802.5	1.5905
0.90	702.0	1.6620

Table 2. Parameters from Correlation of E_c as a Function of Temperature at Specified Compositions (E_c = a+bT)

X_{BeF_2}	Intercept ± σ (a)		(Slope ± σ)x 10^{-3} (b)		$\sigma_{E_c} x10^3$ (volts)
0.30	2.45212	0.0053	- 0.6607	0.0080	0.98
0.33	2.46021	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

IV. DISCUSSION

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^o) are known. As mentioned previously, several attempts were made to determine E^o experimentally, but values of useful accuracy could not be obtained because of high melt viscosity and possibly because of high electrical resistivity.

The values of E_c obtained for various BeF_2 compositions do not lend themselves to direct extrapolation to E^o. 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^o) varies linearly with temperature

(E^o = A+BT)* then eq. (4) may be written

$$E_c = (A+BT) - \frac{RT}{2F} \ell n \; a_{BeF_2}$$

$$\therefore \; \ell n \; a_{BeF_2} = \frac{2F[(A+BT) - E_c]}{RT} \; . \qquad (15)$$

It is then possible to equate eq. (15) to

$$\ell n \; a_{BeF_2} \; (BeF_2 \text{ sat'n}) = - \frac{\Delta H_f}{R}\left(\frac{1}{T} - \frac{1}{T_f}\right) \qquad (16)$$

(where ΔH_f is the heat of fusion of BeF_2 and T_f is the melting point of pure BeF_2) to obtain a relationship between A, B, ΔH_f and E_c calculated at the BeF_2 liquidus temperatures and compositions. Combining eqs. (15) and (16).

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

which simplifies to

$$\frac{2F \; E_c}{T} = \left(2FB - \frac{\Delta H_f}{T_f}\right) + (2FA + \Delta H_f)\frac{1}{T} \; . \qquad (17)$$

This relationship permits correlation of the data (E_c) obtained in the present investigation with the phase diagram data.[12] A plot of the above expression as $2FE_c/T$ vs $1/T$ should be linear since the intercept and slope contain only constants. Using the least square parameters for each composition (Table 2), values for E_c were calculated for the liquidus temperatures at 0.515, 0.60, 0.70, 0.80 and 0.90 BeF_2 (see footnote) and then plotted according to eq. (17) (Fig. 6). The resulting points follow the predicted linear relationship within their pre-

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* Using the heat capacity data in the JANAF Tables (Ref. 21), the ΔCp effect over a temperature range of 450° - 900°C was evaluated and found to be negligible.

dicted uncertainties. Parameters for the least squared line are:

$$\text{Intercept} = -\ 0.03805 \pm 0.0034, (\text{Kcal}/°\text{K}) = 2FB - \frac{\Delta H}{T_f} \qquad (18)$$

$$\text{Slope} = 113.84 \pm 2.48\ , (\text{Kcal}) = 2FA + \Delta H_f \qquad (19)$$

The point at 0.90 BeF_2 was not used because the uncertainty in E_c is relatively large.

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°C for pure BeF_2. A tabulation of these values is shown in Table 3. The values of A and B which are consistent with values obtained in the present investigation are those for which the heat of fusion is assumed to be 2.0 kcal/mole or less as shown in Fig. 7. A heat of fusion for BeF_2 >2.0 kcal/mole yields values of E^o which are greater than corresponding values of E_c at the higher BeF_2 concentration. This creates an impossible situation where the activity of BeF_2 in the mixture is greater than the activity of pure liquid BeF_2. Thus measurements in the present study clearly support the lower values for the heat of fusion for BeF_2.[8,9]

The emf data (E_c) obtained in the present study were fitted by least squares to the expressions listed in Table 4, using the lowest literature value (1.13 kcal/mole) for the heat of fusion of BeF_2. A plot of the smoothed lines for E_c at various BeF_2 concentrations is shown in Fig. 8. The pressure corrected cell potentials (E_c) differed by 1.4097 standard deviations from the smoothed values given by eq. 4-1 (Table 4), and the average deviation of E_c from smoothed values was approximately ± 2.5 mV. The average deviation is consistent with the value predicted by the error analysis for E_c.

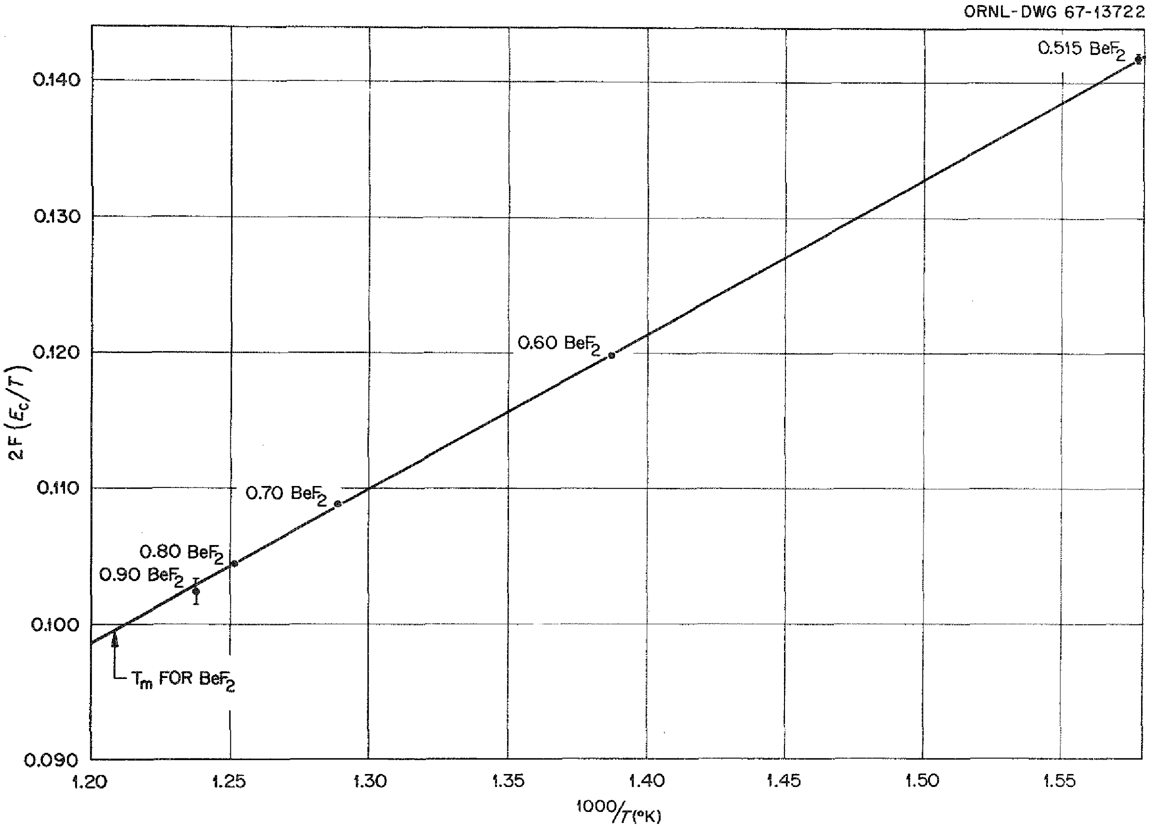

Fig. 6. Correlation of E_c with BeF_2 Liquidus Data.

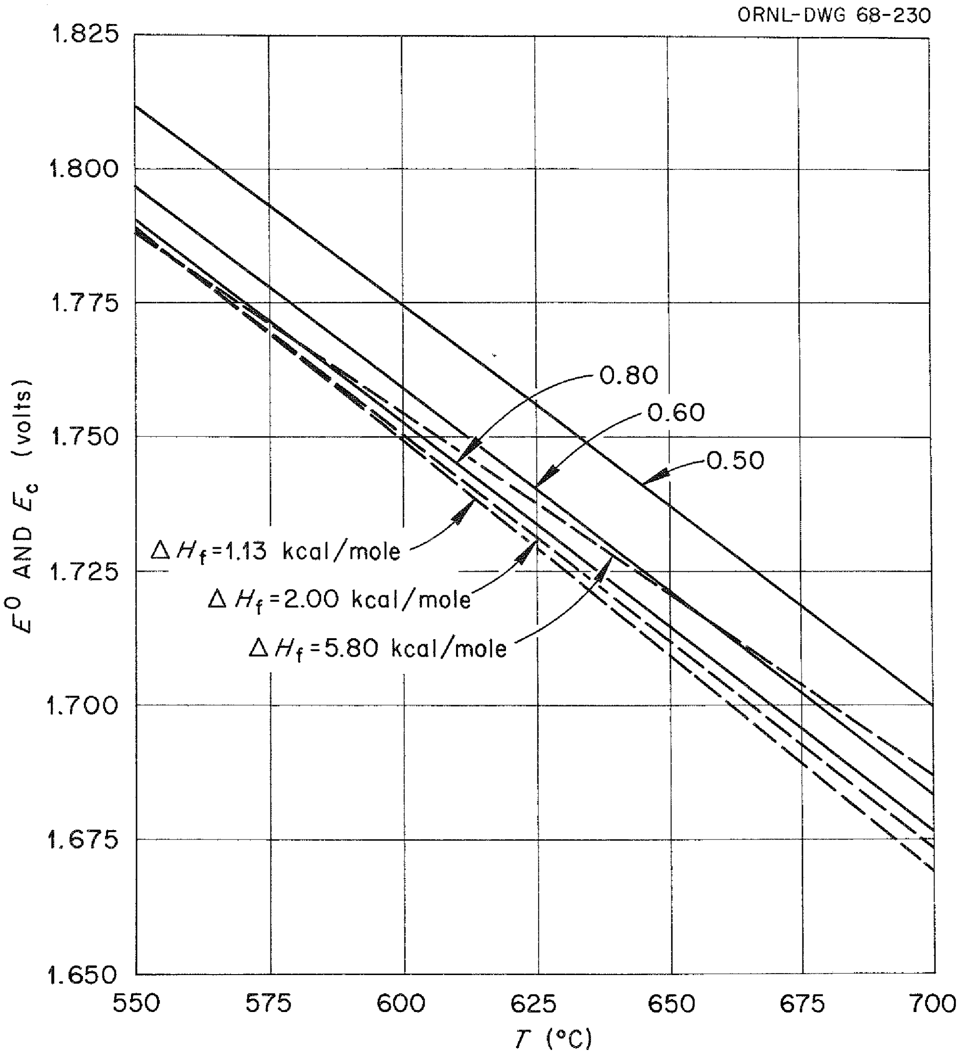

Fig. 7. Effect of the Heat of Fusion of BeF_2 in Determining E^o (dashed lines). The solid lines represent E_c for various mole fraction of BeF_2.

Table 3. Calculated Parameters for the Standard Cell Potential of Pure BeF_2 ($E^o = A + BT$) Assuming Various Values for the Heat of Fusion of BeF_2

Heat of Fusion of BeF_2 (kcal/mole)	$A^{(a)}$	$B^{(b)}_{x\ 10^3}$	Ref. No.
0.70	2.4525	- .8065	
1.00	2.4460	- .7986	
1.13	2.4432	- .7952	9
1.60	2.4330	- .7829	8
2.00	2.4241	- .7725	
2.50	2.4135	- .7594	
5.80	2.3420	- .6730	7

(a) From eq. (19).

(b) From eq. (18).

Table 4. Expressions for Cell Potentials and Activity Coefficients in the LiF-BeF_2 System

Eq. No.	
4-1	$E_c = E^o - \frac{2.3RT}{2F} \log x_{BeF_2} - \frac{2.3RT}{2F} \log \gamma_{BeF_2}$
4-2	$E^o = 2.4430 - 0.0007952T^{(a)}$
4-3	$\log \gamma_{BeF_2} = (3.8780 - \frac{2353.5}{T})x_{LiF}^2$
	$+ (-40.7375 + \frac{36292.8}{T})x_{LiF}^3$
	$+ (94.3997 - \frac{84870.9}{T})x_{LiF}^4$
	$+ (-67.4178 + \frac{52923.5}{T})x_{LiF}^5$
4-4	$\log \gamma_{LiF} = 0.9384 - \frac{232.08}{T}$
	$+ (-36.9734 + \frac{14652.7}{T})x_{BeF_2}^2$
	$+ (126.0947 - \frac{74588.5}{T})x_{BeF_2}^3$
	$+ (-158.4173 + \frac{113592.3}{T})x_{BeF_2}^4$
	$+ (67.4178 - \frac{52923.5}{T})x_{BeF_2}^5$

(a) Calculated using a heat of fusion for BeF_2 = 1.13 kcal/mole.

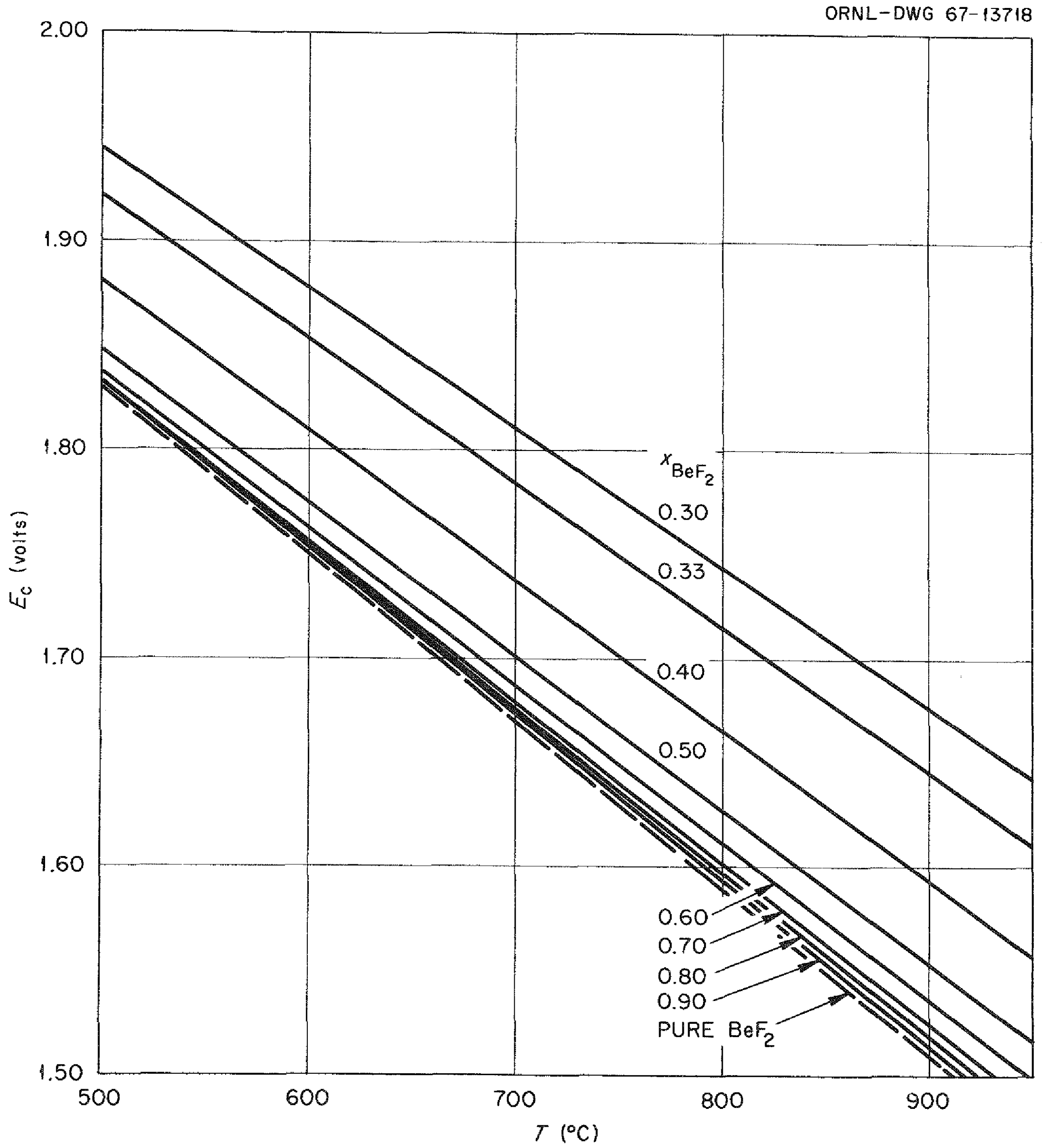

Fig. 8. Correlation of Pressure Corrected Cell Potentials E_c as a Function of Temperature Using Smoothed Parameters.

A Gibbs-Duhem integration of the expression for γ_{BeF_2} Table 4) was carried out to give the corresponding expression for γ_{LiF} (eq. 4-4, Table 4). The integration constant for eq. 4-4 was determined by comparison with γ_{LiF} values derived from the liquidus data[12] and a heat of fusion of 6.47 kcal/mole for LiF. A more accurate evaluation of the integration constant should be possible when the heat of mixing measurements of Holm and Kleppa[22] become available for the LiF-BeF_2 system.

Smoothed values of γ_{BeF_2} are shown as a function of composition at several temperatures in Fig. 9. These results are consistent with those obtained by Mathews and Baes[7] over a composition range 0.30 to 0.60 BeF_2. However, at $x_{BeF_2} > 0.60$ the results are not in agreement. The values obtained in the present study are thought to be the more reliable since they are consistent with both the phase data and with a low heat of fusion for BeF_2. The previous measurements at compositions > 0.60 BeF_2 might be in error because of difficulties in mixing LiF-BeF_2 at high BeF_2 concentrations and because of the effects of 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°C. This procedure was followed for all high BeF_2 concentrations to ensure proper mixing of the LiF-BeF_2. Another possible error in the previous measurements could have been the presence of BeO as a saturating solid. The solubility of BeO might tend to influence the BeF_2 activity more at high BeF_2 concentrations.

The free energy and heat of the cell reaction (eq. 1) were calculated assuming a heat of fusion for BeF_2 = 1.13 kcal/mole. These values combined with the available thermochemical values for HF[21] were used

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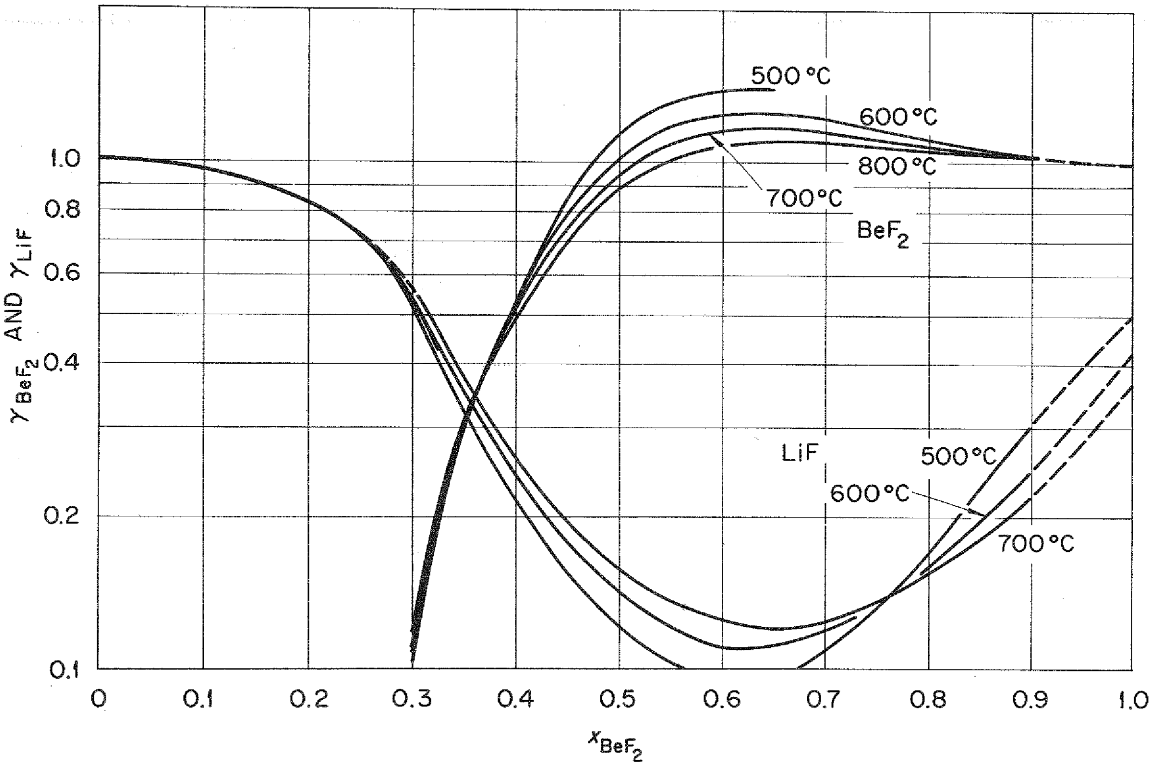

Fig. 9. Activity Coefficients in Molten LiF-BeF$_2$ Mixtures.

to derive the free energy and heat of formation for liquid BeF_2 at 900°K (Table 5). Mathews and Baes[7] measured the equilibrium quotient for the reaction

$$H_2O(g) + BeF_2(d) \rightleftarrows 2HF(g) + BeO(s) \qquad (20)$$

If eq. (20) is combined with the reaction in eq. (1) the resulting reaction is

$$H_2O(g) + Be(s) \rightleftarrows BeO(s) + H_2(g) \qquad (21)$$

The free energy and heat of this last reaction thus could be obtained by combining the two sets of measurements, and, since the thermochemical data for H_2O are accurately known, improved free energy and heats of formation for BeO could be calculated. These are shown in Table 5. The preceding calculations for BeF_2 and BeO were made for a temperature of 900°K. Values for other temperatures were generated using the heat capacity data in the JANAF Tables.[21]

Reference Electrodes

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

Beryllium Electrode

The $Be|Be^{2+}$ electrode should work well in any melt containing beryllium ions and no reducible cations. 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

Table 5. Formation Heats and Free Energies of BeF_2 and BeO

Compound	Temp. (°K)	State	ΔH_f (kcal/mole)		ΔG_f (kcal/mole)	
BeF_2	298	Cryst.	− 246.01	(−242.30 ± 2)[22]	− 234.39	(−230.98 ± 2)[22]
BeF_2	800	Cryst.	− 244.75		− 215.50	
BeF_2	900	Liquid	− 243.12	(± 1.1)	− 211.90	(± 1.1)
BeF_2	1000	Liquid	− 242.54		− 208.47	
BeO	298	Cryst.	− 145.85	(−143.10 ± 0.1)[22]	− 138.36	(−136.12 ± 0.1)[22]
BeO	800	Cryst.	− 145.68		− 125.70	
BeO	900	Cryst.	− 145.57	(± 1.5)	− 123.20	(± 1.5)
BeO	1000	Cryst.	− 145.46		− 120.73	

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 due to spongy deposition of the Be metal, and eventually electrical shorts develop between the electrode and the cell compartment wall.

$HF-H_2$ Electrode

The Pt, $HF,H_2|F^-$ electrode should be a suitable reference electrode in any fluoride-containing melt where there is no possibility of oxidation by HF or reduction by H_2. The solubility of HF in $LiF-BeF_2$ is low[23] (about 0.0003 mole fraction for the partial pressures of HF used in this study), and no significant solubility of H_2 is expected in this system. Potential fluctuations due to this electrode appear to be a function of the melt viscosity. Fluctuations are about ± .1 mV in melts with a viscosity of one poise 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 the H_2-HF mixture will be obtained by passing H_2 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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