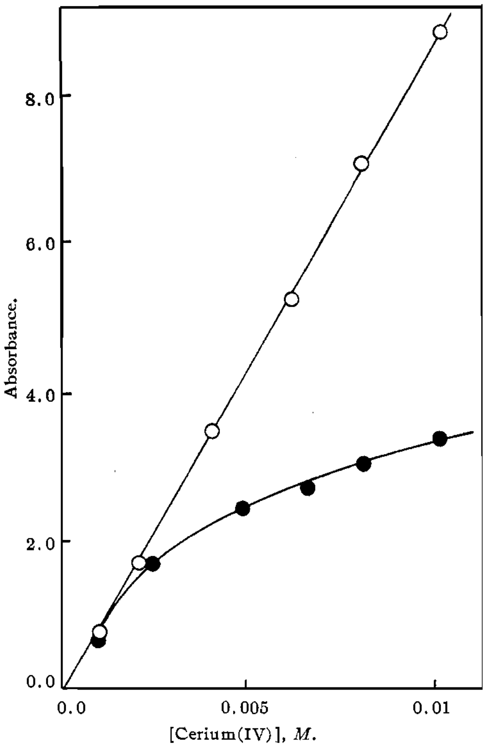

Figure 5.—Effect of nitrate ion on the absorbance of cerium(IV) solutions in 85% acetic acid. The linear relationship is obtained with 0.9 *M* nitrate and the curve corresponds to 0.05 *M* nitrate.

Experimental Section

Materials.—Ceric perchlorate was obtained from the G. F. Smith Chemical Co. as an approximately 0.5 *M* solution in 3 *M* perchloric acid. The cerium(IV) content was determined iodometrically. The acid content was determined by diluting with acetic acid, adding an excess of acetic anhydride to remove water, and titrating potentiometrically with standard sodium acetate in glacial acetic acid. Perchloric acid was obtained from Mallinckrodt as a 70% solution and nitric acid was obtained from Fisher as a 70% solution.

Acetic acid was purified as described previously.[19] The water content was determined spectrophotometrically using acetic anhydride.[20] Water was purified by distillation from chromic acid.

Spectrophotometric Measurements.—The spectra were determined using a Beckman DU quartz spectrometer with 10-mm and shorter cells, or with a Perkin-Elmer Model 350 recording spectrometer using long cells. The Beckman spectrometer was equipped with a thermostated water bath in the light path and made it possible to maintain the temperature at 25.00 ± 0.01°. The temperature in the cell compartment of the Perkin-Elmer spectrometer varied from 23 to 26°. No significant difference was noted in the data obtained using the two spectrometers. The ionic strength was maintained at either 0.6 or 1.0 *M* by the addition of sodium perchlorate. No significant change in absorbance was noted for a change in ionic strength within this range. Cerous ion, in the concentration which might be present as an impurity in the ceric ion solutions, was found to have no significant effect on the observed absorbance values.

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[19] K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 3022 (1958).

[20] S. Bruckenstein, Ph.D. Thesis, University of Minnesota, 1951.

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Oxide Chemistry and Thermodynamics of Molten LiF–BeF$_2$ Solutions[1,2]

BY A. L. MATHEWS AND C. F. BAES, JR.

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A transpiration method was used to equilibrate dilute gaseous mixtures of HF and H_2O in hydrogen with molten LiF–BeF$_2$ solutions, both saturated and unsaturated with crystalline BeO. The observed effluent partial pressures of HF and H_2O were interpreted in terms of equilibrium quotients for the reactions

$$H_2O(g) + BeF_2(d) \rightleftarrows BeO(c) + 2HF(g);\ Q = P_{HF}^2/P_{H_2O}$$

$$H_2O(g) + 2F^-(d) \rightleftarrows O^{2-}(d) + 2HF(g);\ Q_O = P_{HF}^2[O^{2-}]/P_{H_2O}$$

$$H_2O(g) + F^-(d) \rightleftarrows OH^-(d) + HF(g);\ Q_{OH} = P_{HF}[OH^-]/P_{H_2O}$$

Values of Q, Q_O, and Q_{OH} were determined as functions of melt composition ($X_{BeF_2} = 0.3$–0.8) and temperature (500–700°). The ratio Q_O/Q gave the solubility of BeO which was in the range 0.005–0.1 mole of O^{2-}/kg of salt. Since Q should be proportional to the activity of BeF$_2$ in the solutions, activity coefficients were derived for BeF$_2$ (and LiF). Positive deviations from ideal behavior were found at $X_{BeF_2} > 0.5$ and negative deviations at $X_{BeF_2} < 0.5$. Comparison of the observed Q values with the LiF–BeF$_2$ phase diagram suggests that the heat of fusion of BeF$_2$ is ~5.8 kcal/mole. Improved values of the heat and free energy of formation of BeF$_2$(c) were also calculated from these results. If at low LiF concentrations random mixing of bridging and nonbridging fluorides is assumed, it would appear that nonbridging F^- ions occur in groups of four or more.

Introduction

Molten fluoride mixtures in which the principal constituents are LiF and BeF$_2$ have been the subject of extensive investigations at this laboratory for a number of years in connection with the development of a molten salt fueled nuclear reactor (MSRE).[3] In the course of this work the oxide chemistry of these fluoride

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[1] Based upon a Ph.D. Dissertation by A. L. Mathews, submitted to the University of Mississippi, 1965. Also issued as ORNL-TM-1129, May 7, 1965. This research was performed at ORNL under the Oak Ridge Graduate Fellowship Program of The Oak Ridge Associated Universities.

[2] Research sponsored by the USAEC under contract with Union Carbide Corp.

[3] C. F. Bases, Jr., "The Chemistry and Thermodynamics of Molten Salt Reactor Fluoride Solutions," in "Thermodynamics," Vol. 1, IAEA, Vienna, 1966, p 409.

mixtures became of concern primarily because exposure of the melts to water vapor causes hydrolysis

$$H_2O(g) + 2F^-(d) \rightleftharpoons O^{2-}(d) + 2HF(g) \qquad (1)$$

In the binary system LiF–BeF$_2$, this soon leads to precipitation of BeO.[4] The reverse of this reaction, in which oxide impurities are removed by sparging with HF, has been used as a standard purification treatment for years.[5] However, a sufficiently sensitive and reliable method of oxide analysis was not available with which to check the effectiveness of this treatment or to determine the solubility of BeO. It was obviously desirable therefore to investigate the above equilibrium in some detail in order to define better the oxide chemistry and the efficacy of the purification procedure as well as to explore a possibly very sensitive analytical method for oxide.

Another incentive for investigating the heterogeneous equilibria among HF, H$_2$O, and molten LiF–BeF$_2$ can be seen by considering the equilibrium which should occur if BeO is present as a saturating solid

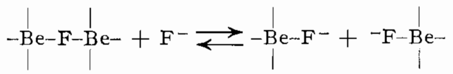
$$H_2O(g) + BeF_2(d) \rightleftharpoons BeO(s) + 2HF(g) \qquad (2)$$

The corresponding equilibrium constant is

$$K = P_{HF}^2/(P_{H_2O}a_{BeF_2})$$

assuming the gases to be ideal. The quotient of gas pressure, $Q = P_{HF}^2/P_{H_2O}$, measured at equilibrium therefore should vary directly as the thermodynamic activity of BeF$_2$ in the melt. Moreover, since the solubility of BeO is small (of the order of 0.01 mole/kg of salt[6]), this activity should correspond closely to that for the binary (*i.e.*, oxide-free) system. Thus in undertaking the present study it was hoped that the thermodynamics of the LiF–BeF$_2$ system as well as the oxide chemistry could be elucidated.

The thermodynamics of the binary system LiF–BeF$_2$ is of more than usual interest since the component salts are quite dissimilar in character. Lithium fluoride is a normal ionic salt while beryllium fluoride is evidently associated since it forms a very viscous liquid which is obviously polymeric. Solid BeF$_2$ has a structure analogous to SiO$_2$, in which the Be^{2+} ions are surrounded tetrahedrally by four fluoride ions and each fluoride ion is bonded to two beryllium ions; *i.e.*, BeF$_4$$^{2-}$ tetrahedra share corners to form a three-dimensional network. The liquid might be expected to have a similar polymeric structure. As LiF is added to molten BeF$_2$, the viscosity drops sharply presumably because bridging fluoride linkages are broken



$$-Be-F-Be- + F^- \rightleftharpoons -Be-F^- + {}^-F-Be- \qquad (3)$$

and the degree of polymerization decreases. The stoichiometric end point for this process occurs when the composition reaches 2LiF–BeF$_2$. Thereafter, the principal beryllium species in the melt is presumably BeF$_4$$^{2-}$. In the crystal structure of the incongruently melting compound Li$_2$BeF$_4$, BeF$_4$$^{4-}$ tetrahedra in fact are present.[7] The variation of the activities of LiF and BeF$_2$ with composition in this system should reflect the polymeric nature of these melts.

Thus far the activity data available for this system in the region of interest (X_{BeF_2} = 0.3–1.0) have been derived from the phase diagram,[8,9] from mass spectroscopic studies of the vapor,[10,11] and from emf measurements.[12] The values derived from phase data besides being nonisothermal have been limited in accuracy because the BeF$_2$ liquidus has been difficult to determine in this region of high liquid viscosities and a poorly crystallizing solid. In addition, the heat of fusion of BeF$_2$ has been relatively uncertain.[13] The mass spectroscopic and emf values are limited in number as well as accuracy.

In the present measurements a transpiration method was used in which gaseous mixtures of HF and H$_2$O in hydrogen were bubbled through the molten mixtures of LiF and BeF$_2$. The primary data obtained were the effluent partial pressures (P_{HF} and P_{H_2O}) as a function of the influent partial pressures (P_{HF}^0 and $P_{H_2O}^0$) and the volume of gas passed. From these measurements it seemed appropriate to assume that, in addition to oxide ion, hydroxide ion also was being formed in the melts

$$H_2O(g) + F^-(d) \rightleftharpoons OH^-(d) + HF(g) \qquad (4)$$

Hence, the data were interpreted in terms of the following equilibrium quotients corresponding to reactions 1, 2, and 4, respectively

$$Q_O = P_{HF}^2[O^{2-}]/P_{H_2O} \quad \text{atm mole kg}^{-1} \qquad (5)$$

$$Q = P_{HF}^2/P_{H_2O} \quad \text{atm (for BeO-saturated melts)} \qquad (6)$$

$$Q_{OH} = P_{HF}[OH^-]/P_{H_2O} \quad \text{mole kg}^{-1} \qquad (7)$$

In addition, for melts in which BeO(c) was not present the following material balance differential equations were used to relate changes in the concentration of oxide and hydroxide ions (in moles/kg) to the influent and effluent partial pressures and the molar volumes (W) of gas at 1 atm passed per kg of melt

$$d[O^{2-}] + d[OH^-] = (P_{H_2O}^0 - P_{H_2O})dW \qquad (8)$$

$$d[OH^-] = (P_{HF}^0 + 2P_{H_2O}^0 - P_{HF} - 2P_{H_2O})dW \qquad (9)$$

By difference

$$d[O^{2-}] = -(P_{HF}^0 + P_{H_2O}^0 - P_{HF} - P_{H_2O})dW \qquad (10)$$

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[4] J. H. Shaffer, G. M. Watson, and W. R. Grimes, USAEC Report ORNL-2931, April 1960, p 84.

[5] J. H. Shaffer, USAEC Report ORNL-3708, Nov 1964, p 288.

[6] B. F. Hitch and C. F. Baes, Jr., USAEC Report ORNL-4076, March 1967, p 19.

[7] J. H. Burns and E. K. Gordon, *Acta Cryst.*, **20**, 135 (1966).

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

[9] J. Lumsden, "Thermodynamics of Molten Salt Mixtures," Academic Press, London, 1966, p 224.

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

[11] A. Büchler and J. L. Stauffer, "Vaporization in the Lithium Fluoride–Beryllium Fluoride System," in "Thermodynamics," Vol. 1, IAEA, Vienna, 1966, p 271.

[12] A. Büchler, "Study of High-Temperature Thermodynamics of Light Metal Compounds," Progress Report No. 7 (Contact DA-19-020-ORD-5584), Army Research Office, Durham, N. C., Sept 30, 1963.

[13] A. R. Taylor and T. E. Gardner (Bureau of Mines Report RI-6664, 1965) have reported a value of 1.13 kcal/mole, based primarily on the difference in the heat of solution of glassy and crystalline BeF$_2$ at 25°. J. A. Blauer, *et al.*, *J. Phys. Chem.*, **69**, 1069 (1965), have reported a similarly low value of 1.6 kcal/mole. These are much lower than recent estimates of Førland[8] and Lumsden[9] based on phase data.

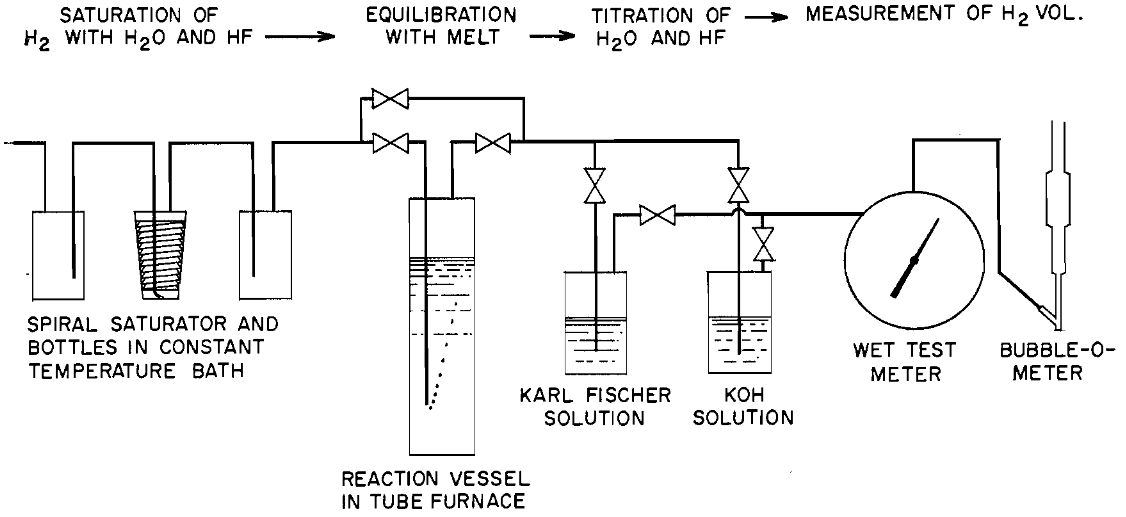

Figure 1.—Schematic diagram of apparatus for equilibration of gaseous HF–H$_2$O–H$_2$ mixtures with molten LiF–BeF$_2$.

The variable W is calculated directly from the volume of gas passed (V) and the melt weight (w)

$$W = \frac{V}{RTw} \text{ mole kg}^{-1} \text{ atm}^{-1} \qquad (11)$$

wherein T is the absolute temperature at which V is measured.

Experimental Section

Chemicals.—Hydrogen was purified before use by passage through a Deoxo unit, a magnesium perchlorate drying tube, and a liquid nitrogen trap. Helium was passed through an Ascarite trap, a magnesium perchlorate drying tube, and a liquid nitrogen trap. Anhydrous HF was used directly from a commercial cylinder without further purification. B & A reagent grade 48% hydrofluoric acid was used to prepare aqueous HF mixtures. Standard base was prepared from reagent grade potassium hydroxide and standardized with potassium acid phthalate. Karl Fischer reagent from Fisher Chemical Co. (So-K-3) was standardized by direct addition of weighed aliquots of water.

The beryllium fluoride, from Brush Beryllium Co., contained less than 750 ppm metallic impurities (principally iron). Lithium fluoride was B & A reagent grade. Various mixtures of these fluorides were prepared by weight, melted together, and then sparged with HF and hydrogen to remove oxide and sulfide impurities. The melts were then sparged with hydrogen alone to reduce nickel and other reducible cationic impurities.[5] After this treatment, analysis of filtered samples of the melts were usually within the limits: Fe, 100–200 ppm; Cu, <100 ppm; Ni, <20 ppm; Cr, <20 ppm; S, <5 ppm. High-purity BeO from Brush Beryllium Co. was used in the preparation of oxide-saturated melts.

Apparatus.—An aqueous HF saturator assembly (Figure 1), used to prepare HF–H$_2$O–H$_2$ gaseous mixtures, consisted of a series of three Teflon containers immersed in a thermostat. The first and last containers were dry bottles, the latter acting as a spray trap. The saturator was a two-piece spiral gas-washing bottle with a capacity of 300 ml. The bath temperature (controlled to ±0.1° in the range of 15–25°) and the concentration of aqueous HF in the saturator were varied to produce the gas compositions desired.

Alternatively, mixtures of HF alone with hydrogen were prepared in which a small flow of HF from a thermostated cylinder, controlled by a mass spectrometer leak valve of Monel and Inconel,[14] was introduced into the hydrogen stream in a small mixing chamber.

The melts were contained in cylindrical vessels (2-in. diameter, 15-in. length; or 4-in. diameter, 15-in. length) constructed of Grade A nickel and equipped with a thermocouple well and a gas-inlet tube each of which reached to within 0.5 in. of the bottom of the vessel, a cover gas line, and a sampling port. A side arm of 0.25-in. tubing on the sampling port served as the gas-outlet line. The reaction vessel was located inside an upright tube furnace, the temperature of which was controlled by an L & N Speedomax H temperature controller with a Model S recorder and a chromel–alumel thermocouple. Temperature was checked periodically with a calibrated Pt—Pt–10% Rh thermocouple and read with an L & N K-2 potentiometer.

The Karl Fischer titration vessel used to determine the water content of the gas stream was a 300-ml round-bottom flask with the following additions: two Pt wires sealed through near the bottom of the flask and about 0.75 in. apart; a side arm added to the bottom to allow drainage of the flask; two buret tips (for 5-ml Koch microburets with 150-ml reservoir) sealed through the top of the vessel about 3 in. apart; and Teflon gas-inlet and gas-outlet lines fitted through a rubber stopper. The solution was stirred by a small bar magnet under the Pt wires. The end point was determined by an amperometric method using the "dead-stop" technique.[15] The indicator circuit consisted of a 1.5-V dc source, a 10^4-ohm variable resistor, a 500-ohm variable resistor, the Pt electrodes, and a microammeter (all connected in series).

The KOH titration vessel used to determine the HF content of the gas stream was a 175-ml test tube closed with a rubber stopper. This was fitted with Teflon gas-inlet and gas-outlet lines and the tip of a 10-ml Lab-Crest microburet.

The total volume of carrier gas passed through the system was measured with a Precision wet-test meter. The gas-exit line from this was connected to a Bubble-O-Meter which was used for precise measurement of the gas flow rate. Connecting lines in the apparatus were copper and the valves were Monel diaphragm types. Both were wrapped with heating tape and held at a temperature of ~100° to minimize HF adsorption. Teflon tubing was used where flexible connections were needed.

Determination of Partial Pressures.—The primary data obtained during a run were the influent partial pressures (P_{HF}^0 and $P_{H_2O}^0$), which were measured usually at the beginning and at the end of a run with the reaction vessel by-passed, and the effluent partial pressures (P_{HF} and P_{H_2O}), which were measured as a function of the volume of gas passed (*cf.* Figures 2 and 3). The pressures were calculated from the formulas

$$P_{HF} = n_{HF}RT/V,\ P_{H_2O} = n_{H_2O}RT/V \qquad (12)$$

wherein n_{HF} and n_{H_2O} are the number of moles equivalent in relation to the volume of standard reagent consumed by the flowing

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[14] Diaphragm-type adjustable leak valve (reference No. C-124492A) obtained from Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tenn.

[15] J. J. Lingane, "Electroanalytical Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1958, p 286.

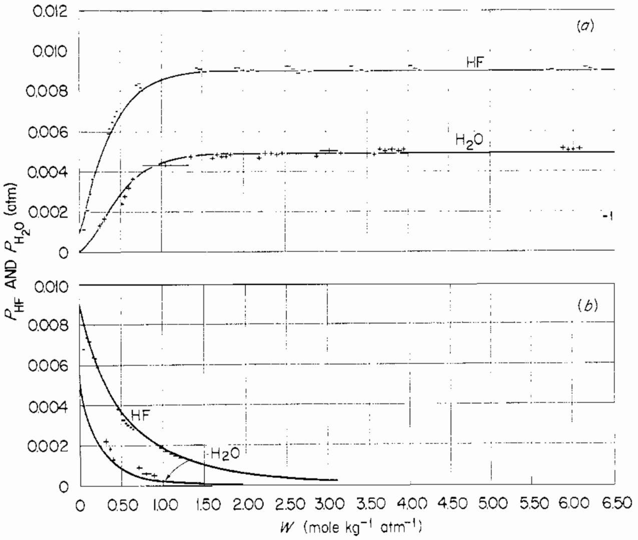

Figure 2.—Effluent partial pressures from a BeO-saturated melt at 700° with $X_{BeF_2} = 0.300$: (a) sparging with influent partial pressures of 0.0057 atm of HF and 0.0065 atm of H_2O; (b) sparging with carrier gas alone. The curves were calculated assuming equilibrium sparging conditions with $Q = 0.0165$ atm and $Q_{OH} = 0.016$ mole/kg.

gas in a measured time. V is the corresponding gas volume determined by comparing this time with the simultaneously determined time for 100 ml of gas to pass through the Bubble-O-Meter. The absolute temperature T is that of the Bubble-O-Meter.

The total volume of gas passed was expressed in units of molar volumes per unit weight of melt W (*cf.* eq 11). The products $P_{HF}dW$ and $P_{H_2O}dW$ thus had units of moles per kilogram and could be related directly to changes in oxide and hydroxide ion concentrations (in moles per kilogram) in the melt (eq 8–10).

The HF and H_2O titration vessels were found to be 99.9% efficient in removing these gases. The partial pressures P_{HF} and P_{H_2O}, which usually did not exceed 0.01 atm, were determined with a precision of approximately 1%. For partial pressures of water less than $\sim 10^{-3}$ atm, a blank correction was made which arose mainly from the in-leakage of moisture into the Karl Fischer titrator. When not in use, the Karl Fischer assembly was kept with excess reagent present in the solution. This desiccated the surface exposed to the gas phase, and, hence, the first determinations in a series of P_{H_2O} values would be low because of absorption of water. Only after approximately the first 0.3 ml of reagent had been consumed were determinations accepted. It was necessary to avoid combinations of P_{HF} and P_{H_2O} in the effluent gas which were supersaturated with respect to aqueous HF at room temperature,[16] since this produced condensation in the lines and erratic results.

Systematic Errors.—The simple relationships (eq 11 and 12) used for calculation of the partial pressures and the molar volumes of gas passed through the reaction vessel are approximations for the following reasons: (1) The gas reaching the wet-test meter and Bubble-O-Meter had been stripped of HF and saturated with H_2O. (2) Depending upon the partial pressure being measured (*i.e.*, P_{HF}^0, $P_{H_2O}^0$, P_{HF}, or P_{H_2O}) there were slightly different total pressures in the various parts of the system. (3) There was a small loss of hydrogen from the reaction vessel by diffusion through the walls. (4) Finally, because of the dead volume in the system there was a lag between the actual equilibrium partial pressures at the surface of the melt and the partial pressures which were measured. When effects (1) to (3) were considered in detail however, the resulting systematic errors in Q and Q_O were only about 2% and no systematic error was introduced into Q_{OH}. These corrections are smaller than the reproducibility with which the quotients could be determined (approximately ±5, ±10, and ±20%, respectively) and consequently they were neglected.

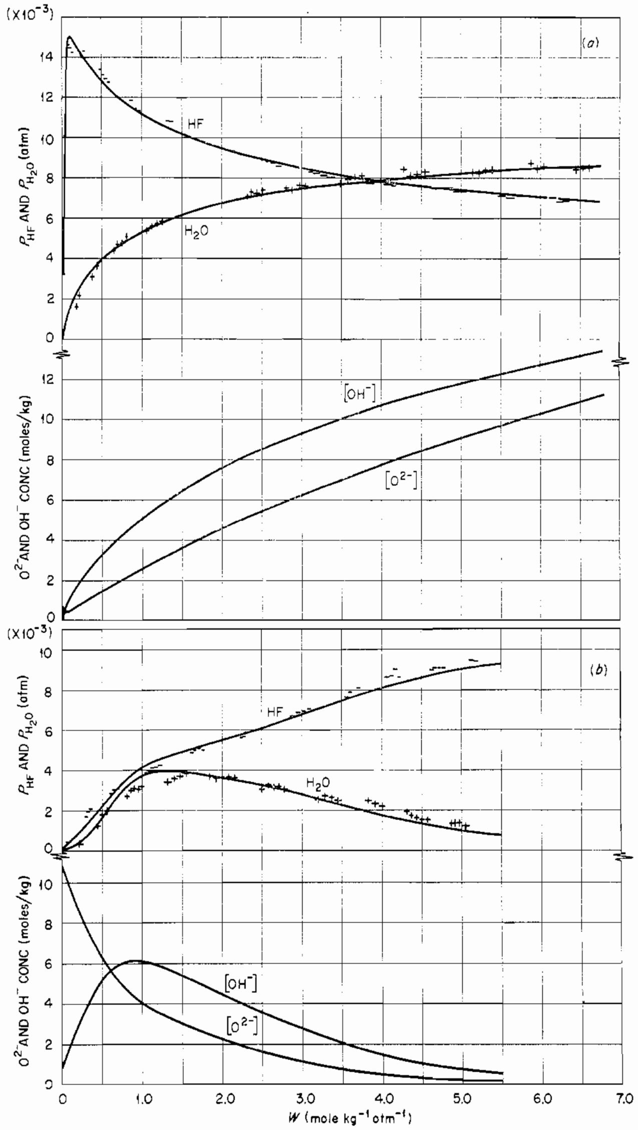

Figure 3.—Effluent partial pressures and melt concentrations for unsaturated melts with $X_{BeF_2} = 0.333$: (a) buildup of oxide and hydroxide concentrations in an initially clean melt upon sparging with influent partial pressures of 0.00382 atm of HF and 0.0105 atm of H_2O at 600°; (b) decrease of oxide and hydroxide concentrations upon sparging with 0.0103 atm of HF alone at 550°. All curves were calculated assuming equilibrium sparging conditions with: (a) $Q_O = 6.05 \times 10^{-5}$ atm mole kg^{-1} and $Q_{OH} = 0.0106$ mole kg^{-1}; (b) $Q_O = 1.84 \times 10^{-5}$ atm mole kg^{-1} and $Q_{OH} = 6.77 \times 10^{-3}$ mole kg^{-1}.

An analysis of the effect of the dead volume on the lag between partial pressures in the reaction vessel and measured partial pressures led to the following correction (ref 1, p 36)

$$P_i = (P_i)_{obsd} + V_R(T_R/T)(d(P_i)_{obsd}/dV) \qquad (13)$$

wherein V_R is the dead volume (the gas volume) in the reaction vessel; T_R and T are the absolute temperature of the reaction vessel and the wet-test meter. The magnitude of the correction is seen to be strictly proportional to the rate at which the partial pressure P_i changes with the measured volume V. Introducing typical values for V_R (in liters), T_R, and Tw

$$P_i = (P_i)_{obsd} + 0.14(d(P_i)_{obsd}/dV) \qquad (14)$$

This correction proved significant only in rare instances at the start of a run and then only over small volumes of flow. At other

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[16] P. A. Munter, O. T. Aepli, and R. A. Kossatz, *Ind. Eng. Chem.*, **41**, 1504 (1949).

times the corrections were less than 10^{-4} atm and so were neglected.

Determination of Equilibrium Quotients

Saturated Melts.—When BeO was present as a saturating solid, the initial effluent partial pressures, P_{HF} and P_{H_2O}, would increase or decrease (depending on the influent pressures, $P_{HF}{}^0$ and $P_{H_2O}{}^0$) and eventually level off at constant values if the run was sufficiently prolonged (Figure 2). By inspection it appeared that as expected the quotient $Q = P_{HF}{}^2/P_{H_2O}$ was a constant during the whole of such a run. However, it was obvious that a difference often existed between the total rate at which protons were entering and leaving the melt. This suggested that some protonated species existed in appreciable amounts in the molten salt. When H_2O and OH^- were considered as possibilities it was found that OH^- formation (reaction 4) was sufficient to explain this effect. The solubility of HF in LiF–BeF$_2$ mixtures has been measured[17] and was too small to be significant here.

If the small solubility of HF is neglected, eq 9 relates changes in hydroxide ion concentration in the melt to the measured partial pressures and the change in molar volumes of gas passed per kg of melt (d*W*). An explicit relationship containing only measured quantities and the equilibrium quotients Q and Q_{OH} may be obtained by making the following substitutions in eq 9

$$P_{H_2O} = P_{HF}{}^2/Q, \quad d[OH^-] = (Q_{OH}/Q)dP_{HF}$$

This yields

$$\frac{dP_{HF}}{(P_{HF}{}^0 + 2P_{H_2O}{}^0) - P_{HF} - (2/Q)P_{HF}{}^2} = (Q/Q_{OH})dW \quad (15)$$

Integrating

$$f(Q, P_{HF}) = \frac{Q\sqrt{A}}{2.303}\left(\frac{1}{Q_{OH}}\right)W + \text{constant} \quad (16)$$

in which

$$f(Q, P_{HF}) = \log\left|\frac{(4P_{HF}/Q) + 1 + \sqrt{A}}{(4P_{HF}/Q) + 1 - \sqrt{A}}\right|$$

$$A = 1 + [8(P_{HF}{}^0 + 2P_{H_2O}{}^0)/Q]$$

The procedure in analyzing the data (done by means of a computer program[18]) was first to estimate Q from P_{HF} and P_{H_2O}, especially in the region of the measurements wherein these pressures were constant or approaching constancy. With this value of Q, the P_{H_2O} measurements were converted to the corresponding calculated P_{HF} values ($P_{HF} = \sqrt{P_{H_2O}Q}$). Then $f(Q, P_{HF})$ was calculated for every observation in the region where partial pressures were changing and plotted *vs.* *W*. Consistent with eq 15, linear plots were obtained, the slopes of which gave Q_{OH}. If necessary, the values of Q were adjusted within their uncertainties to optimize the fit of the data to these plots. Some runs were not continued long enough for P_{HF} and P_{H_2O} to become constant, and here Q was based on other runs at the same temperature and melt composition in order to calculate Q_{OH}. In other runs, P_{HF} and P_{H_2O} were constant almost from the outset, and hence it was not possible to calculate Q_{OH}.

Unsaturated Melts.—For runs in which BeO was not present as a saturating solid, explicit equations could not be found which related Q_O and Q_{OH} to the measured partial pressures and *W*. Hence it was necessary to use a less direct method for determining Q_O and Q_{OH}. The quantities P_{HF} and P_{H_2O} were eliminated from eq 9 and 10 to give

$$\frac{d[OH^-]}{dW} = (P_{HF}{}^0 + 2P_{H_2O}{}^0) - \frac{Q_O[OH^-]}{Q_{OH}[O^{2-}]}(1 + (2[OH^-]/Q_{OH})) \quad (17)$$

$$\frac{d[O^{2-}]}{dW} = \frac{Q_O[OH^-]}{Q_{OH}[O^{2-}]}(1 + ([OH^-]/Q_{OH})) - P_{HF}{}^0 - P_{H_2O}{}^0 \quad (18)$$

Using these equations with Q_O, Q_{OH}, $P_{H_2O}{}^0$, $P_{HF}{}^0$, and the initial concentrations $[OH^-]^0$ and $[O^{2-}]^0$ all specified, it was possible to determine $[OH^-]$ and $[O^{2-}]$ numerically as *W* was increased from zero in small increments. A computer program, which employed the Runge–Kutta method, was used to do this.[19] With values of $[OH^-]$ and $[O^{2-}]$ thus calculated as a function of *W*, it was possible in turn to calculate P_{HF} and P_{H_2O} as a function of *W*

$$P_{HF} = \frac{Q_O[OH^-]}{Q_{OH}[O^{2-}]}, \quad P_{H_2O} = \frac{Q_O[OH^-]^2}{Q_{OH}{}^2[O^{2-}]} \quad (19)$$

These were compared with the observed partial pressures and, finally, the values of Q_O, Q_{OH}, $[OH^-]^0$, and $[O^{2-}]^0$ were adjusted to give the best least-squares fit of the calculated to the observed values of P_{HF} and P_{H_2O}. This method of refining Q_O and Q_{OH} was relatively cumbersome, time consuming, and often unworkable until the initial guesses for the adjustable parameters were reasonably close to the best values.

Validity of Equilibrium Quotients.—The general agreement between the calculated and the observed effluent partial pressures of HF and H_2O, especially in view of the variety of behavior observed as experimental conditions varied (Figures 2 and 3), strongly indicates that the assumed equilibria (eq 1, 2, and 4) are correct and sufficient.

In particular it should be noted that for both unsaturated and saturated melts, inlet gas compositions were varied in such a way that $[OH^-]$ and $[O^{2-}]$ variously increased, changed little, or decreased with continued gas flow. There was no discernible systematic effect upon the resulting values of Q, Q_{OH}, or Q_O. Thus there seems little doubt that equilibrium conditions were adequately approached during the measurements.

Finally, after completion of a series of measurements on saturated melts, the molten salt was transferred from the vessel through a sintered-nickel filter and the material on the filter was examined by X-ray diffraction. Only the characteristic peaks for LiF–BeF$_2$ solids and BeO were observed. There was no indication of hydroxide or oxyfluoride solids or of other oxide solids.

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(17) P. E. Field and J. H. Shaffer, *J. Phys. Chem.*, **71**, 3220 (1967).

(18) Program written by R. J. McNamee, Operations Analysis Division, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tenn.

(19) Program FIASCO written by M. T. Harkrider, Mathematics Division, ORNL, Oak Ridge, Tenn.

TABLE I

EQUILIBRIUM QUOTIENTS IN LiF–BeF$_2$

Equilibrium and quotient	Conditions	Expression
I. $H_2O(g) + BeF_2(d) \rightleftharpoons BeO(c) + 2HF(g)$	BeO satd	
$Q = P_{HF}^2/P_{H_2O}$ (atm)	(a) $X_{BeF_2} = 0.3\text{–}0.8$	$\log Q = \log X_{BeF_2} + 3.900 - (4418/T) + (7.819 - (5440/T))X_{LiF}^2 - (12.66 - (5262/T))X_{LiF}^4$
	(b) LiF satd	$\log Q = 1.534 - (3662/T)$
	(c) BeF$_2$ satd	$\log Q = 6.141 - (6264/T)$
	(d) $X_{BeF_2} = 1.0^a$	$\log K = 6.141 - (\Delta H_f/2.3RT_f) + ((\Delta H_f/2.3R) - 6264)/T$
II. $H_2O(g) + F^-(d) \rightleftharpoons OH^-(d) + Hf(g)$ $Q_{OH} = P_{HF}[OH^-]/P_{H_2O}$ (mole kg^{-1})	BeO satd or soln only	$\log Q_{OH} = -0.503 + 2.843X_{BeF_2} - (2085/T)$
III. $H_2O(g) + 2F^-(d) \rightleftharpoons O^{2-}(d) + 2HF(g)$	Soln only	
$Q_O = P_{HF}^2[O^{2-}]/P_{H_2O}$ (atm mole kg^{-1})	(a) $X_{BeF_2} = 0.273$	$\log Q_O = 4.791 - (8158/T)$
	(b) $X_{BeF_2} = 0.333$	$\log Q_O = 5.673 - (8637/T)$
	(c) $X_{BeF_2} = 0.400$	$\log Q_O = 7.026 - (9032/T)$

[a] ΔH_f is the heat of fusion of BeF$_2$. This equation is obtained by combining eq 26, 27, and Ic.

Results and Discussion

Oxide Chemistry.—The equilibrium quotients Q, Q_{OH}, and Q_O obtained from the transpiration measurements were fitted by least squares to the empirical expressions listed in Table I. The Q values were weighted inversely as their estimated variance (typically ±5%) to determine the six constants in eq Ia (Table I). The average deviation of observed Q values from smoothed values (Figure 4) given by this equation was ~6%. It was evident that eq Ia is increasingly a poor approximation of the data below $X_{BeF_2} = 0.3$. At 700° the expression

$$\log Q = \log X_{BeF_2} - 0.723 + 4.094X_{LiF}^2 - 16.64X_{LiF}^4 + 12.51X_{LiF}^6 \quad (20$$

fits the data in the range $X_{BeF_2} = 0.3\text{–}0.5$ about as well as eq Ia but below $X_{BeF_2} = 0.3$ it is a considerable improvement over it. Equation Ib (Table I) is based on three measurements of Q in which LiF as well as BeO was present as a saturating solid. In a similar way eq Ic corresponds to equilibria along the BeF$_2$ liquidus, *i.e.*, to the reaction

$$H_2O(g) + BeF_2(c) \rightleftharpoons BeO(c) + 2HF(g) \quad (21)$$

Here, however, values of Q were not measured. Instead they were calculated by introducing X_{BeF_2} and T values corresponding to the BeF$_2$ liquidus[20] into eq Ia.

Q_{OH} values derived from saturated melts had estimated variances in the range ±10 to ±20% below $X_{BeF_2} = 0.6$. In unsaturated melts, because of the indirect method used to determine Q_{OH} and Q_O, variances were not estimated; however, Q_{OH} values derived from these measurements were reasonably consistent with those from saturated melts (Figure 5) and, judging from the scatter, smoothed values of Q_{OH} have about a ±10% uncertainty.

The values of Q_O, derived solely from unsaturated melts, are the least accurate of the quotients determined as is indicated by the scatter in Figure 6. The ratio Q_O/Q gives the calculated concentration of oxide (in moles per kilogram) in a melt saturated with BeO. The resulting values (ref 1, Figure 25) reflect the scatter in the Q_O values but are in satisfactory agreement with more recent and more direct measurements of BeO solubility in LiF–BeF$_2$ solutions.[6] While the solubility of BeO increases with both the temperature and the BeF$_2$ content of the melt, the highest value (at X_{BeF_2} = 0.6, 700°) was only 0.1 mole/kg, which is 0.3 mole % of the fluoride. Most solubilities were in the range 0.005–0.02 mole/kg.

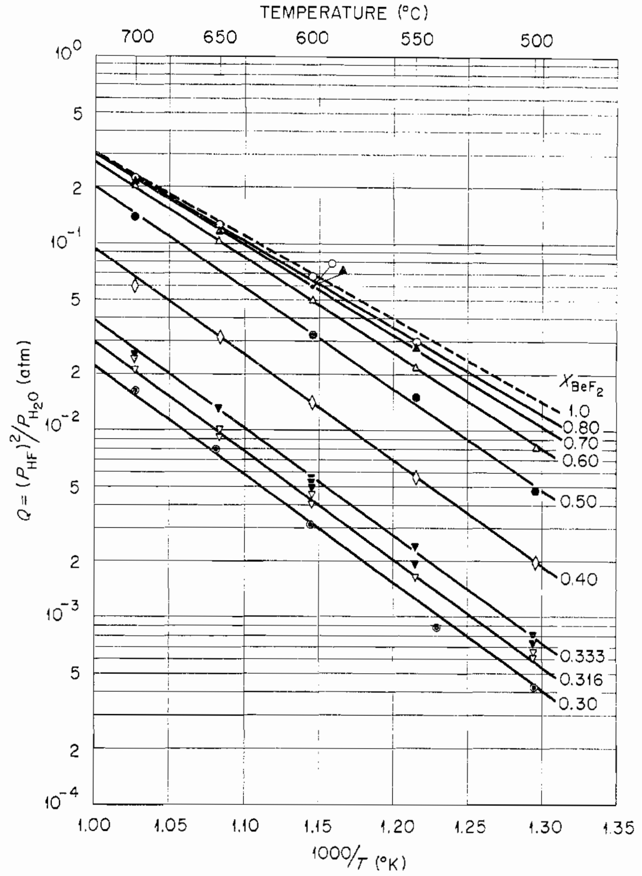

Figure 4.—Values of Q for BeO saturated melts. The lines were derived from eq Ia in Table I.

In the interpretation of all the present measurements, the assumption of OH$^-$ and O^{2-} as the only dissolved species was sufficient; the assumption of H$_2$O and O^{2-}

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[20] Temperature–composition values used here for the LiF liquidus and BeF$_2$ liquidus were supplied by R. E. Thoma of this laboratory. They differ only slightly from the phase diagram reported by Thoma, *et al.*, in USAEC Report ORNL-3789, April 1965, p 3. R. E. Thoma, S. Cantor, H. Insley, and H. A. Friedman have submitted the completed phase diagram for publication.

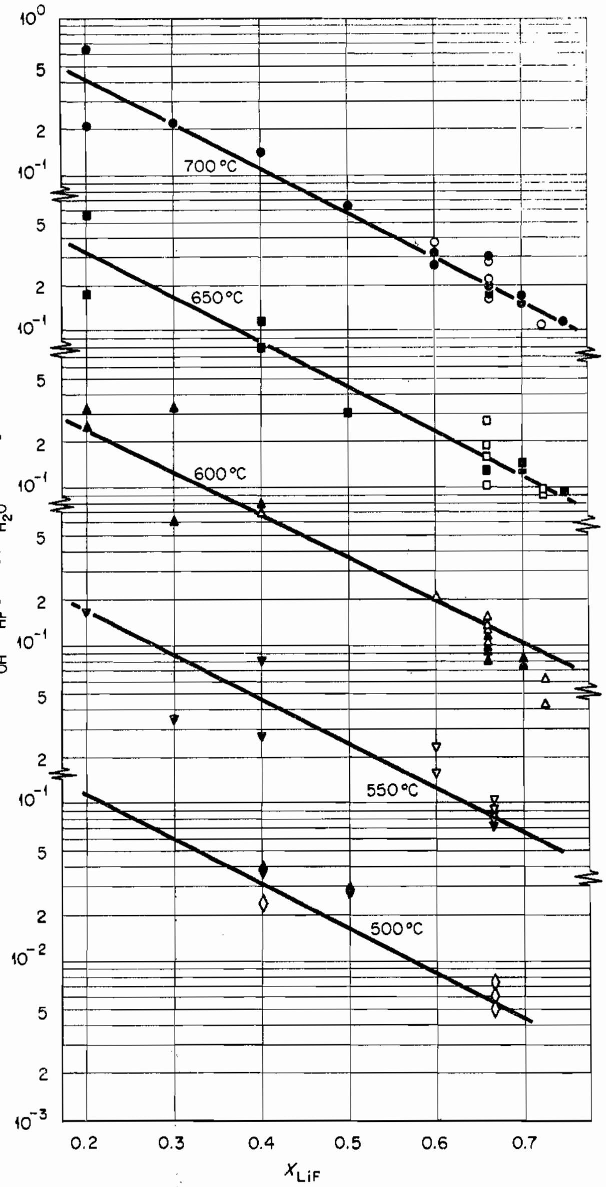

Figure 5.—Values of Q_{OH} from BeO-saturated melts (filled symbols) and from unsaturated melts (open symbols). The lines were derived from eq II in Table I.

on the other hand was not. While it was not possible from the measurements to rule out the presence of both H$_2$O and OH$^-$ as protonated species in solution, this seems unlikely when one considers the following dissociation reactions and their quotients

$$H_2O(d) + F^-(d) \rightleftarrows OH^-(d) + Hf(g) \quad (Q_{OH}/Q_{H_2O}) \quad (22)$$

$$OH^-(d) + F^-(d) \rightleftarrows O^{2-}(d) + HF(g) \quad (Q_O/Q_{OH}) \quad (23)$$

in which Q_{H_2O} is a Henry's law constant

$$Q_{H_2O} = [H_2O]/P_{H_2O} \text{ mole kg}^{-1} \text{ atm}^{-1} \quad (24)$$

The ratio of first to second dissociation constant for water has been estimated by Latimer[21] to be greater than 10^{22}. For H$_2$S it is $\sim 10^7$. If, as seems very likely, the corresponding ratio for the above reaction in molten fluoride is at least 10^4, *i.e.*

$$Q_{OH}^2/Q_O Q_{H_2O} \geqslant 10^4$$

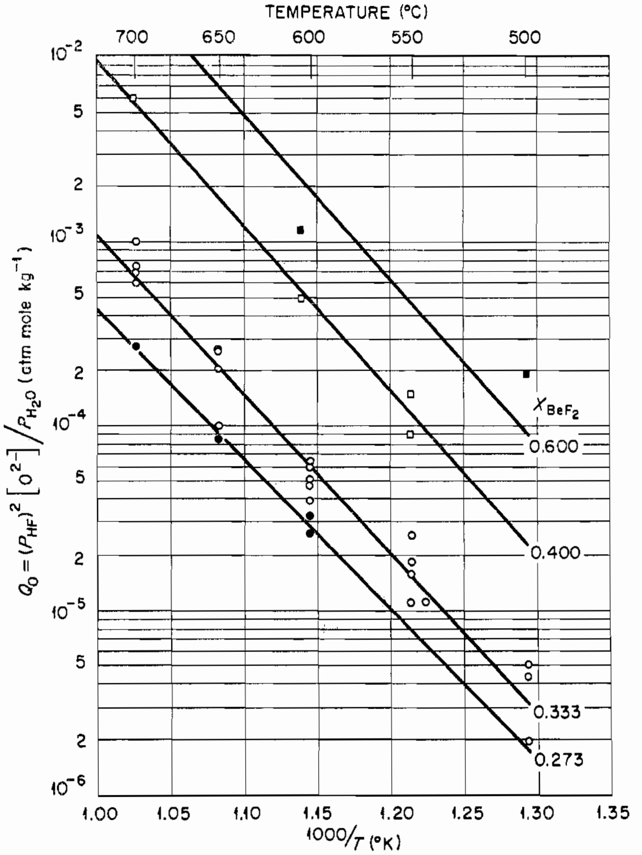

Figure 6.—Values of Q_O from unsaturated melts. The lines at X_{BeF_2} = 0.273, 0.333, and 0.4 were derived, respectively, from eq IIIa, b, and c in Table I.

then from the present estimates of Q_{OH} and Q_O

$$Q_{H_2O} \leqslant 10^{-3} \text{ mole kg atm}^{-1} \quad (25)$$

this would correspond to insignificant amounts of dissolved water at the maximum value of P_{H_2O} used in the present measurements.

While the values of Q and Q_O both increase markedly with temperature, the quotient Q_{OH}—which corresponds to the reaction (eq 4) of H$_2$O with F$^-$ to give HF and OH$^-$—increases only slightly with temperature. The equilibrium quotient for the above reaction between OH$^-$ and F$^-$ (Q_O/Q_{OH}, eq 23) reflects the expected decrease in OH$^-$ stability with increasing temperature. The quotients Q, Q_O, and Q_{OH} all increase with the BeF$_2$ mole fraction. The dependence of these equilibrium quotients on solution composition reflects variations in the activities of BeF$_2$ and F$^-$, and in the activity coefficients of O^{2-} and OH$^-$. Knowledge of these effects should be useful in the development of a model for this molten salt system (see below).

With these values of Q, Q_{OH}, and Q_O as a function of temperature and melt composition, it is possible to specify the conditions and the duration of hydrofluorination necessary to produce a LiF–BeF$_2$ mixture of a given low oxide content.[22] In general the ease of oxide removal by hydrofluorination increases with decreasing temperature and, as might be expected, increases with increasing partial pressure of HF. Oxide

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[21] W. H. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc , New York, N. Y., 1952, p 34.

[22] C. F. Baes, Jr., and B. F. Hitch in USAEC Report ORNL-3812, Feb 1965, p 131.

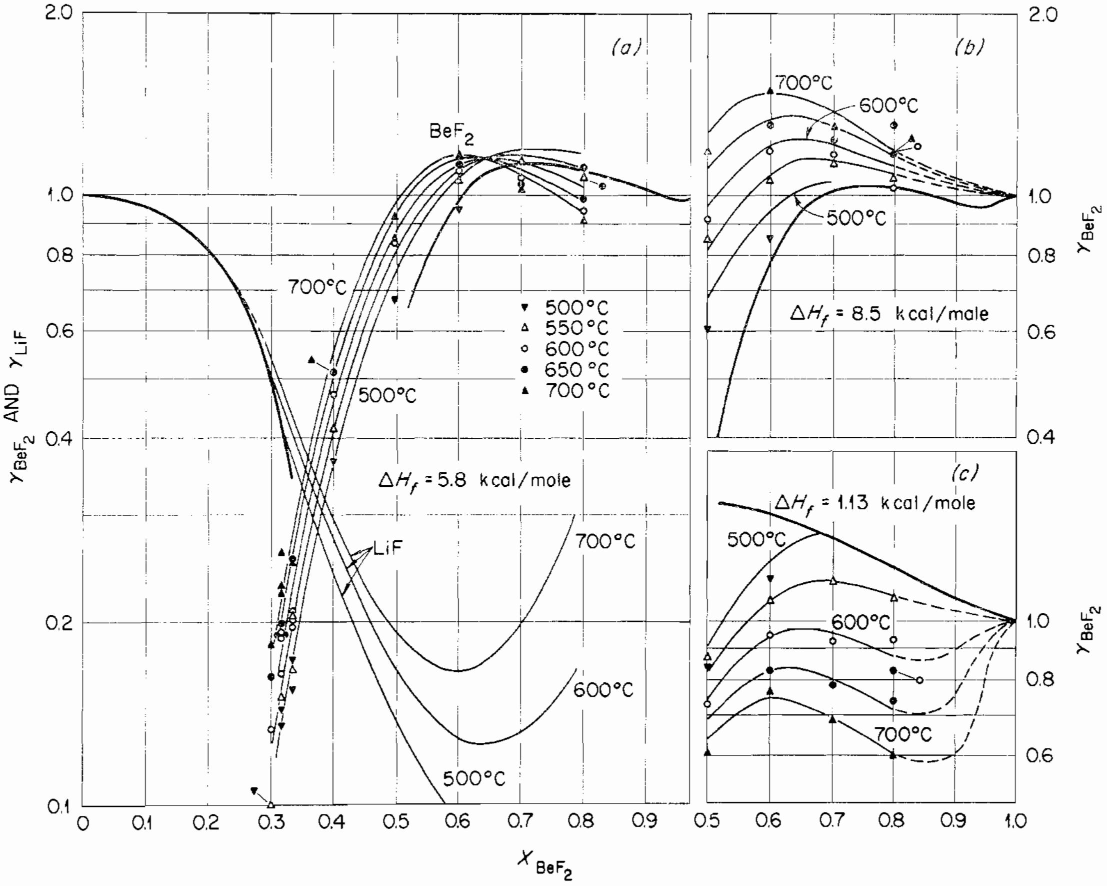

Figure 7.—Activity coefficients in molten LiF–BeF$_2$. Heavy curves are derived from the LiF–BeF$_2$ phase diagram.[20] The heat of fusion of LiF is taken as 6.47 kcal/mole.[26] Three different values are assumed for the heat of fusion of BeF$_2$. The lighter curves are smoothed values from eq I and II in Table II. The dashed portion of the γ_{LiF} curve at 700° is from eq 28. The points are derived from observed Q values (Figure 4), combined with eq 26 and Id (Table I).

removal by hydrofluorination has been adapted for the purpose of oxide analysis in the determination of BeO solubilities[6] and for the oxide analysis of radioactive fluoride fuel salt from the molten salt reactor experiment.[23]

Thermodynamics.—As has already been noted, Q should be proportional to the activity of BeF$_2$

$$Q = Ka_{BeF_2}; \quad \gamma_{BeF_2} = (Q/K)/X_{BeF_2} \tag{26}$$

Here pure liquid BeF$_2$ is the standard state and K is the equilibrium constant for reaction 2. While eq Ia (Table I) can be used to calculate Q, the value of K must be specified in order to determine γ_{BeF_2} by eq 26. If it is assumed that eq Ia is valid all the way to pure BeF$_2$, then K is obtained by introducing $X_{BeF_2} = 1$ and $X_{LiF} = 0$ into this same expression. It is probable, however, that eq Ia cannot safely be extrapolated beyond the range of the present measurements. Alternatively, if, instead, it is assumed only that log K varies linearly with $1/T$, then it is possible to combine eq 26 and Ic with

$$\log a_{BeF_2}\ (\text{BeF}_2\ \text{satn}) = -\frac{\Delta H_f}{2.3R}\left(\frac{1}{T} - \frac{1}{T_f}\right) \tag{27}$$

to obtain a relationship between log K and the heat of fusion of BeF$_2$, ΔH_f (eq Id, Table I). The resulting expression for γ_{BeF_2} and—by a Gibbs–Duhem integration—the expression for γ_{LiF} are given in Table II.

Table II

Activity Coefficients in LiF–BeF$_2$ for X_{BeF_2} = 0.3–0.8 and T = 773–973°K

I. $\log \gamma_{BeF_2} = A + BX_{LiF}^2 + CX_{LiF}^4$ [a]

II. $\log \gamma_{LiF} = D - 2BX_{LiF} + BX_{LiF}^2 - (4/3)CX_{LiF}^3 + CX_{LiF}^4$ [b]

$A = 2.241 + (\Delta H_f/3789) + [1846 - (\Delta H_f/4.576)]/T$ [c]

$B = 7.819 - (5440/T)$

$C = -12.66 + (5262/T)$

$D = 4.379 - (4052/T)$[d]

[a] From eq Ia and Id (Table I) and eq 26. [b] From a Gibbs–Duhem integration of eq I. [c] ΔH_f denotes the heat of fusion of BeF$_2$. [d] From the LiF liquidus data.

In order to extend values of γ_{LiF} below $X_{BeF_2} = 0.3$ at 700°, eq 22 also was subjected to a Gibbs–Duhem integration giving

$$\log \gamma_{LiF} = 0.928 - 8.188X_{LiF} + 4.094X_{LiF}^2 + 22.20X_{LiF}^3 - 16.60X_{LiF}^4 - 15.01X_{LiF}^5 + 12.51X_{LiF}^6 \tag{28}$$

represented by the dashed curve in Figure 7a. The integration constants in these two expressions for γ_{LiF} were determined by comparison with γ_{LiF} values derived from the liquidus data[20] and a heat of fusion of 6.47 kcal/mole for LiF.

If the heat of fusion of BeF$_2$ is chosen as 8.5 kcal/

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(23) R. F. Apple, J. M. Dale, and A. S. Meyer, Jr., in USAEC Report ORNL-3936, Feb 1966, p 154.

mole and this value is inserted into eq Id, this expression becomes equivalent to eq Ia with $X_{BeF_2} = 1$; *i.e.*, the above-mentioned use of eq Ia as an extrapolation function is equivalent to a heat of fusion of 8.5 kcal/mole for BeF$_2$ (assuming the liquidus data[20] on which eq Ic is based are correct). While this value of ΔH_f is well within the range of various other estimated values, it is much higher than a recent calorimetric value of 1.13 kcal/mole reported by Taylor and Gardner.[13] A further difficulty arises in that the resulting activity coefficient curves (Figure 7b) show an increasing positive deviation with temperature which would require that two liquid phases appear above ~650° and at $X_{BeF_2} \sim 0.8$. While a region of two liquid phases has indeed been found in the ternary system LiF–BeF$_2$–ZrF$_4$ in a region near this portion of the LiF–BeF$_2$ binary system, two liquid phases have not been observed[24] in the binary system. If, alternatively, the calorimetric value of $\Delta H_f = 1.13$ kcal/mole is introduced into eq Id, then the activity coefficient curves are shifted (Figure 7c) in such a way that they tend to diverge at $X_{BeF_2} > 0.5$. This behavior is not only peculiar, but it also seems inconsistent with a value of γ_{BeF_2} (1.3 at $X_{BeF_2} = 0.67$ and 604°) derived by Büchler from mass spectroscopy[11] and with Cantor's recently measured vapor pressures of BeF$_2$ over LiF–BeF$_2$ melts at higher temperatures.[25] Cantor's results suggest a log γ_{BeF_2} *vs.* X_{BeF_2} curve at 1000° which is in fact quite similar to the present curve at 550°. This 550° curve is essentially independent of the choice of ΔH_f since it is nearly identical with the melting point (*cf.* eq I, Table II) of BeF$_2$.[20] The similarity of the two activity coefficient curves suggests that γ_{BeF_2} has a low-temperature coefficient above $X_{BeF_2} = 0.5$. If this is so, then the most consistent appearing value of ΔH_f is ~5.8 kcal/mole, a value which minimizes the spread of the present data (Figure 7a) as a function of temperature in this concentration range. This value has a considerable uncertainty, however, because of uncertainties in the other constants in eq Id and in A of Table II. These constants are based primarily on the few measurements at temperatures and compositions (500–550°, $X_{BeF_2} = 0.7$–0.8) approaching the BeF$_2$ liquidus. Emf measurements on this system are presently in progress and should provide additional data with which to define γ_{BeF_2} in this region and to test ΔH_f.

Using available thermochemical data for H$_2$O, HF, and BeO,[26] formation free energies and enthalpies have been derived from eq Ic for crystalline BeF$_2$ (Table III). These are seen to agree well with values given currently in the "JANAF Tables."[26] The values listed for liquid BeF$_2$ in Table III are based on $\Delta H_f = 5.8$ kcal/mole.

Structure of LiF–BeF$_2$ Melts.—Førland has suggested[8] that the BeF$_2$ liquidus data in the LiF–, NaF–, and RbF–BeF$_2$ systems be interpreted in terms of random mixing of bridging F$^-$ ions and nonbridging F$^-$ ions (reaction 3). If these are the only kinds of F$^-$ ions present and if every Be^{2+} ion is surrounded by four F$^-$ ions, then the number of moles of each kind of F$^-$ ion is given by

TABLE III

FREE ENERGY AND HEAT OF FORMATION OF BeF$_2$[a]

Temp, °K	State	ΔG, kcal/mole	ΔH, kcal/mole
298	Cryst	232.2 (230.1 ± 2)[b]	244.1 (242.3 ± 2)[b]
700	Cryst	217.5	243.1
800	Cryst	213.9 ± 1	242.9 ± 1
900	Liq	210.7	237.0
1000	Liq	207.8	236.9

[a] Calculated at 800°K from ΔG and ΔH of reaction given by eq Ic (Table I) along with ΔG_f values given in ref 26 for HF(g), H$_2$O(g), and BeO(c). The values above the melting point (~825°K) are based on an assumed heat of fusion of 5.8 kcal/mole (and entropy of fusion of 7.0 eu). The contribution of ΔC_p to the change of ΔG_f and ΔH_f with temperature was taken from ref 26. [b] See ref 26.

$$n_{-F} = 2n_{LiF};\ n_{-F-} = 2n_{BeF_2} - n_{LiF}$$

Their "mole fractions" are

$$X_{-F} = \frac{2X_{LiF}}{2 - X_{LiF}};\quad X_{-F-} = \frac{2 - 3X_{LiF}}{2 - X_{LiF}}$$

More generally, if the nonbridging F$^-$ ions are present in groups of size p, then the mole fractions are

$$X_{(-F)p} = \frac{(2/p)X_{LiF}}{2 - \left(3 - \dfrac{2}{p}\right)X_{LiF}};\quad X_{-F-} = \frac{2 - 3X_{LiF}}{2 - \left(3 - \dfrac{2}{p}\right)X_{LiF}}$$

Considering only the entropy of mixing of bridging F$^-$ ions and nonbridging F$^-$ ions, or groups of ions, Førland shows that

$$a_{BeF_2} = (X_{-F-})^2$$

Hence

$$\gamma_{BeF_2} = \left[\frac{2 - 3X_{LiF}}{2 - \left(3 - \dfrac{2}{p}\right)X_{LiF}}\right]^2 \frac{1}{X_{BeF_2}} \tag{29}$$

Førland compared the BeF$_2$ liquidus data in all three systems with $p = 1$–4. The corresponding values of ΔH_f obtained were ~19 kcal/mole ($p = 1$), 10 kcal/mole ($p = 2$), and ~5 kcal/mole ($p - 4$). Førland favored the assumption of dimeric nonbridging F$^-$ ions as being a reasonable degree of association over the wide composition ranges involved.

On the basis of this model the present results suggest rather that, as pure BeF$_2$ is approached, nonbridging fluoride ions occur in groups of 4 or more. In particular, the value of ΔH_f for BeF$_2$ chosen above (5.8 kcal/mole) as most consistent with the present data suggests that the association number is ~4. (The much lower calorimetric heat of fusion of 1.13 kcal/mole corresponds to an association number of ~16.) The occurrences of nonbridging fluorides in groups of 4 is reasonable in that it suggests empty "BeF$_4$" tetrahedra in the silica-like network structure which may develop as pure BeF$_2$ is approached in the LiF–BeF$_2$ melts.

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(24) R. E. Thoma and H. A. Friedman in USAEC Report ORNL-3872, Aug 1965, p 126.

(25) S. Cantor in USAEC Report ORNL-3872, Aug 1965, p 123.

(26) "JANAF Thermochemical Tables," Clearing House for Federal Scientific and Technical Information, U. S. Department of Commerce, Aug 1965.

In a subsequent publication, a more detailed model for LiF–BeF$_2$ solutions will be compared with the present data, a model in which polymeric anions $Be_aF_b^{(b-2a)-}$ are assumed. These will extend in composition and structure from the monomer BeF_4^{2-}—the principal species when X_{BeF_2} is less than 0.33—through increasingly polymeric anions as X_{BeF_2} increases, to very large networks or chain structures as pure BeF$_2$ is approached. For the present it may be useful to point out that since in such a model Li$^+$ is the only cation present in solution, its ion fraction is unity and its activity might be approximated as unity. In this case the activity of LiF given by the present results (Table II) should approximate the activity of F$^-$ ion

$$a_{LiF} = (a_{Li})(a_{F^-}) \sim a_{F^-}$$

The rapid drop in γ_{LiF} (Figure 7a)—*i.e.*, in a_{LiF}—as BeF$_2$ is added to LiF thus may be viewed as corresponding to the depletion of free F$^-$ ions as $Be_aF_b^{(b-2a)-}$ polymers are formed.

Notes

CONTRIBUTION FROM THE MORRISTOWN LABORATORY,
INDUSTRIAL CHEMICALS DIVISION, ALLIED CHEMICAL
CORPORATION, MORRISTOWN, NEW JERSEY 07960

N,N-Difluoro-O-fluorocarbonylhydroxylamine, FC(O)ONF$_2$, and N,N-Difluoro-O-trifluoromethylhydroxylamine, CF$_3$ONF$_2$

BY W. B. FOX, G. FRANZ, AND L. R. ANDERSON

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Recent publications have described the synthesis of the novel N-fluorinated hydroxylamines FSO$_2$ONF$_2$,[1] SF$_5$ONF$_2$,[2,3] and CF$_3$ONF$_2$[3,4] through reactions of tetrafluorohydrazine with (FSO$_2$O)$_2$, SF$_5$OF, and CF$_3$OF, respectively. Presumably these reactions proceed *via* simple coupling of difluoramino radicals with the intermediate oxy radicals (FSO$_2$O·, SF$_5$O·, and CF$_3$O·) generated from the substrates.[1–4]

In the light of these reports and our recent esr studies of the oxy radicals generated by homolytic cleavage of the peroxides FC(O)OOC(O)F[5] and CF$_3$OOCF$_3$,[6] it was of interest to examine the reactions of these peroxides with tetrafluorohydrazine. The anticipated synthesis of the corresponding N-fluoro-O-substituted hydroxylamines is described below.

Experimental Section

Materials.—Bis(fluorocarbonyl)peroxide was prepared by a published method[7] and fractionated on the vacuum line through traps at −111, −130, and −196°. The peroxide collected at −130° was used after its identity was confirmed by infrared and mass spectral analysis. Bis(trifluoromethyl) peroxide from Peninsular ChemResearch and tetrafluorohydrazine from E. I. du Pont de Nemours and Co. were sufficiently pure to be used without further treatment.

Preparation of FC(O)ONF$_2$.—The most satisfactory procedure for preparing FC(O)ONF$_2$ is illustrated by the following example. An evacuated 200-ml Pyrex bulb was charged with 150 mm of gaseous N$_2$F$_4$ (1.60 mmol) at 25°, and an equal amount of FC(O)OOC(O)F was then added from a high-pressure reservoir. Within 1 min after the addition, a rapid reaction occurred as evidenced by formation of a white "mist" in the reactor. The bulb was then cooled to −78° and volatile products were pumped off through traps at −111 and −196°. The product FC(O)ONF$_2$ was collected at −111° and a mixture of NF$_3$, CO$_2$, COF$_2$, and SiF$_4$ was found in the −196° trap. The FC(O)ONF$_2$ fraction (0.40 mmol) was contaminated with small amounts of NO$_2$ and unused peroxide from which it could be separated by fractional codistillation.[8] *Anal.* Calcd for FC(O)ONF$_2$: N, 12.2; F, 49.5. Found: N, 11.8; F, 48.7. In nearly a dozen runs conducted in this fashion, yields of FC(O)ONF$_2$ ranged from 10 to 15%.

An unusual requirement of these runs was that a fresh, unused reaction bulb was required for each experiment to ensure reasonable yields of the desired product. Subsequent experiments conducted in bulbs after their initial use produced NF$_3$, COF$_2$, NO$_2$, and oxygen, but no detectable amount of FC(O)ONF$_2$. No manner of rinsing or cleaning restored the apparent catalytic activity of the Pyrex reactor walls. With one exception, experiments conducted in vessels of quartz, nickel, Monel, and stainless steel were unrewarding and led to mixtures of COF$_2$, NF$_3$, NO$_2$, and noncondensable material. In one case, equimolar amounts of N$_2$F$_4$ and FC(O)OOC(O)F in a reactor of Type 316 stainless steel produced a quantitative yield of FC(O)ONF$_2$, but this result could not be reproduced in numerous subsequent trials.

Preparation of CF$_3$ONF$_2$.[9]—The reactor used was a 30-ml Hoke cylinder (316 stainless steel) fitted with a 323A Hoke valve. Tetrafluorohydrazine (2.5 mmol) and bis(trifluoromethyl) peroxide (2.4 mmol) were combined in the tube and heated to 130° for 10 days. Vacuum-line fractionation of products through traps at −130, −142, and −196° afforded unused CF$_3$OOCF$_3$ (1.7 mmol) in the first two traps. A mixture of CF$_3$ONF$_2$, N$_2$F$_4$, NF$_3$ (trace), and COF$_2$ in the third trap was refractionated through −158 and −196° traps which isolated a CF$_3$ONF$_2$–COF$_2$ mixture at −158° and N$_2$F$_4$ (2.2 mmol, contaminated with minor amounts of COF$_2$, CF$_3$ONF$_2$, and NF$_3$) at −196°. Pure CF$_3$ONF$_2$[3] (0.5 mmol) was recovered from the −158° fraction after removing the COF$_2$ (0.5 mmol) by absorption on finely ground CsF. Based on CF$_3$OOCF$_3$ consumed (0.7 mmol), the pure CF$_3$ONF$_2$ recovered (0.5 mmol) represents a 36% yield (83% based on N$_2$F$_4$ consumed). No significant reaction between CF$_3$OOCF$_3$ and N$_2$F$_4$ occurred when mixtures were heated

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[1] M. Lustig and G. H. Cady, *Inorg. Chem.*, **2**, 388 (1963).

[2] J. Ruff, *ibid.*, **4**, 1788 (1965).

[3] W. H. Hale and S. M. Williamson, *ibid.*, **4**, 1342 (1965).

[4] J. M. Shreeve and L. C. Duncan, *ibid.*, **4**, 1516 (1965).

[5] W. B. Fox and G. Franz, *ibid.*, **5**, 946 (1966).

[6] N. Vanderkooi and W. B. Fox, to be published.

[7] (a) A. J. Arvia, P. J. Aymonino, C. Waldow, and H. J. Schumacher, *Angew. Chem.*, **72**, 169 (1960); (b) A. J. Arvia, P. J. Aymonino, and H. J. Schumacher, *Z. Anorg. Allgem. Chem.*, **316**, 327 (1962).

[8] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

[9] Following completion of this work, a similar preparation of CF$_3$ONF$_2$ was reported by G. N. Sausen, U. S. Patent 3,214,465 (Oct 26, 1965).