With the flask open to the vacuum manifold (volume *ca.* 300 ml) but isolated from the pump, *ca.* one-tenth of the lithium aluminum hydride was added to the reaction mixture by twisting the addition tube. Immediate signs of reaction included release of gas bubbles at the surface of the liquid. Eventually a milky suspension of metal halides was formed. After 10 min *ca.* 20 Torr vapor pressure was indicated by a mercury manometer attached to the manifold. The reaction flask was then isolated from the manifold, and the manifold was opened to a previously evacuated 1-l. gas storage bulb whose bottom was immersed in liquid nitrogen. Then the storage bulb was isolated from the manifold which was again opened to the reaction flask. After several such cycles, each lasting 5–10 min, both reaction and storage flasks were simultaneously opened to the manifold for *ca.* 1 min, allowing a small amount of solvent to distil from the reaction flask to the storage flask. Both flasks were then isolated, and *ca.* 8 Torr of noncondensable gas (presumably hydrogen) was exhausted from the vacuum manifold and the storage flask.

This procedure was followed for each of the *ca.* 10 portions of lithium aluminum hydride, which were added over a 3-hr period. Finally *ca.* 10 ml of a mixture of di-*n*-butyl ether and trisilane was obtained in the storage bulb. The reaction flask was frozen in liquid nitrogen, removed from the vacuum manifold after admission of dry nitrogen, and allowed to thaw out of doors, without incident.

Final purification of the product was accomplished by slowly evaporating the trisilane–butyl ether mixture through a cold trap maintained at −50° in a diacetone–alcohol slush bath into a vacuum manifold to which a liquid nitrogen cooled storage bulb was attached. The butyl ether was retained in the cold trap. Finally 255 Torr of gas was obtained in a 1.2-l. volume at 30°. Vapor chromatographic analysis of the purified product on an 18-ft by 0.25-in. column consisting of 60:20:10 (by weight) diethyl phthalate–silicone oil DC710–diatomaceous earth (ABS Anakrom, Analabs, Inc.) with a 44-cm^3/min helium flow rate indicated that the purified product consisted of 75% trisilane, 10% disilane, and 14% silane, with retention times at ambient temperature of 41, 10, and 5 min, respectively. This composition indicates a yield of 12.2 mmol of trisilane, 60% based on octachlorotrisilane. While these figures are taken from one experiment, the preparation has been carried out four times with similar results.

TABLE I

MASS SPECTRUM OF TRISILANE (70 eV)[a]

m/e	Rel intens	*m/e*	Rel intens	*m/e*	Rel intens
94	0.5	86	4.6	58	56.6
93	1.1	85	12.7	57	22.9
92	4.8	84	10.7	56	13.9
91	5.4	63	0.6	42[b]	8.4[b]
90	5.9	62	6.0	30	3.0
89	4.3	61	18.1	29	1.8
88	4.9	60	100	28	8.8
87	3.6	59	20.5	27	7.2

[a] Every observable peak in the spectrum with *m/e* >20 is given. [b] The *m/e* 42 peak belongs to an impurity.

Positive identification of trisilane was based on its mass spectrum (Table I), taken on a sample purified by vapor chromatography using the conditions given. The spectrum, taken on a Varian M66 cycloidal mass spectrometer with an ionizing electron energy of 70 eV, compares favorably with a spectrum in the literature[7] taken on a Nier-type sector mass spectrometer employing 90-eV ionizing electrons. A parent ion mass of 92 was confirmed by lowering the energy of the ionizing electrons.

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Transference Numbers and Mobilities in Molten Mixtures of Beryllium Fluoride and Lithium Fluoride[1]

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Transference numbers in molten salt mixtures, unlike the so-called transference numbers of pure fused salts, are unambiguous properties, and are required to interpret electrical conductance measurements in terms of the relative mobilities of the ionic constituents. The correlation and interpretation of ionic transport properties in molten mixtures of beryllium fluoride with alkali fluorides are of interest because of their extreme variations with composition, which reflect the breakdown of the network-type structure of beryllium fluoride on addition of alkali fluorides. These systems may be considered as weakened analogs of silica–alkaline earth oxide systems, but analogies may be drawn also to the breakdown of the hydrogen-bonded water structure by ionic solutes. (A central atom—Si, Be, or O—is tetrahedrally coordinated by O, F, or H in SiO_2, BeF_2, or H_2O. Addition of solute ultimately breaks up the Si–O–Si, Be–F–Be, or H–O–H bridges.) Information on the transport properties is important also in the development of electroanalytical methods and electrolytic separation processes for the molten salt reactor program.[2]

Behl and Egan[3] and Behl[4] have reported transference numbers in the molten systems LiCl–$CdCl_2$, LiCl–$PbCl_2$, KCl–$PbCl_2$, KCl–$CaCl_2$, KCl–$MgCl_2$, and KCl–NaCl, evaluated from the emf of cells such as

$$\mathrm{Cl_2(g)\text{–}C|KCl(l)}\Big|\;\Big|\begin{matrix}\mathrm{KCl}\\ \mathrm{MCl}_n\end{matrix}\Big|\;\mathrm{C\text{–}Cl_2(g)} \tag{A}$$

and data on the activities of one of the components of the mixture. In KCl–NaCl the transference numbers of potassium and sodium ions, relative to chloride, are equal to their ion fractions over the entire range of concentration ($0.0 < x_{\mathrm{NaCl}} < 0.1$). In the other systems the transference numbers deviated from the ion fractions, but the departures were generally less than 20%. There was no evidence of inordinately low mobilities to suggest strong anionic complexes, although the mobilities of the alkali ions were higher than those of the divalent cations.

In this note we report measurements of the emf of concentration cells

$$\mathrm{Be}\left|\begin{matrix}\mathrm{LiF}\\ \mathrm{BeF_2}\end{matrix}\;\vdots\;\begin{matrix}\mathrm{LiF}\\ \mathrm{BeF_2}\end{matrix}\right|\mathrm{Be} \tag{B}$$

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

(2) K. A. Romberger and J. Braunstein, Reactor Chemistry Division Annual Progress Report, ORNL-4400, Oak Ridge National Laboratory, Oak Ridge, Tenn., Dec 31, 1968, p 11.

(3) W. K. Behl and J. Egan, *J. Phys. Chem.*, **71**, 1765 (1967).

(4) W. K. Behl, Abstracts, 135th Meeting of the Electrochemical Society, New York, N. Y., May 1969, No. 187.

with transference resulting from beryllium electrodes in molten BeF_2–LiF mixtures of differing composition. Cation transference numbers relative to fluoride are calculated from measurements of the above cell and from previously reported measurements of the cell[5]

$$\mathrm{Be}\left|\begin{matrix}\mathrm{LiF}\\ \mathrm{BeF_2}\end{matrix}\right| \mathrm{H_2,\ HF,\ Pt} \tag{C}$$

Our measurements of cell B covered the composition range in indicator half-cell II from 0.33 to 0.51 mol fraction of BeF_2 at 500° and from 0.27 to 0.70 mol fraction of BeF_2 at 610°. Reference half-cell I contained 0.34 mol fraction of BeF_2 at 500° and 0.70 mol fraction of BeF_2 at 610°. We show that these measurements lead to the new result, unusual for molten salt mixtures, that lithium ion is the principal current carrier relative to fluoride in this system.

Experimental Section

The cell, which is shown schematically in Figure 1, and the interior portion of the furnace[6] were of silica. The compatibility of silica containers with BeF_2–LiF mixtures at BeF_2 concentrations greater than 0.33 mol fraction has been demonstrated by spectrophotometric[7] and conductance[8] measurements. LiF was previously sintered under hydrogen, while BeF_2 was a clear glass which had been vacuum distilled in nickel. A stock LiF–BeF_2 mixture (0.34 mol fraction of BeF_2) was filtered through fritted nickel under hydrogen before use. Beryllium rod electrodes dipped into melt in the bulk compartment (II) and in the small reference half-cells. The liquid junction between the two compartments was made through coarse-grade (150 μ) fritted-silica disks. These disks have relatively little surface area and ensure a conduction path through liquid rather than through a silica membrane. Behl and Egan had reported drift of emf with fine-porosity silica frits in emf measurements with molten chlorides and adopted powdered alumina as the diffusion barrier.[3] No such drift was observed with our coarses silica frits, and our results have subsequently been confirmed in all-metal cells which we are using for more extended investigation of BeF_2–alkali fluoride systems.

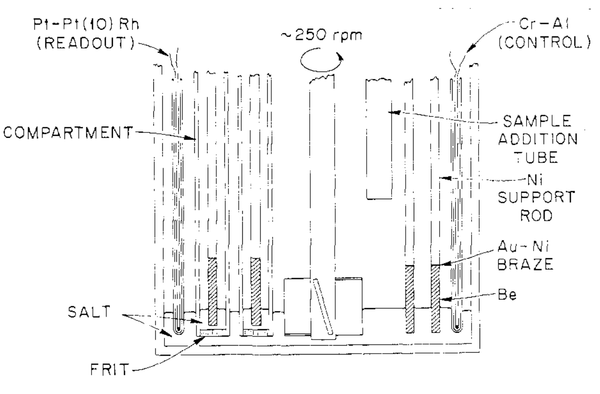

Figure 1.—Silica cell compartment and reference half-cells for the measurement of emf of the cell with transference (B).

The smaller reference compartment (I) was filled initially from melt contained in the larger indicator compartment (II). The initial emfs were 0 ± 1.7 mV. The composition of the bulk compartment was changed by stepwise addition of BeF_2 or LiF at each temperature, while measuring the emf, E_t. Additions of LiF and BeF_2 were made through a ball valve under helium pressure. The emf equilibrated within about 15 min after an addition of BeF_2 or LiF, the approximate time required for salt dissolution and reestablishment of temperature control. Mechanical stirring through a Teflon seal, under a dried helium atmosphere, speeded equilibration.

Results and Discussion

The emf, E_t, of cell B is shown as a function of composition in Table I. At 500°, the composition was first varied from 0.34 to 0.51 mol fraction of BeF_2 by addition of BeF_2. It was then lowered to 0.33 mol fraction of BeF_2 by additions of LiF. At 610°, the composition was varied from 0.70 to 0.27 and then back to 0.33 mol fraction of BeF_2. E_t values for both LiF and BeF_2 additions fell on the same line within ±2 mV. After completion of a set of measurements the melt was analyzed for reducing power (dissolved metallic beryllium or lower valence species). The result, barely within the limits of detection, was <0.1 mol %). Since metallic conduction would not be expected in this system, no error due to dissolved metallic beryllium is expected.

TABLE I

EMF'S OF CELLS WITH TRANSFERENCE IN THE LiF–BeF_2 SYSTEM

Addition sequence	Mol fraction of BeF_2, x_{BeF_2}	ΔE, mV	Addition sequence	Mol fraction of BeF_2, x_{BeF_2}	ΔE, mV
a. 500°, Reference Composition x_{BeF_2} = 0.3400					
8	0.3338	−12.3	5	0.4369	112.1
7	0.3478	5.4	2	0.4485	127.6
6	0.3677	30.5	3	0.4836	153.6
1	0.4040	71.9	4	0.5096	167.9
b. 610°, Reference Composition x_{BeF_2} = 0.7012					
1	0.6211	17.33	8	0.3268	263.61
2	0.5687	35.01	13	0.3087	288.59
3	0.4992	72.73	9	0.3046	293.49
4	0.4721	91.93	12	0.2893	313.33
5	0.4171	145.60	10	0.2831	321.41
6	0.3842	186.23	11	0.2721	>334.3
7	0.3626	214.69			

Hitch and Baes[5] measured the emf of cells C as a function of temperature for BeF_2 mol fractions of 0.30, 0.33, 0.40, 0.50, 0.60, 0.70, 0.80, and 0.90. The difference of emf of two cells such as C, with differing melt concentrations, is the emf, E_w, of a concentration cell without transference with beryllium electrodes, corresponding to the same electrode reactions as in cell B.

If the transference numbers of lithium ion and beryllium ion, relative to fluoride ion as the internal reference, are $t_{Li} = 1 - t_{Be}$, consideration of the electrode reactions, transference, and the Gibbs–Duhem equation gives[3,9] for the change of free energy or emf on

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

(6) K. A. Romberger, MSRP Semiannual Progress Report, ORNL-4254, Oak Ridge National Laboratory, Oak Ridge, Tenn., Feb 29, 1968, p 149.

(7) C. E. Bamberger, C. F. Baes, and J. P. Young, *J. Inorg. Nucl. Chem.*, **30**, 1979 (1968).

(8) G. D. Robbins and J. Braunstein in "Molten Salts: Characterization and Analysis," G. Mamantov, Ed., Marcel Dekker, Inc., New York, N. Y., 1969, p 443.

(9) C. Wagner in "Electrochemistry and Electrochemical Engineering," Vol. 4, P. Delahay, Ed., Interscience Publishers, New York, N. Y., 1966, p 11; A. Klemm in "Molten Salt Chemistry," M. Blander, Ed., John Wiley and Sons, New York, N. Y., 1964.

passage of 1 equiv of charge through cell B with an infinitesimal composition gradient

$$dG_t = t_{Li}d\mu_{LiF} - \frac{1}{2}(1 - t_{Be})d\mu_{BeF_2} \tag{1}$$

$$dE_t = t_{Li}\left[\frac{1 + x}{1 - x}\right]dE_w$$

Thus

$$t_{Li} = \left[\frac{1 - x}{1 + x}\right]\frac{dE_t/dx}{dE_w/dx} = \left[\frac{1 - x}{1 + x}\right]\frac{dE_t}{dE_w} \tag{2}$$

where x is the mol fraction of beryllium fluoride. The mean transference number over a range of composition IIa to IIb in the indicator half-cell is

$$t_{Li} = \frac{E_t^{IIb} - E_t^{IIa}}{\int_{IIa}^{IIb} \frac{1 + x}{1 - x}\,dE_w} \tag{3}$$

Equation 3 may be applied to small composition intervals, to determine the composition dependence of t_{Li}, or over a large interval if t_{Li} varies little with composition.

At 610°, graphical solution of eq 2 and 3, employing plots of E_t *vs.* E_w and of $(1 + x)/(1 - x)$ *vs.* E_w, both yield values for t_{Li} of 1.00 ± 0.05 for intervals in the composition range $0.30 < x < 0.50$. At higher concentrations of BeF_2, the magnitude of the changes in E_t, and especially in E_w, is considerably smaller than at the lower BeF_2 concentrations, as shown in Figure 2. The large relative uncertainties in E_w above $x = 0.5$ render use of the derivative relations of eq 2 imprecise, but $\bar{t}_{Li}$ is estimated to be 1.0 ± 0.2. The mean value of $\bar{t}_{Li}$ calculated with eq 3 from the 500° data is 1.00 ± 0.05 for the interval $0.33 < x < 0.50$. The number of measured values of E_w in this range is too small to warrant use of eq 2.

E_w as a function of composition can be calculated from experimental values of E_t, if t_{Li} is known, with the equation

$$E_w = \int_{IIa}^{IIb} \frac{1}{t_{Li}}\left[\frac{1 - x}{1 + x}\right]dE_t \tag{4}$$

The bands shown on Figure 2 are values of E_w calculated from eq 4 for values of t_{Li} between the extremes 0.95–1.05. A value greater than unity for t_{Li}, if real, would indicate drift of beryllium ions toward the anode. Within their listed uncertainties, the values of E_w given by Hitch and Baes fall within these bands. (The isothermal values of E_w are somewhat less precise than those of E_t since the former were interpolated from the temperature dependence of emf at a series of fixed compositions, whereas E_t was obtained by varying the composition isothermally.) We conclude that $t_{Li} = 1.00 \pm 0.05$ in the range $0.3 < x < 0.5$ and probably in the range $0.3 < x < 0.7$.

The mobility of lithium ion, μ_{Li}, is given by[3,9]

$$\mu_{Li} = \frac{t_{Li}\kappa}{Z_{Li}C_{Li}F} = \frac{t_{Li}\kappa[M_{LiF} + (x/(1 - x)M_{BeF_2}]}{Z_{Li}F\rho} \tag{5}$$

where κ is the specific conductance of the melt; the M's are the formula weights of the components; Z is the charge ($Z_{Li} = 1$), F is the Faraday constant, ρ is the density, and C is the concentration in moles per cubic centimeter. With $t_{Li} = 1$ and the reported conductance[8] and density[10] of $LiF-BeF_2$ mixtures, the calculated mobilities of lithium ion (relative to fluoride) in mixtures containing 0.34 and 0.51 mol fraction of BeF_2 are, respectively, 4.0×10^{-4} and 2.7×10^{-4} cm² sec⁻¹ V⁻¹ at 500° and are estimated to be 6×10^{-4} and 4×10^{-4} $cm^2\ sec^{-1}\ V^{-1}$ at 610°. These values are somewhat lower than those reported for lithium ion in $LiCl-PbCl_2$ mixtures, *ca.* 12×10^{-4} $cm^2\ sec^{-1}\ V^{-1}$ at 650°,[3] even allowing for the temperature difference. Additional conductance measurements, from this laboratory, will permit a more extensive evaluation of the composition dependence of the mobilities.[11]

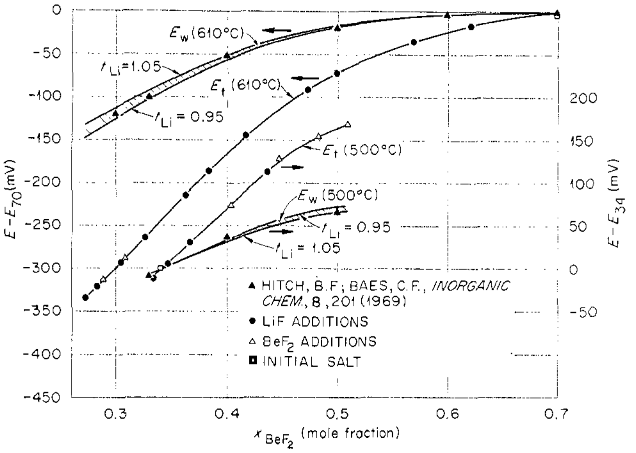

Figure 2.—Emf of concentration cells with (E_t) and without (E_w) transference in the system $LiF-BeF_2$ as a function of mol fraction of BeF_2. The shaded bands indicate values of E_w consistent with the measured E_t and with values of the transference number of lithium ion in the range $0.95 < t_{Li} < 1.05$.

The mobility of beryllium ion is zero within the experimental error. A negative value of t_{Be}, although not impossible (experimentally $t_{Be} = 0 \pm 0.05$), seems highly unlikely since it would imply that the beryllium ion constituent moves toward the anode faster than the fluoride ion constituent. (The transference number of the cadmium ion constituent in concentrated aqueous cadmium iodide solutions becomes slightly negative.[12]) The (virtually) zero mobility of beryllium ions relative to fluoride is consistent with the very strong electrostatic forces between fluoride ion and small doubly charged beryllium ions. The unicationic mechanism of electrical conductance deduced from these results is atypical of molten salt mixtures and analogous to conductance reported in silicate melts.[13]

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(12) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p 90.

(13) J. O'M. Bockris, J. A. Kitchener, and A. E. Davies, *Trans. Faraday Soc.*, **48**, 536 (1952).