

Electrical Conductivity of Molten Fluoride–Oxide Melts[†]

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Empirical equations describing the electrical conductivities of fluorides and fluoride–oxide mixtures have been obtained. These equations are based on two suppositions: (a) electrical conductivity of ionic molten substances is connected with the electronic structure of the cations; (b) the electrical conductivity of ionic melts can be expressed in terms of molar volume. In molten mixtures, the form of the electrical conductivity isotherm depends on the interaction between the components.

Introduction

Fluoride and oxide melts have some common features because they are ionic liquids, but at the same time they have differences, such as the fact that molten oxides are glasslike viscous liquids. Fluoride–oxide molten systems such as calcium fluoride-based fluxes and cryolite alumina melts are often used as media for different technological processes, and therefore, the properties of these systems are very important. At present, the modeling methods describing the properties of halide melts on one hand and oxide melts on the other hand are very different. There is a need to find some common points for modeling the physical properties of halide–oxide melts. The periodic table of the elements can be such a common point. Bockris et al.¹ found that the influences of different components of molten glasses on the electrical conductivity depend on the valences of the cations. The cations were divided into three groups. The first group contained alkali cations: Li⁺, Na⁺, and K⁺. The second, intermediate group consisted of divalent cations: Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Mn²⁺, and Fe²⁺. Al³⁺ and Ti⁴⁺ belonged to the third group. The most conductive cations are those in the first group, and the least conductive are cations in the third group. The close regularity connecting valence and electrical conductivity was found by Biltz and Klemm.² They divided all molten chlorides according to the place of the cation in the periodic table on good and bad conductors. This classification can be explained by the ionic potentials (IPs) of the cations (IP = charge/radius). The strong correlation between the IP of the cation and the physical properties of halides and oxides was found by Cartledge.³ He found the heat of formation to be strongly dependent on IP. The same regularities can be observed for other physical properties, such as electrical conductivity (Figure 1). Particular values of IP correspond to particular values of electrical conductivity. Cations with IPs less than 30 nm⁻¹ form the first group, ideally conducting salts, which are the systems with the lowest IP and highest conductivity. Salts with IPs greater than 30 nm⁻¹ and less than 50 nm⁻¹ form the second group, good conductors. Salts with IPs in range from 50 nm⁻¹ to 100 nm⁻¹ are bad conductors. Salts with IPs greater than 100 nm⁻¹ are insulators. Certainly, this classification is rather relative. In order to describe the properties of salts in

Li ⁺	Be ²⁺	B ³⁺	C ⁴⁺	LiF	BeF ₂	BF ₃	CF ₄
17	64	150	250	7.4	1·10 ⁻⁴		
Na ⁺	Mg ²⁺	Al ³⁺	Si ⁴⁺	NaF	MgF ₂	AlF ₃	SiF ₄
10	31	66	110	3.9	2.3		
K ⁺	Ca ²⁺	Sc ³⁺	Ti ⁴⁺	KF	CaF ₂	ScF ₃	TiF ₄
8	20	40	61	3.1	3.5		
Rb ⁺	Sr ²⁺	Y ³⁺	Zr ⁴⁺	RbF	SrF ₂	YF ₃	ZrF ₄
7	17	33	55	2.7	3.2		0.7
Cs ⁺	Ba ²⁺	La ³⁺	Hf ⁴⁺	CsF	BaF ₂	LaF ₃	HfF ₄
6	15	28	55	2.9	2.9		

Figure 1. Correlation between (A) cation ionic potential (IP/nm⁻¹) and (B) electrical conductivity ($\sigma/S \cdot \text{cm}^{-1}$) of fluoride melts near the melting point. Ionic radii in (A) were taken from ref 4; corresponding values of the electrical conductivities of the molten fluorides ($1000 \cdot \sigma/T_{\text{melting}}$) were taken from ref 5 (the datum for ZrF₄ was taken from ref 7).

accordance with their structures, it is better to base the description on an actual measured property that is determined by ionic potential, such as molar volume. Hence, the electrical conductivity can be also presented as a function of molar volume (V) and temperature (T).

Results and Discussion

Electrical Conductivity of Molten Alkali and Alkaline-Earth Fluorides. Alkali fluorides have the lowest IPs and form the first group, ideally conducting salts. Alkaline-earth fluorides also possess high electrical conductivities, with exception of BeF₂. Magnesium fluoride is also good conductor, but its conductivity is low in comparison with those of other alkaline-earth fluorides. The Mg²⁺ IP is closer to those of rare-earth cations such as La³⁺ and Y³⁺. BeF₂, AlF₃, ZrF₄, HfF₄, TaF₅ and NbF₅ form the group of bad conductors.

The molar volume dependence of the specific conductivities of molten alkali and alkaline-earth fluorides are presented in Figure 2. The specific conductivity values of the alkaline-earth fluorides were extrapolated from data at high temperatures obtained by Voronin et al.¹² Figure 2 shows the same trend for the specific conductivity dependence on molar volume for alkali and alkaline-earth fluorides. However, because of the great melting point differences, the specific conductivities of mixtures cannot be described by one equation.

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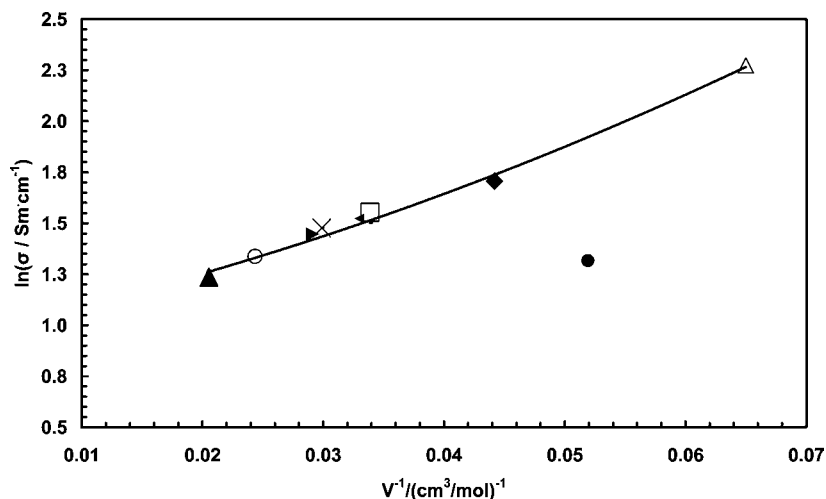


Figure 2. Electrical conductivities of molten alkali and alkaline-earth fluorides as functions of molar volume at 1400 K. Data for alkali fluorides were taken from ref 7: \blacktriangle , CsF; \circ , RbF; \times , KF; \blacklozenge , NaF, \triangle , LiF. Molar volumes of alkali fluorides were taken from ref 6. Values for alkaline-earth fluorides were extrapolated from ref 12: \bullet , MgF_2 ; right-pointing triangle, BaF_2 ; left-pointing triangle, SrF_2 ; \square , CaF_2 . Molar volumes of alkaline-earth fluorides were taken from ref 10.

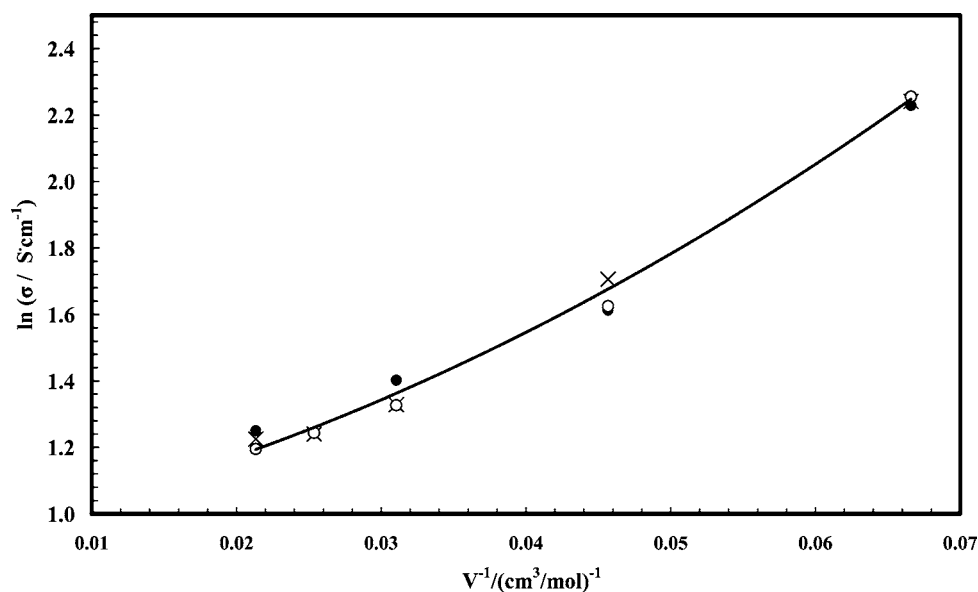


Figure 3. Electrical conductivity of molten alkali fluorides as a function of molar volume at 1300 K: \times , Smirnov et al. (ref 8); \circ , Katyshev and Teslyuk (ref 7); \bullet , Janz et al. (ref 9). Molar volumes were taken from ref 6.

The dependence of the specific conductivity of molten alkali fluorides on molar volume at constant temperature is presented in Figure 3. The data of different authors⁷⁻⁹ show the same trend, which can be described by a logarithmic equation in V at constant temperature (eq 1):

$$\ln \sigma = A + \frac{B}{V} + \frac{C}{V^2} \quad (1)$$

The coefficients A , B , and C are temperature-dependent. Thus, the specific conductivity of molten alkali fluorides can be represented by the following equation:

$$\sigma = 6.67 \exp\left(-\frac{1052 - \frac{13487}{V}}{T}\right) \exp\left(\frac{9.52}{V} + \frac{276}{V^2}\right) \quad (2)$$

in which V is the molar volume in cm^3/mol , σ is the specific conductivity in $\text{S}\cdot\text{cm}^{-1}$, and T is the temperature in K. Equation

Table 1. Calculated and Experimental Specific Conductivities (σ) of Molten Alkali Fluorides at 1300 K

salt	$\sigma/\text{S}\cdot\text{cm}^{-1}$			
	ref 7	ref 8	ref 5	eq 2
LiF	9.56	9.40	9.28	9.55
NaF	4.98	5.50	5.02	5.10
KF	3.75	3.77	4.06	3.83
RbF	3.52	3.46		3.63
CsF	3.53	3.40	3.67	3.53

2 is valid over the temperature range from the melting point to 1400 K. Conductivity values at 1300 K calculated using eq 2 are shown along with some experimental values in Table 1.

Values of electrical conductivities and molar volumes of alkaline-earth fluorides at 1800 K are shown in Figure 4. There is greater dispersion in the experimental data than for the alkali fluorides. However, for calcium fluoride there is good agreement between the data obtained by Voronin et al.¹² and Kim and Sadoway.¹¹ It is possible to apply eq 2 to

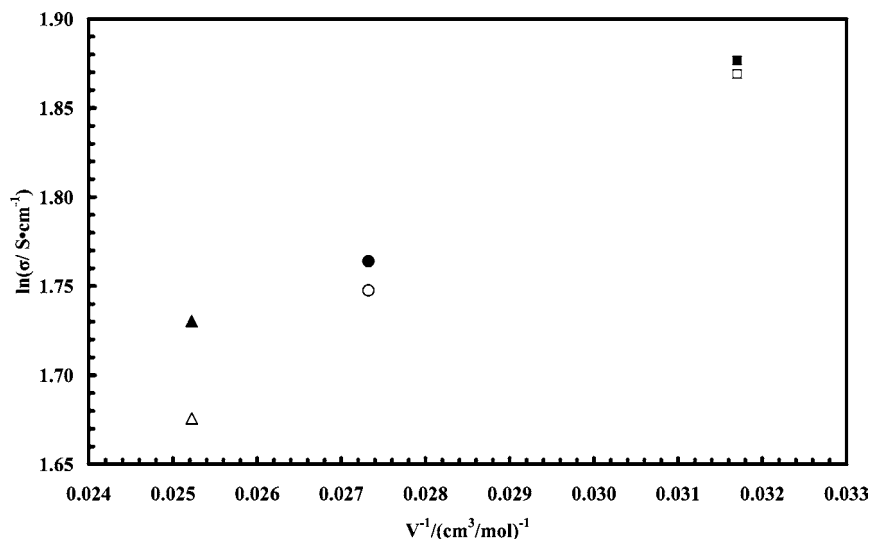


Figure 4. Electrical conductivity of molten alkaline-earth fluorides as a function of molar volume at 1800 K. Solid symbols are data from ref 11, and open symbols are from ref 12: ■/□, CaF₂; ●/○, SrF₂; ▲/△, BaF₂. Molar volumes were taken from ref 10.

Table 2. Calculated and Experimental Conductivities (σ) of Molten CaF₂

T/K	$\sigma/S \cdot \text{cm}^{-1}$		
	ref 11	ref 12	eq 3
1800	6.57	6.48	6.52
1780	6.50	6.42	6.45
1760	6.43	6.35	6.39
1740	6.36	6.29	6.32
1720	6.29	6.21	6.25
1700	6.57	6.48	6.52

CaF₂. In this case, it should contain an additional coefficient, D , as shown in eq 3:

$$\sigma = 6.67 \exp\left(-\frac{1052 - \frac{13487}{V}}{T}\right) \exp\left(\frac{9.52}{V} + \frac{276}{V^2}\right) D \quad (3)$$

The temperature dependence of D over the temperature range 1700 K to 1870 K is given by $D = 0.92 + 1.82 \cdot 10^{-4} \cdot (T/K)$. In Table 2, experimental conductivities of CaF₂ from 1700 K to 1800 K are compared with values calculated using eq 3.

Electrical Conductivity of Molten Alkali Fluoride Mixtures. Mixtures of alkali fluorides can be considered as ideal mixtures because the change in molar volume at constant temperature is close to additive (the deviations do not exceed 3 %).⁴ This is due to the similar IPs of alkali cations. The thermodynamic data for alkali fluoride mixtures³² also show that the interaction in these systems is much lower than in mixtures of alkali fluorides with alkaline-earth fluorides.¹⁸ This means that these mixtures are close to ideal ones. Thus, their electrical conductivities must change in some ideal way. Equation 2 reflects the electrical conductivity change with cation–anion distance and can be the equation of ideal conductivity. The validity of eq 2 was verified for all alkali fluoride mixtures. The maximal difference between calculated and experimental data does not exceed 10 %. Comparisons of experimental conductivities⁹ and values calculated using eq 2 for the KF + NaF, LiF + NaF, and LiF + KF systems are given in Tables 3 and 4.

Electrical Conductivity of Nonideal Fluoride Mixtures. Molten mixtures of alkali fluorides with other fluoride salts demonstrate different behavior. Very few systematic data on

Table 3. Conductivities (σ) Calculated Using Eq 2 and Experimental Values from Ref 9 for the KF + NaF and LiF + NaF Systems at 1300 K

X_{NaF}	KF + NaF			LiF + NaF			
	$\frac{\sigma_{\text{calcd}}}{S \cdot \text{cm}^{-1}}$	$\frac{\sigma_{\text{exptl}}}{S \cdot \text{cm}^{-1}}$	% dev ^a	X_{NaF}	$\frac{\sigma_{\text{calcd}}}{S \cdot \text{cm}^{-1}}$	$\frac{\sigma_{\text{exptl}}}{S \cdot \text{cm}^{-1}}$	% dev ^a
0	3.82	4.27	10.50	0	9.55	9.97	4.20
0.12	3.89	4.26	8.50	0.15	8.32	8.64	3.70
0.25	3.92	4.28	8.30	0.30	7.41	7.52	1.50
0.50	4.15			0.38	7.05	7.04	0.10
0.60	4.27	4.49	3.70	0.50	6.52	6.75	3.40
0.63	4.29			0.60	6.16	6.00	2.70
0.75	4.47			0.80	5.57	5.83	4.50
0.80	4.62	4.62	0.20	1	5.09	5.28	3.60
0.88	4.77						
1	5.07	5.28	3.80				

^a Percent relative deviation, calculated as $100 \cdot (\sigma_{\text{calcd}} - \sigma_{\text{exptl}}) / \sigma_{\text{exptl}}$.

Table 4. Conductivities (σ) Calculated Using Eq 2 and Experimental Values from Ref 9 for the LiF (1) + KF (2) System at 1300 K

X_2	$\frac{\sigma_{\text{exptl}}}{S \cdot \text{cm}^{-1}}$	$\frac{\sigma_{\text{calcd}}}{S \cdot \text{cm}^{-1}}$	% dev ^a
0	9.97	9.55	5.42
0.12		6.82	
0.15	6.75	6.48	4.09
0.25		5.58	
0.3	5.06	5.35	5.84
0.37		4.95	
0.5	4.24	4.49	6.09
0.63	4.10	4.22	3.03
0.75		4.07	
0.8	4.06	3.95	2.78
0.88		3.85	
1	3.43	3.74	9.13

^a Percent relative deviation, calculated as $100 \cdot (\sigma_{\text{calcd}} - \sigma_{\text{exptl}}) / \sigma_{\text{exptl}}$.

both density and electrical conductivity are available for other mixtures, but one example, alkali fluoride mixtures with thorium and uranium fluorides, shows how the chemical interaction between components influences the electrical conductivity. The changes in molar volume for the molten systems LiF + UF₄ and NaF + UF₄ are shown in Figure 5. The isotherms are close to additive ones. The electrical conductivities for these systems are presented in Figures 6 and 7. The experimental data are close to the ones calculated according to eq 4:

$$\sigma = 6.67 \exp\left(-\frac{1052 - \frac{13487}{V}}{T}\right) \exp\left(\frac{9.52}{V} + \frac{276}{V^2}\right) \exp(EX_2) \quad (4)$$

in which X_2 is the mole fraction of UF_4 , $E = -2.05 + 0.0012 \cdot (T/\text{K})$ (the temperature interval varies from 1300 K to 1400 K), and the temperature dependence of the coefficient D

over the temperature range from 1300 K to 1400 K is given by $D = 0.00147 \cdot (T/\text{K}) - 1.54059$.

The uranium tetrafluoride mixtures with potassium fluoride, rubidium fluoride, and cesium fluoride show strong interactions between the components. This is reflected in the molar volumes (Figure 8). The electrical conductivities of these mixtures

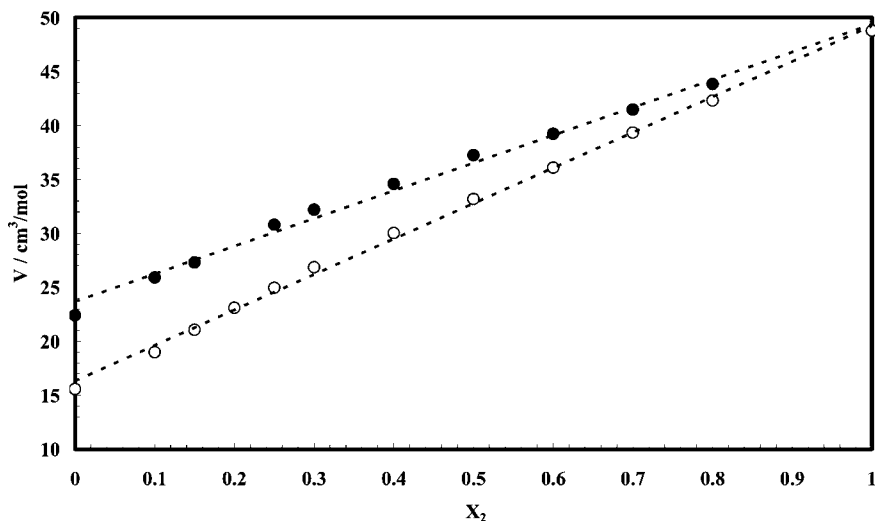


Figure 5. Molar volumes of the LiF (1) + UF_4 (2) and NaF (1) + UF_4 (2) molten systems at 1400 K (ref 13): \circ , LiF + UF_4 ; \bullet , NaF + UF_4 .

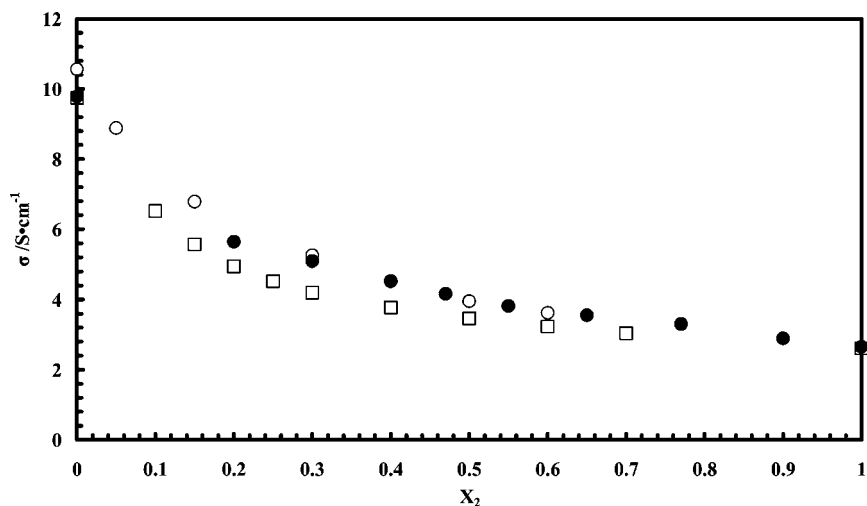


Figure 6. Specific conductivity of the LiF (1) + UF_4 (2) molten system at 1400 K: \circ , Janz et al. (ref 9); \bullet , Koverda (ref 16); \square , calculated values.

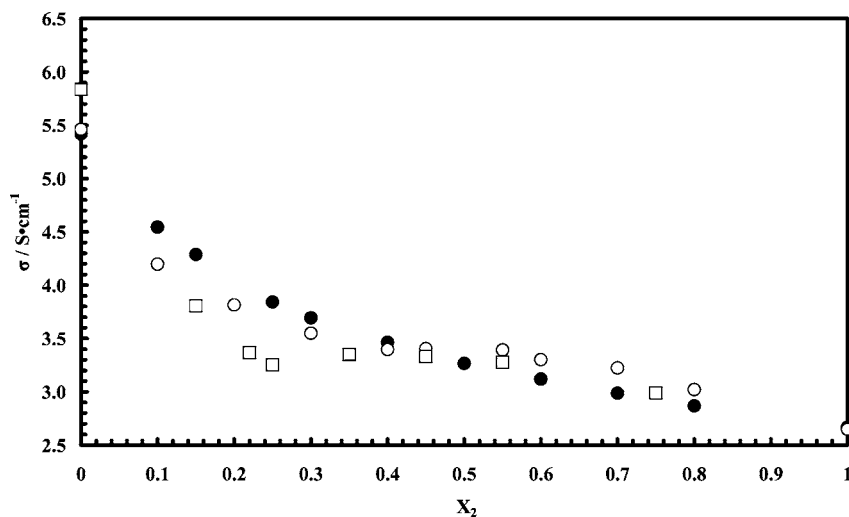


Figure 7. Specific conductivity of the NaF (1) + UF_4 (2) molten system at 1400 K: \square , Janz et al. (ref 9); \circ , Koverda (ref 16); \bullet , calculated values.

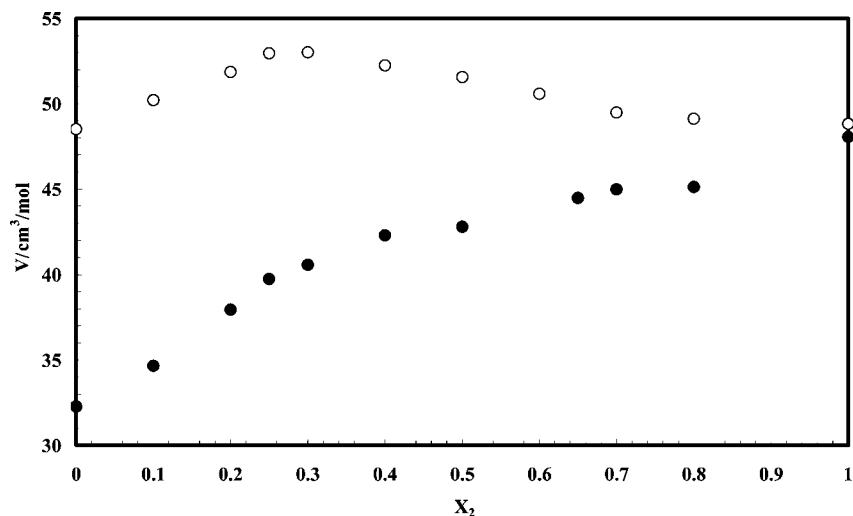


Figure 8. Molar volume in the KF (1) + UF₄ (2) and CsF (1) + UF₄ (2) systems at 1400 K (ref 14): ○, CsF + UF₄; ●, CsF + UF₄.

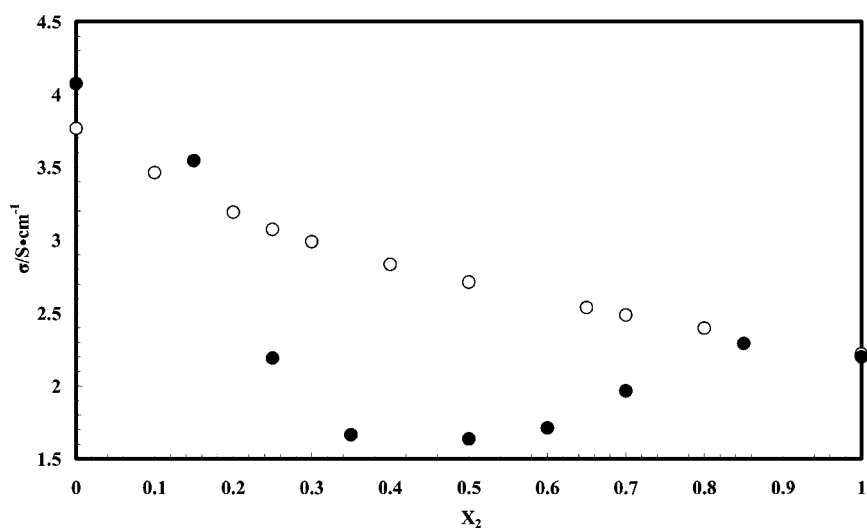


Figure 9. Specific conductivity in the KF (1) + UF₄ (2) system at 1400 K: ○, calculated values; ●, experimental values from ref 15.

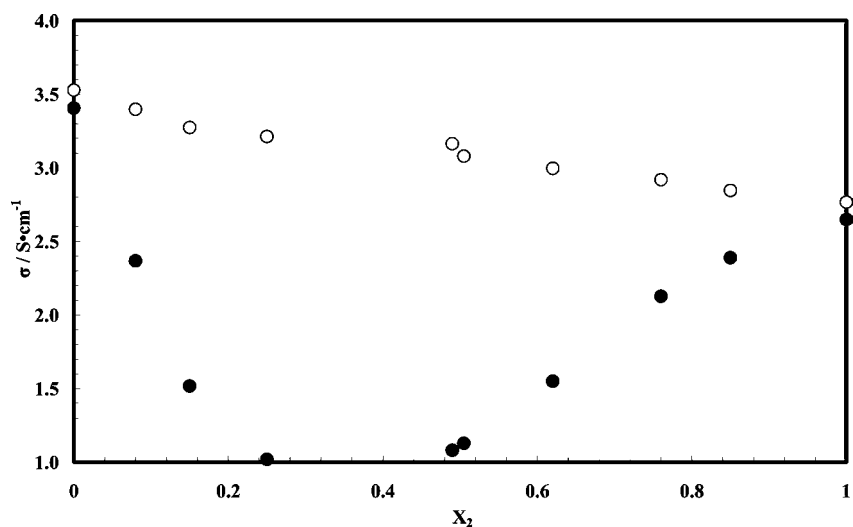


Figure 10. Specific conductivity in the CsF (1) + UF₄ (2) system at 1400 K: ○, calculated values; ●, experimental values from ref 15.

demonstrate large deviations from the calculated values (Figures 9 and 10). The deviations of the experimental specific conductivities from the calculated values are shown in Figure 11. The differences between the molar volumes and the additive values are shown in Figure 12. Thus, it is possible to make the conclusion that the mixture of lithium and sodium fluorides with

uranium tetrafluoride can be considered as close to ideal for two reasons: (1) the molar volume is close to additive, and (2) the deviation of the specific conductivity from the ideal value is small. The mixtures of potassium, rubidium, and cesium fluoride are nonideal as a result of the strong interactions, which result in large positive deviations of the molar volume from

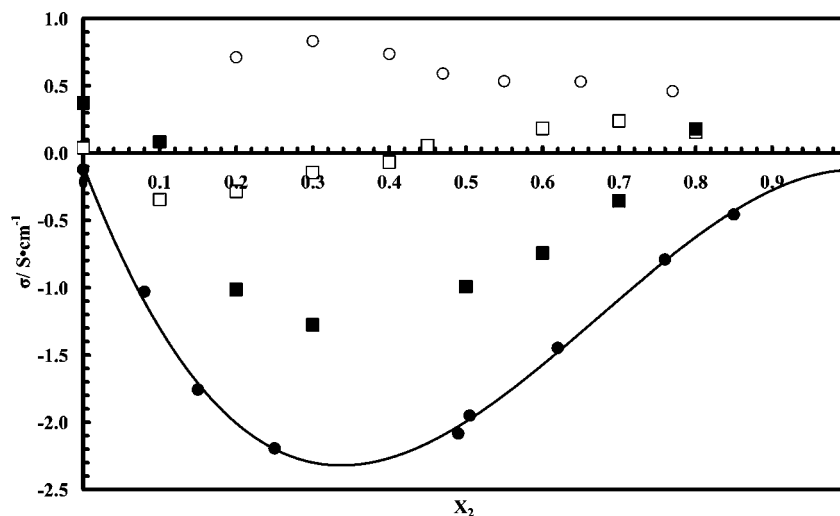


Figure 11. Deviations of the experimental electrical conductivities from the calculated values: \circ , LiF (1) + UF₄ (2); \bullet , CsF (1) + UF₄ (2); \square , NaF (1) + UF₄ (2); \blacksquare , KF (1) + UF₄ (2).

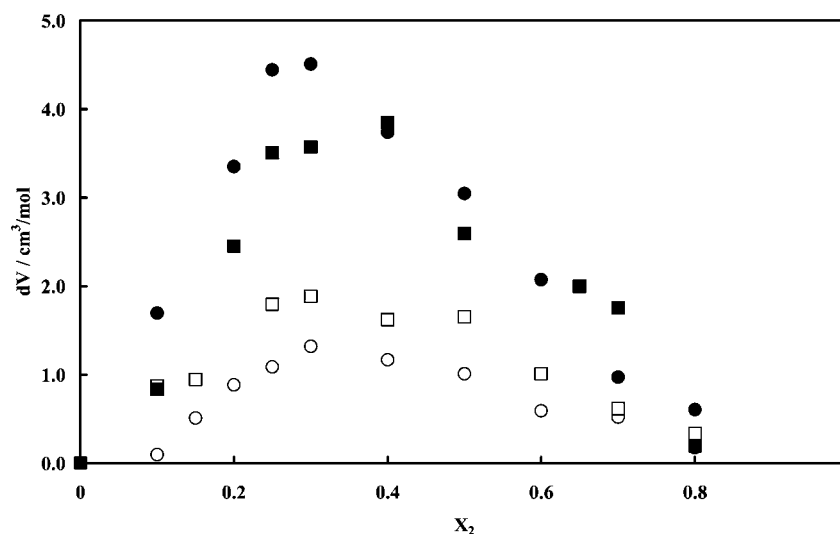


Figure 12. Excess molar volumes: \circ , LiF (1) + UF₄ (2); \bullet , CsF (1) + UF₄ (2); \square , NaF (1) + UF₄ (2); \blacksquare , KF (1) + UF₄ (2).

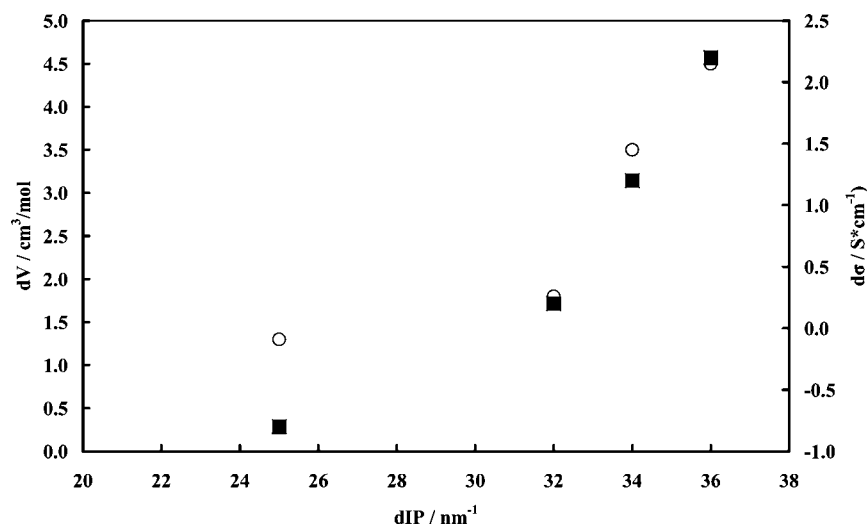


Figure 13. Excess molar volumes (\circ , left axis) and deviations of experimental specific conductivities from calculated values (\blacksquare , right axis) as functions of the difference in the cation ionic potentials of U⁴⁺ and the alkali cations.

the additive values and large negative deviations of the specific conductivity from the ideal values. These deviations can be explained from the point of view proposed by Hong and Kleppa for enthalpy of mixing.¹⁷ They found the enthalpy of mixing to

be dependent on the IP difference. The deviations of the electrical conductivities from calculated ones are also dependent on the IP difference, as are the deviations of the molar volumes from the additive values (Figure 13). The values were taken at

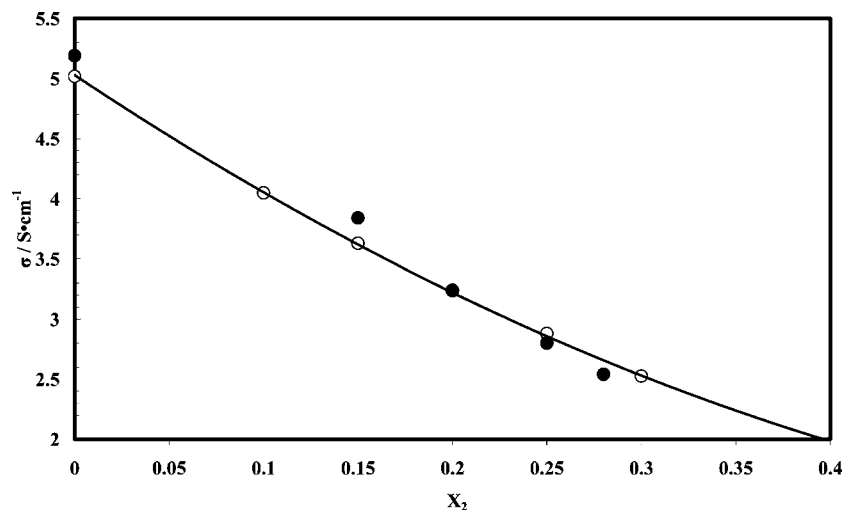


Figure 14. Electrical conductivity (σ) of the NaF (1) + AlF₃ (2) system at 1273 K: ○, calculated using eq 5; ●, experimental values from ref 19.

Table 5. Conductivities (σ) Calculated Using Equation 5 and Experimental Values from Reference 17 for the LiF (1) + BeF₂ (2) System at 1200 K

X_2	$\frac{\sigma_{\text{calcd}}}{\text{S} \cdot \text{cm}^{-1}}$	$\frac{\sigma_{\text{exptl}}}{\text{S} \cdot \text{cm}^{-1}}$	% dev ^a
0	8.91	8.93	0.30
0.10	6.94	6.42	7.40
0.20	5.42	4.97	8.20
0.30	4.03	4.03	0.01
0.40	3.27	3.37	3.10

^a Percent relative deviation, calculated as $100 \cdot (\sigma_{\text{calcd}} - \sigma_{\text{exptl}}) / \sigma_{\text{exptl}}$.

compositions in which the UF₄ mole fraction was 0.25. Thus, the electrical conductivity can be presented as a function of temperature, molar volume, and some thermodynamic property (e.g., enthalpy of mixing), but there are no such data for alkali fluoride mixtures with uranium fluorides.

Electrical Conductivity of Cryolite Melts. Molten fluorides have found broad use as electrolytes for aluminum production. The mixture contains sodium fluoride and aluminum fluoride in different proportions and also alkaline-earth fluorides as additives. The electrical conductivity is a very important parameter because it determines the energetic efficiency of the process. Sodium cryolite can be considered as one composition of the molten mixture NaF (1) + AlF₃ (2). The conductivity of this mixture is an example of an ideal conducting salt + bad conducting salt system. Its specific conductivity up to $X_2 = 0.5$ can be described by eq 4 with its own coefficient D in exponential form:

$$\sigma = 6.67 \exp\left(-\frac{1052 - \frac{13487}{V}}{T}\right) \exp\left(\frac{9.52}{V} + \frac{276}{V^2}\right) \times \exp(-1.65X_2) \quad (5)$$

where X_2 is the mole fraction of AlF₃. A comparison of experimental and calculated data is given in Figure 14. Density data were taken from the paper of Fernandez and Ostvold,¹⁸ and conductivity data were taken from the paper of Frank and Foster.¹⁹ It is possible to evaluate more sophisticated cryolite melts using eq 5. Comparisons of calculated and experimental data for some quaternary mixtures are given in Tables 6 and 7. The molar volumes of these mixtures were calculated as additive sums based on the quaternary system (NaF + AlF₃) + CaF₂ + BaF₂.

Electrical Conductivity of Glasslike Fluorides. Some fluoride melts are glasslike, such as BeF₂. Their properties are very similar to glasses: high viscosity, high temperature coefficient of electrical

Table 6. Calculated and Experimental Specific Conductivities (σ) in the NaF (1) + CaF₂ (2) + BaF₂ (3) + AlF₃ (4) System at 1273 K

sample	100 w				V_{calcd} cm ³ ·mol ⁻¹	$\sigma/\text{S} \cdot \text{cm}^{-1}$	
	1	2	3	4		exptl ^a	calcd ^b
1	68.8	16.4	11.0	3.8	22.80	4.45	4.56
2	63.6	17.1	11.4	7.9	23.75	4.21	4.19
3	51.8	18.6	12.4	17.2	24.37	3.68	3.66
4	37.8	20.3	13.6	28.3	27.03	3.06	2.88
5	20.9	22.4	15	41.7	31.60	2.3	1.74

^a Data from ref 20. ^b Values calculated using eq 5.

Table 7. Calculated and Experimental Specific Conductivities (σ) in the Na₃AlF₆ (1) + CaF₂ (2) + BaF₂ (3) + NaF (4) System at 1273 K

sample	100 w				V_{calcd} cm ³ ·mol ⁻¹	$\sigma/\text{S} \cdot \text{cm}^{-1}$	
	1	2	3	4		exptl ^a	calcd ^b
1	4.3	18.6	12.4	64.7	24.02	4.47	4.42
2	10.4	22.4	15.0	52.2	24.55	4.21	4.19
3	35.8	38.5	25.7	0	27.81	3.11	3.24

^a Data from ref 20. ^b Values calculated using eq 5.

conductivity, and so on. The electrical conductivity change with melt composition in the LiF (1) + BeF₂ (2) system is shown in Figure 15. The isotherm can be divided into two parts. The mixture has high conductivity in the concentration range from $X_2 = 0$ to 0.5. The properties of such mixtures are determined mainly by the lithium fluoride properties. This is seen from the dependences of the temperature coefficients of density and conductivity^{21,22} ($\rho = \rho_0 - bT$ and $\ln \sigma = A - B/T$), as shown in Figure 16. The temperature coefficients of physical properties reflect the structure peculiarities of any system. The temperature coefficients in the LiF-rich region do not change significantly and are close to the coefficients of pure lithium fluoride. This means that in this concentration range, the electrical conductivity of this mixture is determined by the alkali cations, and it can be considered as a mixture of good-conducting salts.

The absolute values of electrical conductivity also reflect the difference between ionic and glasslike melts (beryllium fluoride-rich region) in the LiF + BeF₂ system. Thus, the electrical conductivity of this system over the concentration range $X_2 = 0$ to 0.5 can be described by eq 6:

$$\sigma = 6.67 \exp\left(-\frac{1052 - \frac{13487}{V}}{T}\right) \exp\left(\frac{9.52}{V} + \frac{276}{V^2}\right) \times \exp(-1.0X_2) \quad (6)$$

where X_2 is the BeF₂ mole fraction and, as before, V is the molar volume in cm³/mol, σ is the specific conductivity in S·cm⁻¹,

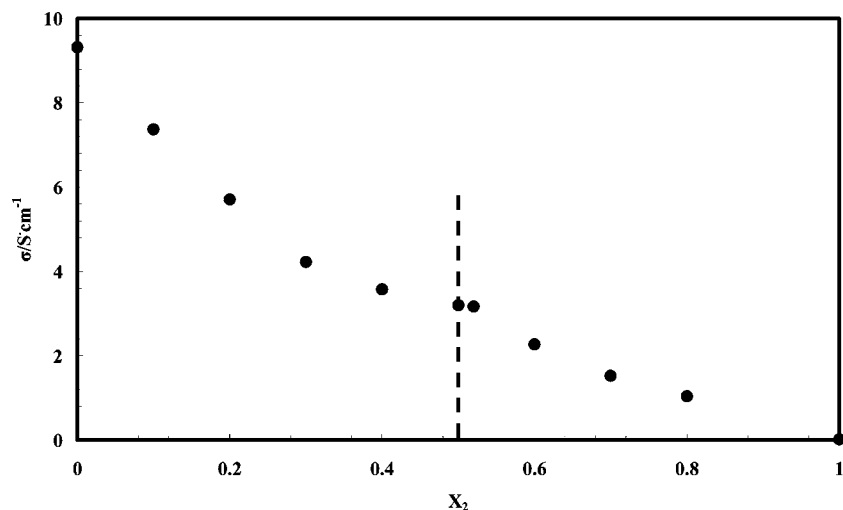


Figure 15. Electrical conductivity in the LiF (1) + BeF₂ (2) system at 1200 K (ref 21).

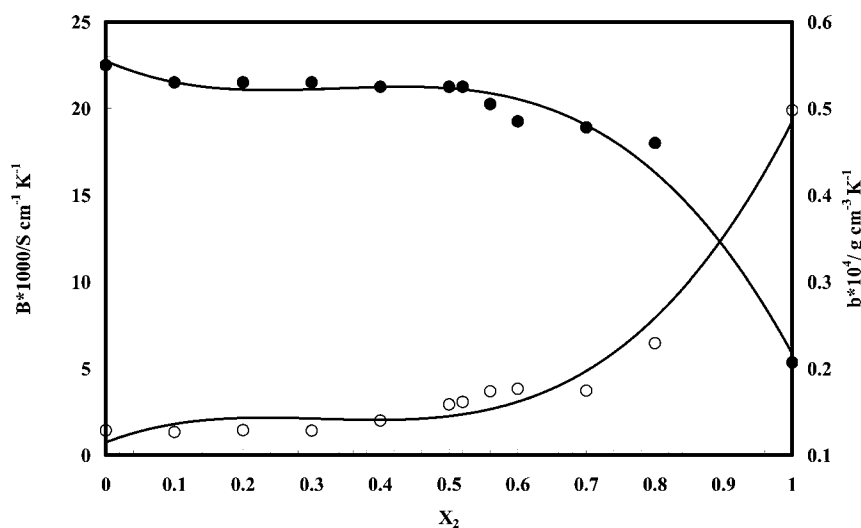


Figure 16. Electrical conductivity (○, ref 21) and density (●, ref 22) temperature coefficients in the LiF (1) + BeF₂ (2) system.

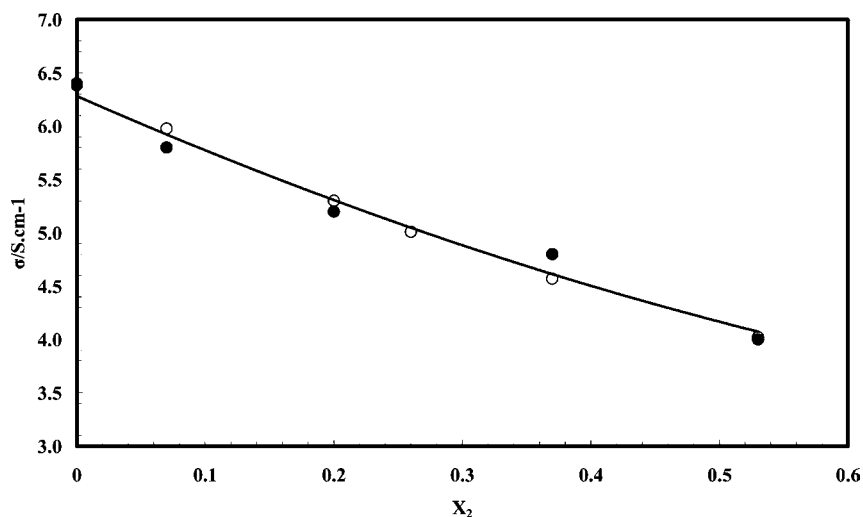


Figure 17. Electrical conductivity (σ) in the CaF₂ (1) + CaO (2) system at 1873 K: ○, calculated using eq 2; ●, experimental values from ref 23. Densities were taken from ref 24.

and T is the temperature in K. A comparison of the experimental and calculated data is given in Table 5.

Electrical Conductivity of the CaF₂ + CaO Molten System. The LiF + BeF₂ system can be used as a model system for describing fluoride–oxide melt properties. The change in the

temperature coefficient with oxide composition is similar to the change in the temperature coefficient with beryllium fluoride content in the LiF + BeF₂ system. Thus, a version of eq 6 with an additional coefficient (see eq 7) can be applied to describe the electrical conductivity of fluoride–oxide melts, such as the CaF₂

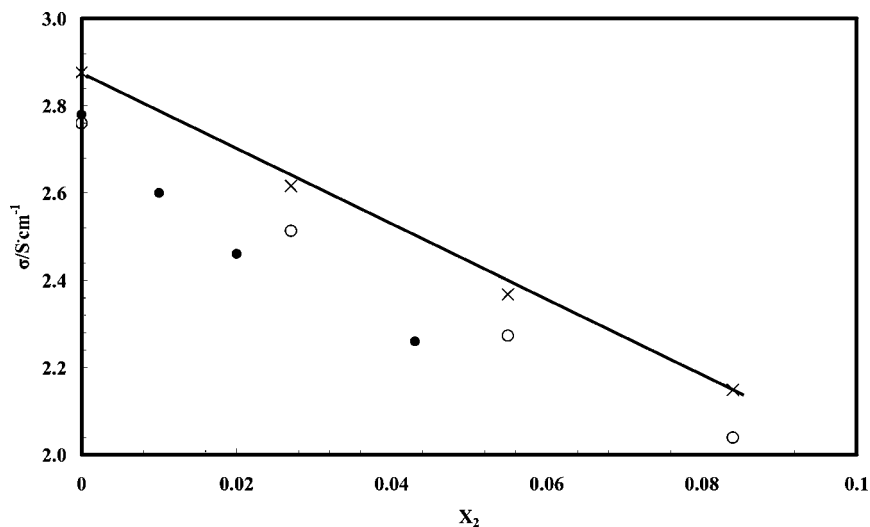


Figure 18. Electrical conductivity (σ) in the Na_3AlF_6 (1) + Al_2O_3 (2) system at 1273 K: \times , calculated using eq 8; O , experimental values from ref 26; \bullet , experimental values from ref 28.

+ CaO system. In this case, calcium oxide can be considered as a glasslike salt. The conductivity of this system is given by

$$\sigma = 6.67 \exp\left(-\frac{1052 - \frac{13487}{V}}{T}\right) \exp\left(\frac{9.52}{V} + \frac{276}{V^2}\right) \times \exp(-1.0X_1 + 0.2X_2) \quad (7)$$

where X_1 is the CaO mole fraction and X_2 the CaF_2 mole fraction. The equation is valid for $X_1 = 0$ to 0.5. A comparison of experimental and calculated electrical conductivity values is presented in Figure 17. Data on density and electrical conductivity were taken from refs 23 and 24.

Electrical Conductivity of Cryolite–Alumina Melts. Cryolite–alumina melts are the basic electrolytes for industrial production of aluminum. They contain fluoride salts (NaF , AlF_3) and aluminum oxide (Al_2O_3) and thus are an example of fluoride–oxide melts. The effect of alumina concentration on the electrolyte electrical conductivity is very important. There have been many investigations of the electrical conductivity of alumina-containing cryolites.^{25–31} It is a matter of fact that the conductivity values decrease with alumina content. The analysis of existing information has allowed the derivation of the following equation:

$$\sigma = 6.67 \exp\left(-\frac{1052 - \frac{13487}{V}}{T}\right) \exp\left(\frac{9.52}{V} + \frac{276}{V^2}\right) \times \exp(-1.65X_1) \exp(-2.5X_2) \quad (8)$$

where X_1 is the mole fraction of Na_3AlF_6 and X_2 the mole fraction of Al_2O_3 . A comparison of experimental and calculated data is given in Figure 18. There is good agreement. The difference between the calculated and experimental values does not exceed 5 %.

Conclusions

This work leads to the following conclusions: (1) The specific conductivity of molten fluoride salts can be connected with the ionic potentials of the cations. (2) The specific conductivities of molten alkali fluorides depend on their molar volumes and can be described by a molar volume–temperature equation. (3) The electrical conductivities of other conducting fluoride salts can be described by similar equations containing additional

coefficients. (4) The specific conductivities of molten mixtures of good-conducting salts with badly conducting salts can be also described by a similar equation with additional coefficients over the concentration range in which the mole fraction of the badly conducting salt varies from 0 to 0.5. (5) The specific conductivities of molten mixtures of good-conducting salts with oxides can be described in the same way as the mixtures of good-conducting salts with badly conducting ones over the concentration range with $X_{\text{oxide}} = 0$ to 0.5.

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