

Conductivity, Thermal Measurements, and Phase Diagram of the $\text{Na}_2\text{S}_2\text{O}_7$ – NaHSO_4 SystemG. Hatem,[†] M. Gaune-Escard,[†] S. B. Rasmussen,[‡] and R. Fehrmann^{*,‡}*Institut Universitaire des Systèmes Thermiques Industriels (IUSTI), Technopole de Chateau-Gombert, 13453 Marseille, France, and Department of Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark**Received: October 6, 1998; In Final Form: November 25, 1998*

The conductivity of the $\text{Na}_2\text{S}_2\text{O}_7$ – NaHSO_4 binary system has been measured for 15 different compositions in the full composition range, and in the temperature range 400–700 K. Phase transition temperatures were obtained, and the phase diagram was constructed. It is of the simple eutectic type, where the eutectic is found to have the composition $X_{\text{NaHSO}_4} = 0.97$, as calculated from the measured thermodynamic properties, and to melt at 179 °C. The partial enthalpy and entropy of mixing have been obtained, and the negative entropy points to a structural order of the melt, presumably due to hydrogen bonding, as found earlier for the $\text{K}_2\text{S}_2\text{O}_7$ – KHSO_4 system. For each composition measured of the $\text{Na}_2\text{S}_2\text{O}_7$ – NaHSO_4 system in the molten state, the conductivity has been expressed by equations of the form $\kappa = A(X) + B(X)(T - T_m) + C(X)(T - T_m)^2$, where T_m is the intermediate temperature of the measured temperature range.

Introduction

The molten salt–gas system $\text{M}_2\text{S}_2\text{O}_7$ – V_2O_5 – $\text{SO}_2/\text{O}_2/\text{O}_3/\text{N}_2$ (M = alkali) at 400–500 °C is considered a realistic model system for the industrial catalyst used for SO_2 oxidation.¹ Catalysts containing mixtures of K and Na as promoting alkali ions are very common. They are also used for purification of wet industrial off-gases by oxidation of SO_2 to SO_3 , followed by condensation of H_2SO_4 as a commercial product.² In the wet flue gases, $\text{M}_2\text{S}_2\text{O}_7$ is partly transformed to MHSO_4 , making the catalyst solvent system a $\text{M}_2\text{S}_2\text{O}_7$ – MHSO_4 (M = Na, K) mixture. Recently³ we have investigated the $\text{K}_2\text{S}_2\text{O}_7$ – KHSO_4 system by conductivity, NMR spectroscopy, and thermal methods and constructed the phase diagram of this binary system. The present paper concerns our measurements on the $\text{Na}_2\text{S}_2\text{O}_7$ – NaHSO_4 system and the results are compared with the phase diagram published⁴ more than 75 years ago and the previously⁵ measured conductivity of the pure molten component NaHSO_4 .

Other fundamental thermodynamic data as densities, conductivities, heats of mixing, and heat capacities of the $\text{Na}_2\text{S}_2\text{O}_7$ – NaHSO_4 system, as well as the heat of fusion of the pure components, are virtually missing in the literature. These properties are the object of our previous⁶ and present paper as well as ongoing investigations.

Experimental Section

Chemicals. The hygroscopic $\text{Na}_2\text{S}_2\text{O}_7$ was prepared by thermal decomposition of $\text{Na}_2\text{S}_2\text{O}_8$ (Merck, p.a.) in N_2 as earlier described,⁷ kept on sealed ampules, and handled only in the drybox, with a measured water content less than about 5 ppm. NaHSO_4 (Merck, suprapur (99%)) was dried at 110 °C and also kept in sealed ampules until used.

Conductivity Measurements. The borosilicate cell with gold electrodes and other experimental details have been described previously.³ The temperature of the furnace was regulated to

within ± 0.1 °C. It was decreased from the highest measuring temperature in steps of 2.5 or 10 °C to the temperature of crystallization, often obtained at large subcooling of the melt. Then the temperature was raised stepwise until the measured conductivity coincided with the value obtained on cooling, i.e., at the liquidus temperature of the mixture. Finally, the temperature was increased to the initially measured temperature, where the reproducibility of the measured conductivity was checked. The temperature was measured by a thermocouple, precalibrated against a Pt100 resistance thermometer, placed at the capillary tube of the cell. A Radiometer CDM-230 conductivity meter was used for the conductivity measurements, and the cell constants in the range 100–200 cm^{-1} could be measured, as earlier described,⁸ by use of a 0.1 M KCl standard solution.

Thermal Measurements. The thermal measurements were carried out by use of a Setaram DSC 121 differential scanning calorimeter, where the temperature was changed in the range 2–5 °C/min. The samples were contained in Pyrex cells, sealed under vacuum. The partial enthalpy of mixing of $\text{Na}_2\text{S}_2\text{O}_7$ in the $\text{Na}_2\text{S}_2\text{O}_7$ – NaHSO_4 melts has been measured at the following experimental conditions: $X_{\text{NaHSO}_4} = 0.540$ ($T = 663$ K) and $X_{\text{NaHSO}_4} = 0.954$ ($T = 544$ K), by using a Calvet microcalorimeter. The melts were contained in a Pyrex crucible and the sodium pyrosulfate in a fragile Pyrex ampule. The measurements were carried out by breaking the ampules in the crucible.

Results and Discussion

The conductivity of 15 different compositions of the solid and liquid $\text{Na}_2\text{S}_2\text{O}_7$ – NaHSO_4 binary system was measured in the composition range $X_{\text{NaHSO}_4} = 0$ –1. These conductivities are plotted as $-\ln(\kappa)$ vs $1/T$ in Figures 1 and 2. As observed previously^{3,9–11} for the systems $\text{K}_2\text{S}_2\text{O}_7$ – KHSO_4 , $\text{K}_2\text{S}_2\text{O}_7$ – V_2O_5 , $\text{Cs}_2\text{S}_2\text{O}_7$ – V_2O_5 , and $\text{M}_2\text{S}_2\text{O}_7$ – V_2O_5 (M = 20% Na + 80% K), respectively, a marked change of the conductivity takes place at the phase transition temperatures of the measured mixtures, i.e., the liquidus and solidus temperatures. However, for mixtures rich in NaHSO_4 only one transition temperature could be identified; i.e., the temperature of fusion of the eutectic

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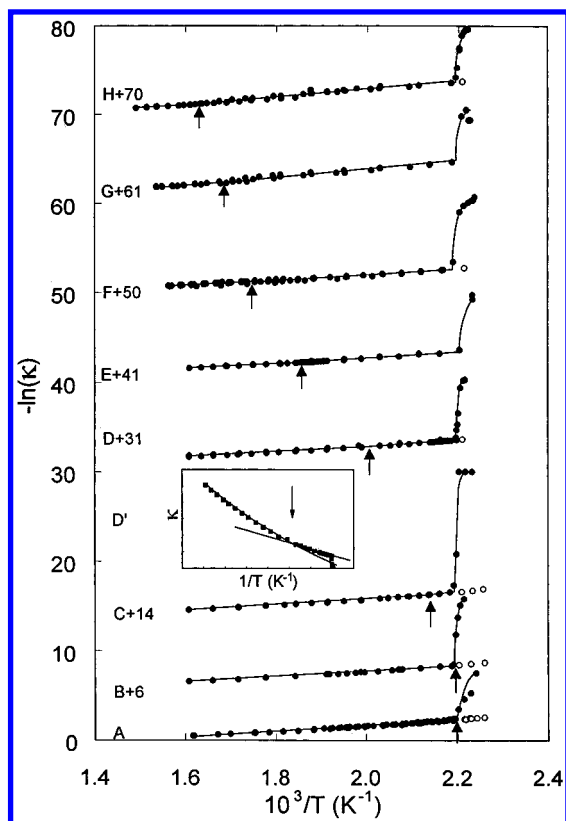


Figure 1. Electrical conductivity vs temperature of the $\text{Na}_2\text{S}_2\text{O}_7$ – NaHSO_4 system at various compositions X_{NaHSO_4} : (A) 1.000; (B) 0.975; (C) 0.925; (D) 0.900; (D') 0.900; (E) 0.825; (F) 0.750; (G) 0.677; (H) 0.600. The curves are offset by the specified values. Open circles indicate subcooling, and arrows indicate the liquidus temperatures. If the liquidus point was difficult to determine, a nonlogarithmic plot was used instead of the usual logarithmic one, as shown by the insert D'.

mixture of the $\text{Na}_2\text{S}_2\text{O}_7$ – NaHSO_4 system and the liquidus temperature are too close to each other. Therefore, DSC measurements of two samples in this region were carried out but also in this case the transition temperatures were too close to be separated.

All observed temperatures of transition are shown in Figure 3. The phase diagram is of the simple eutectic type as for the $\text{K}_2\text{S}_2\text{O}_7$ – KHSO_4 system but without the break in the liquidus curve found in that system at the solid–solid ($\alpha \rightarrow \beta$) phase transition temperature for $\text{K}_2\text{S}_2\text{O}_7$, in accordance with our recent⁶ thermal measurements on solid $\text{Na}_2\text{S}_2\text{O}_7$ showing no separate transition below the temperature of fusion of 402 °C. The fusion of the eutectic is found to be 179 ± 1 °C as an average of the measured values. The composition of the eutectic mixture is apparently found in the range $X_{\text{NaHSO}_4} = 0.8$ – 1 . The heat of fusion of NaHSO_4 was found to be 17.3 kJ/mol obtained by DSC, rather far from the only value found in the literature¹² of 10.4 kJ/mol, based on a heating curve in the range 100–200 °C. No low-temperature solid–solid transition is found for NaHSO_4 , contrary³ to KHSO_4 . From the temperature of fusion of 182 °C found here for NaHSO_4 and the fusion temperature of the eutectic of 179 °C deduced from our conductivity measurements, we may calculate the liquidus temperature in this region (assuming ideality) from the slope given by

$$\frac{\Delta T}{\Delta X_{\text{NaHSO}_4}} = \frac{RT_{\text{fus}}^2(\text{NaHSO}_4)}{\Delta H_{\text{fus}}^\circ(\text{NaHSO}_4)} \quad (1)$$

where ΔT is equal to 3 K.

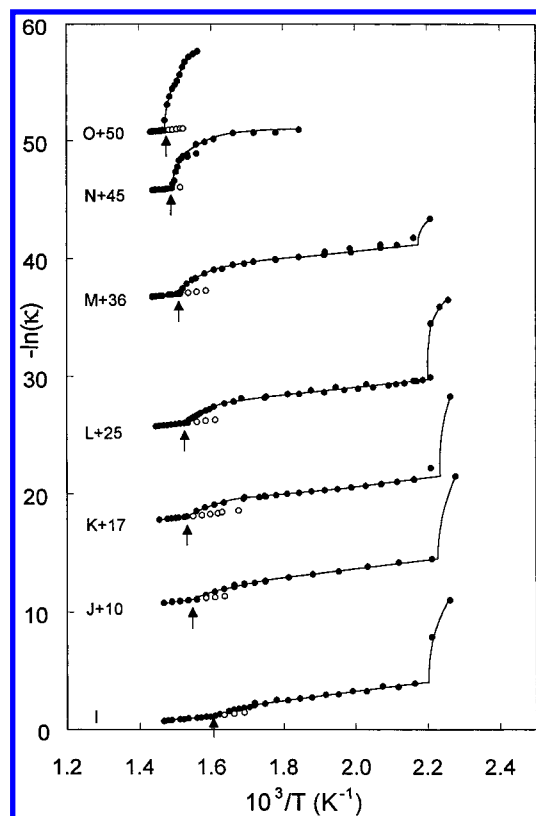


Figure 2. Electrical conductivity vs temperature of the $\text{Na}_2\text{S}_2\text{O}_7$ – NaHSO_4 system at various compositions X_{NaHSO_4} : (I) 0.545; (J) 0.390; (K) 0.316; (L) 0.300; (M) 0.200; (N) 0.100; (O) 0.000. The curves are offset by the specified values. Open circles indicate subcooling, and arrows indicate the liquidus temperatures.

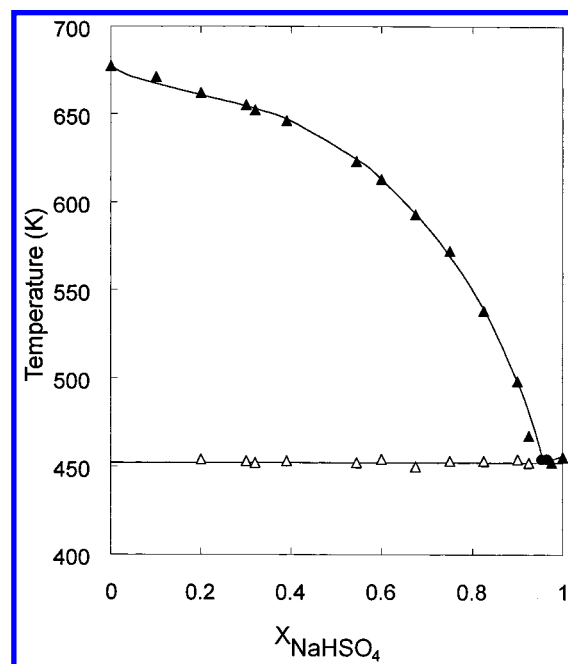


Figure 3. Phase diagram of the $\text{Na}_2\text{S}_2\text{O}_7$ – NaHSO_4 system obtained from conductance (\blacktriangle) and DSC (\bullet) measurements. Open symbols indicate the melting point of the eutectic.

A value of $\Delta X_{\text{NaHSO}_4} = 0.03$ could be calculated by giving the composition $X_{\text{NaHSO}_4} = 0.97$ for the eutectic. These values can be compared with 205 °C and $X_{\text{NaHSO}_4} = 0.94$ found by us,³ respectively, for the fusion and composition of the eutectic of the $\text{K}_2\text{S}_2\text{O}_7$ – KHSO_4 system. In the range $0 < X_{\text{NaHSO}_4} < 0.97$ the temperature, T , of fusion and thus the liquidus curve

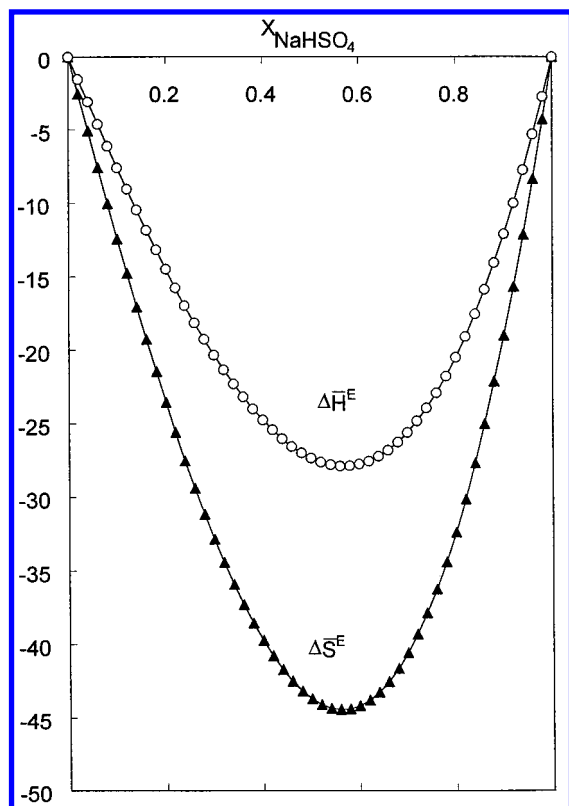


Figure 4. Calculated excess enthalpies (○) and entropies (▲) of mixing, ΔH^E (kJ·mol⁻¹) and ΔS^E (J·mol⁻¹·K⁻¹), for the Na₂S₂O₇–NaHSO₄ system at 650 K.

can be calculated from the classical equation

$$-\Delta G_{\text{fus},T}^{\circ}(\text{Na}_2\text{S}_2\text{O}_7(\text{s})) = RT \ln X_{\text{Na}_2\text{S}_2\text{O}_7} + \Delta \bar{G}_T^E(\text{Na}_2\text{S}_2\text{O}_7(\text{l})) \quad (2)$$

where the Gibbs energy of fusion of Na₂S₂O₇ is calculated from our measured⁶ values of $C_p(\text{s})$, $C_p(\text{l})$, $\Delta H_{\text{fus}}^{\circ}$, and T_{fus} or Na₂S₂O₇ and the excess Gibbs energy from the empirical expression¹³

$$\Delta \bar{G}_T^E = X(1-X)(A_0 + A_1T + A_2T(1 - \ln T) + X(B_0 + B_1T + B_2T(1 - \ln T))) \quad (3)$$

where $X = X_{\text{Na}_2\text{S}_2\text{O}_7}$.

From this expression the excess enthalpy and entropy can be obtained by using classical thermodynamic relations. All six coefficients are calculated by a multilinear regression method using all the experimental liquidus points, and the partial enthalpies of mixing. The values $A_0 = 491.56$ kJ, $A_1 = -6.08$ kJ T⁻¹, $A_2 = -0.97$ kJ T⁻², $B_0 = 1327.84$ kJ, $B_1 = -12.69$ kJ T⁻¹, and $B_2 = -1.95$ kJ T⁻² could be calculated (with a regression coefficient of 0.9998) as well as the liquidus curve shown on the phase diagram in Figure 3. An excellent fit to the experimental data points is observed. The partial enthalpy of mixing of Na₂S₂O₇(l) in NaHSO₄(l) can be calculated to be $\Delta H_{\text{mix}}^{\circ}(\text{Na}_2\text{S}_2\text{O}_7(\text{l})) = -11.94$ kJ/mol. The experimental value, found by calorimetry using the method of indirect drop via the ampule breaking method of solid Na₂S₂O₇ to liquid NaHSO₄ at 544 K, is -11.95 kJ/mol using our previously⁶ obtained experimental values of $\Delta H_{\text{fus}}^{\circ}$ and C_p for Na₂S₂O₇(s). Thus a very good agreement is found between the calculated and the measured value of $\Delta H_{\text{mix}}^{\circ}(\text{Na}_2\text{S}_2\text{O}_7(\text{l}))$. The calculated and experimental partial enthalpy of mixing of Na₂S₂O₇ in the mixture with $X_{\text{NaHSO}_4} = 0.54$ at $T = 663$ K are found to be

TABLE 1: Coefficients for Empirical Equations^a for the Specific Conductivity of Different Compositions, X_{NaHSO_4} , of the Molten Na₂S₂O₇–NaHSO₄ System, Their Liquidus Temperatures, T_{liq} , and the Middle Temperature, T_m , of the Measured Temperature Range^b

X_{NaHSO_4}	T_{liq} (K)	T_m (K)	$A(X)$ (Ω ⁻¹ cm ⁻¹)	$B(X)$ (10 ⁻³ Ω ⁻¹ cm ⁻¹ deg ⁻¹)	$C(X)$ (10 ⁻⁶ Ω ⁻¹ cm ⁻¹ deg ⁻²)	SD (Ω ⁻¹ cm ⁻¹)
1.000	455	487	0.17091	2.499	6.7334	0.0010
0.971	452	515	0.23085	2.646	4.4047	0.0037
0.925	467	523	0.23631	2.750	4.2015	0.0036
0.900	498	562	0.31870	2.752	0.7102	0.0215
0.825	538	576	0.38679	2.968	4.0343	0.0068
0.750	572	606	0.35685	2.676	10.194	0.0091
0.675	593	622	0.34208	2.696	5.8391	0.0027
0.600	613	640	0.37907	2.765	1.5444	0.0021
0.545	623	650	0.38887	2.690	2.0792	0.0037
0.390	646	666	0.40129	3.650	82.931	0.0147
0.316	652	667	0.38351	2.822	-10.190	0.0025
0.300	655	671	0.41068	3.092	-17.790	0.0030
0.200	662	680	0.41818	2.834	19.792	0.0033
0.100	671	682	0.41642	2.417	-38.890	0.0058
0.000	677	688	0.42808	2.874	9.4928	0.0011

^a $\kappa = A(X) + B(X)(T - T_m) + C(X)(T - T_m)^2$, $T \geq T_{\text{liq}}$ (T in kelvin).

^b Consult Figures 1 and 2 for the highest measuring temperature.

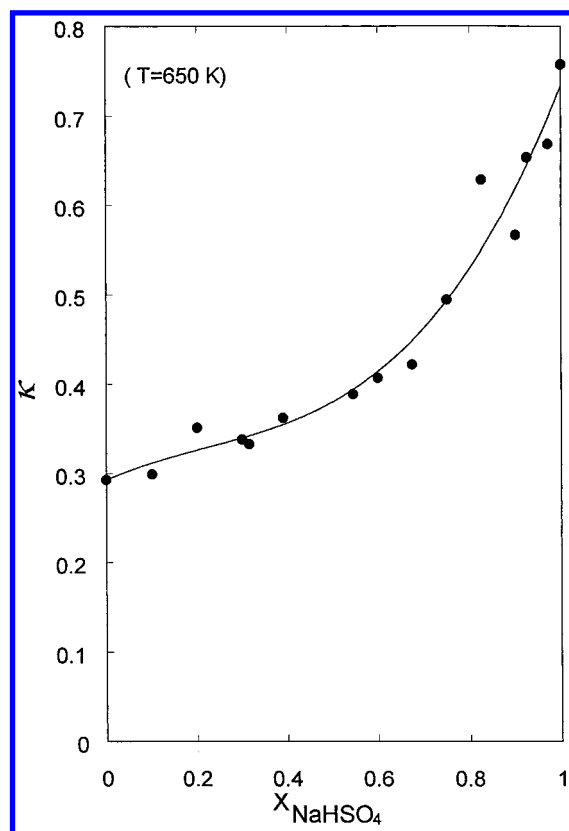


Figure 5. Conductivity isotherm for the Na₂S₂O₇–NaHSO₄ system at 650 K, with curve fits corresponding to $\kappa = 0.293 + 0.225X - 0.420X^2 + 0.636X^3$, and with a regression coefficient of 0.97.

exactly the same: -34.69 kJ/mol. The calculated excess enthalpies and entropies of mixing, ΔH^E and ΔS^E (Figure 4), are negative in the whole composition range of the binary Na₂S₂O₇–NaHSO₄ system and comparable with values obtained on the analogous K₂S₂O₇–KHSO₄ system. The negative values of ΔS^E points for both systems to an ordered liquid, most probably due to H-bonding between the species HSO₄⁻ and S₂O₇²⁻, dominating the liquid.³ The calculations have been done at 650 K, the average temperature of the conductivity measurements.

The phase diagram depicted in Figure 3 agrees rather well, within about 15 K at maximum, with the earlier⁴ published diagram contrary to about 50 K deviation found for the $\text{K}_2\text{S}_2\text{O}_7$ – KHSO_4 system.^{3,4} The position of the eutectic found⁴ at $X_{\text{NaHSO}_4} = 0.965$ and its temperature of fusion of 183 °C agrees well with our values of $X_{\text{NaHSO}_4} = 0.97$ and 179 °C, respectively. Also the temperature of fusion found⁴ for NaHSO_4 of 186 °C and $\text{Na}_2\text{S}_2\text{O}_7$ of 401 °C are in very good agreement with our values of 182 and 402 °C, respectively.

Conductivity of the Liquid $\text{Na}_2\text{S}_2\text{O}_7$ – NaHSO_4 System. The conductivities of the 15 different compositions measured in the liquid region have been fitted as previously³ to polynomials of the form $\kappa = A(X) + B(X)(T - T_m) + C(X)(T - T_m)^2$ where $T \geq T_{\text{liquidus}}$ and T_m is the middle temperature of the measured range, as indicated in Table 1. Using the polynomials in Table 1 to calculate the conductivity for all compositions at the average temperature of all the measured temperatures leads to rather large extrapolations, outside the measured temperature ranges, especially for the extreme compositions. The conductivity isotherm calculated at 650 K and displayed in Figure 5 should therefore be taken with caution and considered as qualitative. It is noted, as was the case³ for the $\text{K}_2\text{S}_2\text{O}_7$ – KHSO_4 system, that the conductivity increases with the mole fraction of NaHSO_4 , most probably due to the increased concentration of H^+ . H^+ seems indeed to carry most of the current judged from the molar conductivities of 34.9 and 46.2 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, respectively, for $\text{Na}_2\text{S}_2\text{O}_7$ and NaHSO_4 at 650 K, which can be calculated from Table 1 and the densities of $\text{Na}_2\text{S}_2\text{O}_7$ ⁶ and NaHSO_4 , assuming the same density as found¹⁴ for KHSO_4 .

Our measured conductivities for molten NaHSO_4 as well as for KHSO_4 ³ do not fit very well with the only previously

published data⁵ that we know of. In the temperature range 200–300 °C our conductivities ($\ln(\kappa)$) are about 2 times the values found in ref 5 for both salts. However, no indication is given in ref 5 concerning the calibration of the conductivity cell.

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References and Notes

- (1) Topsøe, H. F. A.; Nielsen, A. *Trans. Dan. Acad. Technol. Sci.* **1947**, 1, 18.
- (2) Smith, D. J. *Power Eng. Int.* 1994, Apr. 21.
- (3) Eriksen, K. M.; Fehrmann, R.; Hatem, G.; Gaune-Escard, M.; Lapina, O. B.; Mastikhin, V. M. *J. Phys. Chem.* **1996**, 100, 10771.
- (4) Cambi, L.; Bozza, G. *Ann. Chim. Appl.* **1923**, 13, 221.
- (5) Rogers, S. E.; Ubbelohde, A. R. *Trans. Faraday Soc.* **1950**, 46, 1051.
- (6) Hatem, G.; Abdoun, F.; Gaune-Escard, M.; Eriksen, K. M.; Fehrmann, R. *Thermochim. Acta* **1998**, 319, 33.
- (7) Boghosian, S.; Fehrmann, R.; Bjerrum, N. J.; Papatheodorou, G. N. *J. Catal.* **1989**, 119, 121.
- (8) Jones, G.; Bradshaw, B. C. *J. Am. Chem. Soc.* **1933**, 55, 1780.
- (9) Folkmann, G. E.; Eriksen, K. M.; Fehrmann, R.; Gaune-Escard, M.; Hatem, G.; Lapina, O. B.; Terskikh, V. *J. Phys. Chem.* **1998**, 102, 24.
- (10) Folkmann, G. E.; Hatem, G.; Fehrmann, R.; Gaune-Escard, M.; Bjerrum, N. J. *Inorg. Chem.* **1991**, 30, 4057.
- (11) Karydis, D. A.; Boghosian, S.; Fehrmann, R. *J. Catal.* **1994**, 145, 312.
- (12) Reznitskii, L. A.; Khomyakov, K. G. *Vestn. Mosk. University Ser. Mater. Mekhan. Astron. Fiz. I Khim.* **1959**, 14 (2), 199/202; *Chem. Abstr.* **1960**, 54, 8261.
- (13) Lukas, H. L.; Henig, E. T.; Zimmerman, B. *Calphad* 1–3, **1977**, 225.
- (14) Hansen, N. H.; Bjerrum, N. J. *Chem. Eng. Data*, **1981**, 26, 13.