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Electronic Conduction and Electron Mobilities in Molten NaCl-Na Solutions

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ABSTRACT

The electronic conductivity of molten NaCl-Na solutions was determined as a function of the activity of Na at 850° and 900°C by using the Wagner polarization technique. A transient technique was used to determine the diffusion coefficient and the mobility of electrons. A thermodynamic defect model was applied for calculating the concentration of defects as a function of the activity of Na in NaCl.

The study of mixtures of molten salts and metals has received much attention. Bredig and co-workers (1) carried out a comprehensive examination of physical properties of binary mixtures of salts and metals, focusing on alkali and alkaline earth systems. Phase diagrams and electrical conductivities were determined for a large number of systems, among them the NaCl-Na system. Dissolution of Na in molten NaCl gives rise to an increase in the total electrical conductivity, which increases as the activity of Na increases.

The excess conductivity is believed to be electronic. Molten alkali halide-alkali metal mixtures are completely miscible above a certain critical temperature, and the solutions exhibit a continuous transformation of the electronic structure from metallic to nonmetallic states. Spectroscopic measurements in salt-rich alkali systems, reported by Freyland and co-workers (2), suggest the formation of localized electronic states similar to F-centers in solid crystals, *i.e.*, electrons are localized at anion vacancies. At higher metal activity approaching the metal-nonmetal transition, associated F-centers may be formed. The thermodynamic properties of some molten alkali halide-alkali metal mixtures were studied by Smirnov *et al.* (3). Data for the activity of Na in molten NaCl were reported.

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Egan and Freyland (4) have proposed a thermodynamic defect model for molten NaBr-Na mixtures similar to that used for crystalline alkali halides with excess metal developed by Kroger (5) and Wagner (6). The model takes into account equilibria between different defects. The concentration of anion vacancies, electrons, F-centers, and F-center dimers in molten NaBr was obtained as a function of the activity of Na fitting thermodynamic data to the model. In a recent paper by Haarberg *et al.* (7) this model was used to describe molten NaBr-Na and NaI-Na. The electronic conductivity was measured, and a good agreement between the thermodynamic properties and the electron transport properties was obtained. In the present paper the same approach was applied to molten NaCl-Na solutions along with measurements of the electron mobility.

Techniques for the Measurement of Electronic Conduction and Electron Mobilities

Electronic conductivity.—The Wagner polarization technique is usually used to study electrical conduction in solids exhibiting both ionic and electronic transport. The method has been thoroughly treated in the literature especially by Wagner (8) and Kroger (9). It has also been employed to study the movement of electrons in molten salts (10, 11). A brief description is presented here for the convenience of the reader.

This is a dc method using cells of the following type

$$\mathrm{Fe(s)|NaCl(l)|Na - Bi(l)}_{x\mathrm{Na}=0.1} \quad [\mathrm{I}]$$

where the Na-Bi(l) alloy serves as a reference electrode with known activity of sodium and the iron serves as an inert electron conductor or blocking electrode. One applies potentials across the cell which are lower than those necessary to decompose the NaCl, the iron electrode being negative. In this way ionic currents are suppressed and only electronic current flows. There is no gradient of electrical potential within the bulk of the NaCl, otherwise ions would move. Under steady-state conditions which take 10-15 min after each potential change, the current density is given by

$$J_e = \frac{\kappa_e}{\mathbf{F}}\left(\frac{\partial \eta_e}{\partial x}\right) \quad [1]$$

where κ_e is the electronic conductivity in NaCl, $\mathbf{F}$ is the Faraday, and η_e is the electrochemical potential of electrons [see Wagner (8) or Kroger (9)]. The ionic current density is given by

$$J_{\mathrm{ion}} = -\frac{\kappa_{\mathrm{ion}}}{\mathbf{F}}\left(\frac{\partial \mu_{\mathrm{Na}}}{\partial x} - \frac{\partial \eta_e}{\partial x}\right) = 0 \quad [2]$$

where μ_{Na} is the chemical potential of Na in NaCl. Since $J_{\mathrm{ion}} = 0$

$$\frac{\partial \mu_{\mathrm{Na}}}{\partial x} = \frac{\partial \eta_e}{\partial x} \quad [3]$$

Since the cell is designed (see Experimental section) so that the compartment between the two electrodes has a constant cross section, integration of Eq. [1] using Eq. [3] gives

$$l\,J_e = \frac{1}{\mathbf{F}}\int_{\mu_{\mathrm{Na}}^{\mathrm{ref}}}^{\mu_{\mathrm{Na}}^{\mathrm{Fe}}} \kappa_e d\mu_{\mathrm{Na}} \quad [4]$$

The chemical potential of Na at the iron electrode is related to the voltage impressed across the cell, E, by

$$\mu_{\mathrm{Na}}^{\mathrm{Fe}} - \mu_{\mathrm{Na}}^{\mathrm{ref}} = -\mathbf{F}E \quad [5]$$

Differentation of [4] and [5] with respect to $\mu_{\mathrm{Na}}^{\mathrm{Fe}}$ and substitution gives

$$\kappa_e = l\frac{d|J_e|}{dE} = G\frac{d|I|}{dE} \quad [6]$$

where G is the cell constant and I is the steady-state current of cell (I).

In order to obtain the electronic conductivity in NaCl, steady-state current-potential curves were obtained and then differentiated to yield κ_e. Further, the conductivity was obtained as a function of sodium activity using

$$a_{\mathrm{Na}} = \exp\left[\frac{(E - E^0)\mathbf{F}}{RT}\right] \quad [7]$$

where E^0 is the potential of the Na-Bi electrode *vs.* pure sodium taken from the extensive literature on this system (12-15).

Electron mobilities.—The diffusion coefficient and mobility of electrons in the melt may also be measured by observing the cell's approach to steady state. When a potential is imposed on the iron electrode, a chemical potential of sodium is produced in the NaCl at this point and with it a given concentration of electrons. These electrons then diffuse toward the reference electrode according to Fick's second law. The concentration of electrons as a function of time and distance from the iron electrode is given by the following equation [see, for example, Cranck (6)]

$$c = c_1 + (c_0 - c_1)\frac{x}{l} + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{c_0 \cos n\pi - c_1}{n} \sin\frac{n\pi x}{l}\exp\left(-\frac{Dn^2\pi^2 t}{l^2}\right) \quad [8]$$

where c_1 is the electron concentration at the iron electrode, c_0 is the concentration at the reference electrode, x is the distance from the iron electrode, D is the diffusion coefficient of electrons, l the distance between the iron electrode and the reference electrode, and t is the time in seconds. The flow of electrons, j, is then given by

$$j = -D\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{D(c_1 - c_0)}{l} - \frac{2Dc_0}{l}\sum_{n=1}^{\infty}(-1)^n \exp\left(-\frac{Dn^2\pi^2 t}{l^2}\right) + \frac{2Dc_1}{l}\sum_{n=1}^{\infty}\exp\left(-\frac{Dn^2\pi^2 t}{l^2}\right) - \frac{4Dc_0}{l}\sum_{m=0}^{\infty}\left(-\frac{D(2m+1)^2\pi^2 t}{l^2}\right) \quad [9]$$

The quantity of electrons flowing in the cell is given by

$$Q_t = \int_0^t j dt = \frac{D(c_1 - c_0)}{l}t - \frac{2l}{\pi^2}\sum_{n=1}^{\infty}\frac{c_0 \cos n\pi - c_1}{n^2}\left[1 - \exp\left(-\frac{Dn^2\pi^2 t}{l^2}\right)\right] - \frac{4c_0 l}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{n^2}\left[1 - \exp\left(-\frac{Dn^2\pi^2 t}{l^2}\right)\right] \quad [10]$$

At longer times with $t \to \infty$, Eq. [10] reduces to

$$Q_t = \frac{D(c_1 - c_0)}{l}t + \frac{l}{3}(c_1 - c_0) \quad [11]$$

The total number of coulombs passed through the cell as a function of time is given by

$$Q = \frac{D(c_1 - c_0)\,\mathbf{F}A}{l}t + \frac{l}{3}(c_1 - c_0)\,\mathbf{F}A \quad [12]$$

where $\mathbf{F}$ is the Faraday constant and A is the area of the sodium chloride compartment. Thus, if one imposes a voltage across the cell at $t = 0$ and measures the coulombs until steady state, one obtains the diffusion coefficient of electrons as follows. The slope of a plot of Q *vs.* t is given by

$$\text{Slope} = \frac{D(c_1 - c_0)\,\mathbf{F}A}{l} \cong \frac{Dc_1\mathbf{F}A}{l} \qquad [13]$$

when the concentration of electrons at the reference electrode is much smaller than that generated at the iron electrode. The intercept of the plot is given by

$$\text{Intercept} = \frac{l}{3}(c_1 - c_0)\mathbf{F}A \cong \frac{l}{3}c_1\mathbf{F}A \qquad [14]$$

$$D = \frac{\text{Slope}}{\text{Intercept}}\,\frac{l^2}{3} \qquad [15]$$

Since $I = dQ/dt$

$$D = \frac{Il^2}{(Q - It)3} \qquad [16]$$

Therefore measurements of Q were taken for a time t until steady state was reached and Eq. [16] used to obtain values of D. The mobility of electrons was then calculated from the Nernst-Einstein equation

$$u_e = (D\mathbf{F})/(RT) \qquad [17]$$

Experimental Details

The experimental cell is shown in Fig. 1. A tantalum crucible contains the salt (NaCl single crystals of optical grade) in contact with a Na-Bi alloy (= 10 mole percent (m/o) Na). The Fe electrode is placed inside a sapphire capillary (4.2 cm long, 3 mm id). A vacuum-tight seal is formed between iron and sapphire. This seal prevents the evaporation of Na, which is essential for obtaining good results. A constant potential is imposed across the cell making the Ta cup positive and the Fe electrode negative. The current through the cell is measured as a function of time, and the steady-state value is recorded. A series of such corresponding data is measured so that the electronic conductivity can be calculated as a function of potential. The cell constant is determined by the geometry of the sapphire capillary. AC resistance measurements are also made periodically between the Ta cup and the Fe electrode as a control.

A transient technique is applied to the same cell in order to measure the diffusion coefficient of electrons. The current response to a potential applied across the electrodes is measured until steady state is attained. The total number of coulombs passed is recorded and the diffusion coefficient calculated from Eq. [16].

A reference electrode consisting of a Na-Bi alloy placed inside an alumina tube is also shown. The amount of Bi is accurately known. This reference electrode is used to check the composition of the Na-Bi alloy in the tantalum cup which can vary over a period of several days due to evaporation of sodium. All Na is coulometrically removed from the reference electrode and then added again until the potential between the reference alloy and the larger Na-Bi alloy is zero. The composition of the Na-Bi alloy in the tantalum cup is then known, and the activity of Na is calculated from thermodynamic data for Na-Bi alloys (12-15).

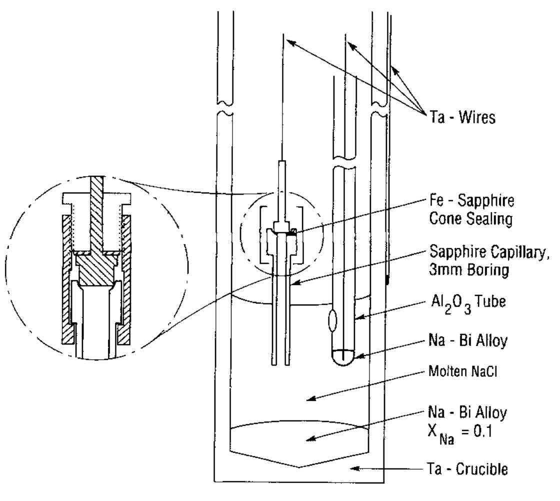

Fig. 1. Experimental arrangement used for cell [I]

Defect Model

It has been found helpful to explain the results reported in this paper in terms of a defect model generally used for ionic solids. Details are presented by Kroger (5) and Wagner (6). The complete analysis has been previously set forth in the two publications dealing with NaBr and NaI (4, 7). A brief review will be given here for convenience of the reader. The notation of Kroger is used.

The addition of Na to liquid NaCl can be represented by the following set of equations and associated equilibrium constants. The concentration of defects is small so that concentrations are used in place of activities.

$$\text{Na} + \text{Cl}_{\text{Cl}}^x = V_{\text{Cl}}^{\cdot} + e' + \text{NaCl} \quad K_{\text{II}} = \frac{[V_{\text{Cl}}^{\cdot}][e']}{a_{\text{Na}}} \qquad [18]$$

$V_{\text{Cl}}^{\cdot}$ is an anion vacancy [see Ref. (5)] and e' is an electron in the conduction band

$$\text{Na} + \text{Cl}_{\text{Cl}}^x = V_{\text{Cl}}^x + \text{NaCl} \quad K_{\text{III}} = \frac{[V_{\text{Cl}}^x]}{a_{\text{Na}}} \qquad [19]$$

where V_{Cl}^x is an F-center in the melt

$$2\text{Na} + 2\text{Cl}_{\text{Cl}}^x = (V_{\text{Cl}})_2^x + 2\text{NaCl} \quad K_{\text{IV}} = \frac{[(V_{\text{Cl}})_2^x]}{a_{\text{Na}}^2} \qquad [20]$$

with $(V_{\text{Cl}})_2^x$ representing an F-center dimer. In addition, the following internal equilibria are present

$$e' + h^{\cdot} = 0 \qquad [21]$$

where $h^{\cdot}$ is an electron hole

$$V_{\text{Cl}}^{\cdot} + V_{\text{Na}}' = \text{NaCl} \qquad [22]$$

V_{Na}' being a cation vacancy.

$$V_{\text{Cl}}^x = V_{\text{Cl}}^{\cdot} + e' \quad K_{\text{VII}}^{-1} = \frac{[V_{\text{Cl}}^{\cdot}][e']}{[V_{\text{Cl}}^x]} \qquad [23]$$

$$2V_{\text{Cl}}^x = (V_{\text{Cl}})_2^x \quad K_{\text{VIII}}^{-1} = \frac{[(V_{\text{Cl}})_2^x]}{[V_{\text{Cl}}^x]} \qquad [24]$$

$$(V_{\text{Cl}})_2^x = (V_{\text{Cl}})_2^{\cdot} + e' \quad K_{\text{IX}}^{-1} = \frac{[(V_{\text{Cl}})_2^{\cdot}][e']}{[(V_{\text{Cl}})_2^x]} \qquad [25]$$

Also, electroneutrality demands that

$$[e'] = [V_{\text{Cl}}^{\cdot}] + [(V_{\text{Cl}})_2^{\cdot}] \qquad [26]$$

neglecting the concentration of cation vacancies which is very small in the activity regions studied here. The deviation from exact stoichiometry in the melt is given by

$$\delta = [V_{\text{Cl}}^{\cdot}] + 2[(V_{\text{Cl}})_2^{\cdot}] + [V_{\text{Cl}}^x] + 2[(V_{\text{Cl}})_2^x] \qquad [27]$$

Combining these equations as shown in Ref. (4) one obtains expressions for the deviation from exact stoichiometry δ as a function of a_{Na}

$$\delta = K_{\text{VIII}}^{-1}\frac{a_{\text{Na}}}{a_{\text{Na}}^{\text{II}}} + 2K_{\text{VIII}}^{-1}\left(\frac{a_{\text{Na}}}{a_{\text{Na}}^{\text{II}}}\right)^2 + \left[K_{\text{VII}}^{-1/2}K_{\text{VIII}}^{-1/2}\left(\frac{a_{\text{Na}}}{a_{\text{Na}}^{\text{II}}}\right)^{-1/2} + 2K_{\text{IX}}^{-1}\frac{K_{\text{VIII}}^{-1/2}}{K_{\text{VII}}^{-1/2}}\left(\frac{a_{\text{Na}}}{a_{\text{Na}}^{\text{II}}}\right)^{3/2}\right]B^{-1/2} \qquad [28]$$

where $B = 1 + (K_{\text{IX}}^{-1}/K_{\text{VII}}^{-1}\, a_{\text{Na}}/a_{\text{Na}}^{\text{II}})$ and $a_{\text{Na}}^{\text{II}}$ is a constant equal to the activity of sodium where $[V_{\text{Cl}}^x] = [(V_{\text{Cl}})_2^x]$.

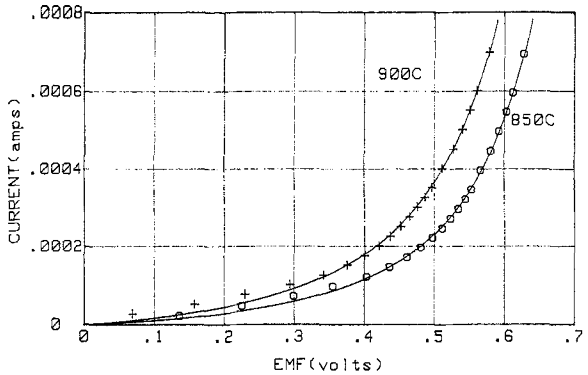

Fig. 2. Current vs. potential at 850° and 900°C for cell [I]

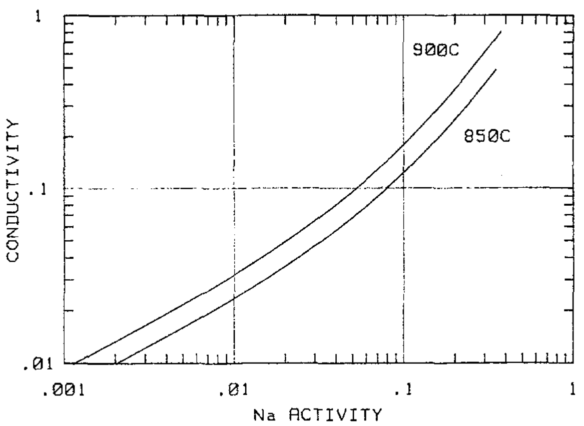

Fig. 3. Electronic conductivity vs. sodium activity at 850° and 900°C

Further, one obtains an equation for the concentration of conduction electrons as a function of a_{Na}

$$[e'] = \left[K_{VII}^{-1/2}K_{VIII}^{-1/2}\left(\frac{a_{Na}}{a_{Na}^{II}}\right)^{-1/2} + 2K_{IX}^{-1}\frac{K_{VIII}^{-1/2}}{K_{VII}^{-1/2}}\left(\frac{a_{Na}}{a_{Na}^{II}}\right)^{3/2}\right]B^{-1/2} \quad [29]$$

One may also obtain an expression for the electronic conductivity as a function of a_{Na} when the mobility of electrons u_e does not vary with the concentration

$$\kappa_e = ([e']u_e)/(V_m) \quad [30]$$

Knowing the equilibrium constants one may then calculate the concentration of any defect in the melt at various sodium activities. Thus

$$[V_{Cl}^{x}] = K_{VIII}^{-1}\frac{a_{Na}}{a_{Na}^{II}} \quad [31]$$

and

$$[(V_{Cl})_2^{x}] = K_{VIII}^{-1}\left(\frac{a_{Na}}{a_{Na}^{II}}\right)^2 \quad [32]$$

Results and Discussion

The currents measured at various applied potentials on cell (I) are shown in Fig. 2 for temperatures of 850° and 900°C. These points were fit to an exponential curve as explained in Ref. (7) and the derivative of this curve is then used to obtain the conductivity as a function of Na activity according to Eq. [6] and [7]. Results are shown in Fig. 3. Transient measurements were also taken on cell (I) for various applied potentials to obtain the electron mobilities using Eq. [16] and [17] and these results are shown in Tables I and II for 850° and 900°C.

The above results were used to test the validity of the defect model in the following way. Equation [28] was fit to the thermodynamic data of Smirnov *et al.* (3) using a general least squares method (17). Equation [30] using [29] was fit to the conductivity data reported here by the same method. From these fits one obtains values for K_{VII}^{-1}, K_{VIII}^{-1}, K_{IX}^{-1}, and a_{Na}^{II}. If the model is a valid representation of the system

Table I. Results of transient measurements on cell [I]

$T = 850°C$ $E° = 0.867$ $V_m = 38.20$			
E (V)	D ($cm^2\ s^{-1}$)	I_{steady} (μA)	u_e ($cm^2\ V^{-1}\ s^{-1}$)
0.650	0.0094	284	0.097
0.675	0.0093	349	0.096
0.700	0.0095	454	0.098
0.725	0.0095	590	0.098
0.750	0.0101	787	0.104

Table II. Results of transient measurements on cell [I]

$T = 900°C$ $E° = 0.874$ $V_m = 38.91$			
E (V)	D ($cm^2\ s^{-1}$)	I_{steady} (μA)	u_e ($cm^2\ V^{-1}\ s^{-1}$)
0.675	0.0120	596	0.119
0.700	0.0123	670	0.122
0.725	0.0123	814	0.122
0.750	0.0125	1011	0.124

Table III. Equilibrium constants and mobilities for molten NaCl

	a_{Na}^{II}	K_{VII}^{-1}	K_{VIII}^{-1}	K_{IX}^{-1}/K_{VII}^{-1}	u_e
850°C	0.522	$1.37 \cdot 10^{-4}$	$2.69 \cdot 10^{-3}$	10.89	0.109
900°C	0.520	$1.27 \cdot 10^{-4}$	$4.38 \cdot 10^{-3}$	15.3	0.108

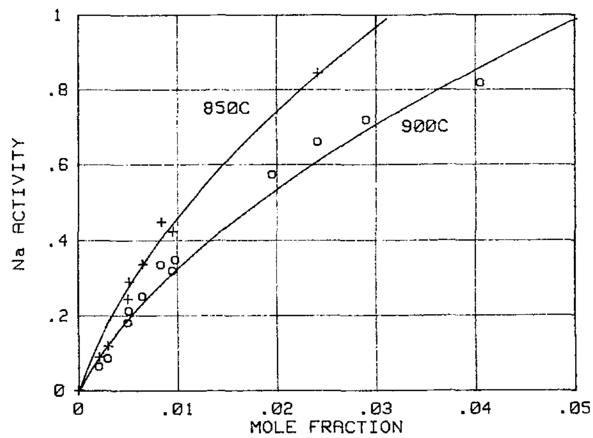

Fig. 4. Sodium activity vs. mole fraction sodium at 850° and 900°C. Smirnov *et al.* (+ or o), calculated from the model (—).

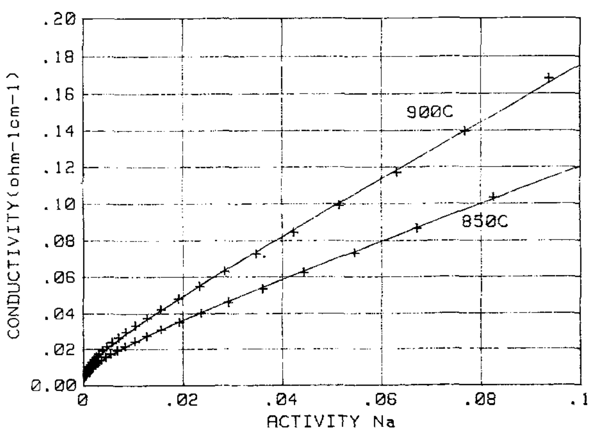

Fig. 5. Electronic conductivity vs. sodium activity at 850° and 900°C. Model (—), experiment (+).

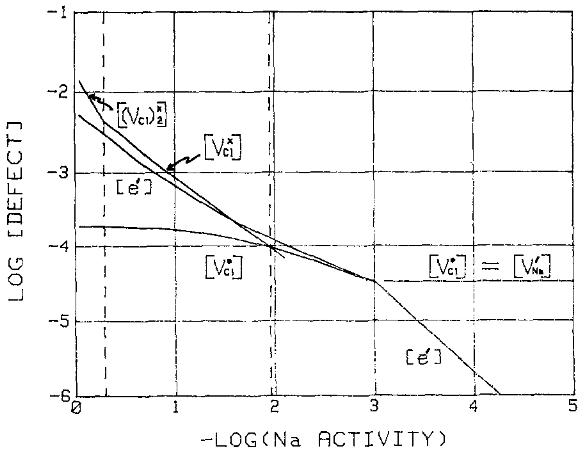

Fig. 6. Various defect concentrations in molten NaCl at 850°C calculated from the defect model.

then the values of the equilibrium constants will be the same for both fits.

Figure 4 shows the activity of sodium in molten NaCl as a function of the mol fraction of sodium x_{Na} determined by (3) [$x_{Na} = \delta/(1 + \delta)$]. The least squares fit with values for K_{VII}^{-1}, K_{VIII}^{-1}, K_{IX}^{-1}, and a_{Na}^{II} given in Table III is also shown. Figure 5 shows the comparison for the conductivity using the same constants. The agreement in both cases is excellent. A model developed for ionic solids is found to be equally valid for a molten salt. One also gets values of the electron mobilities from Eq. [30] and these values are given in Table III. The agreement with the values obtained by experiment is quite good which is another indication that the model is accurate and useful. Figure 6 shows the concentration of several defects in molten sodium chloride calculated from the model using the constants shown in Table III.

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Induced Surface States on p-WSe_2

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ABSTRACT

Capacitance-voltage measurements made on the p-WSe_2/electrolyte interface after exposure to silver or triiodide ions reveal two types of results before either species desorbs again within a few hours. For a few samples only a shift of their flatband potential is observed; silver producing a small anodic and triiodide a larger cathodic shift in the flatband potential. However, for most samples surface states are observed in addition to the shifts in the flatband potential. These surface states are thought to be caused by a stronger, possibly specific interaction between the chalcogenides and the adsorbate. After exposure to triiodide low frequency measurements reveal a broad distribution of surface states with a maximum density of states of about $4(10^{11})$ cm^{-2} eV^{-1} which peaks near E_v + 0.5 eV, while silver-treated surfaces consistently reveal two monoenergetic levels at E_v + 0.61 and E_v + 0.73 eV with a history dependent density of states.

Recent *in situ* investigations of surface states on semiconductors immersed in an electrolyte have centered on capacitance-voltage (1-4), conductance-voltage (1, 2), modulated and steady-state photocurrents (5, 6) as well as electroreflectance (7-10). We have concentrated on the first two techniques in an initial study of induced surface states on tungsten diselenide which, to the authors' knowledge, has not been done previously.

WSe_2 is one of the semiconducting members of the transition metal dichalcogenide family. The metal atoms are in hexagonally packed planes that are sandwiched between chalcogen layers. Strong covalent bonds within a sandwich alternate with weak, van der Waals type bonds between sandwiches. Surfaces relatively free of defects, *i.e.*, steps and dangling bonds, can therefore be prepared by simply peeling away successive sandwiches with sticky