ELECTRONIC CONDUCTION AND ELECTRON MOBILITIES IN MOLTEN KBr-K SOLUTIONS

G.M. Haarberg* and J.J. Egan
Brookhaven National Lab, Department of Applied Science, Upton, NY

Abstract
The electronic conductivity of molten KBr-K solutions was determined as a function of the activity of K at 780, 800 and 850°C by using the Wagner polarization technique. A transient technique was used to determine the diffusion coefficient and the mobility of electrons.

INTRODUCTION
The study of mixtures of molten salts and metals has received much attention. Bredig and coworkers /1/ determined the phase diagram for the KBr-K system and measured the electrical conductivity of solutions of potassium in molten potassium bromide. It was found that dissolution of K in molten KBr gives rise to electronic conduction. The system undergoes a continuous transition of the electronic structure from nonmetallic to metallic states as the content of K in solution increases. The properties of dilute solutions of alkali metals in molten alkali halides can be explained by using a thermodynamic model proposed by Egan and Freyland /2/. The formation of defects such as electrons and F-centers is considered. Results from spectroscopy /3/ and conductivity measurements /4,5/ are in accordance with predictions from the thermodynamic defect model.

*Present address: University of Trondheim
Laboratories of Industrial Electrochemistry
N-7034 Trondheim, Norway
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 /6/ and Kroger /7/. It has also been employed to study the movement of electrons in molten salts /4,5,8/. A brief description is presented here for the convenience of the reader.

This is a dc method using cells of the following type

\[ \text{Fe(s) | KBr(l) | K - Bi(l)}_{x_{K}=0.04} \]  

where the K-Bi (l) alloy serves as a reference electrode with known activity of potassium 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 KBr, 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 KBr otherwise ions would move. Under steady state conditions which take about 30 minutes after each potential change the current density is given by

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

where \( \kappa_e \) is the electronic conductivity in KBr, \( F \) is the Faraday and \( \eta_e \) is the electrochemical potential of electrons (see Wagner /6/ or Kroger /7/). The ionic current density is given by

\[ J_{\text{ion}} = -\frac{\kappa_{\text{ion}}}{F} \left( \frac{\partial \mu_K}{\partial x} - \frac{\partial \eta_e}{\partial x} \right) = 0 \quad (2) \]

where \( \mu_K \) is the chemical potential of K in KBr. Since \( J_{\text{ion}} = 0 \)

\[ \frac{\partial \mu_K}{\partial x} = \frac{\partial \eta_e}{\partial x} \quad (3) \]
Since the cell is designed (see experimental section) so that the compartment between the two electrodes has a constant cross section, integration of eqn. (1) using eqn. (3) gives

$$l J_e = \frac{1}{F} \int_{\mu_{K}^{\text{ref}}}^{\mu_{K}^{\text{Fe}}} \kappa_e d\mu_K$$  

(4)

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

$$\mu_{K}^{\text{Fe}} - \mu_{K}^{\text{ref}} = -FE$$  

(5)

Differentiation of (4) and (5) with respect to $\mu_{K}^{\text{Fe}}$ and substitution gives

$$\kappa_e = \frac{l d|J_e|}{dE} = G \frac{d|I|}{dE}$$  

(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 KBr, steady state current-potential curves were obtained and then differentiated to yield $\kappa_e$. Further, the conductivity was obtained as a function of potassium activity using

$$a_K = \exp \left[ \frac{(E - E^0)F}{RT} \right]$$  

(7)

where $E^0$ is the potential of the K-Bi electrode vs. pure potassium taken from the literature on this system /9,10/.

**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 potassium is produced in the KBr 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 Crank /11/)

\[
\begin{align*}
c &= c_1 + (c_0 - c_1) \frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{c_0 \cos n\pi - c_1}{n} \frac{\sin \frac{n\pi x}{l}}{l} \exp \left(-\frac{Dn^2\pi^2t}{l^2}\right) \\
&\quad + \frac{4c_0}{\pi} \sum_{m=0}^{\infty} \frac{1}{2m+1} \frac{\sin \frac{(2m+1)\pi x}{l}}{l} \exp \left(-\frac{D(2m+1)^2\pi^2t}{l^2}\right)
\end{align*}
\] (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

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

The quantity of electrons flowing in the cell is given by

\[
Q_t = \int_0^t j \, dt = \frac{D(c_1 - c_0)}{l} t - \frac{2Dc_0}{l^2} \sum_{n=1}^{\infty} \frac{c_0 \cos \pi n - c_1}{n^2} \left[1 - \exp \left(-\frac{Dn^2\pi^2t}{l^2}\right)\right] \\
&\quad - \frac{4c_0}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \left[1 - \exp \left(-\frac{D(2m+1)^2\pi^2t}{l^2}\right)\right]
\] (10)

At longer times with \(t \to \infty\) equation (10) reduces to

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

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

\[
Q = \frac{D(c_1 - c_0)FA}{l} t + \frac{l}{3} (c_1 - c_0)FA
\] (12)

where \(F\) 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

\[
Slope = \frac{D(c_1 - c_0)F \Delta A}{l} \approx \frac{Dc_1F \Delta A}{l}
\]

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

\[
Intercept = \frac{l}{3}(c_1 - c_0)F \Delta A \approx \frac{l}{3}c_1F \Delta A
\]

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

\[
u_e = \frac{(DF)}{(RT)}
\]

**EXPERIMENTAL DETAILS**

The experimental cell is shown in Figure 1. A tantalum crucible contains the salt (KBr single crystals of optical grade) in contact with a K-Bi alloy (= 4mole%K). The Fe electrode is placed inside a sapphire capillary (4.2 cm long, 3 mm inside diameter). A vacuum tight seal is formed between iron and sapphire. This seal prevents the evaporation of K, 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 eqn. (16).

A reference electrode consisting of a K-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 K-Bi alloy in the tantalum cup which can vary over a period of several days due to evaporation of potassium. All K is coulometrically removed from the reference electrode and then added again until the potential between the reference alloy and the larger K-Bi alloy is zero. The composition of the K-Bi alloy in the tantalum cup is then known, and the activity of K is calculated from thermodynamic data for K-Bi alloys /9,10/.

RESULTS

The currents measured at various applied potentials on cell (I) are shown in Figure 2 for temperatures of 780, 800 and 850°C. These points were fit to an exponential curve as explained in ref./4/ using the least square routine of Marquart/12/ and the derivative of this curve is then used to obtain the conductivity as a function of K activity according to equation (6) and (7). Results are shown in Figure 3. Transient measurements were also taken on cell (I) for various applied potentials to obtain the electron mobilities using equation (16) and (17) and these results are shown in Tables 1, 2 and 3 for 780, 800 and 850°C.

ACKNOWLEDGEMENTS

This work was supported by the Division of Chemical Sciences, U.S. Department of Energy under Contract No. DE-AC02-76CH00016.
Table 1: Results of Transient Measurements on cell (I).

| $T = 780^\circ C$ | $E^o = 0.985$ | $V_m = 56.96$ |
|-------------------|---------------|----------------|
| $E$ [volts] | $D$ [cm$^2$sec$^{-1}$] | $I_{steady}$ [\mu amps] | $u_e$ [cm$^2$volt$^{-1}$sec$^{-1}$] |
| 0.700 | 0.016 | 617 | .176 |
| 0.780 | 0.016 | 1207 | .176 |
| 0.800 | 0.017 | 1391 | .187 |

Table 2: Results of Transient Measurements on cell (I).

| $T = 800^\circ C$ | $E^o = 0.986$ | $V_m = 57.41$ |
|-------------------|---------------|----------------|
| $E$ [volts] | $D$ [cm$^2$sec$^{-1}$] | $I_{steady}$ [\mu amps] | $u_e$ [cm$^2$volt$^{-1}$sec$^{-1}$] |
| 0.730 | 0.016 | 962 | .173 |
| 0.750 | 0.018 | 1130 | .194 |
| 0.770 | 0.016 | 1291 | .173 |

Table 3: Results of Transient Measurements on cell (I).

| $T = 850^\circ C$ | $E^o = 0.987$ | $V_m = 58.58$ |
|-------------------|---------------|----------------|
| $E$ [volts] | $D$ [cm$^2$sec$^{-1}$] | $I_{steady}$ [\mu amps] | $u_e$ [cm$^2$volt$^{-1}$sec$^{-1}$] |
| 0.608 | 0.0170 | 543 | .176 |
| 0.750 | 0.0170 | 1444 | .176 |
| 0.770 | 0.0170 | 1712 | .176 |
REFERENCES

1. M. A. Bredig, "Mixtures of Metals with Molten Salts" in *Molten Salt Chemistry*, M. Blander, Editor, p. 365, Interscience, New York, 1964.
2. J. J. Egan, W. Freyland, *Ber. Bunsenges. Phys. Chem.* 89, 381 (1985).
3. W. Freyland, K. Garbade, H. Heyer, E. Pfeiffer, *J. Phys. Chem.* 88, 3745 (1984); *Phys. Rev. Lett.* 51, 1304 (1983).
4. G. M. Haarberg, K. S. Osen, J. J. Egan, H. Heyer, W. Freyland, *Ber. Bunsenges. Phys. Chem.* 92, 139 (1988).
5. G. M. Haarberg, K. S. Osen, R. J. Heus, J. J. Egan, *J. Electrochem. Soc.* 137, 2777 (1990).
6. C. Wagner, *Proc. CITCE* 7, 361 (1957).
7. F. A. Kroger, *The Chemistry of Imperfect Crystals*, Vol. 3, p. 149 North Holland Pub., American Elsevier, 1974.
8. G. J. Reynolds, M. C. Y. Lee, R. A. Huggins, *Proc Fourth Int. Symp. Molten Salts*, p. 519 (1983).
9. A. Petric A. D. Pelton, M.-L. Saboungi, *J. Phys. F: Met. Phys.* 18, 1473 (1988).
10. J. J. Egan, *High Temp. Science* 19, 111 (1985).
11. J. Crank, *The Mathematics of Diffusion*, 2nd. ed., Oxford University Press, Ely House, London (1975).
12. D. W. Marquardt, *J. Soc. Ind. Appl. Math.* 2, 431 (1963).
Fig. 1 Experimental Arrangement used for Cell(I)
Fig. 2 Current vs. potential at 780, 800, and 850 °C for cell (I). (top curve 850 °C)

Fig. 3 Electronic Conductivity vs. potassium activity at 780, 800, and 850 °C (top curve 850 °C)