

An Incomplete-Dissociation Model for Diffusion and Ionic Conduction in Pure Molten Salts

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Diffusion and ionic conduction in pure 1:1 molten salts is described by an incomplete-dissociation model comprising neutral diatomic molecules and monoatomic ions. The internal mobility b_{+-} and the self-diffusion coefficients D_+ and D_- are given in terms of the six inter-particle friction coefficients and the degree of dissociation. By an approximation it is possible to derive from experimental b_{+-} , D_+ and D_- values an apparent degree of dissociation which ranges from 0.93 for NaCl to 0.51 for TiCl and decreases with temperature.

The notion that molten salts become more molecular with rising temperature was first deduced from a comparison of their diffusivities with their conductances [1] and became quite popular when Grantham and Yosim [2] were able to show that the conductance vs. temperature curve of some salts passes over a maximum. A quantitative description of self-diffusion and ionic conduction of incompletely dissociated molten salts has, however, not yet been given and shall be the subject of the present paper. For this purpose we use the concept of friction coefficients.

The friction coefficients r_{ik} are defined such that the frictional force exerted by the particles i on one mole of particles k is

$$x_i r_{ik} v_{ik}, \quad (1)$$

where x_i is the mole fraction of the particles i and v_{ik} is the transport velocity of the particles i with respect to the particles k ($v_{ik} = -v_{ki}$). From the balance of the frictional forces acting between two kinds of particles, as expressed by the relation

$$x_k x_i r_{ik} v_{ik} + x_i x_k r_{ki} v_{ki} = 0, \quad (2)$$

it follows that

$$r_{ik} = r_{ki}. \quad (3)$$

In the first paper dealing with friction coefficients in molten salts [3] the following expressions for 1:1

salts were given:

$$\frac{b_{+-}}{F} = \frac{2\zeta}{r_{+-}}, \quad \frac{D_+}{RT} = \frac{2}{r_{+-} + r_{++}},$$

$$\frac{D_-}{RT} = \frac{2}{r_{+-} + r_{--}}. \quad (4a, b, c)$$

Here b_{+-} , D_+ and D_- are the internal mobility and the self-diffusion coefficients, respectively, F is Faraday's constant and ζ was said to be "a number which takes into account incomplete dissociation and the molecular fine structure of the electric field". As a matter of fact, ζ was only introduced in the second and published version of the paper in order to provide a means of diminishing r_{+-} and thus preventing r_{++} and r_{--} from becoming negative; such a negativity seems to contradict the definition of the friction coefficients (1).

In a subsequent paper Laity [4] did show that the introduction of ζ was inconsistent. He correctly put

$$\frac{b_{+-}}{F} = \frac{2}{r_{+-}}, \quad \frac{D_+}{RT} = \frac{2}{r_{+-} + r_{++}}$$

$$\frac{D_-}{RT} = \frac{2}{r_{+-} + r_{--}} \quad (5a, b, c)$$

and owned that "whenever negative friction coefficients are encountered, it may be inferred that the choice of entities is unrealistic".

Angell and Tomlinson [5] give $r_{--} = (0.1 \pm 0.1) \cdot 10^8$ (in $\text{J sec cm}^{-2} \text{ mole}^{-1}$) for TiCl, and Ketelaar and Kwak [6] give $r_{++} = (0.03 \pm 0.30) \cdot 10^8$ for NaNO_3 . What "realistic" entities, then, are to be chosen if these values are negative or become negative at elevated temperatures? In an MD simulation one would certainly continue to work with the simple

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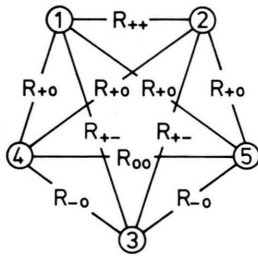
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cations and anions only. We shall, however, in this paper look into what happens with the friction coefficients if neutral diatomics are introduced in addition to the two simple ions.

In the complete-dissociation model (CDM) one has three friction coefficients and, in order to treat self-diffusion of the cations, one has to consider three species (1, 2 and 3) and two friction coefficients (r_{+-} and r_{++}). The cations 1 and 2 are physically identical but differently tagged. Without loss of generality one can assume that there are equal amounts of 1 and 2, so that the mole fractions of the three species are

$$x_1 = x_2 = \frac{1}{4}, \quad x_3 = \frac{1}{2}. \quad (6)$$

In the incomplete-dissociation model (IDM) there are six friction coefficients, and in order to treat self-diffusion of the positive ionic constituent one has to consider five species and five friction coefficients which build up a kind of Solomon's seal:



The species 1, 2 and 3 are those of the CDM while the species 4 and 5 are diatomic neutrals containing the species 1 and 2, respectively. The mole fractions, friction coefficients and velocities in the IDM shall be written in capital letters. With the degree of dissociation

$$\alpha = X_1/(X_1 + X_4) = X_2/(X_2 + X_5) \quad (7)$$

the mole fractions in the IDM become

$$\begin{aligned} X_1 = X_2 &= \frac{1}{2} \alpha / (1 + \alpha), & X_3 &= \alpha / (1 + \alpha), \\ X_4 = X_5 &= \frac{1}{2} (1 - \alpha) / (1 + \alpha). \end{aligned} \quad (8)$$

Exchange of the tagged ions is supposed to be so rapid that $X_1/X_2 = X_4/X_5$ even if X_1/X_2 varies in space.

The velocity difference v_{13} is related to the velocity differences V_{13} , V_{43} and V_{53} by the relation

$$v_{13} = (X_1 V_{13} + X_4 V_{43}) / (X_1 + X_4) - (X_4 V_{43} + X_5 V_{53}) / (X_3 + X_4 + X_5). \quad (9)$$

By introducing (8) into (9) one obtains

$$v_{13} = \alpha V_{13} + \frac{1}{2} (1 - \alpha) (V_{43} - V_{53}), \quad (10a)$$

and by analogy

$$v_{23} = \alpha V_{23} + \frac{1}{2} (1 - \alpha) (V_{53} - V_{43}). \quad (10b)$$

The relations between the friction coefficients in the two models result from two requirements:

- (i) Given v_{13} and v_{23} , the energy dissipation per unit volume must be the same in the two models.
- (ii) Given v_{13} and v_{23} , the energy dissipation must be minimal in the IDM.

The first requirement is expressed by the relation

$$\begin{aligned} \sum_k \left(\sum_i x_i r_{ik} v_{ik} \right) x_k v_{k3} \\ = \frac{1}{2} (1 + \alpha) \sum_k \left(\sum_i x_i R_{ik} V_{ik} \right) X_k V_{k3}, \end{aligned} \quad (11)$$

where the factor $\frac{1}{2} (1 + \alpha)$ takes account of the fact that in the IDM the number of particles in a given volume depends on α . The mole fractions given by (6) and (8), respectively, and our friction coefficients

$$\begin{aligned} r_{+-} &= r_{13} = r_{23}, & r_{++} &= r_{12}, \\ R_{+-} &= R_{13} = R_{23}, & R_{++} &= R_{12}, \\ R_{+0} &= R_{14} = R_{15} = R_{24} = R_{25}, \\ R_{-0} &= R_{34} = R_{35}, & R_{00} &= R_{45} \end{aligned} \quad (12)$$

must be introduced into (11). We also relate all velocities to the species 3 in the respective model and drop the subscript 3 in the velocity differences for simplicity. One then obtains from (11)

$$\begin{aligned} (2r_{+-} + r_{++}) (v_1^2 + v_2^2) - 2r_{++} v_1 v_2 \\ = A(V_1^2 + V_2^2) - B V_1 V_2 - C(V_1 + V_2)(V_4 + V_5) \\ + D(V_4 - V_5)^2 + E(V_4^2 + V_5^2) \end{aligned} \quad (13)$$

with

$$\begin{aligned} A &= 2[x^2(2R_{+-} + R_{++}) + 2\alpha(1 - \alpha)R_{+0}]/(1 + \alpha), \\ B &= 4x^2 R_{++}/(1 + \alpha), \\ C &= 4\alpha(1 - \alpha)R_{+0}/(1 + \alpha), \\ D &= 2(1 - \alpha)^2 R_{00}/(1 + \alpha), \\ E &= 4\alpha(1 - \alpha)(R_{+0} + R_{-0})/(1 + \alpha). \end{aligned} \quad (14a, b, c, d, e)$$

With (10) the l.h.s. of (13) becomes

$$a(V_1^2 + V_2^2) - bV_1V_2 + c(V_1 - V_2)(V_4 - V_5) + d(V_4 - V_5)^2$$

with

$$\begin{aligned} a &= x^2(2r_{+-} + r_{++}), \\ b &= 2x^2r_{++}, \\ c &= 2x(1-x)(r_{+-} + r_{++}), \\ d &= (1-x)^2(r_{+-} + r_{++}). \end{aligned} \quad (15 \text{ a, b, c, d})$$

The second requirement is expressed by the relation

$$\begin{aligned} &[2AV_1 - BV_2 - C(V_4 + V_5)]dV_1 \\ &+ [2AV_2 - BV_1 - C(V_4 + V_5)]dV_2 \\ &+ [-C(V_1 + V_2) + 2D(V_4 - V_5) + 2EV_4]dV_4 \\ &+ [-C(V_1 + V_2) - 2D(V_4 - V_5) + 2EV_5]dV_5 = 0 \end{aligned} \quad (16)$$

with the accessory conditions $dv_1 = 0$ and $dv_2 = 0$, i.e., using (10), with the accessory conditions

$$\begin{aligned} x dV_1 + \frac{1}{2}(1-x)dV_4 - \frac{1}{2}(1-x)dV_5 &= 0, \\ x dV_2 - \frac{1}{2}(1-x)dV_4 + \frac{1}{2}(1-x)dV_5 &= 0. \end{aligned} \quad (17 \text{ a, b})$$

By adding (17a) and (17b), after multiplication with two arbitrary multipliers, to (16) one obtains (Lagrange) four independent relations between V_1 , V_2 , V_4 , and V_5 which, by elimination of the multipliers, lead to two relations between these velocities. These two relations allow us to express V_4 and V_5 as functions of V_1 and V_2 .

One then eliminates V_4 and V_5 on both sides of (13) and obtains a homogeneous linear equation in $(V_1^2 + V_2^2)$ and V_1V_2 . Since V_1 and V_2 are free variables, the coefficients in this equation of both $(V_1^2 + V_2^2)$ and V_1V_2 , which are functions of r_{+-} , r_{++} , R_{+-} , R_{++} , R_{+0} , R_{-0} , R_{00} and x , must be zero, and these two equations allow us to express r_{+-} and r_{++} as functions of R_{+-} , R_{++} , R_{+0} , R_{-0} , R_{00} and x .

The performance of this calculation is tedious, the result, however, is so obvious that one wonders if there does not exist an easier way to derive it:

$$r_{+-} = \frac{2}{x(1+x)} \left[xR_{+-} + (1-x) \left(\frac{1}{R_{+0}} + \frac{1}{R_{-0}} \right)^{-1} \right], \quad (18 \text{ a})$$

$$r_{++} = \frac{2}{1+x} \left[\frac{x}{x(R_{+-} + R_{++}) + (1-x)R_{+0}} + \frac{1-x}{x(R_{+0} + R_{-0}) + (1-x)R_{00}} \right]^{-1} - r_{+-}, \quad (18 \text{ b})$$

and by analogy

$$r_{--} = \frac{2}{1+x} \left[\frac{x}{x(R_{+-} + R_{--}) + (1-x)R_{-0}} + \frac{1-x}{x(R_{+0} + R_{-0}) + (1-x)R_{00}} \right]^{-1} - r_{+-}. \quad (18 \text{ c})$$

By combining (5) with (18) one obtains

$$\frac{b_{+-}}{F} = x(1+x) \left[xR_{+-} + (1-x) \left(\frac{1}{R_{+0}} + \frac{1}{R_{-0}} \right)^{-1} \right]^{-1}, \quad (19 \text{ a})$$

$$\frac{D_+}{RT} = (1+x) \left[\frac{x}{x(R_{+-} + R_{++}) + (1-x)R_{+0}} + \frac{1-x}{x(R_{+0} + R_{-0}) + (1-x)R_{00}} \right], \quad (19 \text{ b})$$

$$\frac{D_-}{RT} = (1+x) \left[\frac{x}{x(R_{+-} + R_{--}) + (1-x)R_{-0}} + \frac{1-x}{x(R_{+0} + R_{-0}) + (1-x)R_{00}} \right]. \quad (19 \text{ c})$$

If the IDM-friction coefficients are to have a physical meaning in the sense of the expression (1), they have to be positive. This shall be assumed in the following.

From (18) and (19) one sees that

i) for $x = 1$: $r_{+-} = R_{+-}$, $r_{++} = R_{++}$, $r_{--} = R_{--}$,

$$\begin{aligned} \frac{b_{+-}}{F} &= \frac{2}{R_{+-}}, \quad \frac{D_+}{RT} = \frac{2}{R_{+-} + R_{--}}, \\ \frac{D_-}{RT} &= \frac{2}{R_{+-} + R_{--}}; \end{aligned}$$

ii) for $x = 0$: $r_{+-} = \infty$, $r_{++} = -\infty$, $r_{--} = -\infty$,

$$\frac{b_{+-}}{F} = 0, \quad \frac{D_+}{RT} = \frac{1}{R_{00}}, \quad \frac{D_-}{RT} = \frac{1}{R_{00}};$$

iii) r_{+-} and b_{+-} are independent of R_{++} , R_{--} and R_{00} ,

r_{++} and D_+ are independent of R_{--} ,

r_{--} and D_- are independent of R_{++} .

In case of solid cation conductors the coefficients R_{00} and R_{-0} are very large compared to the other

friction coefficients. One then obtains from (19):

$$\frac{RT}{F} \frac{b_{+-}}{D_+ + D_-} = \frac{\alpha(R_{+-} + R_{++}) + (1 - \alpha) R_{+0}}{\alpha R_{+-} + (1 - \alpha) R_{+0}}. \quad (20)$$

As expected from (20), $RTb_{+-}/F(D_+ + D_-)$ has been found to be greater than unity for solid cation conductors, e.g. 2.0 for α -AgI [7].

In case of partly ionized rarified gases the distribution of the particles is random and multiparticle collisions are not involved. The friction coefficients occurring in (19) result then from the physics of binary collisions.

For molten salts it can reasonably be assumed that the six friction coefficients are of the same order of magnitude. In view of the lack of further information about the friction coefficients one could try to cut the Gordian knot by putting

$$R_{+-} = R_{+0} = R_{-0} = R_{00} = R_{++} = R_{--} \equiv \tilde{R}, \quad (21)$$

which with (19) would lead to (22a, b, c)

$$b_{+-}/F = 2\alpha/\tilde{R}, \quad D_+/RT = 1/\tilde{R}, \quad D_-/RT = 1/\tilde{R}.$$

Equations (22b and c) would, however, not be satisfactory since generally $D_+ \neq D_-$. As to (22a), one may pragmatically replace $1/\tilde{R}$ by the arithmetic mean $(D_+ + D_-)/2RT$ and obtain an apparent degree of dissociation of molten 1:1 salts:

$$\alpha_{\text{app}} = \frac{RT}{F} \frac{b_{+-}}{D_+ + D_-}. \quad (23)$$

α_{app} ranges from 0.93 for NaCl [8] to 0.51 for TiCl [5] and decreases with temperature.

It should be possible to find an analogue of the apparent degree of dissociation of molten salts in Ion Dynamics Simulations. Okada et al. [9] have introduced a transport property which they call Self Exchange Velocity (SEV) of neighbouring unlike ions. The SEV divided by a suitable average center of mass velocity of the unlike ions is a candidate for such an analogue. It should be larger for NaCl than for TiCl melts and should decrease with temperature if the density is adjusted to that at constant pressure at every temperature.

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