Electrical Transport Phenomena in Molten Salts

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The equivalent conductivity of molten salts containing more than two ion constituents will be discussed using *the equivalent fractions* (Äquivalentanteile). The ionic conductivities of the ion constituents follow from this equivalent conductivity and the transport numbers. The electrical transport phenomena are referred to the *idealized* ionic melt which is defined by the limiting values of the ionic conductivities of the ion constituents in the pure components. The equations are calculated for the system $KNO_3 + AgNO_3$.

Es wird die Äquavilentleitfähigkeit bei Salzschmelzen mit mehr als zwei ionischen Bestandteilen mit Hilfe von *Äquivalentanteilen* diskutiert. Aus dieser Äquivalentleitfähigkeit und den Überführungszahlen ergeben sich mit den Äquivalentanteilen die Ionenleitfähigkeiten der ionischen Bestandteile. Die elektrischen Transportphänomene werden auf eine *idealisierte* Salzschmelze normiert, die mit den Grenzwerten der Ionenleitfähigkeiten der ionischen Bestandteile in den reinen Komponenten definiert wird. Die Gleichungen werden berechnet für das System $KNO_3 + AgNO_3$.

The purpose of the following investigation is the definition of the equivalent conductivity of molten salts containing more than two ion constituents. In the literature the term "equivalent conductivity" is ambiguous and in most cases one does not seem to be aware of this ambiguity. By a logical definition, deduced from the conditions of electrical neutrality, one can define the equivalent concentration and with that the equivalent conductivity of multicomponent molten salts (and mixtures of organic acids without water). From this we can derive the ionic conductivities of the ion constituents and the limiting values of these in the pure components. By these limiting values we define an *idealized* ionic melt, to which the electrical transport phenomena can be referred.

Equivalent Conductance

We consider an ionic melt with n components which are composed each of two ion constituents:

$$A_{\nu_{1+}} B_{\nu_{1-}} + C_{\nu_{2+}} D_{\nu_{2-}} + \dots + Y_{\nu_{n+}} Z_{\nu_{n-}} . \qquad (1)$$

The subscript of the components is $k = 1, \dots, n$ and of the ion constituents $a = 1+, 1-, \dots, n+, n-$. In particular, $k+$ is the cationic and $k-$ the anionic constituent of component k. The symbol ν_a denotes the dissociation number of the ion constituent a. System (1) includes molten salts in which one ion constituent belongs to several components. Then the melt consists of $N \leqq 2\,n$ ion constituents.

The internal condition of electrical neutrality for *one* component of the system is

$$z_{k+}\, c_{k+} + z_{k-}\, c_{k-} = 0 , \qquad (2)$$

where z_{k+} and z_{k-} denote the charge numbers and c_{k+} and c_{k-} the molarities of the cationic and anionic constituent of the component considered, respectively. The equivalent concentration c_k^* of this component is defined by

$$c_k^* \equiv z_{k+}\, c_{k+} = |\, z_{k-} \,|\, c_{k-} . \qquad (3)$$

For the *total* system (1) the condition of electric neutrality is

$$\sum_a^N z_a\, c_a = 0 . \qquad (4)$$

Thus we can define the equivalent concentration c of the melt (1):

$$c^{\square} \equiv \sum_k^n c_k^* = \sum_k^n z_{k+}\, \nu_{k+}\, c_k = \sum_k^n |\, z_{k-} \,|\, \nu_{k-}\, c_k \qquad (5)$$

using the relations

$$c_{k+} = \nu_{k+}\, c_k , \qquad c_{k-} = \nu_{k-}\, c_k \qquad (6)$$

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where c_k denotes the molarity of component k.

The conductance $\varkappa$ of system (1) is related to the ionic mobility ${}_\mathrm{i}u_a$ and the ionic conductivity ${}_\mathrm{i}\lambda_a$, respectively, of the ion constituent a with reference to the ion constituent i (${}_\mathrm{i}\lambda_a = F\,{}_\mathrm{i}u_a$, ${}_\mathrm{i}\lambda_\mathrm{i} = {}_\mathrm{i}u_\mathrm{i} = 0$, F = Faraday constant) in the following way[1]:

$$\varkappa = F \sum_a^N |z_a|\, c_a\, {}_\mathrm{i}u_a = \sum_a^N |z_a|\, c_a\, {}_\mathrm{i}\lambda_a \,. \qquad (7)$$

From Eq. (5) and (7) we obtain the equivalent conductivity Λ:

$$\Lambda \equiv \varkappa / c^\square = F \sum_a^N |z_a|\, c_a\, {}_\mathrm{i}u_a / c^\square = \sum_a^N y_a\, {}_\mathrm{i}\lambda_a \,. \qquad (8)$$

The abbreviation

$$y_a \equiv |z_a|\, c_a / c \qquad (9)$$

will be called the "equivalent fraction" (Äquivalentanteil) of the ion constituent a **.

For aqueous electrolyte solutions with two components (water + one electrolyte), we have

$$y_+ = y_- = 1 \quad \text{and thus} \quad \Lambda = {}_1\lambda_+ + {}_1\lambda_- \,.$$

If the system contains more solute components, the equivalent conductivity of such a system is also given by Eq. (8).

From Eq. (5) and (9) we obtain the identity

$$\sum_k^n y_{k+} = \sum_k^n y_{k-} = 1 \,, \qquad (10)$$

and from Eq. (3) and (9) for the equivalent fractions of each component

$$y_{k+} = y_{k-} \equiv y_k \,. \qquad (11)$$

With Eq. (11) we can write Eq. (8) in the form

$$\Lambda = \sum_k^n y_k ({}_\mathrm{i}\lambda_{k+} + {}_\mathrm{i}\lambda_{k-}) \,. \qquad (12)$$

The proper composition variables for molten salts are the true mole fractions of the ion constituents

$$x_{k+} \equiv \frac{c_{k+}}{\sum\limits_k^n \nu_{k+}\, c_k} \,, \qquad x_{k-} \equiv \frac{c_{k-}}{\sum\limits_k^n \nu_{k-}\, c_k} \qquad (13\,\mathrm{a})$$

and the stoichiometric mole fraction of the component k

$$x_k \equiv \frac{c_k}{\sum\limits_k^n c_k} \,, \qquad (13\,\mathrm{b})$$

respectively. The equivalent fractions are then

$$y_{k+} = \frac{z_{k+}\, \nu_{k+}\, x_k + \sum\limits_l z_{l+}\, \nu_{l+}\, x_l}{\sum\limits_k^n z_{k+}\, \nu_{k+}\, x_k} \,. \qquad (13\,\mathrm{c})$$

The sum in the numerator is to be extended over the components, which have an ion constituent in common with k, the sum in the denominator over all components. y_{k-} is analogous.

The stoichiometric transport number ${}_\mathrm{i}\vartheta_a$ of the ion constituent a referred to the ion constituent i is defined by

$${}_\mathrm{i}\vartheta_a \equiv (|z_a|\, c_a / \varkappa)\, {}_\mathrm{i}\lambda_a \,, \qquad {}_\mathrm{i}\lambda_a = y_a\, {}_\mathrm{i}\lambda_a / \Lambda \,. \qquad (14)$$

From this we obtain:

$${}_\mathrm{i}\lambda_a = {}_\mathrm{i}\vartheta_a\, \Lambda / y_a \,. \qquad (15)$$

Limiting Cases

The definition (8) of the equivalent conductivity is clear and convenient because Λ of the mixture can be related to the equivalent conductivity $\Lambda_k^\cdot$ of the pure component k. We must distinguish between two cases for these limiting values:

1. *The pure component k contains the reference constituent* i. The counter-ion of component k belonging to i will be called j. Then there follows from Eq. (12):

$$\lim_{y_k \to 1} \Lambda \equiv \Lambda_k^\cdot = {}_\mathrm{i}\lambda_j^\cdot \qquad (16)$$

with

$$\Lambda_k^\cdot = \frac{\varkappa_k^\cdot}{c_k^{*\cdot}} = \varkappa_k^\cdot / |z_i|\, \nu_{ki}\, c_k^\cdot = \varkappa^\cdot\, V_k^\cdot / |z_i|\, \nu_{ki} \,. \qquad (17)$$

Here $\varkappa_k^\cdot$ denotes the the conductance, $c_k^{*\cdot}$ the equivalent concentration, $c_k^\cdot$ the molarity and $V_k^\cdot$ the molar volume of component k in the pure state.

2. *The pure component k does not contain the reference constituent* i. In this case ${}_\mathrm{i}\lambda_{k+}$ and ${}_\mathrm{i}\lambda_{k-}$ are

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[1] J. RICHTER, Ber. Bunsenges. Physik. Chem. **72**, 681 [1968].

** BLOOM and HEYMANN[2] used the "equivalent fractions f_i" for the calculation of the equivalent weights and AZIZ and WETMORE[3] defined the "transport fractions Θ_i", in order to avoid any ambiguity about defining transport numbers for salt melts. These terms are not identical with our „equivalent fractions y_a", which are suitable for the definition of the equivalent conductivity and of all consequences following from this. Blooms "equivalent fractions f_i" do not exist in the later literature any more. The "transport fractions Θ_i" of Aziz and Wetmore are sometimes used for the definition of the transport numbers, cf. e. g. LAITY[4].

[2] H. BLOOM and E. HEYMANN, Proc. Roy. Soc. London **A 188**, 392 [1947].

[3] P. M. AZIZ and F. E. W. WETMORE, Can. J. Chem. **30**, 779 [1952].

[4] R. LAITY, J. Chem. Phys. **30**, 682 [1952].

meaningless at $c^{\square} = c_k^{*\cdot}$. However, it is to be expected that ${}_{\mathrm{i}}\lambda_{k+}$ and ${}_{\mathrm{i}}\lambda_{k-}$, as well as the transport numbers ${}_{\mathrm{i}}\vartheta_{k+}$ and ${}_{\mathrm{i}}\vartheta_{k-}$ have finite limiting values. Thus we derive from Eq. (12):

$$\lim_{y_k \to 1} \Lambda \equiv \Lambda_k^{\cdot} = {}_{\mathrm{i}}\lambda_{k+}^{\cdot} + {}_{\mathrm{i}}\lambda_{k-}^{\cdot} \tag{18}$$

and from Eq. (14):

$$\lim_{y_k \to 1} {}_{\mathrm{i}}\vartheta_{k+} \equiv {}_{\mathrm{i}}\vartheta_{k+}^{\cdot} = \frac{{}_{\mathrm{i}}\lambda_{k+}^{\cdot}}{\Lambda_k^{\cdot}}, \quad \lim_{y_k \to 1} {}_{\mathrm{i}}\vartheta_{k-} \equiv {}_{\mathrm{i}}\vartheta_{k-}^{\cdot} = \frac{{}_{\mathrm{i}}\lambda_{k-}^{\cdot}}{\Lambda_k^{\cdot}}$$

where (19)

$${}_{\mathrm{i}}\vartheta_{k+}^{\cdot} + {}_{\mathrm{i}}\vartheta_{k-}^{\cdot} = 1 \, . \tag{20}$$

[At finite concentrations, we have ${}_{\mathrm{i}}\vartheta_{k+} + {}_{\mathrm{i}}\vartheta_{k-} \neq 1$ (<1).]

Eqs. (16), and (18) to (20) are logical limiting cases. They show that the treatment developed above is consistent and straightforward.

The contrary limiting cases are obtained for $y_k \to 0$. The transport numbers at these limits tend towards zero, according to Eq. (14), irrespective of the value of the ionic conductivity (except ${}_{\mathrm{i}}\lambda_{\alpha} = \infty$). The limiting value of the ionic conductivity ${}_{\mathrm{i}}\lambda_{\alpha}^{\infty}$ is a measure of the mobility of the ion constituent α at infinite dilution in one of the other components and therefore finite and non-zero.

It is to be expected that ${}_{\mathrm{i}}\vartheta_{\alpha}$ at $y_m \to 1$ (m denotes the component considered as solvent) is a linear function in y_{α}:

$${}_{\mathrm{i}}\vartheta_{\alpha} = {}_{\mathrm{i}}g_{\alpha}^{\infty(m)}\, y_{\alpha}\, , \quad (y_m \to 1) \tag{21}$$

where ${}_{\mathrm{i}}g_{\alpha}^{\infty(m)}$ is a constant characteristic of α and of m and finite as well as non-zero.

From Eq. (15) and (21) there follows:

$$\lim_{y_m \to 1} {}_{\mathrm{i}}\lambda_{\alpha} \equiv {}_{\mathrm{i}}\lambda_{\alpha}^{\infty(m)} = {}_{\mathrm{i}}g_{\alpha}^{\infty(m)} \Lambda_m^{\cdot} \, . \tag{22}$$

${}_{\mathrm{i}}\lambda_{\alpha}^{\infty(m)}$ is finite and different from zero, too. But it does not contribute anything to the equivalent conductivity of the system in this limiting state, because, according to Eq. (9), the equivalent fraction is zero. So the consistence of our method is achieved.

For each ion constituent there are one value of ${}_{\mathrm{i}}\lambda_{\alpha}^{\cdot}$ and $n-1$ values of ${}_{\mathrm{i}}\lambda_{\alpha}^{\infty(m)}$, which are determined by etxtrapolation of ${}_{\mathrm{i}}\vartheta_{\alpha}$ versus y_{α}.

Idealized Salt Melt

We call a molten salt "idealized", if the ionic conductivity remains constant within the total range of composition:

$${}_{\mathrm{i}}\lambda_{\alpha} = {}_{\mathrm{i}}\lambda_{\alpha}^{\cdot} = {}_{\mathrm{i}}\lambda_{\alpha}^{\infty} \, . \tag{23}$$

For a better estimation of the deviation from the idealized case, we introduce the excess function

$$\Lambda^{\mathrm{E}} \equiv \Lambda - \Lambda^{\mathrm{id}} \tag{24}$$

where, due to Eq. (12), (18), and (23):

$$\Lambda^{\mathrm{id}} = \sum_{k}^{n} y_k ({}_{\mathrm{i}}\lambda_{k+}^{\cdot} + {}_{\mathrm{i}}\lambda_{k-}^{\cdot}) = \sum_{k}^{n} y_k \Lambda_k^{\cdot} \, . \tag{25}$$

Λ^{id} is the equivalent conductivity in the idealized state defined above. From Eq. (24) there follows with Eq. (12) and (25):

$$\Lambda^{\mathrm{E}} = \sum_{k}^{n} y_k [({}_{\mathrm{i}}\lambda_{k+} - {}_{\mathrm{i}}\lambda_{k+}^{\cdot}) + ({}_{\mathrm{i}}\lambda_{k-} - {}_{\mathrm{i}}\lambda_{k-}^{\cdot})] \, . \tag{26}$$

If we insert Eq. (23) into Eq. (14) and consider Eq. (25), we obtain the transport numbers of the idealized melt:

$${}_{\mathrm{i}}\vartheta_{\alpha}^{\mathrm{id}} = y_{\alpha}\, {}_{\mathrm{i}}\lambda_{\alpha}^{\cdot} / \Lambda^{\mathrm{id}} \, . \tag{27}$$

We shall test these equations for a type of melt which is most frequently investigated in the literature. The melt consists of two components and three ion constituents, e. g.

$$\mathrm{NaCl}(1) + \mathrm{CaCl_2}(2) \, . \tag{28}$$

The common ion constituent is chosen as reference ion i. The ion constituent occurring in component 1 only will be denoted by a, the one occurring in component 2 only will be denoted by b. The equivalent conductivity results from Eq. (8) with (5) in the x-scale:

$$\Lambda = \varkappa / c^{\square} = \varkappa \bar{V} / (z_{\mathrm{a}} \nu_{\mathrm{a}} x_1 + z_{\mathrm{b}} \nu_{\mathrm{b}} x_2) = \varkappa V^{\square} \, . \tag{29}$$

$\bar{V}$ is the molar volume, $V^{\square}$ the equivalent volume of the melt.

From Eq. (15) with (10) we obtain the ionic conductivities:

$${}_{\mathrm{i}}\lambda_{\mathrm{a}} = {}_{\mathrm{i}}\vartheta_{\mathrm{a}}\, \Lambda / y_{\mathrm{a}}\, , \quad {}_{\mathrm{i}}\lambda_{\mathrm{b}} = (1 - {}_{\mathrm{i}}\vartheta_{\mathrm{a}}) \Lambda / (1 - y_{\mathrm{a}}) \, . \tag{30}$$

In particular, for uni-univalent electrolytes we have:

$$y_{\mathrm{a}} = x_1\, , \qquad y_{\mathrm{b}} = 1 - x_1\, , \tag{31}$$

$${}_{\mathrm{i}}\lambda_{\mathrm{a}} = {}_{\mathrm{i}}\vartheta_{\mathrm{a}}\, \Lambda / x_1\, , \quad {}_{\mathrm{i}}\lambda_{\mathrm{b}} = (1 - {}_{\mathrm{i}}\vartheta_{\mathrm{a}}) \Lambda / (1 - x_1) \, . \tag{32}$$

From Eq. (12) there follows:

$$\Lambda = y_{\mathrm{a}}\, {}_{\mathrm{i}}\lambda_{\mathrm{a}} + (1 - y_{\mathrm{a}})\, {}_{\mathrm{i}}\lambda_{\mathrm{b}} \, . \tag{33}$$

From Eq. (31) we thus obtain:

$$\Lambda = x_1\, {}_{\mathrm{i}}\lambda_{\mathrm{a}} + (1 - x_1)\, {}_{\mathrm{i}}\lambda_{\mathrm{b}} \, . \tag{34}$$

In view of Eqs. (33) and (34), the limiting values of Λ are:

$$\lim_{y_1 \to 1} \Lambda \equiv \Lambda_1^{\cdot} = {}_i\lambda_a^{\cdot}\,, \quad \lim_{y_2 \to 1} \Lambda \equiv \Lambda_2^{\cdot} = {}_i\lambda_b^{\cdot}\,. \tag{35}$$

According to Eq. (25), we have:

$$\Lambda^{id} = y_a\, {}_i\lambda_a^{\cdot} + (1 - y_a)\, {}_i\lambda_b^{\cdot}\,. \tag{36}$$

This is a linear function in y_a. The excess function Λ^E follows from Eq. (26):

$$\Lambda^E = y_a ({}_i\lambda_a - {}_i\lambda_a^{\cdot}) + (1 - y_a)({}_i\lambda_b - {}_i\lambda_b^{\cdot})\,. \tag{37}$$

The graphical plots of Λ, Λ^{id} and Λ^E versus y_a give the usual pictures of the thermodynamic excess functions [5]. Just like in the last case the deviations from Λ^{id} may be positive or negative. Thus we can expect positive or negative deviations of the ionic conductivities from ${}_i\lambda_\alpha^{\cdot} = {}_i\lambda_\alpha^{\infty}$.

For the transport numbers, the schematic diagram (Fig. 1) follows from Eq. (30), if we choose ${}_i\lambda_a > \lambda_a^{\cdot}$, ${}_i\lambda_b < {}_i\lambda_b^{\cdot}$ and ${}_i\lambda_a^{\cdot} > {}_i\lambda_b^{\cdot}$:

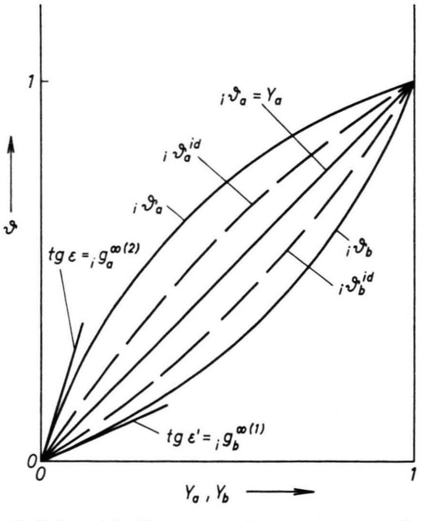

Fig. 1. Schematic diagram of the transport numbers.

The drawn lines represent the transport numbers of the melt, the tangent of its initial slope is the constant of Eq. (21). The shaded lines are the transport numbers of the idealized melt and the straight line is the case

$${}_i\vartheta_a = y_a\,, \qquad {}_i\vartheta_b = 1 - y_a\,. \tag{38}$$

According to Eq. (30) this is equal to

$${}_i\lambda_a = {}_i\lambda_b = \Lambda\,. \tag{39}$$

This case will seldom occur. It is much more likely that the conditions (38) and (39) are satisfied for a certain composition of the system (Fig. 2). The two ion constituents have the same mobility at this composition, i. e. the system can be considered to be a pseudo-unicomponent-system as far as the conductivity at this particular composition is concerned. A typical example of this phenomen is the system [6] $NaNO_3 + AgNO_3$.

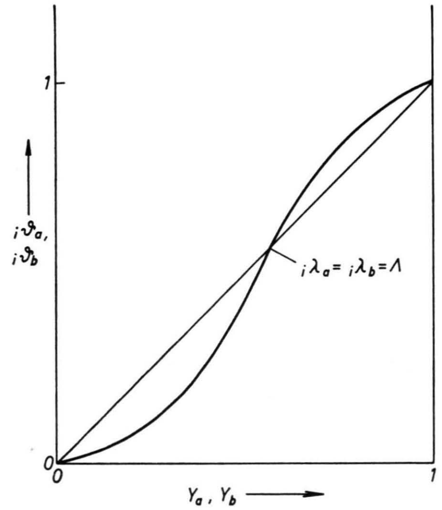

Fig. 2. Schematic diagram of the case ${}_i\lambda_a = {}_i\lambda_b = \Lambda$.

The transport numbers of the idealized melt, to which we referred the electrical transport phenomena in a melt of type (28), are, in view of Eq. (27):

$${}_i\vartheta_a^{id} = y_a\, {}_i\lambda_a^{\cdot}/\Lambda^{id}, \quad {}_i\vartheta_b^{id} = (1 - y_a)\, {}_i\lambda_b^{\cdot}/\Lambda^{id}\,. \tag{40}$$

Example

To illustrate our equations, we choose a system expected to be an idealized melt in view of the similar values of the ionic radii. Of course, there are many examples where the conductivities deviate from the conductivity of the idealized melt, but these examles are not so informative in our case. Moreover, there are no experimental values of transport numbers for most melts, and these values, besides conductivities, are necessary for the calculations.

We consider the melt

$$KNO_3(1) + AgNO_3(2) \tag{41}$$

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[5] J. Richter, Z. Naturforsch. **24 a**, 835 [1969].

[6] J. Richter and E. Amkreutz, Z. Naturforsch., to be published.

Table 1. The conductivities of the melt KNO_3+AgNO_3 and of the corresponding idealized melt at 300 °C, as functions of the mole fraction x_{AgNO_3} of silver nitrate.

x_{AgNO_3}	$\frac{\Lambda \cdot 10^4}{\Omega^{-1}\,m^2\,mol^{-1}}$	$\frac{\lambda_{K^+} \cdot 10^4}{\Omega^{-1}\,m^2\,mol^{-1}}$	$\frac{\lambda_{Ag^+} \cdot 10^4}{\Omega^{-1}\,m^2\,mol^{-1}}$	$\frac{\Lambda^{id} \cdot 10^4}{\Omega^{-1}\,m^2\,mol^{-1}}$	$\frac{\Lambda^{E} \cdot 10^4}{\Omega^{-1}\,m^2\,mol^{-1}}$
1,0	45,8390	—	—	45,8390	—
0,9	44,0938	37,9210	44,7797	43,9341	+ 0,1597
0,8	42,0409	33,8430	44,0904	42,0292	+ 0,0117
0,7	40,2235	31,2403	44,0734	40,1243	+ 0,0992
0,6	38,2497	29,4523	44,1147	38,2194	+ 0,0303
0,5	36,2872	28,7394	43,8350	36,3145	— 0,0273
0,4	34,5130	29,0485	42,7098	34,4096	+ 0,1034
0,3	32,5964	29,1040	40,7457	32,5047	+ 0,0918
0,2	30,3980	28,4981	37,9975	30,5998	— 0,2018

at 300 °C. The densities and conductivities of this system were determined by BRILLANT[7], the transport numbers by OKADA and KAWAMURA[8]. The quantities Λ, Λ^{id} and Λ^{E} of the melt (41) are computed according to Eqs. (29), (31), (36), and (37). λ_{K^+} and λ_{Ag^+} are obtained from Eq. (32).

The values are given in Table 1. They are plotted in Fig. 3. Neither λ_{Ag^+} nor λ_{K^+} observe the condition (23) of the idealized melt. λ_{Ag^+} decreases in the total concentration range, whereas λ_{K^+} increases. It is: $\lambda_{K^+} > \lambda^{\cdot}_{K^+}$, $\lambda_{Ag^+} < \lambda^{\cdot}_{Ag^+}$ and $\lambda^{\cdot}_{Ag^+} > \lambda^{\cdot}_{K^+}$. Λ and Λ^{id} give straight lines, within experimental accuracy. Therefore we need no graph for Λ^{E}, which would only be a measure of this accuracy. The decrease of the ionic conductivity λ_{Ag^+} and the simultaneous increase of λ_{K^+} effect a compensation so that Λ of the melt is equal to Λ^{id} of the idealized melt. In this way the conductivity of melt (41) shows the same behaviour as does the conductivity of the idealized melt, although the ionic conductivities of the ion constituents do not behave in the idealized manner.

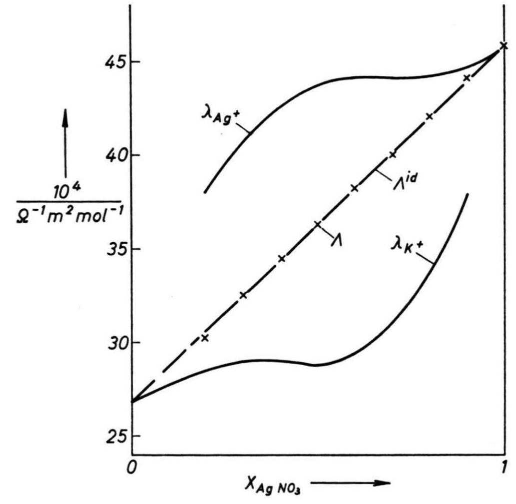

Fig. 3. λ_{Ag^+}, λ_{K^+}, Λ, and Λ^{id} of the melt KNO_3+AgNO_3 at 300 °C.

That means that we can split ${}_{\mathrm{i}}\lambda_{\mathrm{a}}$ and ${}_{\mathrm{i}}\lambda_{\mathrm{b}}$ in a constant and in a term depending on composition:

$$ {}_{\mathrm{i}}\lambda_{\mathrm{a}} = {}_{\mathrm{i}}\lambda^{\cdot}_{\mathrm{a}} + \varphi_{\mathrm{a}} , \tag{42} $$

$$ {}_{\mathrm{i}}\lambda_{\mathrm{b}} = {}_{\mathrm{i}}\lambda^{\cdot}_{\mathrm{b}} + \varphi_{\mathrm{b}} . \tag{43} $$

φ_{a} and φ_{b} are the quantities which describe the deviation of ${}_{\mathrm{i}}\lambda^{\cdot}_{\mathrm{a}}$ and ${}_{\mathrm{i}}\lambda^{\cdot}_{\mathrm{b}}$ depending on the composition.

From Eq. (34) we obtain

$$ \Lambda = x_1\, {}_{\mathrm{i}}\lambda^{\cdot}_{\mathrm{a}} + x_1\, \varphi_{\mathrm{a}} + (1-x_1)\, {}_{\mathrm{i}}\lambda^{\cdot}_{\mathrm{b}} + (1-x_1)\, \varphi_{\mathrm{b}} . \tag{44} $$

In consequence of the compensation mentioned above we find

$$ x_1\, \varphi_{\mathrm{a}} + (1-x_1)\, \varphi_{\mathrm{b}} = 0 . \tag{45} $$

This condition is satisfied very well by system (41).

We see that it is easier to find some properties of an idealized melt than some of an ideal ionic melt in the thermodynamic sense[9] which is defined by

$$ \mu_k \equiv \mu^{\cdot}_k + R\,T \ln x_k \tag{46} $$

where μ_k denotes the chemical potential of the component k in the mixture, $\mu^{\cdot}_k$ that of the pure component k, and R the gas constant. Such an ideal melt seems to be rare. Even melt (41) deviates a little from condition (46) as the activity coefficients of KETELAAR[10] show.

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[7] S. BRILLANT, Rapport CEA-R-3545 (1968), CEN-Saclay P.B. Nr. 2, 91 — Gif sur Yvette, France.

[8] M. OKADA and K. KAWAMURA, Electrochim. Acta **15**, 1 [1970].

[9] R. HAASE, Z. Physik. Chem. (Frankfurt) **63**, 95 [1969].

[10] J. A. A. KETELAAR and A. DAMMERS-DE KLERK, Proc. Nederl. Ak. **68**, B, 169 [1965].

$x_{\mathrm{AgNO_3}}$	$\vartheta_{\mathrm{Ag^+}}$	$\vartheta^{\mathrm{id}}_{\mathrm{Ag^+}}$	$\vartheta_{\mathrm{K^+}}$	$\vartheta^{\mathrm{id}}_{\mathrm{K^+}}$
1,0	1,000	1,000	0,000	0,000
0,9	0,914	0,939	0,086	0,061
0,8	0,839	0,873	0,161	0,127
0,7	0,767	0,800	0,233	0,200
0,6	0,692	0,720	0,308	0,280
0,5	0,604	0,631	0,396	0,369
0,4	0,495	0,533	0,505	0,467
0,3	0,375	0,423	0,625	0,577
0,2	0,250	0,300	0,750	0,700
0,0	0,000	0,000	1,000	1,000

Table 2. The transport number of the melt KNO_3+AgNO_3 and of the corresponding idealized melt at 300 °C, as functions of the mole fraction $x_{\mathrm{AgNO_3}}$ of silver nitrate.

The transport numbers of system (41) and the values of $\vartheta^{\mathrm{id}}_{\mathrm{Ag^+}}$ and $\vartheta^{\mathrm{id}}_{\mathrm{K^+}}$ derived from Eq. (40) are summarized in Table 2. They are plotted in Fig. 4. We find $\vartheta^{\mathrm{id}}_{\mathrm{Ag^+}} > \vartheta_{\mathrm{Ag^+}}$ and $\vartheta^{\mathrm{id}}_{\mathrm{K^+}} < \vartheta_{\mathrm{K^+}}$, although they do not deviate much from the idealized behaviour, as a consequence of the compensation effect mentioned above.

The constants $g^{\infty}_{\mathrm{K^+}}$ and $g^{\infty}_{\mathrm{Ag^+}}$ of Eq. (21) cannot be safely determined from Fig. 4; for the jump in the composition from $x=0$ to $x=0.1$ and 0.2, respectively, is too great to derive limiting values – the usual situation in molten salts.

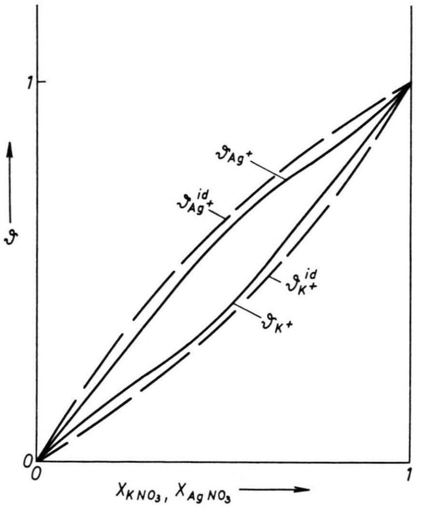

Fig. 4. The transport numbers of the melt KNO_3+AgNO_3 at 300 °C.

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