

The series and parallel models of electrical conductivity of molten salt mixtures

I. Binary mixtures with simple halide anions

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The series and parallel models of electrical conductivity of molten mixtures are derived. It is shown that the parallel model is identical with the additive model of molar electrical conductivity. The series model appears to be suitable for definition of the ideal conductance of molten mixtures. Applying these models conductivity of molten halide mixtures is calculated and compared with experimental data.

Представлены групповая и параллельная модели электропроводности расплавленных смесей. Показано, что параллельная модель идентична аддитивной модели мольной электропроводности. Групповая модель оказывается подходящей для определения идеальной проводимости расплавленных смесей. Эти модели применены к расчету электропроводностей расплавленных галогенидных смесей и результаты сравнены с экспериментальными данными.

Recently it has been shown that using a suitable model we can successfully calculate the electrical conductivity of three component molten salt mixtures [1—3]. The calculations were based on the assumption that the ideal conductance behaviour can be represented by the additive model of molar conductivity of electrolyte. The model was considered to be empirical.

In this paper we shall give a physical background to this model. We shall also introduce a new model for electrical conductivity which appears to be more suitable for definition of the ideal conductance of molten mixtures.

Let us assume that we have an amount of molten substance A, n_A , and amount of molten substance B, n_B . If we denote volume of these melts as V_A and V_B it holds

$$V_A = n_A M_A / \rho_A = n_A V_A^0 \quad V_B = n_B M_B / \rho_B = n_B V_B^0 \quad (1)$$

where M_A and M_B are the molar masses of substance A and B, respectively, ρ_A , ρ_B are the densities of pure melts, and V_A^0 , V_B^0 are the molar volumes of pure molten

substances. We can imagine that these melts are placed in the conductivity cells which have a shape of cuboid. Let us connect the two cells in series (Fig. 1). The electrical resistance of the corresponding cell is given by the relationships

$$R_{A,s} = \frac{l_A}{\kappa_A S} \quad R_{B,s} = \frac{l_B}{\kappa_B S} \quad (2)$$

where κ_A and κ_B are the conductivities of pure substances A and B and l_A , l_B are the lengths of the corresponding cells and S is the area of the base of the conductivity cells.

As both cells are connected in series the total resistance of the system equals sum of the resistances $R_{A,s}$ and $R_{B,s}$. Now we mix the melts of molten substances A and B. According to the proposed series model we assume that resistance R_{mix} of the new (mixed) system equals sum of the resistances of the original cells

$$R_{\text{mix},s} = R_{A,s} + R_{B,s} \quad (3)$$

$$\frac{V_{\text{mix}}}{\kappa_{\text{mix},s} \cdot S^2} = \frac{V_A}{\kappa_A S^2} + \frac{V_B}{\kappa_B S^2} \quad (4)$$

where $\kappa_{\text{mix},s}$ is the conductivity of molten mixture A + B (the index s denotes that the conductivity was calculated according to the series model).

Since we deal with an ideal model we can assume in this approximation that also the volume of the molten mixture behaves ideally. Then we readily obtain from eqn (4) the final relationship

$$\frac{x_A V_A^0 + x_B V_B^0}{\kappa_{\text{mix},s}} = \frac{x_A V_A^0}{\kappa_A} + \frac{x_B V_B^0}{\kappa_B} \quad (5)$$

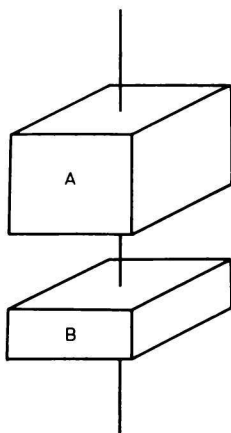


Fig. 1. Scheme of the series connection of conductivity cells.

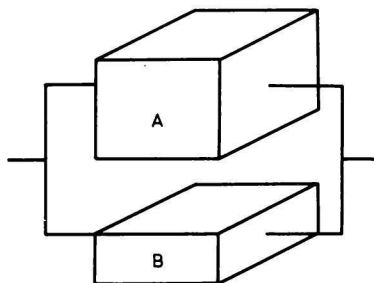


Fig. 2. Scheme of the parallel connection of conductivity cells.

Now we shall consider a parallel connection of both conductivity cells as it is illustrated in Fig. 2. Let us assume that the base of the cells is a square. Then it holds for resistance of each compartment (p denotes the parallel connection of the cells as shown in Fig. 2)

$$R_{A,p} = \frac{S}{\kappa_A V_A} \quad R_{B,p} = \frac{S}{\kappa_B V_B} \quad (6)$$

Conductance of the system equals sum of the reciprocal values of resistances of both cells. It follows

$$\frac{1}{R_{\text{mix},p}} = \frac{1}{R_{A,p}} + \frac{1}{R_{B,p}} \quad (7)$$

$$\frac{\kappa_{\text{mix},p} \cdot V_{\text{mix}}}{S} = \frac{\kappa_A V_A}{S} + \frac{\kappa_B V_B}{S} \quad (8)$$

After introducing mole fractions into eqn (8) (we again assume a thermodynamic ideal behaviour of the mixture) we obtain

$$\kappa_{\text{mix},p} (x_A V_A^0 + x_B V_B^0) = x_A V_A^0 \kappa_A + x_B V_B^0 \kappa_B \quad (9)$$

$\kappa_{\text{mix},p}$ is the conductivity calculated according to the parallel model. Because $\kappa_A V_A^0$ and $\kappa_B V_B^0$ are the molar conductivities of pure components it readily follows that this model is identical with the additive model for the molar conductivity of electrolyte.

Comparison of the experimentally determined conductivity and that calculated according to the parallel and series models for some molten mixtures of alkali metal halides and alkaline earth halides is presented in Table 1. The deviation of experimental data from the model is expressed as

$$\Delta / \% = 100(\kappa_{\text{exp}} - \kappa_{\text{calc}}) / \kappa_{\text{calc}} \quad (10)$$

Δ_p denotes deviation from the parallel model, Δ_s the deviation from the series model, and Δ_M deviation from Markov's model [4]. According to the latter model it holds (λ denotes the "equivalent" conductivity)

$$\lambda_{\text{mix},M} = x_A^2 \lambda_A^0 + x_B^2 \lambda_B^0 + 2x_A x_B \lambda_A^0 \quad (11)$$

$$\lambda_A^0 < \lambda_B^0$$

Experimental data on conductivity of mixtures of molten fluorides and chlorides are taken from [5, 6]. The data on conductivity of mixtures of molten bromides are taken from [7]. From the comparison of fitness of different models to experimentally determined conductivity at $x_A = 0.5$ (which corresponds approximately to the

Table 1

Comparison of the experimental conductivity and the conductivity calculated according to the parallel and series models for some molten halide mixtures

System		$\frac{\kappa_{\text{exp}}}{\text{S cm}^{-1}}$	$\frac{\kappa_p}{\text{S cm}^{-1}}$	$\frac{\kappa_s}{\text{S cm}^{-1}}$	$\left. \begin{array}{l} \Delta_p/\% \\ \Delta_s/\% \\ \Delta_M/\% \end{array} \right\} x_A = 0.5$
LiF—NaF $T = 1300 \text{ K}$	0.20	5.83	5.645	5.383	
	0.40	5.95	6.360	5.868	− 0.8
	0.50	6.70	6.756	6.177	+ 8.5
	0.62	7.04	7.271	6.630	+ 5.6
	0.70	7.52	7.642	7.001	
	0.85	8.64	8.403	7.907	
LiF—KF $T = 1200 \text{ K}$	0.20	3.72	4.311	4.012	
	0.35	3.69	4.812	4.267	− 29.9
	0.50	3.80	5.420	4.623	− 17.8
	0.70	4.59	6.471	5.402	− 27.9
	0.85	6.21	7.524	6.502	
NaCl—KCl $T = 1100 \text{ K}$	0.20	2.40	2.525	2.452	
	0.41	2.60	2.774	2.643	− 6.8
	0.51	2.71	2.907	2.758	− 1.7
	0.65	2.93	3.101	2.945	− 1.7
	0.73	3.05	3.217	3.069	
	0.85	3.30	3.403	3.292	
NaCl—BaCl ₂ $T = 1280 \text{ K}$	0.16	2.29	2.394	2.311	
	0.32	2.59	2.613	2.451	− 9.1
	0.52	2.66	2.926	2.683	− 0.9
	0.87	3.36	3.666	3.460	− 3.9
LiBr—CaBr ₂ $T = 1073 \text{ K}$	0.25	1.772	2.192	1.783	− 13.9
	0.50	2.557	2.970	2.128	+ 20.2
	0.75	3.775	3.994	2.850	+ 2.3
NaBr—CaBr ₂ $T = 1073 \text{ K}$	0.25	1.445	1.846	1.736	− 25.2
	0.50	1.615	2.158	1.961	− 17.6
	0.75	2.075	2.530	2.319	− 18.6
KBr—CaBr ₂ $T = 1073 \text{ K}$	0.25	1.219	1.742	1.736	− 31.6
	0.50	1.154	1.686	1.679	− 31.3
	0.75	1.357	1.742	1.736	− 30.2
NaBr—SrBr ₂ $T = 1073 \text{ K}$	0.25	1.358	1.604	1.450	− 18.3
	0.50	1.604	1.967	1.677	− 4.4
	0.75	2.082	2.415	2.078	− 10.2

Table 1 (Continued)

System		$\frac{\kappa_{exp}}{S\ cm^{-1}}$	$\frac{\kappa_p}{S\ cm^{-1}}$	$\frac{\kappa_s}{S\ cm^{-1}}$	$\left. \begin{array}{l} \Delta_p/\% \\ \Delta_s/\% \\ \Delta_M/\% \end{array} \right\} x_A = 0.5$	
NaBr—BaBr ₂ T = 1073 K	0.25	1.427	1.571	1.395	— 15.5	
	0.50	1.661	1.966	1.623	+ 2.3	
	0.75	2.128	2.466	2.050	— 7.1	
KBr—BaBr ₂ T = 1153 K	0.25	1.255	1.394	1.351	— 16.2	
	0.50	1.301	1.553	1.483	— 12.3	
	0.75	1.488	1.732	1.665	— 11.5	

maximum deviation) it follows that the Markov model and the series model give rather similar results. They describe well conductivity of the systems which are ideal from the thermodynamical point of view.

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