RELATIONSHIP BETWEEN THERMAL DIFFUSION AND CONDUCTIVITY FOR TWO-COMPONENT CRYSTALLINE STRUCTURES

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This paper gives a more accurate form of Reinhold's formula, which connects the concentration thermal diffusion effect with the transport number and electrical conductivity. The obtained formula correctly predicts the direction of thermal diffusion and the order of magnitude, but the results are a little too high.

Reinhold [1–3] showed experimentally that a concentration gradient is set up in a nonisothermal solid solution only if the transport numbers depend appreciably on the temperature.

In the derivation of an analytic relationship between these quantities, Reinhold assumed that the difference between the elementary heats of transport of cations in the formula obtained by Wagner [4] for the thermal diffusion effect is equal to the difference in the values of the work of dissociation of cations in the expression he obtained for the transport numbers at different temperatures. The final result was the expression

$$\frac{\Delta C_2}{\Delta T} = \frac{C_1 C_2 \ln (n_1' n_2''/n_2' n_1'')}{T_1 - T_2}.$$

This expression can easily be written in differential form as the Soret coefficient of the second component:

$$S_2 \equiv \frac{1}{C_2}\frac{dC_2}{dT} = C_1 \frac{d[\ln (n_1/n_2)]}{dT}.$$

The Soret coefficient of a two-component system, according to this formula, is written in the form

$$S_T \equiv \frac{d[\ln (C_1/C_2)]}{dT} = \frac{1}{C_1 C_2}\frac{dC_1}{dT} =$$

$$= C_1 \frac{d[\ln (n_1/n_2)]}{dT} + C_2 \frac{d[\ln (n_1/n_2)]}{dT}.$$

Taking into account that $C_1 + C_2 = 1$ and $n_1 + n_2 = 1$, we obtain

$$S_T = \frac{1}{n_1 n_2}\frac{dn_1}{dT}. \tag{1}$$

The determination of the heat of transport in solids has been the subject of several papers [5–7], which indicate that it is not equal to the work of dissociation. Reinhold does not give convincing arguments to show that their differences should be equal. In the present paper the transport numbers are regarded in accordance with their definition as relationships between the partial conductivities of the ions involved in the transport of electricity and the over-all conductivity.

The aim of the work was to connect the transport numbers with the previously obtained expression for the Soret effect [8] by means of kinetic relationships.

If at temperature T_1 the partial conductivity of the first cation is $\varkappa_1 = A_1 \exp(-Q_1/RT)$ and of the second $\varkappa_2 = A_2 \exp(-Q_2/RT)$, then for the transport numbers we can write

$$n_1 = \varkappa_1/(\varkappa_1 + \varkappa_2); \quad n_2 = \varkappa_2/(\varkappa_1 + \varkappa_2).$$

Raising the right and left sides of the expression for n_1 to the power C_1D_1 and the expression for n_2 to the power C_2D_2, we can write

$$n_1^{C_1D_1}/n_2^{C_2D_2} = (A_1^{C_1D_1}/A_2^{C_2D_2})(\varkappa_1 + \varkappa_2)^{C_2D_2 - C_1D_1}$$

$$\exp[-(Q_1C_1D_1 - Q_2C_2D_2)/RT]$$

or

$$\ln (n_1^{C_1D_1}/n_2^{C_2D_2}) = \ln (A_1^{C_1D_1}/A_2^{C_2D_2}) - (Q_1C_1D_1 - Q_2C_2D_2)/RT +$$

$$+ (C_2D_2 - C_1D_1)\ln (\varkappa_1 + \varkappa_2).$$

Differentiating with respect to T, we obtain

$$\frac{d[\ln (n_1^{C_1D_1}/n_2^{C_2D_2})]}{dT} = \frac{d[\ln (A_1^{C_1D_1}/A_2^{C_2D_2})]}{dT} - \tag{2}$$

$$- \frac{d[(Q_1C_1D_1 - Q_2C_2D_2)/RT]}{dT} + \frac{d[(C_2D_2 - C_1D_1)\ln (\varkappa_1 - \varkappa_2)]}{dT}.$$

We analyze all the terms in the steady state. The left side can be written in the form

Values of Soret Coefficients Obtained from Different Formulas on the Basis of Experimental Data of [2]

C_1 (Ag)	T_1, °C	T_2, °C	τ in days	S_T from (5)	$S_T = \frac{1}{C_1C_2}\frac{\Delta C_1}{\Delta T_2}$	S_T from (1)	S_T from (6)
0.9	248	308	20	−0.068	−0.0111 −0.0118	0.0043 0.0040	−0.075 −0.048
0.8	223	290	40	−0.038	−0.0092	−0.0065	−0.0248
0.8	214	275	40		−0.0133	−0.0072	−0.0280
0.8	229	304	20		−0.0113	−0.0058	−0.0253
0.8	215	302	20		−0.0095	−0.0051	−0.0227
0.65	217	281	40	−0.0014	−0.0052	−0.0039	−0.0084
0.5	245	304	40		−0.0046	−0.000002	−0.000002

$$\left(\frac{dC_1}{dT}D_1+C_1\frac{dD_1}{dT}\right)\ln n_1+C_1D_1\frac{1}{n_1}\frac{dn_1}{dT}-$$
$$-\left(\frac{dC_2}{dT}D_2+C_2\frac{dD_2}{dT}\right)\ln n_2-C_2D_2\frac{1}{n_2}\frac{dn_2}{dT}.$$

Since in the steady state $S_1=\frac{1}{C_1}\frac{dC_1}{dT}$ and $S_1=-\frac{dD_1}{dT}\Big/D_1$, the first term is zero. It can be shown in the same way that the third term is also zero.

Since the first term on the right side after differentiation has the form

$$\left(\frac{dC_1}{dT}D_1+C_1\frac{dD_1}{dT}\right)\ln A_1-$$
$$-\left(\frac{dC_2}{dT}D_2+C_2\frac{dD_2}{dT}\right)\ln A_2, \qquad (3)$$

then, according to the foregoing, it is zero.

Differentiation of the second term gives the expression

$$\frac{1}{RT}\left(Q_1\frac{dC_1}{dT}D_1+Q_1C_1\frac{dD_1}{dT}-Q_2\frac{dC_2}{dT}D_2-\right.$$
$$\left.-Q_2C_2\frac{dD_2}{dT}\right)-\frac{Q_1C_1D_1-Q_2C_2D_2}{RT^2}. \qquad (4)$$

It is easy to show that the expression in the brackets is zero. The previously obtained expression for the Soret coefficient [8] can easily be converted to the form

$$S_T=\frac{C_2D_2Q_2-C_1D_1Q_1}{C_1C_2(D_1+D_2)RT^2}, \qquad (5)$$

and then (4) can be written in the form $C_1C_2(D_1+D_2)S_T$.

Carrying out differentiation and similar transformations in the last term of formula (2), we bring it to the form

$$C_1D_1\frac{1}{n_1}\frac{dn_1}{dT}-C_2D_2\frac{1}{n_2}\frac{dn_2}{dT}=$$
$$=-C_1C_2(D_1+D_2)S_T+\frac{C_2D_2-C_1D_1}{\varkappa}\frac{d\varkappa}{dT}.$$

Since $n_2 = 1 - n_1$,

$$S_T=-\frac{C_2n_1D_2+C_1n_2D_1}{C_1C_2(D_1+D_2)n_1n_2}\frac{dn_1}{dT}+$$
$$+\frac{C_2D_2-C_1D_1}{C_1C_2(D_1+D_2)\varkappa}\frac{d\varkappa}{dT}.$$

For the case of low mobility of the anions in comparison with that of the cations [4] we know that $D_1 = D_2$ and, hence, for the last formula we obtain

$$S_T=\frac{1}{2}\left(-\frac{C_2n_1+C_1n_2}{C_1C_2n_1n_2}\frac{dn_1}{dT}+\frac{C_2-C_1}{G_2C_1}\frac{1}{\varkappa}\frac{d\varkappa}{dT}\right). \qquad (6)$$

These formulas for the determination of Soret coefficients can be tested if experimental data for the conductivity and transport numbers at different temperatures and concentrations are available. Sufficient data is given in Reinhold and Schulz's paper [2] for a CuBr-AgBr system (see the table). The values given in the sixth column of the table are the result of a direct determination of the Soret coefficient from the value of the concentration gradient produced by the temperature gradient. A comparison of the tabulated results shows that the values obtained from formula (6) correctly predict the direction of thermal diffusion, but are a little too high. The fourth column of the graph gives the time for which the specimens were kept in nonisothermal conditions.

The reason for the systematic error responsible for the overestimated results should obviously be sought in the fact that the heat flow is neglected in this paper and the obtained formulas correspond to relationships of quasi-static thermodynamics. Thermal diffusion is a phenomenon which is regarded in the theory of irreversible thermodynamics as an effect on the borderline between diffusion and thermal conduction.

NOTATION

C_i—concentrations of components in mole fractions: n_i' and n_i''—transport numbers of i-th cation at temperatures T_1 and T_2, respectively; S_i—Soret coefficient of i-th component; S_T—total Soret coefficient; x_i—partial conductivity of i-th component; $\varkappa$—over-all conductivity; Q_i—energy of activation of i-th cation; D_i—coefficient of diffusion of i-th cation.

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