Soret Coefficient and Thermoelectric Power of Thermocells Containing Molten Binary Mixtures

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For an ionic melt consisting of two components and of three ion constituents, we derive the interrelation between the Soret coefficient and the initial and final values of the thermoelectric power of a thermocell containing the melt considered. We only use the general formulas of Thermodynamics of Irreversible Processes and there is no restriction with respect to the valency types of the electrolytes.

For a solution of a single electrolyte in a neutral solvent, the interrelation between the Soret coefficient and the thermoelectric power of a thermocell has been established long ago[1]. For a molten binary mixture, however, such a relation has not yet been derived except in the special case of uni-univalent electrolytes[2]. We will, therefore, develop the general formula[3] for two-component ionic melts with three ion consistuents.

The melt consisting of the two components 1 and 2 contains the following ion constituents: α (occurring in component 1 only), β (occurring in component 2 only), and γ (common to both components). For transport quantities such as the heats of transport $^*Q_\alpha$ and $^*Q_\beta$ and the transported entropies $^*S_\alpha$ and $^*S_\beta$ the reference substance is the ion constituent γ.

The state of the melt is described by the thermodynamic temperature T, the pressure P, and the mole fraction x of component 2. The Faraday constant is denoted by F. The chemical potentials of the two components are denoted by μ_1 and μ_2, those of the three ion constitutents by μ_α, μ_β, and μ_γ. The symbol $(\text{grad}\,\mu_i)_{T,P}$ refers to that part of the gradient of the chemical potential of substance i which is due to a gradient of x for uniform values of T and P.

Let us consider a melt in which there are gradients of temperature and composition, the pressure being uniform. Then both thermal diffusion (Soret effect) and (ordinary) diffusion (interdiffusion) occur. Eventually a stationary (non-equilibrium) state or steady state will be established where the transport of matter is zero. The general equations governing this steady state in our case (steady Soret effect in ionic melts with three ion constituents) can be shown to be[5]

$$z_\alpha F \,\text{grad}\, \psi + (\text{grad}\, \mu_\alpha)_{T,P} + (^*Q_\alpha/T)\,\text{grad}\, T = 0\,, \tag{1}$$

$$z_\beta F \,\text{grad}\, \psi + (\text{grad}\, \mu_\beta)_{T,P} + (^*Q_\beta/T)\,\text{grad}\, T = 0 \tag{2}$$

where z_i is the charge number of the ion constituent i (positive or negative for cation or anion constituents, respectively) and ψ is the (inner) electric potential.

We have the relations

$$z_\alpha \nu_\alpha + z_\gamma \nu_\gamma = 0\,, \quad z_\beta \nu_\beta + z_\gamma \nu_\gamma' = 0\,, \tag{3}$$

$$\mu_1 = \nu_\alpha \mu_\alpha + \nu_\gamma \mu_\gamma\,, \quad \mu_2 = \nu_\beta \mu_\beta + \nu_\gamma' \mu_\gamma\,, \tag{4}$$

$$(1-x)\,(\text{grad}\,\mu_1)_{T,P} + x\,(\text{grad}\,\mu_2)_{T,P} = 0\,. \tag{5}$$

Here ν_i denotes the dissociation number of the ion constituent i, the two values for γ (ν_γ and ν_γ') relating to the two components 1 and 2, respectively.

Combining Eqs. (3) and (4), we find:

$$\mu_\alpha/z_\alpha - \mu_\beta/z_\beta = \mu_1/(z_\alpha \nu_\alpha) - \mu_2/(z_\beta \nu_\beta)\,. \tag{6}$$

We obtain from (5) and (6):

$$(1/z_\alpha)\,(\text{grad}\,\mu_\alpha)_{T,P} - (1/z_\beta)\,(\text{grad}\,\mu_\beta)_{T,P} = -\,[\zeta/(1-x)]\,(\text{grad}\,\mu_2)_{T,P} \tag{7}$$

with [see Eq. (3)]

$$\zeta \equiv \frac{z_\alpha \nu_\alpha (1-x) + z_\beta \nu_\beta x}{z_\alpha \nu_\alpha z_\beta \nu_\beta} = -\,\frac{\nu_\gamma' x + \nu_\gamma (1-x)}{z_\gamma \nu_\gamma \nu_\gamma'}\,. \tag{8}$$

For $\nu_\gamma' = \nu_\gamma$ the dimensionless quantity ζ becomes

$$\zeta = -1/(z_\gamma \nu_\gamma) \tag{9}$$

which for $z_\gamma = \pm 1$, $\nu_\gamma = 1$ reduces to

$$\zeta = \mp 1\,. \tag{10}$$

The last relation implies that the two electrolytes (components 1 and 2) are uni-univalent (example: the molten salt mixture $KNO_3 + AgNO_3$ where $\zeta = 1$).

Dividing Eqs. (1) and (2) by z_α and z_β, respectively, subtracting the resulting equations, and taking account of (7), we find:

$$\zeta\, \mu_{22}\, \text{grad}\, x = (^*Q/T)\,(1-x)\,\text{grad}\, T \quad \text{(steady state)} \tag{11}$$

where the relation

$$(\text{grad}\,\mu_2)_{T,P} = (\partial \mu_2/\partial x)_{T,P}\,\text{grad}\, x \tag{12}$$

and the abbreviations

$$\mu_{22} \equiv (\partial \mu_2/\partial x)_{T,P} \tag{13}$$

$$^*Q \equiv {}^*Q_\alpha/z_\alpha - {}^*Q_\beta/z_\beta \tag{14}$$

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have been used. Obviously $^*Q$ is a linear combination of the two heats of transport.

We introduce the Soret coefficient σ by

$$\operatorname{grad} x = \sigma\, x\,(1-x) \operatorname{grad} T \text{ (steady state)} . \quad (15)$$

This definition is analogous to that used for binary nonelectrolyte solutions and for solutions of a single electrolyte in a neutral solvent.

It follows from (11) and (15) that

$$^*Q = \sigma\, T\, x\, \zeta\, \mu_{22} . \quad (16)$$

Thus the quantity $^*Q$ can be derived from measured values of σ.

The transported entropies $^*S_\alpha$ and $^*S_\beta$ and the heats of transport $^*Q_\alpha$ and $^*Q_\beta$ of the ion constituents α and β are interrelated by

$$^*S_\alpha = {^*Q_\alpha}/T + S_\alpha , \quad {^*S_\beta} = {^*Q_\beta}/T + S_\beta \quad (17)$$

where S_α and S_β are the partial molar entropies of the ion constituents α and β. The partial molar entropies S_1 and S_2 of the components 1 and 2 are given by relations analogous to the Equations (4). We thus derive in view of (3):

$$S_\alpha/z_\alpha - S_\beta/z_\beta = S_1/(z_\alpha\, \nu_\alpha) - S_2/(z_\beta\, \nu_\beta) , \quad (18)$$

an equation corresponding to (6). Combining (14), (17), and (18), we obtain:

$$^*S_\alpha/z_\alpha - {^*S_\beta}/z_\beta = {^*Q}/T + S_1/(z_\alpha\, \nu_\alpha) - S_2/(z_\beta\, \nu_\beta) , \quad (19)$$

another useful relation.

We now consider a thermocell containing the melt and two chemically identical electrodes reversible[6] to the ion constituent β (e. g. two silver electrodes dipping into the molten salt mixture $KNO_3 + AgNO_3$). Then the expression for the difference between the final (steady-state) value ε_∞ and the initial value ε_0 of the thermoelectric power of the thermocell can be shown to be[7]

$$F(\varepsilon_\infty - \varepsilon_0) = t_\alpha\, {^*Q}/T = (1 - t_\beta)\, {^*Q}/T \quad (20)$$

where Eq. (19) has been used and t_α or t_β denotes the (internal) transport number of the ion constituent α or β, respectively, the ion constituent γ being again the reference substance.

We derive our final formula from (16) and (20):

$$F(\varepsilon_\infty - \varepsilon_0) = \sigma\, t_\alpha\, \zeta\, x\, \mu_{22} = \sigma (1 - t_\beta)\, \zeta\, x\, \mu_{22} . \quad (21)$$

Thus there is a general relation among the three measurable quantities σ, ε_0, and ε_∞ referring to nonisothermal transport processes. The quantity ζ may be replaced by $(1-x)/(z_\beta\, \nu_\beta\, X_1)$ where X_1 denotes the equivalent fraction of component 1.

Since $\mu_{22} > 0$ (stability condition) and $\zeta > 0$ for $z_\gamma < 0$ or $\zeta < 0$ for $z_\gamma > 0$ [see Eq. (8)], it follows from (21) that $\varepsilon_\infty - \varepsilon_0$ and σ have the same sign if γ is an anion constituent while $\varepsilon_\infty - \varepsilon_0$ and σ have opposite signs if γ is a cation constituent.

For $\nu_\gamma' = \nu_\gamma$ Eq. (21), when combined with (3) and (9), reduces to the relation

$$F(\varepsilon_\infty - \varepsilon_0) = \sigma\, [\,(1 - t_\beta)/(z_\beta\, \nu_\beta)\,]\, x\, \mu_{22} . \quad (22)$$

We may compare Eq. (22) to the corresponding formula[8] valid for a solution of a single electrolyte (with two ion constituents) in a neutral solvent:

$$F(\varepsilon_\infty - \varepsilon_0) = \sigma\, [\,(1 - t_\mathrm{i})/(z_\mathrm{i}\, \nu_\mathrm{i})\,]\, m\, (\partial \mu_2/\partial m)_{T,P} . \quad (23)$$

Here t_i, z_i, and ν_i are the (Hittorf) transport number, the charge number, and the dissociation number of that ion constituent (i) for which the electrodes are reversible and m and μ_2 denote the molality and the chemical potential of the electrolyte.

For any binary ionic melt with three ion constituents, the transported entropies $^*S_\alpha$ and $^*S_\beta$ can be derived from measurements of either ε_0 and ε_∞ or ε_0 and σ or ε_∞ and σ. This follows from Eqs. (16) and (19) and from relations given earlier[7]. So in this respect, too, the two-component melts resemble electrolyte solutions.

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[1] R. Haase, Trans. Faraday Soc. **49,** 724 [1953].

[2] U. Prüser, Dissertation Technische Hochschule Aachen, 1976.

[3] Though the general equations given by Schönert and Sinistri[4] implicitly contain the desired formula, we will give a new derivation since we do not want to change the reference system, as do the authors mentioned.

[4] H. Schönert and C. Sinistri, Z. Elektrochem. **66,** 413 [1962].

[5] R. Haase, Thermodynamics of Irreversible Processes, Reading (Mass.) 1969, p. 330, Equation [4–24.24].

[6] The question of whether α or β is taken to be the "reversible ion" r is only a matter of choice of the components. The case, however, where the electrodes are reversible to the common ion constituent γ $(r = \gamma)$ is really different. Here we find that t_α in (20) and (21) has to be replaced by $t_\alpha - X_1$. The formula for the thermoelectric power ε at any instant (for any value of the mole fraction difference Δx corresponding to the temperature difference ΔT in the melt) results from (21), or from the equation replacing it for $r = \gamma$, if one substitutes ε for ε_∞ and $\lim\limits_{\Delta T \to 0} \Delta x/\Delta T$ for $\sigma\, x\,(1-x)$.

[7] R. Haase and J. Richter, Z. Naturforsch. **24 a,** 418 [1969], Eqs. (1), (5) and (6).

[8] R. Haase[5], p. 391 to 393, Eqs. [4–29.27], [4–29.33], and [4–29.37].