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Thermal Diffusion in Ionic Systems[1]

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Starting from the complete set of equations of hydrodynamics and nonequilibrium thermodynamics for a binary uni-univalent salt in an electrolyte solution contained between electrodes, we have solved, in part, both the transient and the steady-state thermal diffusion problems. Full account is taken of nonvanishing space charge near the electrodes. Formulas are obtained for the temperature distribution, the electric field, the salt concentration distribution, the charge distribution, and the voltage. The effect of Joule heating on the temperature distribution is very small. The effect of space charge on the electric field and on the salt concentration distribution is also small. Applications both to solid-state ionic devices such as batteries and to thermal diffusion measurements in aqueous electrolyte solutions are mentioned.

KEY WORDS: ion transport; solid-state batteries; thermal diffusion; thermocells.

1. INTRODUCTION

Thermocells have been studied and used for over 125 years, and their nonequilibrium thermodynamic description is readily available [1]. The major features of the nonequilibrium thermodynamic description are two sets of equations: (i) the set of differential equations of hydrodynamics, the conservation equations; and (ii) the set of flux-force relationships, the Onsager equations. In order to obtain accurate values of transport properties from experimental data, and in order to design devices and experiments that involve transport, it is in principle necessary to solve the complete set of transport equations subject to the initial and boundary conditions appropriate to the problem at hand.

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A "pure" (i.e., one-dimensional) thermal diffusion experiment begins when the temperatures of two opposite walls are suddenly changed from their initial, identical values to their final, different values. The temperature gradient thus produced induces matter flow and the establishment of a concentration gradient. In this experiment, the initial conditions are that the temperature and composition are uniform. In the usual experiment, the boundary conditions for the composition of each species are due to the fact that matter does not flow through the walls. The boundary conditions for temperature are time dependent since it is, in fact, impossible to change the wall temperatures instantaneously. The time-dependent pure thermal diffusion problem for impermeable walls has been solved [2].

When electrodes are present in a solution containing ions, there are additional boundary conditions due to chemical transfer at the electrodes. In general, these boundary conditions are well represented by writing the ith ion flux J_i into the solution at the electrode as a sum of forward and backward processes [3–5].

$$J_i = k_{if} c_{i,\text{electrode}} - k_{ib} c_{i,\text{solution}} \tag{1}$$

where k_{if} and k_{ib} are, respectively, the forward and backward rate constants, and c_i is the interface concentration in the region indicated. Thus, $c_{i,\text{solution}}$ is the concentration of ion i at the solution side of the interface between the solution and the electrode. This general boundary condition accommodates a variety of situations, including reversible electrodes and blocking electrodes.

If the mass flux of cations in the regions close to the electrodes, or indeed anywhere, is different from that of anions, then a macroscopic electrical charge will be present. It is essential to take account of the existence of space charge when considering interfacial transport of ions. Brumleve and Buck [3] have obtained space-charge distributions for various electrolyte systems by solving the transport equations numerically. Space charge is of course much more important near the walls than in the bulk of the solution. In aqueous electrolyte solutions in conventional electrochemical settings, the charged region is very small compared with the rest of the system. This is not the case, however, in living cells or in thin film solid-state batteries.

In order to obtain analytic solutions of the transport equations including nonelectroneutrality, it is necessary to retain the charge as an explicit property. For uni-univalent solutions, the two composition variables of choice [6, 7] are the salt concentration c and the charge concentration ζ,

$$c = \frac{1}{2}(c_1 + c_2), \qquad \zeta = \frac{1}{2}(c_2 - c_1) \tag{2}$$

where c_1 is the concentration of cations and c_2 is the concentration of anions. Clearly, $\zeta = 0$ in electrically neutral regions.

In this paper we present the general transport equations for thermal diffusion in a uni-univalent electrolyte solution, liquid or solid, with ion boundary conditions of the type expressed by Eq. (1). Analytic solutions are given for an idealized system whose salt concentration is small enough for the Nernst–Planck equations to be valid [7].

2. GENERAL TRANSPORT EQUATIONS

In a nonreacting, one-dimensional system with immobile solvent, the equation of conservation of mass of each component is

$$(\partial c_i/\partial t) = -(\partial J_i/\partial x) \tag{3}$$

where c_i is the concentration of component i, t is time, x is the spatial coordinate, and J_i is the Hittorf diffusion flux defined by

$$J_i = c_i(v_i - v_0) \tag{4}$$

where v_i is the velocity of component i and v_0 is the velocity of the solvent [taken as zero in Eq. (3)]. The equation of conservation of energy for the system is well approximated by [5, 7]

$$(C_p/V)(\partial T/\partial t) = (\partial/\partial x)\, \kappa_T(\partial T/\partial x) + EI_F \tag{5}$$

where C_p is the molar constant-pressure heat capacity of the system, V is the molar volume, T is the temperature, κ_T is the steady-state thermal conductivity of the system, E is the electric field, which is related to the electrostatic potential ϕ by

$$E = -(\partial\phi/\partial x) \tag{6}$$

and I_F is the Faradaic electric current,

$$I_F = F\sum_i z_i J_i \tag{7}$$

with z_i the charge per mole of component i and F the Faraday constant. The total current I is the sum of the Faraday current and Maxwell's displacement current [3, 7],

$$I = I_F + \varepsilon(\partial E/\partial t) \tag{8}$$

where ε is the permittivity. Electric-field strength is related to charge by the Poisson equation,

$$\varepsilon(\partial E/\partial x) = F \sum_i z_i c_i \tag{9}$$

The Onsager equations, which relate the diffusion and heat fluxes to the gradients of chemical potential and temperature, are [1, 7]

$$\begin{aligned} -J_i &= \sum_j l_{ij}(\partial_T \mu_j/\partial x) + l_{iQ}(\partial \ln T/\partial x) \\ -J_Q &= \sum_j l_{Qj}(\partial_T \mu_j/\partial x) + l_{QQ}(\partial \ln T/\partial x) \end{aligned} \tag{10}$$

where l_{ij}, l_{iQ}, l_{Qj}, and l_{QQ} are Onsager coefficients, Q denotes heat, and the electrochemical-potential gradient in an isobaric system is related to the concentration and electric potential by

$$(\partial_T \mu_j/\partial x) = \sum_i \mu_{ji}(\partial c_i/\partial x) + z_j F(\partial \phi/\partial x) \tag{11}$$

with

$$\mu_{ji} = (\partial u_j/\partial c_i)_{T,p,c_{k \neq i}} \tag{12}$$

3. DILUTE SOLUTION, UNI-UNIVALENT SOLUTE

In a sufficiently dilute solution, the l_{ij} in the first of Eqs. (10) vanish for $i \neq j$ and the solution behaves ideally with respect to chemical interactions [7]. Then the first of Eqs. (10) becomes

$$-J_i = D_i(\partial c_i/\partial x) + (\lambda t_i/F z_i)(\partial \phi/\partial x) + (c_i D_i Q_i^*/RT^2)(\partial T/\partial x) \tag{13}$$

where the Nernst–Planck diffusion coefficients D_i, the conductance λ, the transference numbers t_i, and the heats of transport Q_i^* are defined by [5, 7]

$$\begin{aligned} D_i &= RT l_{ii}/c_i, & \lambda &= F^2 \sum_i z_i^2 l_{ii} \\ t_i &= (F^2/\lambda)\, z_i^2 l_{ii}, & Q_i^* &= (l_{iQ}/l_{ii}) = RT l_{iQ}/c_i D_i \end{aligned} \tag{14}$$

For a single uni-univalent solute, we have, with 1 denoting cations and 2 anions,

$$\begin{aligned} -J_1 &= D_1(\partial c_1/\partial x) + (\lambda t_1/F)(\partial \phi/\partial x) + (c_1 D_1 Q_1^*/RT^2)(\partial T/\partial x) \\ -J_2 &= D_2(\partial c_2/\partial x) - (\lambda t_2/F)(\partial \phi/\partial x) + (c_2 D_2 Q_2^*/RT^2)(\partial T/\partial x) \end{aligned} \tag{15}$$

Conversion to c and ζ as the composition variables and to

$$J_c = \frac{1}{2}(J_1 + J_2), \qquad J_\zeta = \frac{1}{2}(J_2 - J_1) \tag{16}$$

as the fluxes yields

$$\begin{aligned} -J_c &= D(\partial c/\partial x) - D'(\partial \zeta/\partial x) + (F/RT)(cD' - \zeta D)(\partial \phi/\partial x) \\ &\quad + (cD\sigma_T - \zeta D'\sigma'_T)(\partial T/\partial x) \\ -J_\zeta &= D'(\partial c/\partial x) - D(\partial \zeta/\partial x) + (F/RT)(cD - \zeta D')(\partial \phi/\partial x) \\ &\quad + (cD'\sigma'_T - \zeta D\sigma_T)(\partial T/\partial x) \end{aligned} \tag{17}$$

where

$$\begin{aligned} D &= \frac{1}{2}(D_1 + D_2), \qquad D' = \frac{1}{2}(D_1 - D_2) \\ \sigma_T &= (D_1 Q_1^* + D_2 Q_2^*)/2RT^2 D, \qquad \sigma'_T = (D_1 Q_1^* - D_2 Q_2^*)/2RT^2 D' \end{aligned} \tag{18}$$

and where we have eliminated λ and the t_i in favor of D and D'. The coefficient σ_T is similar to the Soret coefficient, the coefficient D is similar to the "ambipolar" diffusion coefficient, and the coefficients, σ'_T and D' represent, respectively, thermal diffusion and mass diffusion of the electric charge.

The conservation equations for c and ζ are

$$(\partial c/\partial t) = -(\partial J_c/\partial x), \qquad (\partial \zeta/\partial t) = -(\partial J_\zeta/\partial x) \tag{19}$$

Since $I_F = F(J_1 - J_2) = -2FJ_\zeta$, we also have

$$\varepsilon(\partial E/\partial t) = I + 2FJ_\zeta \tag{20}$$

Moreover, the Poisson equation is

$$\varepsilon(\partial E/\partial x) = -2F\zeta \tag{21}$$

4. STEADY STATE

At the steady state, J_c and J_ζ are constants, with values fixed by Eq. (1). Solving Eqs. (17) for $(\partial c/\partial x)$ and $(\partial \zeta/\partial x)$, we find

$$\begin{aligned} (\partial c/\partial x) &= -[DJ_c - D'J_\zeta)/(D^2 - D'^2)] - (F/RT)\,\zeta E - (2RT^2)^{-1} \\ &\quad \times [c(Q_1^* + Q_2^*) + \zeta(Q_2^* - Q_1^*)](\partial T/\partial x) \\ (\partial \zeta/\partial x) &= -[(D'J_c - DJ_\zeta)/(D^2 - D'^2)] - (F/RT)\,cE - (2RT^2)^{-1} \\ &\quad \times [c(Q_2^* - Q_1^*) + \zeta(Q_1^* + Q_2^*)](\partial T/\partial x) \end{aligned} \tag{22}$$

where we have used Eq. (6). For constant thermal conductivity, the steady-state temperature equation is

$$(\partial^2 T/\partial x^2) = -(I_{\mathrm{F}}/\kappa_{\mathrm{T}})E \tag{23}$$

4.1. Isothermal Case

When the temperature is uniform throughout the system. Eqs. (22) become

$$(\partial c/\partial x) = -K - (F/RT)\,\zeta E, \qquad (\partial \zeta/\partial x) = -K' - (F/RT)\,cE \tag{24}$$

where

$$K = (DJ_{\mathrm{c}} - D'J_{\zeta})/(D^2 - D'^2), \qquad K' = (D'J_{\mathrm{c}} - DJ_{\zeta})/(D^2 - D'^2) \tag{25}$$

With Eq. (21), Eqs. (24) become

$$\begin{aligned} (\partial c/\partial x) &= -K + (\varepsilon/4RT)(\partial E^2/\partial x^2) \\ (\partial^2 E/\partial x^2) - (2F^2/\varepsilon RT)\,cE &= (2F/\varepsilon)\,K' \end{aligned} \tag{26}$$

The solutions to the coupled Eqs. (26) are obtained by a perturbation approach defined by

$$\begin{aligned} c &= \bar{c} + \delta c_1 + \delta^2 c_2 + \cdots \\ E &= E_0 + \delta E_1 + \delta^2 E_2 + \cdots \end{aligned} \tag{27}$$

The lowest-order results are

$$\begin{aligned} E_0 &= -(2F/\varepsilon\kappa^2)\{K' + \kappa\rho[\cosh(\kappa x)]/[\sinh(\kappa L/2)]\} \\ \zeta_0 &= \rho[\sinh(\kappa x)]/[\sinh(\kappa L/2)] \\ c_1 &= -Kx - (\rho K'/\bar{c}\kappa)(2/\kappa L)\{1 - (\kappa L/2)[\cosh(\kappa x)]/[\sinh(\kappa L/2)]\} \\ &\quad - [\rho^2/4\bar{c}\kappa L\sinh^2(\kappa L/2)][\sinh(\kappa L) - (\kappa L)\cosh(2\kappa x)] \end{aligned} \tag{28}$$

where κ^{-1}, the inverse debye length, is defined by

$$\kappa^2 = (2F^2/\varepsilon RT)\bar{c} \tag{29}$$

and where we have required for the charge density at the walls that

$$\zeta(L/2) = \rho = -\zeta(-L/2) \tag{30}$$

This condition is used only to provide relatively simple results—Eq. (1) or other estimates should be used in particular applications.

Of principal importance for application is the electric-potential difference across the cell. This is obtained by integrating E to obtain $\phi(x)$ and then subtracting to get $\Delta\phi = \phi(L/2) - \phi(-L/2)$. The perturbation approach yields E_0 as an even function of x, E_1 as an odd function of x, E_2 as an even function of x, and so forth. The second-order equations for E, c, and ζ are very cumbersome and are displayed elsewhere [5]. For $\Delta\phi$ we find

$$\Delta\phi = (RT/\bar{c}F)[K'L - (KL/2\bar{c})^2(KL/3) + 2\rho - (3\rho/8)(KL/2\bar{c})^2] \quad (31)$$

In order to estimate the relative importance of the various terms in Eqs. (28) and (31), we note that κ ranges from about $10^8\ \mathrm{m}^{-1}$ for 0.01 M aqueous solutions at 298 K to about $10^9\ \mathrm{m}^{-1}$ for a 5 M solid solution of low dielectric constant at 1000 K.

If the electrodes allow the passage of cations only, then

$$K = (I_F/2FD_1) = -K' \quad (32)$$

and the leading terms in the equations for E, c, and $\Delta\phi$ become

$$\begin{gathered} E \approx I_F/\varepsilon D_1\kappa^2, \qquad c \approx \bar{c} - (I_F/2FD_1)x \\ \Delta\phi \approx -(RT/\bar{c}F)(I_F L/2FD_1) \end{gathered} \quad (33)$$

A potential difference of about 0.4 V is produced by a current density of $300\ \mathrm{amp}\cdot\mathrm{m}^{-2}$ across a cell 0.01-m thick.

4.2. Nonisothermal Case

A perturbation approach similar to that just discussed leads to the temperature distribution

$$T = T_M + (x/L)\,\Delta T + [(L/2)^2 - x^2](2I_F^2/\lambda\kappa_T) \quad (34)$$

where

$$T_M = \frac{1}{2}[T(L/2) + T(-L/2)], \qquad \Delta T = [T(L/2) - T(-L/2)] \quad (35)$$

and where λ and κ_T are, respectively, the conductance and the thermal conductivity. The last term on the right-hand side of Eq. (34) is due to Joule heating. Its maximum contribution occurs at the center of the cell, where $x = 0$. For $\kappa_T = 10\ \mathrm{J}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}\cdot\mathrm{s}^{-1}$, $\lambda = 10\ \Omega^{-1}\cdot\mathrm{m}^{-1}$, a current density of $300\ \mathrm{amp}\cdot\mathrm{m}^{-2}$ across a cell 10^{-2} m thick will produce a temperature increase of about 5 K, which is negligible compared to T_M. The temperature gradient is

$$(\partial T/\partial x) = (\Delta T/L) - (x/L)(4LI_F^2/\lambda\kappa_T) \quad (36)$$

The maximum contribution to $(\partial T/\partial x)$ of the Joule-heating term under the conditions stated above is $18\ \mathrm{K \cdot m^{-1}}$, which is negligible for our present purposes if $(\Delta T/L)$ is, say, $10^3\ \mathrm{K \cdot m^{-1}}$ or $10\ \mathrm{K \cdot cm^{-1}}$. Moreover, because the Joule-heating effect has opposite parity to the temperature-difference effect, there is no contribution of Joule heating to the change in $\Delta\phi$ produced by the imposition of a temperature difference.

With neglect of the Joule-heating term in Eq. (36), Eqs. (23) become

$$(\partial c/\partial x) = -H - (F/RT)\,\zeta E, \qquad (\partial \zeta/\partial x) = -H' - (F/RT)\,cE \tag{37}$$

where

$$H = K + c[(Q_1^* + Q_2^*)/2RT^2], \qquad H' = K' + c[(Q_2^* - Q_1^*)/2RT^2] \tag{38}$$

and where we have neglected, in comparison to the c terms, the contribution of ζ terms to H and H'.

The additions to the isothermal results are

$$\begin{aligned} E &= E_{\text{isothermal}} - (2F/\varepsilon\kappa^2)\,\bar{c}[(Q_2^* - Q_1^*)/2RT^2](\Delta T/L) \\ c &= c_{\text{isothermal}} - x\bar{c}[(Q_1^* + Q_2^*)/2RT^2](\Delta T/L) \\ \Delta\phi &= (\Delta\phi)_{\text{isothermal}} + [(Q_2^* - Q_1^*)/2FT]\,\Delta T \end{aligned} \tag{39}$$

For aqueous electrolyte solutions, Haase [1] reports Q_2^* values for typical anions (Cl^-, Br^-, NO_3^-, ClO_4^-) from 1.5 to $1.7\ \mathrm{kcal \cdot mol^{-1}}$; for typical cations ($Na^+$, K^+, Ag^+) the values of Q_1^* range from -0.3 to $-1.0\ \mathrm{kcal \cdot mol^{-1}}$. Thus, $Q_1^* - Q_2^* \approx 2\ \mathrm{kcal \cdot mol^{-1}} \approx 10^4\ \mathrm{J \cdot mol^{-1}}$, while $Q_1^* + Q_2^* \approx 5 \times 10^3\ \mathrm{J \cdot mol^{-1}}$. The contribution to $\Delta\phi$ is about $(\Delta T/20T)$ volts, which is only a few millivolts for small ΔT. Clearly, large ΔT will increase $\Delta\phi$ significantly. Tables and graphs illustrating this, along with a discussion of the electrical efficiency of a solid-state cell, are presented elsewhere [5, 8].

5. TIME DEPENDENCE

Four macroscopic relaxation times characterize thermal diffusion in charged systems.

(i) The "warming-up" time is due to the fact that it is not possible to shift from identical wall temperatures to different wall temperatures instantaneously. The value of this relaxation time, γ, depends on the apparatus and the interface between the apparatus and the system under study. It may be determined empirically by fitting the observed time dependence of the wall temperature to an exponential function. For example, if the temperature at the wall is changed from T_M to T_H, the exponential expression for the wall temperature T_W is

$$T_W = T_M + (T_H - T_M)(1 - e^{-t/\gamma}) \tag{40}$$

Typically [2], γ is small, of the order of 1 min or less, since it reflects the time required to change the temperature of a thin solid, usually metallic, wall.

(ii) The thermal relaxation time, τ_T, characterizes the time required to reach the thermal steady state. This relaxation time is related to system properties and dimensions by [2]

$$\tau_T = (L^2/\pi^2)(C_p/V\kappa_T) \tag{41}$$

If both walls have the same warming-up time γ, and if Joule heating is negligible, the solution of Eq. (5) for constant thermal conductivity, heat capacity, and molar volume is [2]

$$\begin{aligned} T = T_M + \Delta T \Big\{ & (x/L) - \frac{1}{2} e^{-t/\gamma} [\sin(\pi x/L)(\tau/\gamma)^{\frac{1}{2}}] / [\sin(\pi/2)(\tau/\gamma)^{\frac{1}{2}}] \\ & - (\tau_T/\pi) \sum_{m=1}^{\infty} (-1)^m [m(4m^2\gamma - \tau_T)]^{-1} [\sin(2m\pi x/L)]\, e^{-4m^2 t/\tau_T} \Big\} \end{aligned} \tag{42}$$

For nonelectrolytes and, presumably, polymers, τ_T is about 1 min for material 0.01 m thick. Reduction of the thickness to 0.001 m reduces τ_T to less than 1 s.

(iii) The dielectric relaxation time, τ_D, characterizes the time required for the electric field E to attain its steady-state value in the absence of concentration gradients. This time is related to system properties by

$$\tau_D = (\varepsilon/\gamma) \tag{43}$$

Its value for dilute aqueous solutions is about 10^{-9} s [6].

(iv) The diffusion relaxation time, θ, is defined by

$$\theta = (L^2/\pi^2 D_F) \tag{44}$$

where D_F is the Fick's law diffusion coefficient, which is related to the dilute solution ionic diffusion coefficients D_1 and D_2 by [7]

$$D_F = 2D_1 D_2/(D_1 + D_2) \tag{45}$$

For liquids, in a cell 0.01 m thick, $\theta \approx 1$ h. Diffusion coefficients for solids are generally much lower than for liquids, and θ is generally, therefore, much greater, even for thinner cells. The chief point for the present discussion is that the relaxation time for diffusion is some 100 times greater than for the three processes discussed above. This means that all thermal and electrical processes (except for minor readjustments due to concentration changes) reach steady state long before measurable diffusion occurs.

With the initial condition that of uniform composition but fully established thermal and electrical fields, the conservation equation for composition is [5]

$$(\partial c/\partial t) = (\partial/\partial x)\, D_{\mathrm{F}}[(\partial c/\partial x) - c\omega(\Delta T/L)] \tag{46}$$

where the Hittorf Soret coefficient ω is defined by [1, 5]

$$\omega = \sigma - \alpha \tag{47}$$

where α is the thermal expansivity of the solution and the Soret coefficient σ is related to the ionic heats of transport by

$$\sigma = \frac{1}{2}\,(Q_1^* + Q_2^*)/RT^2 \tag{48}$$

for a dilute solution. The boundary conditions on Eq. (46) are

$$D_{\mathrm{F}}[(\partial c/\partial x) - c\omega(\Delta T/L)] = -J_{\mathrm{c}}^{\infty}, \qquad x = \pm(L/2) \tag{49}$$

where J_{c}^{∞} is the steady-state constant wall flux of Section 4.

The solution of Eq. (46) for constant D_{F} and ω and for times greater than $(\theta/2)$ is [5]

$$c = c^{\infty} + (2\beta/\pi)^2\, \Gamma(x)\exp\{-(t/\theta)[1 + (\beta/\pi)^2]\} \tag{50}$$

where c^{∞} is the steady-state concentration distribution of Section 4 and where

$$\beta = -(\omega/2)\,\Delta T \tag{51}$$

and where

$$\begin{aligned} \Gamma(x) &= \Gamma(0)[\cos(\pi x/L) + (\pi/\beta)\sin(\pi x/L)]\, e^{-\beta(x/L)} \\ \Gamma(0) &= [\bar{c} + (LJ_{\mathrm{c}}^{\infty}/2\beta D_{\mathrm{F}})](2/\pi)[1 + (\beta/\pi)]^{-2}\, e^{\beta/2} \end{aligned} \tag{52}$$

In order to find analytic solutions for E, ζ, and $\Delta\phi$ for $(\theta/2) < t < \infty$, it is necessary to solve

$$(\partial^2 E/\partial x^2) - K^2(c/\bar{c})E = (2F/\varepsilon)\, H' \tag{53}$$

for E, Eq. (21) for ζ, and then perform a further integration to obtain $\Delta\phi$. This task has not yet been accomplished because of the mathematical difficulties introduced by the substitution of Eqs. (50)–(52) into Eq. (53). It is likely that only numerical solutions can be found. This is worth doing because the time required to reach the steady state of aqueous or solid-state electrolytic cells is of considerable practical importance.

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