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Fundamental analysis on a thermocell with a mixture of the soluble redox couple aqueous potassium ferrocyanide and potassium ferricyanide solution

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Abstract

The transport coefficients in the flux equations of two soluble salts of the redox couple, the electric current and the heat in a thermocell were generally determined with the specific conductivity of the electrolyte solution, the transport numbers of the ions, the charge numbers of the ions, the heats of transfer of the salts and the steady-state thermoelectric power. The heats of transfer of potassium ferrocyanide and potassium ferricyanide in aqueous solution ($0.36\ \mathrm{mol/dm^3} + 0.36\ \mathrm{mol/dm^3}$) were calculated as 8.0 and −1.2 kJ/mol, respectively, at 298 K from measurement results of the initial and steady-state thermoelectric powers of the thermocell of the redox couple and the critical concentration of natural convection in a thin-layer thermocell placed horizontally.

INTRODUCTION

Thermocells, which are also called non-isothermal galvanic cells, are a kind of thermoelectric converter which consists of an electrolyte solution and two identical electrochemical electrodes placed at different temperatures [1–4]. Some redox-type cells have been developed as a thermal energy converter from low-grade heat sources in different laboratories [5–7]. In these cells, an aqueous solution containing a soluble redox couple, e.g. potassium ferrocyanide and potassium ferricyanide, is placed between two platinum electrodes. The absolute value of the thermoelectric power of this type of cell, of the order of 1–2 mV/K, is higher than (or equal to, at least) that of semiconductor thermoelectric devices.

Since the performance of these cells has been analysed only experimentally, there is no exact way of obtaining the optimum conditions of high electric power and high efficiency. One necessary analysis is of the fluxes of matter, electric charge and heat

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under diffusion control. Another important analysis is of the natural convection taking place in the cell with temperature gradients. This paper concerns the former analysis from the aspect of irreversible thermodynamics. This will also be used in calculations on the natural convection by computer in further work.

The thermoelectric phenomena of soluble redox couples have been analysed with the initial thermoelectric powers [8] and heat evolution [9] using the transported entropies or heats of transfer of ions in the redox couples. In these analyses, only heat or thermoelectric power is considered. In the practical use of a thermocell as an energy converter, it is necessary to know how much current passes through the cell with given potential and temperature differences. It is also necessary to know how big a concentration difference is generated due to the electrode reaction, migration and thermal diffusion in the cell; this concentration difference promotes the convection in the electrolyte solution. For these purposes, the Onsager flux equations must be solved. Detailed solutions of flux equations in electrochemical cells under temperature gradients have been presented by Agar [1], Haase [2] and deBethune [10], who have been referenced by many workers. Since this paper concerns only the current and the observable potential difference between electrodes, the method presented by Førland et al. [11], in which the potential difference can be obtained directly without its separation into a diffusion contribution, a thermal contribution and so on, is used.

In this paper, the transport coefficients in the flux equations for a thermocell with a soluble redox couple are first solved generally with the Nernst–Planck assumption to calculate the characteristic properties of the thermocell. Some important equations for thermoelectric effects are also given. Finally, the measurement and calculation results for a thermocell with potassium ferrocyanide and potassium ferricyanide are presented.

THEORETICAL ANALYSIS

Onsager flux equations

We consider an electrochemical cell with two soluble salts of a redox couple, $A_{\nu_1}M$ and $A_{\nu_2}M$, which fill the region between two electrodes as illustrated in Fig. 1. M represents the redox couple, A the counter-ion, and ν_1 and ν_2 are the stoichiometric numbers of the salts. It is assumed that these salts dissociate into the common counter-ion A^{z_0}, and the redox couple ions $A_{\nu_1-n_1}M^{z_1}$ and $A_{\nu_2-n_2}M^{z_2}$ associated partly with the counter ion:

$$A_{\nu_1}M \rightarrow n_1\ A^{z_0} + A_{\nu_1-n_1}M^{z_1} \qquad n_1 = |z_1/z_0| \tag{1.1}$$

$$A_{\nu_2}M \rightarrow n_2\ A^{z_0} + A_{\nu_2-n_2}M^{z_2} \qquad n_2 = |z_2/z_0| \tag{1.2}$$

where z_1 and z_2 are the charge numbers of the associated ions and z_0 is that of the counter-ion. A charge-transfer reaction of n electrons takes place on the electrode:

$$A_{\nu_1-n_1}M^{z_1} \rightleftarrows A_{\nu_2-n_2}M^{z_2} + n\ e^- + n_A\ A^{z_0} \tag{2.1}$$

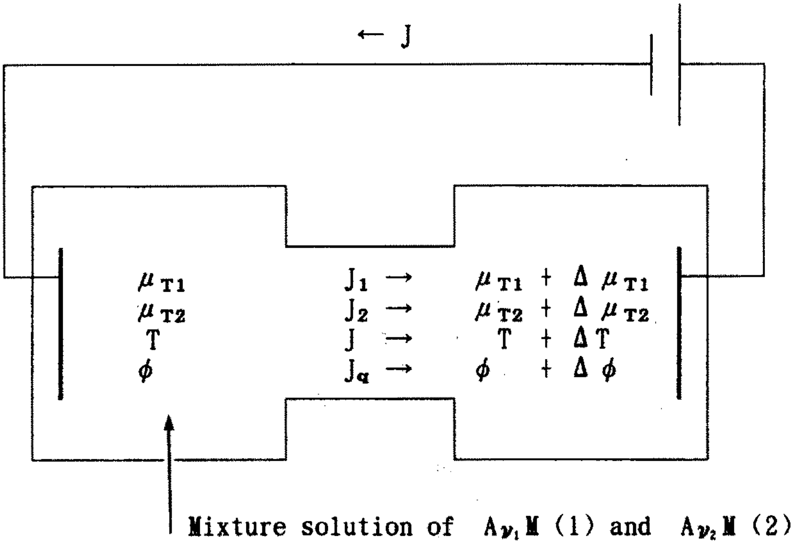

Fig. 1. Schematic illustration of the cell for theoretical analysis. Direction of fluxes, J_1, J_2, J, and J_q, are defined in the above direction. Chemical potentials, μ_{T1} and μ_{T2}, electric potential, ϕ, and temperature, T, in two compartments differ by small amounts.

where n_A is the difference of the association numbers of the redox ions, given by

$$n_A = (\nu_1 - n_1) - (\nu_2 - n_2) = \{n - (z_2 - z_1)\}/z_0 \tag{2.2}$$

The complete set of fluxes are the two mass fluxes, J_1 and J_2, of $A_{\nu_1}M$ and $A_{\nu_2}M$, respectively; the electric current, J; and the heat flux, J_q. These mass and heat fluxes include the formation or consumption of the masses and heat by the electrode reaction. The complete set of conjugate forces are the gradients of the chemical potentials, $\nabla\mu_{T1}$ and $\nabla\mu_{T2}$, of $A_{\nu_1}M$ and $A_{\nu_2}M$, respectively; the electric potential, $\nabla\phi$; and the logarithm of the temperature, ∇ ln T. $\nabla\phi$ used here is the observable potential difference using the electrode on which the electron-transfer reaction in eqn. (2.1) takes place. The Onsager flux equations with transport coefficients, L_{ij}, are as follows, where the Onsager reciprocal relation, $L_{ij} = L_{ji}$, is valid:

$$J_1 = -L_{11}\nabla\mu_{T1} - L_{12}\nabla\mu_{T2} - L_{13}\nabla\phi - L_{14}\nabla \ln T \tag{3.1}$$

$$J_2 = -L_{21}\nabla\mu_{T1} - L_{22}\nabla_{mT2} - L_{23}\nabla\phi - L_{24}\nabla \ln T \tag{3.2}$$

$$J = -L_{31}\nabla\mu_{T1} - L_{32}\nabla\mu_{T2} - L_{33}\nabla\phi - L_{34}\nabla \ln T \tag{3.3}$$

$$J_q = -L_{41}\nabla\mu_{T1} - L_{42}\nabla\mu_{T2} - L_{43}\nabla\phi - L_{44}\nabla \ln T \tag{3.4}$$

Determination of L_{ij}, $i = 3$ and $j = 1, 2, 3$

Since the electric current is proportional to the specific conductivity of the solution, κ, under the condition of no gradient in both the chemical potential and the temperature, L_{33} should be equal to κ:

$$L_{33} = \kappa = |z_1| C_1\lambda_1 + |z_2| C_2\lambda_2 + |z_0| C_0\lambda_0, \tag{4}$$

$$C_0 = n_1C_1 + n_2C_2$$

where C_1 and C_2 are the concentrations of $A_{\nu_1}M$ and $A_{\nu_2}M$, respectively, in volume, and λ_1, λ_2 and λ_0 are ionic conductivities of $(1/z_1)(A_{\nu_1-n_1}M^{z_1})$, $(1/z_2)(A_{\nu_2-n_2}M^{z_2})$, and $(1/z_0)A^{z_0}$, respectively. When an electric current passes under the same condition of $\nabla\mu_{T1} = \nabla\mu_{T2} = \nabla \ln T = 0$, $A_{\nu_1-n_1}M^{z_1}$ is produced and $A_{\nu_2-n_2}M^{z_2}$ is consumed in the right side compartment due to electron transfer on the electrode at rates equal to J/nF, where F is the Faraday constant. The migration rates of the ions $A_{\nu_1-n_1}M^{z_1}$ and $A_{\nu_2-n_2}M^{z_2}$ are $+(t_1/z_1)J/F$ and $+(t_2/z_2)J/F$, respectively, where t_1 and t_2 are the transport numbers of the respective ions. The total mass-transfer rates as salts $A_{\nu_1}M$ and $A_{\nu_2}M$ give L_{13} and L_{23}:

$$L_{13}/L_{33} = (J_1/J)_{\nabla\mu_{T1}=\nabla\mu_{T2}=\nabla \ln T=0} = \{1/n + (t_1/z_1)\}/F \tag{5}$$

$$L_{23}/L_{33} = (J_2/J)_{\nabla\mu_{T1}=\nabla\mu_{T2}=\nabla \ln T=0} = \{-1/n + (t_2/z_2)\}/F \tag{6}$$

Determination of L_{ij}, $i, j = 1, 2$

In order to use the Nernst–Planck assumption in the solution of L_{ij} (i, $j = 1, 2$), we consider a cell with another set of electrodes in which the mass fluxes of $A_{\nu_1}M$ and $A_{\nu_2}M$ are equal to the migration speeds of the ions $A_{\nu_1-n_1}M^{z_1}$ and $A_{\nu_2-n_2}M^{z_2}$, respectively. In this case, the mass transfer of these ions is not coupled with the electrode reaction. A possible electrode reaction giving such a condition is one which is reversible to the counter-ion, A^{z_0}, as

$$A \rightleftarrows A^{z_0} + z_0\, e^- \tag{7}$$

where A is not soluble and the charge-transfer reaction (2.1) between the redox couple does not take place on this electrode. The flux equations in the cell with this electrode can be written with a new observable electric potential ϕ' and transport coefficients K_{ij} $(= K_{ji})$ as follows:

$$J_1 = -K_{11}\ \nabla\mu_{T1} - K_{12}\ \nabla\mu_{T2} - K_{13}\ \nabla\phi' - K_{14}\ \nabla \ln T \tag{8.1}$$

$$J_2 = -K_{21}\ \nabla\mu_{T1} - K_{22}\ \nabla\mu_{T2} - K_{23}\ \nabla\phi' - K_{24}\ \nabla \ln T \tag{8.2}$$

$$J = -K_{31}\ \nabla\mu_{T1} - K_{32}\ \nabla\mu_{T2} - K_{33}\ \nabla\phi' - K_{34}\ \nabla \ln T \tag{8.3}$$

$$J_q = -K_{41}\ \nabla\mu_{T1} - K_{42}\ \nabla\mu_{T2} - K_{43}\ \nabla\phi' - K_{44}\ \nabla \ln T \tag{8.4}$$

According to Førland et al. [11], $K_{12} = K_{21} = 0$ corresponds to the Nernst–Planck assumption, and $K_{11} = K_{31}/z_1$ and $K_{22} = K_{32}/z_2$ are valid if there is no migration as ion pairs. K_{i3} are obtained in the same manner as L_{i3}:

$$K_{13} = (t_1/z_1)\kappa/F \qquad K_{23} = (t_2/z_2)\kappa/F \qquad K_{33} = \kappa \tag{9}$$

We next consider the flux equations under pure diffusion with new transport coefficients l_{ij} $(= l_{ji})$, in which the electric potential ϕ' in flux equations (8.1)–(8.4) can be eliminated using eqn. (8.3) with $J = 0$:

$$J_1 = -l_{11}\ \nabla\mu_{T1} - l_{12}\ \nabla\mu_{T2} - l_{14}\ \nabla\ \ln T \tag{10.1}$$

$$J_2 = -l_{21}\ \nabla\mu_{T1} - l_{22}\ \nabla\mu_{T2} - l_{24}\ \nabla\ \ln T \tag{10.2}$$

$$J_\mathrm{q} = -l_{41}\ \nabla\mu_{T2} - l_{42}\ \nabla\mu_{T2} - l_{44}\ \nabla\ \ln T \tag{10.3}$$

$$l_{11} = K_{11} - K_{13}K_{31}/K_{33} = \left(1/z_1^2\right)(1 - t_1)t_1\kappa/F^2 \tag{11.1}$$

$$l_{22} = K_{22} - K_{23}K_{32}/K_{33} = \left(1/z_2^2\right)(1 - t_2)t_2\kappa/F^2 \tag{11.2}$$

$$l_{12} = K_{12} - K_{13}K_{32}/K_{33} = -(1/z_1z_2)t_1t_2\kappa/F^2 \tag{11.3}$$

Since, in the case of pure diffusion, the flux equations should not depend on the choice of electrodes, the above transport coefficients are valid for the cell with the former electrode, on which charge-transfer reaction (2.1) takes place. Therefore

$$L_{11} = l_{11} + L_{13}L_{31}/L_{33} = \left\{1/n^2 + (1/z_1 + 2/n)t_1/z_1\right\}\kappa/F^2 \tag{12}$$

$$L_{22} = l_{22} + L_{23}L_{32}/L_{33} = \left\{1/n^2 + (1/z_2 - 2/n)t_2/z_2\right\}\kappa/F^2 \tag{13}$$

$$L_{12} = l_{12} + L_{13}L_{32}/L_{33} = -\left\{1/n^2 + t_1/z_1n - t_2/z_2n\right\}\kappa/F^2 \tag{14}$$

Determination of L_{ij} (i, j = 1, 2) by ionic diffusion

L_{ij} $(i,\ j = 1, 2)$ can also be obtained using ionic fluxes assuming that three ions, $A_{\nu_1-n_1}M^{z_1}$, $A_{\nu_2-n_2}M^{z_2}$, and A^{z_0}, in the solution move by the gradient of the respective ionic chemical potentials μ_{z_1}, μ_{z_2} and μ_{z_0}, and the electric potential, Φ, which is defined as 1 at the position of the ions [12]. The respective ionic fluxes j_1, j_2 and j_0 may be under the isothermal condition

$$j_1 = \left(\lambda_1/F^2\right)\left\{\mp Fc_1\,\nabla\Phi - \nabla\mu_{z_1}/|z_1|\right\} \tag{15.1}$$

$$j_2 = \left(\lambda_2/F^2\right)\left\{\mp Fc_2\,\nabla\Phi - \nabla\mu_{z_2}/|z_2|\right\} \tag{15.2}$$

and

$$j_0 = \left(\lambda_0/F^2\right)\left\{\mp Fc_0\,\nabla\Phi - \nabla\mu_{z_0}/|z_0|\right\} \tag{15.3}$$

(− for cation: + for anion)

Here, c_1, c_2 and c_0 $(= n_1c_1 + n_2c_2)$ are the concentrations of the ions $A_{\nu_1-n_1}M^{z_1}$, $A_{\nu_2-n_2}M^{z_2}$ and A^{z_0}, respectively. In the case of no electric current, the three mass fluxes of the ions are not independent, since in order to keep electric neutrality

$$z_1j_1 + z_2j_2 + z_0j_0 = 0 \tag{15.4}$$

By eliminating $\nabla\Phi$ with eqns. (15.1)–(15.4) and introducing the relations of the chemical potentials

$$\mu_{T1} = \mu_{z_1} + n_1\mu_{z_0} \tag{16.1}$$

and

$$\mu_{T2} = \mu_{z_2} + n_2\mu_{z_0} \tag{16.2}$$

the same mass flux equations as eqns. (10.1)–(10.3) are obtained with the transport coefficients equal to eqns. (11.1)–(11.3).

Determination of L_{ij}, $i = 4$

Before determining L_{4j}, the heats of transfer of $A_{\nu_1}M$ and $A_{\nu_2}M$, Q_1^* and Q_2^*, respectively, are defined as the ratio of the heat flux and an individual mass flux under the condition of being able to observe only the mass flux of the respective salts:

$$Q_1^* = (J_q/J_1)_{J_2=J=\nabla T=0} \tag{17.1}$$

$$Q_2^* = (J_q/J_2)_{J_1=J=\nabla T=0} \tag{17.2}$$

The transport coefficient, l_{4j} ($j =$ 1, 2, 3) in eqn. (10.3), under no current is expressed with the heats of transfer as

$$l_{41} = Q_1^* l_{11} + Q_2^* l_{21} \tag{18.1}$$

$$l_{42} = Q_1^* l_{12} + Q_2^* l_{22} \tag{18.2}$$

The initial thermoelectric power, ϵ_i, observed just after the temperature change under the uniform concentration and the steady-state thermoelectric power, ϵ_{st}, observed in the Soret equilibrium are related by

$$F(\epsilon_i - \epsilon_{st})T = (-1/n - t_1/z_1)Q_1^* + (1/n - t_2/z_2)Q_2^* \tag{19}$$

where the two thermoelectric powers are defined as

$$\epsilon_i = (\nabla\phi/\nabla T)_{\nabla\mu_{T1}=\nabla\mu_{T2}=J=0} \tag{20}$$

and

$$\epsilon_{st} = (\nabla\phi/\nabla T)_{J_1=J_2=J=0} \tag{21}$$

If a new term Q_e^* is introduced which is the heat transferred only by the current, and is defined as

$$Q_e^* = (J_q/J)_{J_1=J_2=\nabla T=0} = -\epsilon_{st}T \tag{22}$$

then L_{4j} ($j = 1, 2, 3$) are determined as follows.

$$L_{41} = Q_1^* L_{11} + Q_2^* L_{21} + Q_e^* L_{31} \tag{23}$$

$$L_{42} = Q_1^* L_{12} + Q_2^* L_{22} + Q_e^* L_{32} \tag{24}$$

$$L_{43} = Q_1^* L_{13} + Q_2^* L_{23} + Q_e^* L_{33} = -T\kappa\epsilon_i \tag{25}$$

Since heat is transferred purely by thermal conductance in the case of no current and no mass fluxes, the transport coefficient L_{44} is determined from the thermal conductivity, $\mathscr{K}$:

$$L_{44} = \mathscr{K}T + l_{41}Q_1^* + l_{42}Q_2^* + L_{43}^2/L_{33} \tag{26}$$

Transported entropy and heat of transfer

We consider the entropy balance at the right-hand electrode compartment in Fig. 1, when the electric current passes. The entropy which must be added to keep the temperature in the compartment constant is $J_1S_1 + J_2S_2$, where S_1 and S_2 are the entropies of $A_{\nu_1}M$ and $A_{\nu_2}M$, respectively. There is another entropy which must be taken away to compensate the transported entropies. When there is no chemical potential or temperature gradient, the entropy taken away is equal to S_{salt}^*J, where S_{salt}^* is the entropy transported by the whole salts in the solution:

$$S_{\text{salt}}^* = (t_1/z_1)s_1^* + (t_2/z_2)s_2^* + (t_0/z_0)s_0^* \tag{27}$$

Here, s_1^*, s_2^* and s_0^* are the transported entropies of ions $A_{\nu_1-n_1}M^{z_1}$, $A_{\nu_2-n_2}M^{z_2}$ and A^{z_0}, respectively. Thus, ϵ_i is expressed with these entropies:

$$\begin{aligned} F\epsilon_i &= -FL_{43}/T\kappa \\ &= \{1/n + (t_1/z_1)\}S_1 + \{-1/n + (t_2/z_2)\}S_2 - S_{\text{salt}}^* \end{aligned} \tag{28}$$

Under the condition of $J_2 = J = \nabla \ln T = 0$ used in the definition of Q_1^*, the entropy taken away is $(s_1^* + n_1s_0^*)J_1$. Thus, the heats of transfer are expressed with the entropies of the salt and the transported entropies of the ions:

$$Q_1^* = T(s_1^* + n_1s_0^* - S_1) \tag{29.1}$$

$$Q_2^* = T(s_2^* + n_2s_0^* - S_2) \tag{29.2}$$

From eqns. (19), (28), (29.1) and (29.2), ϵ_{st} is expressed only with the transported entropies:

$$F\epsilon_{\text{st}} = (1/n)(s_1^* - s_2^*) \tag{30}$$

Steady state

After the masses move due to the applied temperature and electric potential gradients, a steady state of no net transfer of masses is observed. The electric current, J_{st}, under this condition is simply written with the steady-state conductivity, κ_{st}, and thermoelectric power:

$$J_{\text{st}} = -\kappa_{\text{st}}(\nabla\phi - \epsilon_{\text{st}}\nabla T) \tag{31}$$

$$n^2/\kappa_{\text{st}} = n_A^2|z_0|/\lambda_0C_0 + |z_1|/\lambda_1C_1 + |z_2|/\lambda_2C_2 \tag{32}$$

The chemical potential gradients under this condition are the sum of those due to the electric potential and the temperature gradients:

$$(\nabla\mu_{T1}/\nabla\phi)_{J_1=J_2=J=0}=z_1\{1/C_1\lambda_1-n_A/C_0\lambda_0\}\kappa_{st}F/n \tag{33.1}$$

$$(\nabla\mu_{T2}/\nabla\phi)_{J_1=J_2=J=0}=z_2\{1/C_2\lambda_2-n_A/C_0\lambda_0\}\kappa_{st}F/n \tag{33.2}$$

$$(\nabla\mu_{T1}/\nabla\ \ln\ T)_{J_1=J_2=J=0}=-Q_1^* \tag{34.1}$$

$$(\nabla\mu_{T2}/\nabla\ \ln\ T)_{J_1=J_2=J=0}=-Q_2^* \tag{34.2}$$

EXPERIMENTAL

Procedures

In the measurement of the initial thermoelectric powers, an inverted U-shaped glass cell [13,14], which had a large distance (ca. 200 mm) between two platinum electrodes, was used. An aqueous solution of a mixture of potassium ferrocyanide and potassium ferricyanide was put in the cell. After a stable potential difference (< 0.01 mV) was observed with two legs of the cell immersed in the same water thermostat (293 K), one of the two legs was moved to another controlled thermostat at a different temperature (303 K). The potential difference then became stable within 10 min.

In the measurement of steady-state thermoelectric powers, a thin-layer cell made of acrylic resin as illustrated schematically in Fig. 2 was used. The cell was designed to make deaeration possible, though the detail is not illustrated in Fig. 2. The same solution of potassium ferrocyanide and potassium ferricyanide was put between two platinum disk electrodes (10 mm in diameter and 1 mm thick) using silicone rubber (0.95 mm thick), which had a hole 5.5 mm in diameter. The temperature of the electrodes was controlled by water circulating through the backs of the electrodes, which were insulated by thin plastic film. Temperatures were measured by thermocouples placed in the water near the electrodes. After a stable potential difference (< 0.1 mV, including a small potential difference due to the small temperature difference between two electrodes) was observed by circulating water from the same thermostat kept at 293 K, the water circulating behind one electrode was changed to another thermostat kept at 303 K to change the temperature of the electrode. For measurement of the steady-state conductivities, a potential difference (10 mV) was applied between two electrodes under isothermal conditions (298 K). After a few tens of minutes the potential difference and current became stable in both cases.

In the steady-state measurements, the disk electrodes were placed horizontally. The temperature and electric potential gradients were applied vertically with the upper electrode hotter or positive. It was not necessary to keep the electrodes rigorously horizontal as L'vov et al. suggested [15], since the short distance between the two electrodes impedes natural convection. The real temperature differences between the two electrodes for the calculation of the thermoelectric powers were estimated after correction of the temperature decrease in the platinum electrodes.

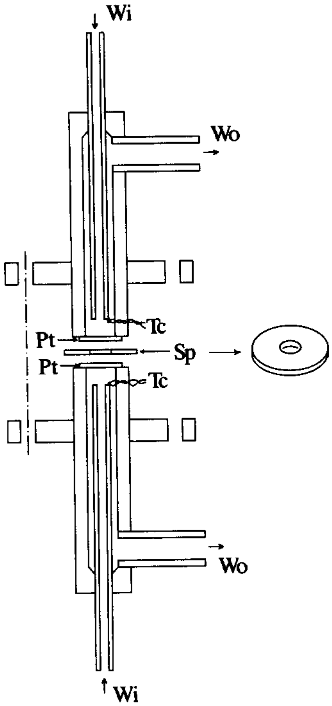

Fig. 2. Thin-layer cell for the steady-state measurements. (Sp) Silicone rubber space; (Tc) thermocouple; (Pt) platinum disc electrode; (Wi) water inlet; (Wo) water outlet.

The correction due to the thermal conductances of platinum and water is nearly 3%. After correction, the steady-state thermoelectric powers obtained with a 0.95 mm and 0.50 mm thickness spacer were similar within experimental error.

Equipment

A Solartron 1286 Electrochemical Interface was used as a potentiostat and to measure the potential difference. The thermostats used were Toyo Rikakikai NCB-211 and NESLAB instruments RTE-5, which had the ability to control the temperature of water within ±0.02 K. The voltage of the thermocouples was measured with a Hewlett-Packard HP-3457A multimeter. The potentiostat and multimeter were connected to an HP-9000-310 personal computer.

Chemicals

Potassium ferrocyanide and potassium ferricyanide of guaranteed grade were used without further purification.

RESULTS

Measurements were made in two ionic strengths with different concentration ratios of potassium ferrocyanide and potassium ferricyanide; one was $I' = 0.16$ M ($\mathrm{M} = \mathrm{mol/dm^3}$), corresponding to 0.01 M + 0.01 M solution and the other was $I' = 5.8$ M, corresponding to 0.36 M + 0.36 M solution, where I' is the apparent ionic strength calculated under the assumption of complete dissociation of both salts ($I' = 10C_1 + 6C_2$). The solution of low ionic strength was deaerated by bubbling highly pure argon gas, although the deaeration did not cause any change in the measurement results. The solution of high ionic strength was not deaerated, since a small volume of the solution was used. The conductivities and thermoelectric powers obtained are plotted against the concentration ratios in Figs. 3 and 4.

CALCULATION AND DISCUSSION

The general forms of the atomic groups and some numbers such as stoichiometric numbers, charge numbers and so on considered in the Theoretical Analysis section are modified to the following forms in this specific case: $\nu_1 = 4$, $\nu_2 = 3$, $z_0 = 1$, $z_1 = 0$ to -4, $z_2 = 0$ to -3, $n_1 = -z_1$, $n_2 = -z_2$, $n = 1$, $n_A = 1 - (|z_1| - |z_2|)$, $\mathrm{A} = \mathrm{K}$, $\mathrm{M} = [\mathrm{Fe(CN)_6}]$, $\mathrm{A}_{\nu_1}\mathrm{M} = \mathrm{K_4[Fe(CN)_6]}$, $\mathrm{A}_{\nu_2}\mathrm{M} = \mathrm{K_3[Fe(CN)_6]}$, $\mathrm{A}^{z_0} = \mathrm{K}^+$, $\mathrm{A}_{\nu_1 - n_1}\mathrm{M}^{z_1} = \mathrm{K}_{4+z_1}[\mathrm{Fe(CN)_6}]^{z_1}$, $\mathrm{A}_{\nu_2 - n_2}\mathrm{M}^{z_2} = \mathrm{K}_{3+z_2}[\mathrm{Fe(CN)_6}]^{z_2}$.

Estimation of conductivities from the literature

In order to calculate the ionic conductivities and heats of transfer using the equations in the Theoretical Analysis section, it was necessary to have some

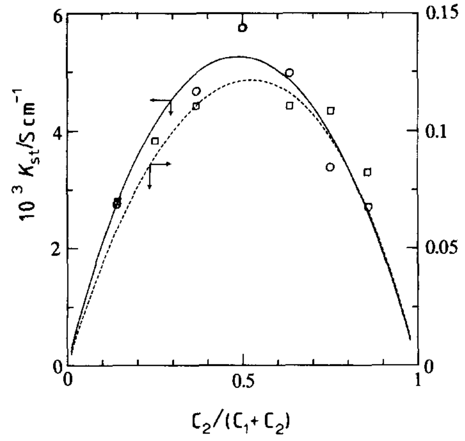

Fig. 3. Conductivity (κ_{st}) changes under the steady state vs. the concentration of the redox couple at 298 K. The lines are calculated from eqn. (32) with the calculated ionic conductivities in Table 1. (○, ———) $I' = 0.16$ M; (□, - - - - - -) $I' = 5.8$ M.

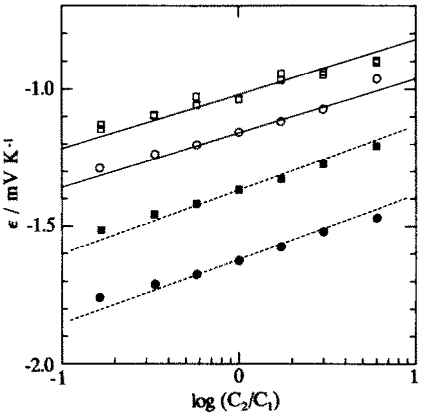

Fig. 4. Change of the thermoelectric powers at initial time (ϵ_i) and under the steady state (ϵ_{st}) vs. the concentration ratio of the redox couple between 293 and 303 K. The solid lines are theoretical straight lines of ϵ_{st} by eqn. (39.1) with a slope of 0.198 mV K^{-1}. The dashed lines show ϵ_i calculated by eqn. (19) using ϵ_{st} on the straight lines. (○) ϵ_{st} ($I' = 0.16$ M); (●) ϵ_i ($I' = 0.16$ M); (□) ϵ_{st} ($I' = 5.8$ M); (■) ϵ_i ($I' = 5.8$ M).

TABLE 1

Calculated properties of the thermocell with potassium ferrocyanide and potassium ferricyanide at 298 K

	Lower ionic strength	Higher ionic strength
Apparent ionic strength [a]		
I'/mol dm^{-1}	0.16	5.8
Estimated values from data in the literature [b]		
λ_0/S cm mol^{-1}	63	50
Λ_1/4 S cm mol^{-1}	104	70
Λ_2/3 S cm mol^{-1}	119	81
Calculated from measurement results		
I/mol dm^{-3} [c]	0.101 ± 0.001	2.6 ± 0.1
$\lambda_1/\lvert z_1 \rvert$ S cm mol^{-1}	21	24
$\lambda_2/\lvert z_2 \rvert$ S cm mol^{-1}	37	34
z_1	-3.2	-2.4
z_2	-2.5	-2.0
ϵ_{st}^{o}/mV K^{-1}	-1.16	-1.02
ϵ_i^{o}/mV K^{-1}		
Q_1^*/kJ mol^{-1}	$12.2 + 0.82Q_2^*$ [d]	$8.9 + 0.77Q_2^*$ [d]
$(C_2/C_1)_{cr}$	(12) [e]	12
Q_1^*/kJ mol^{-1}	(11.2) [e]	8.2
Q_2^*/kJ mol^{-1}	(-1.2) [e]	-0.9

[a] $I' = \{16C_1 + 9C_2 + (4C_1 + 3C_2)\}/2$.

[b] Ref. 16.

[c] $I = \{z_1^2 C_1 + z_2^2 C_2 + (\lvert z_1 \rvert C_1 + \lvert z_2 \rvert C_2)\}/2$.

[d] Q_2^* in kJ mol^{-1}.

[e] Estimated from $(C_2/C_1)_{cr}$ of higher ionic strength.

conductivities from literature data [16]. The ionic molar conductivity of potassium ion was estimated from the molar conductivity of aqueous potassium chloride solution with its transport number. The molar conductivities Λ_1 and Λ_2 of potassium ferrocyanide and potassium ferricyanide, respectively, were determined from the conductivities of the solution of the single salt. In each case, the conductivities were determined for the same ionic strength, I, which was calculated using the equation in the footnote of Table 1 assuming the association with the counter-ion. The results are listed in the table.

Ionic conductivities and charge numbers of ions

Conductivity under the steady state is a function of two variables, $1/C_1$ and $1/C_2$, as seen in eqn. (32), which can also be written as

$$n^2/\kappa_{st} - n_A^2 |z_0|/\lambda_0 C_0 = (|z_1|/\lambda_1)/C_1 + (|z_2|/\lambda_2)/C_2 \tag{35}$$

In this equation, the left-hand term is an observable value which is a function of the two variables. $|z_1|/\lambda_1$ and $|z_2|/\lambda_2$ were obtained by the least-mean-square method for a multivariable from the data in Fig. 3. In the calculation of the left-hand term, n_A and C_0 were first obtained assuming appropriate z_1 and z_2 values. After calculation of z_1 and z_2 as explained later in this section, $|z_1|/\lambda_1$ and $|z_2|/\lambda_2$ were calculated by the least-mean-square method for the same data again. Since the second term of the left-hand side represents a small correction, only a small difference was obtained after the replication of the least-mean-square calculation.

Combining the molar conductivity of the solution of the single salt,

$$\Lambda_i = |z_i|\lambda_i + n_i|z_0|\lambda_0 \qquad (i = 1 \text{ or } 2) \tag{36}$$

with $\lambda_i/|z_i|$ obtained from the steady-state conductivities, z_1 and z_2 were determined as shown in Table 1. As can be seen in this table, z_1 and z_2 were not integers due to the equilibrium of the association reaction in eqns. (1.1) and (1.2). Although the flux equations must be solved with the equilibrium reaction to obtain rigorous equations, in this paper a real number for z_i is used as an approximation. The charge numbers of the ions can be determined from the following dissociation constants from ref. 17:

$$[\mathrm{Fe(CN)_6}]^{4-} + \mathrm{K}^+ \rightleftarrows \mathrm{K[Fe(CN)_6]}^{3-} \tag{37.1}$$

$\log K = 1.5$ ($I = 0.1$ M)

$$[\mathrm{Fe(CN)_6}]^{3-} + \mathrm{K}^+ \rightleftarrows \mathrm{K[Fe(CN)_6]}^{2-}, \tag{37.2}$$

$\log K = 0.85$ ($I = 0.1$ M)

$\log K = 0.18$ ($I = 2.0$ M)

The expected closest integer numbers are $z_1 = -3$ and $z_2 = -3$ at the low ionic strength and $z_1 = -3$ and $z_2 = -2$ at the higher ionic strength. These numbers are very similar to the real numbers obtained here.

The steady-state conductivities calculated by eqn. (32) from these ionic equivalent conductivities and z_i are shown by the solid and dashed lines in Fig. 3. Maximum conductivities were obtained at $C_2/(C_1 + C_2)$ equal to 0.49 ($I' = 0.16$ M) and 0.52 ($I' = 5.8$ M).

Steady-state thermoelectric power

Since the excess entropy of the transported entropy is very small [1], i.e.

$$s_i^* = s_i^{*\circ} - R \ln c_i \qquad (i = 1,2), \tag{38}$$

where $s_1^{*\circ}$ and $s_2^{*\circ}$ are the standard transported entropies of $A_{\nu_1-n_1}M^{z_1}$ and $A_{\nu_2-n_2}M^{z_2}$, respectively, eqn. (30) gives ϵ_{st} linearly proportional to the logarithm of the concentration ratio of the redox couple as

$$F\epsilon_{st} = F\epsilon_{st}^\circ + (1/n)R \ln(C_2/C_1) \tag{39.1}$$

$$F\epsilon_{st}^\circ = (1/n)(s_1^{*\circ} - s_2^{*\circ}) \tag{39.2}$$

The observed values of ϵ_{st} are almost on a straight line of slope equal to 2.303 R/F ($= 0.198$ mV/K) as shown in Fig. 4. Small deviations from a straight line may be due to the concentration dependence of $s^{*\circ}$. The steady-state thermoelectric powers at a concentration ratio equal to 1, ϵ_{st}°, are given in Table 1.

Heats of transfer

From eqn. (19) it seems possible to obtain Q_1^* and Q_2^* by the least-mean-square method for two variables. $F(\epsilon_i - \epsilon_{st})T$ is the observed value, and $(-1/n - t_1/z_1)$ and $(1/n - t_2/z_2)$ two variables. The data in Fig. 4, however, gave abnormally large heats of transfer, more than 100 kJ/mol. This demonstrates that these two variables is not completely independent. The ratio of these two variables is in very close approximation to 0.82 ± 0.02 ($I' = 0.16$ M) and 0.77 ± 0.03 ($I' = 5.8$ M). If the measurement can be made more precisely and the heats of transfer are completely constant, individual Q_1^* and Q_2^* will be obtained by eqn. (19). In ordinary measurement, only the relation between Q_1^* and Q_2^* in the form

$$Q_1^* = r_Q Q_2^* + Q^* \tag{40.1}$$

can be obtained as shown in Table 1, where r_Q and Q^* are calculated from the observed data as

$$r_Q = \langle (1/n - t_2/z_2)/(1/n + t_1/z_1) \rangle \tag{40.2}$$

$$Q^* = -\langle F(\epsilon_i - \epsilon_{st})T/(1/n + t_1/z_1) \rangle \tag{40.3}$$

$\langle\ \rangle$ = average

In order to determine Q_1^* and Q_2^* separately, it is necessary to use another relation between them. A possible data set which gives such a relation is S_1, S_2 and s_0^*, which are in the literature [1,17,18]. From eqns. (27)–(30), the difference of the heat of transfer is

$$Q_1^* - Q_2^* = T\{nF(\epsilon_i - \epsilon_{st}) + (n_1 - n_2)s_0^* - (S_1 - S_2)\} \tag{41}$$

The simultaneous equation of eqns. (40.1) and (41) may give Q_1^* and Q_2^* separately. It was again impossible to obtain reliable values, because only a small error of 1 e.u. (= 4.8 J/K mol) in the entropies brings about a large change (~ 20 kJ/mol) in the heat of transfer. Since the two relations in eqns. (40.1) and (41) are almost in the same form, the determinant of the simultaneous equation was very small.

Another way to determine the individual heats of transfer is to measure the concentration difference between the two electrodes. In this work, a critical point of natural convection taking place due to the concentration difference was used instead of the measurement of the individual concentration difference of the salts. The convection can be detected from the time change of the potential difference after the temperature gradient is applied. As shown in Fig. 5(a–h) at the high ionic strength, when the upper electrode was set at the higher temperature, a smooth decrease (in absolute values) after a peak in the potential difference was observed due to thermal diffusion (Soret effect) with no convection. In the opposite temperature gradient, the convection took place at a smaller concentration ratio than $C_2/C_1 = 9$ as seen in Fig. 5(a–f′), in which the potential difference gave oscillations. The convection did not take place under a higher concentration ratio than $C_2/C_1 = 12$ as seen in Fig. 5(g′ and h′), in which the potential change in time is very smooth. Since no convection took place at $C_2/C_1 \geqslant 12$ in either direction of the temperature gradient, the small concentration difference was generated by the thermal diffusion in this concentration region. Therefore, the critical concentration ratio, $(C_2/C_1)_{cr}$, may be equal to around 12. In the case of the low ionic strength,

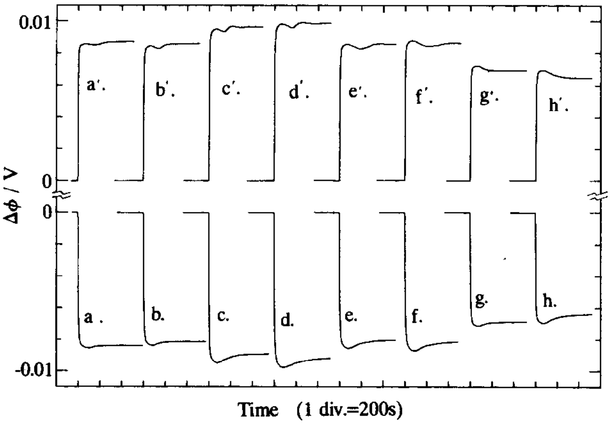

Fig. 5. Potential difference ($\Delta\phi$, against lower electrode) with time for various concentration ratios. (Since the temperature difference in this measurement was varied from curve to curve, the observed $\Delta\phi$ was not equal to $\epsilon_{st} \times 10$ K.) $r = C_2/C_1$ (a, a′) $r = 0.33$; (b, b′) $r = 1$; (c, c′) $r = 1.73$; (d, d′) $r = 3$; (e, e′) $r = 6$; (f, f′) $r = 9$; (g, g′) $r = 12$; (h, h′) $r = 100$. (a–h) Higher temperature at the upper electrode; (a′–h′) lower temperature at the upper electrode.

the convection was not observed in any direction of the temperature gradient or in any concentration ratio, since the concentration difference generated by the thermal diffusion is so small.

The critical point calculated from the Rayleigh number is complicated in the case of simultaneous diffusion of matter and temperature [19]. The approximate critical point of the concentration may be calculated from the balance point of the density change due to concentration and that due to temperature as

$$\beta_1(\nabla C_1/\nabla T)_{J_1=J_2=J=0} + \beta_2(\nabla C_2/\nabla T)_{J_1=J_2=J=0} + \beta = 0 \tag{42}$$

where β_1, β_2 and β are coefficients of the density (ρ) change by concentration and temperature in the following equation:

$$\rho = \beta_1 C_1 + \beta_2 C_2 + \beta T \tag{43}$$

Inserting eqns. (34.1) and (34.2) into eqn. (43) under the assumption of constant activity coefficients, we arrive at the following expression of the critical concentration ratio:

$$(C_2/C_1)_{\text{cr}} = -\beta_1 Q_1^*/\beta_2 Q_2^* - \beta T/\beta_2 Q_2^* C_1 \tag{44.1}$$

Since the second term in eqn. (44.1) can be neglected in the case of high concentrations, eqn. (44.1) can now be written as

$$Q_1^*/Q_2^* = -(C_2/C_1)_{\text{cr}}(\beta_2/\beta_1) \tag{44.2}$$

Q_1^* and Q_2^* calculated from eqn. (44.2) and eqn. (40) are given in Table 1, where the heats of transfer at low ionic strength were also calculated assuming that $(C_2/C_1)_{\text{cr}} = 12$. The values of Q_1^* obtained, 11.2 and 8.2 kJ/mol for $I' = 0.16$ and 5.8, respectively, are reasonably in the region of the heat of transfer of many other salts, 1–10 kJ/mol [1,2]. No literature data of Q_1^* and Q_2^* are available to our knowledge. The negative sign obtained for Q_2^*, -1.2 and -0.9 J/mol for $I' = 0.16$ and 5.8, respectively, is not common for the heat of transfer; a few salts such as alkali iodides have a negative value [1].

CONCLUSION

The transport coefficients in the flux equations of a thermocell with soluble redox couples could be determined by the observable values. Using these transport coefficients, the following properties of a thermocell with potassium ferrocyanide and potassium ferricyanide were calculated from the measurement results with various concentration ratios of the redox couple and data in the literature.

The steady-state conductivity of the cell gave the charge numbers of the redox ions. Although the initial and steady-state thermoelectric powers can fundamentally give the heats of transfer of potassium ferrocyanide and potassium ferricyanide, it was impossible to obtain reliable values. The thermoelectric powers can give only the relation between them. Another relation obtained from the critical concentration of the natural convection gave the individual heats of transfer. The properties obtained reproduced the experimental results.

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LIST OF SYMBOLS

$A_{\nu_1}M$, $A_{\nu_2}M$	soluble salts of the redox couple
$A_{\nu_1-n_1}M^{z_1}$, $A_{\nu_2-n_2}M^{z_2}$	ions of the redox couple
A^{z_0}	counter-ion
c_1, c_2, c_0	concentrations of the ions, $A_{\nu_1-n_1}M^{z_1}$, $A_{\nu_2-n_2}M^{z_2}$ and A^{z_0}, respectively (mol m^{-3})
C_1, C_2	concentrations of the salts $A_{\nu_1}M$ and $A_{\nu_2}M$, respectively (mol m^{-3})
$(C_2/C_1)_{cr}$	critical concentration ratio for the convection
F	Faraday constant (96485 C mol^{-1})
I'	apparent ionic strength assuming complete dissociation (mol m^{-3})
I	ionic strength (mol m^{-3})
j_1, j_2, j_0	fluxes of the ions $A_{\nu_1-n_1}M^{z_1}$, $A_{\nu_2-n_2}M^{z_2}$, and A^{z_0}, respectively (mol s^{-1} m^{-2})
J_1, J_2	fluxes of the salts $A_{\nu_1}M$ and $A_{\nu_2}M$, respectively (mol s^{-1} m^{-2})
J	electric current density (A m^{-2})
J_q	heat flux (W m^{-2})
J_{st}	electric current density under the steady state (A m^{-2})
K	association constant
K_{ij}	transport coefficient in eqn. (8)
$\mathscr{K}$	thermal conductivity (W m^{-1} K^{-1})
l_{ij}	transport coefficient in eqn. (10) under pure diffusion
L_{ij}	transport coefficient in eqn. (3)
n	electron number of electron-transfer reaction
n_A	difference of the association number of the redox ions
n_1, n_2	numbers of counter-ions dissociated from $A_{\nu_1}M$ and $A_{\nu_2}M$, respectively
Q_1^*, Q_2^*,	heats of transfer of $A_{\nu_1}M$ and $A_{\nu_2}M$, respectively (J mol^{-1})
Q_e^*	heat transferred only by the current (J mol^{-1})
r_Q, Q^*	constants in eqn. (40)
R	gas constant (8.314 J mol^{-1} K^{-1})
s_0^*, s_1^*, s_2^*	transported entropies of the ions A^{z_0}, $A_{\nu_1-n_1}M^{z_1}$ and $A_{\nu_2-n_2}M^{z_2}$, respectively (J mol^{-1} K^{-1})
$s_1^{*\circ}$, $s_2^{*\circ}$	standard transported entropies of $A_{\nu_1-n_1}M^{z_1}$ and $A_{\nu_2-n_2}M^{z_2}$, respectively (J mol^{-1} K^{-1})

S^{*}_{salt}	transported entropy of the whole salts in the solution (J mol^{-1} K^{-1})
S_1, S_2	partial molar entropies of the salts $A_{\nu_1}M$ and $A_{\nu_2}M$, respectively (J mol^{-1} K^{-1})
t_0, t_1, t_2	transport numbers of the ions A^{z_0}, $A_{\nu_1-n_1}M^{z_1}$ and $A_{\nu_2-n_2}M^{z_2}$, respectively
T	temperature (K)
z_0	charge number of the counter-ion
z_1, z_2	charge numbers of the associated ions $A_{\nu_1-n_1}M^{z_1}$ and $A_{\nu_2-n_2}M^{z_2}$, respectively
β	coefficient of the density change by temperature (kg m^{-3} K^{-1})
β_1, β_2	coefficients of the density change by concentration of $A_{\nu_1}M$ and $A_{\nu_2}M$, respectively (kg mol^{-1})
ϵ_i	initial thermoelectric power (V K^{-1})
ϵ_{st}	steady-state thermoelectric power (V K^{-1})
ϵ°_{st}	ϵ_{st} at $c_2 = c_1$ (V K^{-1})
κ	specific conductivity of the solution (S m^{-1})
κ_{st}	specific conductivity under the steady state (S m^{-1})
λ_1, λ_2, λ_0	ionic molar conductivities of $(1/z_1)A_{\nu_1-n_1}M^{z_1}$, $(1/z_2)A_{\nu_2-n_2}M^{z_2}$ and $(1/z_0)A^{z_0}$, respectively (S m^2 mol^{-1})
Λ_1, Λ_2	molar conductivities of $A_{\nu_1}M$ and $A_{\nu_2}M$, respectively (S m^2 mol^{-1})
$\nabla\mu_{T1}$, $\nabla\mu_{T2}$	chemical potentials at temperature T of $A_{\nu_1}M$ and $A_{\nu_2}M$, respectively (J mol^{-1})
ν_1, ν_2	stoichiometric numbers in the salts $A_{\nu_1}M$ and $A_{\nu_2}M$, respectively
ρ	density (kg m^{-3})
ϕ	electric potential observed by electron-transfer reaction (2.1) (V)
ϕ'	electric potential observed by electron-transfer reaction (7) (V)
Φ	electric potential at the ion (V)

REFERENCES

1 J.N. Agar in P. Delahay (Ed.), Advances in Electrochemistry and Electrochemical Engineering, Vol. 3, Wiley, New York, 1961.
2 R. Haase, Thermodynamics of Irreversible Processes, Addison-Wesley, Reading, MA, 1962.
3 H.L. Chum and R.A. Osteryoung, US DOE Rep., SERI-TR-332-416-VOL-1 (1980) and -VOL-2 (1981)
4 T. Ikeshoji, Rep. Gov. Ind. Res. Inst. Tohoku, 17 (1984) 39.
5 B. Burrows, J. Electrochem. Soc., 123 (1976) 154.
6 T.I. Quickenden and C.F. Vernon, Sol. Energy, 36 (1986) 63.
7 T. Ikeshoji, Bull. Chem. Soc. Jpn., 60 (1987) 1505.
8 P. Blanc and C. Madic, Inorg. Chim. Acta, 95 (1984) 141.
9 R. Tamamushi, J. Electroanal. Chem., 65 (1975) 263.
10 A.J. deBethune, J. Electrochem. Soc., 107 (1969) 829.
11 K. Førland, T. Førland and S.K. Ratkje, Irreversible Thermodynamics, Wiley, New York, 1989.
12 In the case of a solution of a single salt, see, for example, J.O'M. Bockris and A.K.N. Reddy, Modern Electrochemistry, Vol. 1, Plenum, New York, 1970.

13 T. Ikeshoji and S.K. Ratkje, J. Electrochem. Soc., 133 (1986) 1107.
14 S.K. Ratkje, T. Ikeshoji and K. Syverud, J. Electrochem. Soc., 137 (1990) 2088.
15 S.N. L'vov, Ya.D. Rakhmilevich and I.A. Dibrov, Zh. Fiz. Khim., 60 (1986) 2896.
16 H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolyte Solutions, 3rd ed., Reinhold, 1958.
17 R.M. Smith and A.E. Martell, Critical Stability Constants, Vol. 4, 1976 and Vol. 5, 1982, Plenum, New York.
18 D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney and R.L. Nuttall, J. Phys. Chem. Ref. Data, 11, Suppl. 2 (1982).
19 P. Glansdorff and I. Prigogine, Thermodynamic Theory of Structure, Stability and Fluctuations, Wiley, New York, 1971.