NOTES

The Seebeck Effect in an Electrolytic Thermocouple Involving Ion-permselective Membranes

By Toshio IKEDA and Masao TSUCHIYA*

(Received March 30, 1964)

Several years ago, Tyrrell and his co-workers¹⁾ reported on the Seebeck effect on the purely electrolytic thermocouple of the following system:

$$\begin{array}{l|c|l} \mathrm{Ag/AgX,\ MX}(m) & \begin{array}{c}\text{Ion exchanger}\\ \text{in M}^+\text{ form (MR)}\end{array} & \mathrm{MX}(m),\ \mathrm{AgX/Ag} \\ T \qquad\quad T & & T+\Delta T \qquad\quad T \end{array} \tag{1}$$

Their purpose was to explain the thermal sensation of nerve systems. Recently, we have studied an electrolytic thermocouple of the following type:

$$\begin{array}{lcccl} & \mathrm{D} & & \mathrm{D'} & \\ \mathrm{Hg/HgCl,\ KCl}(m^{\circ}) & \vdots & \mathrm{KCl}(m) & \vdots & \mathrm{KCl}(m^{\circ}),\ \mathrm{HgCl/Hg} \\ T & T & & T+\Delta T & T \end{array} \tag{2}$$

where D and D′ are ion-permselective membranes of an identical nature, but kept at different temperatures, T and $T+\Delta T$ respectively; the whole system is symmetrical in its construction, except for the temperature gradient applied to it.

As can easily be seen from the structure, the EMF of the cell 2 consists of two parts: one is the difference between the two isothermal membrane potentials arising at two membranes kept at different temperatures, T and $T+\Delta T$ respectively; the other is the difference between the two thermal diffusion potentials²⁾ which are revealed in opposite directions in two solution phases of different concentrations, m° and m. By taking the sign convention of EMF, ΔE, of the cell 2 to follow the sign of the calomel electrode on the hot side, we have, then, for the first approximation:

$$\boldsymbol{F}\Delta E=\frac{\partial}{\partial T}\left[\sum\nolimits_k \frac{t_k'}{z_k}\boldsymbol{R}T\ln\frac{m_k\gamma_k}{m_k^{\circ}\gamma_k^{\circ}}\right]\Delta T - \frac{\partial}{\partial m}\left[\sum\nolimits_k \frac{t_k Q_k^*}{z_k T}\Delta T\right](m-m^{\circ}) \tag{3}$$

where $\boldsymbol{F}$ and $\boldsymbol{R}$ have their usual meanings; T is the absolute temperature; t_k and t_k' are the transport numbers of k-th ion species of z_k valency in the solution and membrane phases respectively; m_k and γ_k are the molality and the activity coefficient of k-th ion species on the molality scale, and the symbols with the superfix o refer to those in the outer electrolytic solution. Q_k^* is the ionic heat of transfer of k-th ion species. As judged from the Q_k^* values,³⁾˒⁴⁾ the second term on the right side of Eq. 3 can be ignored as compared with the first. Moreover, if a single 1, 1 valent electrolyte is used and if the membranes are perfectly permselective exclusively to one ion species (for example, to K^+), (i.e., in the case of $t'_{K^+}=1$, $t'_{Cl^-}=0$; accordingly, $\partial t'_{K^+}/\partial T=0$, $\partial t'_{Cl^-}/\partial T=0$), Eq. 3 can practically be approximated to $\boldsymbol{F}\mathrm{d}E/\mathrm{d}T = 2.303\boldsymbol{R}\log_{10}(m_{K^+}\gamma_{K^+}/m^{\circ}_{K^+}\gamma^{\circ}_{K^+})$, since the contribution from $\partial\ln\gamma_{K^+}/\partial T$ is very small, not exceeding 3% of the total in most cases.

Oxidized collodion membranes⁵⁾˒⁶⁾ prepared in a bag form, of nearly equivalent nature, were pasted with collodion to the nozzles of both terminal calomel electrodes. The membranes used were nearly completely permselective to cations, as judged from their apparent cation transport number being found to be about 0.97. Anion permselective membranes

---

* Present address: Tokyo Metropolitan Isotope Centre, Setagaya, Tokyo

1) H. J. V. Tyrrell, D. A. Taylor and C. M. Williams, *Nature*, **177**, 668 (1956).

2) E.g., H. J. V. Tyrrell, "Diffusion and Heat Flow in Liquids," Butterworths, London (1961), p. 59.

3) T. Ikeda, *Rep. Liberal Arts Sci. Fac., Shizuoka Univ., Nat. Sci.*, **2**, 153 (1959).

4) P. N. Snowdon, and J. C. R. Turner, *Trans. Faraday Soc.*, **56**, 1409 (1960).

5) H. P. Gregor and K. Sollner, *J. Phys. Chem.*, **50**, 53 (1946).

6) T. Ikeda and K. Tarumoto, *Rep. Liberal Arts Sci. Fac., Shizuoka Univ., Nat. Sci.*, **3**, 109 (1961); ibid., **3**, 165 (1962).

were prepared by forming a resin in the cellophane matrix by diffusing formaldehyde and aniline hydrochloride in aqueous media from either side of a cellophane that was tied with cotton thread to the endings of the nozzeles of two terminal calomel electrodes. The apparent anion transport numbers of these membranes were found to be about 0.91. The electrode nozzles so prepared were inserted into the appropriate compartments of an H-shaped cell filled with an m molal potassium chloride sulution. The temperature of two legs of the H-cell was controlled by thermostated water in Dewar vessels, fixed on one side, while it was varied around the mean temperature of 25°C on the other side. The EMF of the cell 2 was measured by varying, for the sake of experimental convenience, the concentration, m, of the inner pottasium chloride solution, while that of the outer was fixed at a convenient value. The EMF was found, for all values of m, to be proportional to the temperature difference, ΔT, in the temperature range studied. In Fig. 1 the temperature coefficient, $\mathrm{d}E/\mathrm{d}T$, was plotted against $\log m\gamma_\pm$, where $\gamma_\pm$ is the mean ionic activity coefficient. A nearly linear relation with a slope of about 197 μV./deg. (which was very close to the theoretical value, $2.3\,\boldsymbol{R/F}$) was found there, well agreeing with the present theory and with Tyrrell's results for the system 1. Reverse phenomena were found when anion-selective membranes were used in place of cation-selective membranes. The slope was somewhat higher than the theoretical expectation; however, this might be due to some change in the chemical nature of the anion-selective membranes used here, because these membranes were found to exhibit a faster fading of the isothermal membrane potential at higher temperatures.

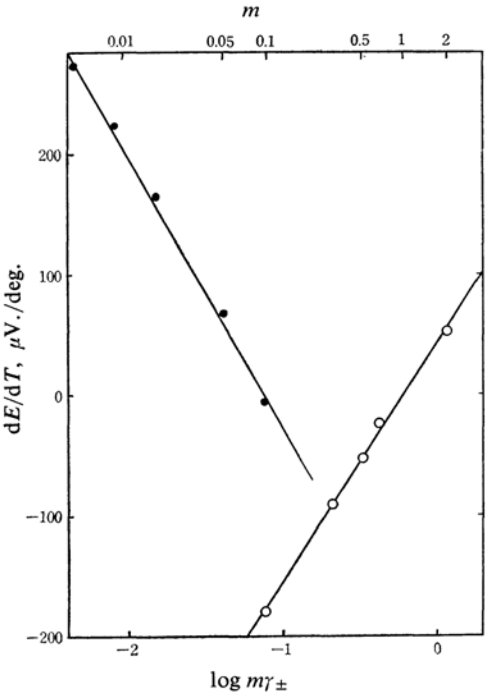

Fig. 1. Initial thermoelectric power $\mathrm{d}E/\mathrm{d}T$ of the system 2.

- ○, for the system, oxidized collodion membranes being used, where m° was fixed at 1 M.
- ●, for the system, aniline-formaldehyde resin membranes being used, where m° was fixed at 0.1 M.

These facts indicate that the mechanism for the generation of EMF is perhaps the same in both systems, 1 and 2. The magnitude of $\mathrm{d}E/\mathrm{d}T$ here obtained is in itself probably insufficient to explain why it is a stimulant in producing the thermal sensation, but several tens of nerve fibers would serve, if the cooperative function of the nerve fiber systems is taken into consideration.

Department of Chemistry
Shizuoka University
Oiwa, Shizuoka