Electrolytic Thermocouple for the Determining Soret Coefficients and Heats of Transfer of Hydrochloric Acid

By Toshio IKEDA

(Received July 29, 1964)

It is impossible to determine the Soret coefficients or the ionic heats of transfer directly from the initial thermoelectric power of a thermocell alone, though there is an intimate relation between them. It is possible, however, to determine the value of one electrolyte relative to the other electrolyte when two thermocells with a common electrode system are coupled. This procedure was employed on hydrochloric acid in the present work.

General Relations.—We used an electrolytic thermocouple of the following system:

$$\begin{array}{lll} \mathrm{Hg/HgCl,\ KCl}(m), & & \\ \quad T & & \\ & \mathrm{HgCl/Hg/HgCl,\ HCl}(m), & \mathrm{HgCl/Hg} \\ & \quad T+\varDelta T & \quad T \end{array} \qquad (1)$$

The initial thermoelectric powers, $\varepsilon_0^{\mathrm{KCl}}$ and $\varepsilon_0^{\mathrm{HCl}}$, for two thermocells constituting the left and right halves of cell system 1 can be written, respectively, as follows:[1]

$$\boldsymbol{F}\varepsilon_0^{\mathrm{KCl}} = -t_{\mathrm{K^+}}^{\mathrm{KCl}}\frac{Q_{\mathrm{K^+}}^{*\mathrm{KCl}}}{T} + t_{\mathrm{Cl^-}}^{\mathrm{KCl}}\frac{Q_{\mathrm{Cl^-}}^{*\mathrm{KCl}}}{T} + S_{\mathrm{Cl^-}}^{\mathrm{KCl}} + S_{\mathrm{Hg}} - S_{\mathrm{HgCl}} - S_{\mathrm{el}} - \frac{Q_{\mathrm{el}}^{*}}{T} \qquad (2)$$

and

$$\boldsymbol{F}\varepsilon_0^{\mathrm{HCl}} = -t_{\mathrm{H^+}}^{\mathrm{HCl}}\frac{Q_{\mathrm{H^+}}^{*\mathrm{HCl}}}{T} + t_{\mathrm{Cl^-}}^{\mathrm{HCl}}\frac{Q_{\mathrm{Cl^-}}^{*\mathrm{HCl}}}{T} + S_{\mathrm{Cl^-}}^{\mathrm{HCl}} + S_{\mathrm{Hg}} - S_{\mathrm{HgCl}} - S_{\mathrm{el}} - \frac{Q_{\mathrm{el}}^{*}}{T} \qquad (3)$$

where $\boldsymbol{F}$ is the Faraday; T is the absolute temperature; $t_{\mathrm{K^+}}^{\mathrm{KCl}}$ and $Q_{\mathrm{K^+}}^{*\mathrm{KCl}}$ are, respectively, the transport number and the ionic heat of transfer of potassium ions in an aqueous solution of potassium chloride at the molality of m, and $t_{\mathrm{Cl^-}}^{\mathrm{KCl}}$ and $Q_{\mathrm{Cl^-}}^{*\mathrm{KCl}}$ are the similar quantities for the chloride ions; $S_{\mathrm{Cl^-}}^{\mathrm{KCl}}$ represents the partial molar entropy of the chloride ions in an aqueous m molal solution of potassium chloride; S_{Hg} and S_{HgCl} are, respectively, the molar entropies of the liquid mercury and of the solid mercurous chloride of the calomel electrode, and S_{el} and Q_{el}^{*} are, respectively, the molar entropy and the molar heat of transfer of electrons in the metallic leads of the electrodes. Equation 3 may be read in a similar fashion.

Now, if the following two conditions:

$$Q_{\mathrm{Cl^-}}^{*\mathrm{KCl}} = Q_{\mathrm{Cl^-}}^{*\mathrm{HCl}} \text{ and } S_{\mathrm{Cl^-}}^{\mathrm{KCl}} = S_{\mathrm{Cl^-}}^{\mathrm{HCl}} \qquad (4)$$

are allowed simultaneously, the resultant initial thermoelectric power, $(\mathrm{d}E/\mathrm{d}T)_0$, for the electrolytic thermocouple of system 1 may be written as follows:

$$\boldsymbol{F}\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_0 = -t_{\mathrm{K^+}}^{\mathrm{KCl}}\frac{Q_{\mathrm{K^+}}^{*\mathrm{KCl}} + Q_{\mathrm{Cl^-}}^{*\mathrm{KCl}}}{T} + t_{\mathrm{H^+}}^{\mathrm{HCl}}\frac{Q_{\mathrm{H^+}}^{*\mathrm{HCl}} + Q_{\mathrm{Cl^-}}^{*\mathrm{HCl}}}{T} \qquad (5)$$

where the identity conditions, $t_{\mathrm{K^+}}^{\mathrm{KCl}} + t_{\mathrm{Cl^-}}^{\mathrm{KCl}} = 1$ and $t_{\mathrm{H^+}}^{\mathrm{HCl}} + t_{\mathrm{Cl^-}}^{\mathrm{HCl}} = 1$, are used. Further, Eq. 5 can be rewritten in terms of the Soret coefficients, σ^{KCl} and σ^{HCl}, as follows:

$$\boldsymbol{F}\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_0 = 2t_{\mathrm{K^+}}^{\mathrm{KCl}}\ \boldsymbol{RT}\sigma^{\mathrm{KCl}}\boldsymbol{B}^{\mathrm{KCl}} - 2t_{\mathrm{H^+}}^{\mathrm{HCl}}\ \boldsymbol{RT}\sigma^{\mathrm{HCl}}\boldsymbol{B}^{\mathrm{HCl}} \qquad (6)$$

where

$$\left.\begin{aligned} \sigma^{\mathrm{KCl}} &= -(Q_{\mathrm{K^+}}^{*\mathrm{KCl}} + Q_{\mathrm{Cl^-}}^{*\mathrm{KCl}})/2\boldsymbol{RT}\boldsymbol{B}^{\mathrm{KCl}} \\ \sigma^{\mathrm{HCl}} &= -(Q_{\mathrm{H^+}}^{*\mathrm{HCl}} + Q_{\mathrm{Cl^-}}^{*\mathrm{HCl}})/2\boldsymbol{RT}\boldsymbol{B}^{\mathrm{HCl}} \\ \boldsymbol{B}^{\mathrm{KCl}} &= 1 + (\mathrm{d}\ln\gamma_{\pm}{}^{\mathrm{KCl}}/\mathrm{d}\ln m)_{\mathrm{T,P}} \\ \boldsymbol{B}^{\mathrm{HCl}} &= 1 + (\mathrm{d}\ln\gamma_{\pm}{}^{\mathrm{HCl}}/\mathrm{d}\ln m)_{\mathrm{T,P}} \end{aligned}\right\} \qquad (7)$$

$\boldsymbol{R}$ is the gas constant, and $\gamma_{\pm}{}^{\mathrm{KCl}}$ and $\gamma_{\pm}{}^{\mathrm{HCl}}$ are the mean ion activity coefficients of potassium chloride and of hydrochloric acid in aqueous m molal solutions respectively.

If the Soret coefficient is known accurately for an aqueous m molal solution of potassium chloride, for example, then one may obtain, by means of Eq. 6, the Soret coefficient of hydrochloric acid at the same concentration and at the same temperature, and may further calculate the heats of transfer by the aid of Eq. 7.

Experimental

All solutions were prepared from G. R. chemicals by using ordinary distilled water. The concentration of the solution was checked by titration and

---

[1] E. g., H. J. V. Tyrrell, "Diffusion and Heat Flow in Liquids," Butterworths, London (1961).

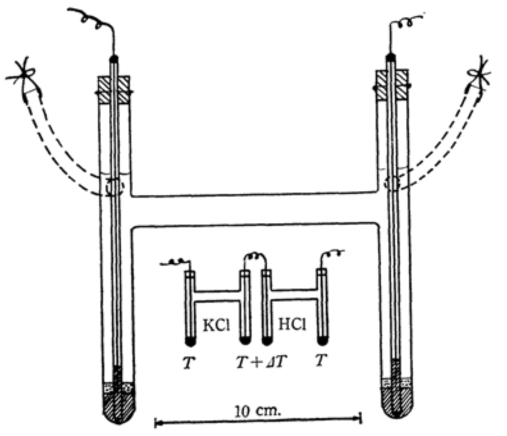

Fig. 1. Cell system, the parts drawn with dotted line representing the side tubes on the front of paper.

was adjusted to yield definite values in molality, values accurate within ±1% in the present work. Two H-shaped glass cells were convenient for the present purpose (Fig. 1). Two H-shaped calomel thermocells involving, respectively, the solutions of potassium chloride and hydrochloric acid at the same concentration were joined together by the legs and then placed in water thermostated in two respective Dewar vessels. The temperature was changed from 17°C to 32°C on only one side of of these two Dewar vessels by adding cold or hot water to yield the mean 25°C, while the temperature on the colder side was always fixed at 17°C. Under a moderate agitation with air bubbling, the thermal equilibrium of the cell system was attained in about ten minutes after the change of the temperature of thermostat water in the Dewar vessels. The temperature was read with a calibrated mercury thermometer with 0.1°C divisions. The terminals of two thermocells were joined together electrically on the warmer side, and the remaining terminals on the colder side were served to the measurements of the e. m. f. The e. m. f., E, of cell system 1 was measured for a given temperature difference, ΔT, by the use of a Yokogawa precision potentiometer (Type P-7, for low voltage use, with a sensitivity as low as 0.1 μV.) by the use of a sensitive galvanometer as a zero indicator.

Here, the sign convention for e. m. f. of system (1) was taken as positive if the sign of the electrode on the colder side of hydrochloric acid was found be positive against the sign of the electrode on the colder side of potassium chloride.

In measuring every care was taken to get accurate and reproducible data. Even the best-prepared thermocells were let stand for about three days after having been prepared in order to bring them to a stationary state. A battery, the electric source, must be connected to the potentiometer for at least three hours prior to measurement so that the normalized state of the potentiometer does not drift. The shielding of the system from inconvenient heat effects is also important.

Results and Discussion

The plots of the e. m. f., E, of 1 against the applied temperature difference, ΔT, fell on a straihgt line, with a definite slope depending on the concentration. Here, the non-linear data were abandoned because they were taken when the system was not in a steady state. The results are presented in Figs. 2 and 3. The initial thermoelectric power, $(\mathrm{d}E/\mathrm{d}T)_0$, was found to be positive at the present sign

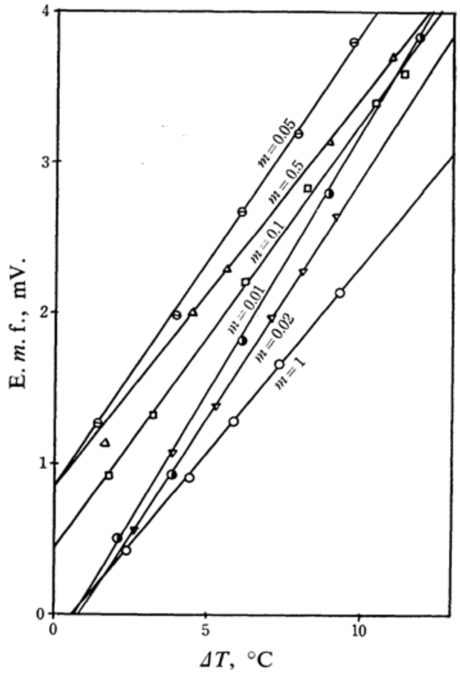

Fig. 2. E. m. f.'s of electrolytic thermocouple system of KCl/HCl with respect to temperature difference ΔT, for different molalities m, at 25°C.

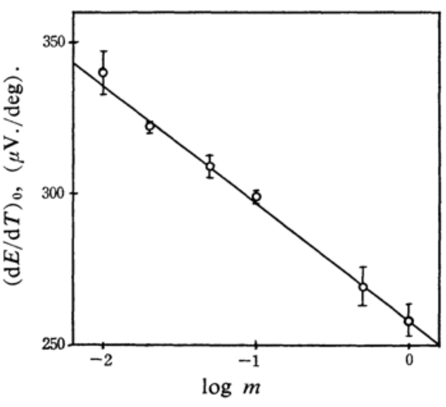

Fig. 3. Relation between the initial thermoelectric powers of electrolytic thermocouple of KCl/HCl and logarithm of molality at 25°C.

TABLE I. INITIAL THERMOELECTRIC POWER, $(\mathrm{d}E/\mathrm{d}T)_0$, OF THE ELECTROLYTIC THERMOCOUPLE SYSTEM OF KCl/HCl, AND THE ESTIMATION OF THE SORET COEFFICIENTS AND HEATS OF TRANSFER OF HYDROCHLORIC ACID AT 25°C

$$Q^*_{\mathrm{HCl}} \equiv Q^{*\mathrm{HCl}}_{\mathrm{H^+}} + Q^{*\mathrm{HCl}}_{\mathrm{Cl^-}}$$

m	$t^{\mathrm{KCl}}_{\mathrm{K^+}}$	B^{KCl}	$t^{\mathrm{HCl}}_{\mathrm{H^+}}$	B^{HCl}	$-\sigma^{\mathrm{KCl}}$ $\times 10^3$ deg^{-1}	$\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_0$ $\frac{\mu\mathrm{V.}}{\mathrm{deg.}}$	$-\sigma^{\mathrm{HCl}}\times 10^3$ deg^{-1}				Q^*_{HCl} $\frac{\mathrm{cal.}}{\mathrm{mol.}}$
						this work	calcd.	obs.	obs.e)	obs.f)	
0.01	0.4902	0.954	0.8251	0.958	1.43a)	340±7	9.21	9.01a)	11	8.4	3120
0.02	0.4901	0.941	0.8266	0.946	1.22b)	322±3	8.73	7.8d)	8.2	—	2920
0.05	0.4899	0.925	0.8292	0.942	0.99b)	309±4	8.23	—	6.4	6.3	2740
0.1	0.4898	0.909	0.8314	0.943	0.86*	299±3	7.90	—	5.6	5.3	2630
0.2	0.4894	0.900	0.8337	0.956	0.76*	—	—	—	5.0	—	—
0.5	0.4888	0.892	0.838	1.044	0.79*	269±7	6.36	6.71c)	6.2	—	2350
1.0	0.4882	0.931	0.841	1.160	0.94c)	258±5	5.58	5.82c)	6.0	—	2280

a) Ref. 3.
b) Ref. 2.
c) Ref. 4.
d) E. D. Eastman, *J. Am. Chem. Soc.*, **50**, 283, 292 (1928)
e) Values at 40°C, Ref. 5.
f) Values at 35°C, Ref. 6.
* Interpolation.

convention; it seems to diminish linearly with the logarithms of molality, as is indicated in Fig. 3.

Early data on the Soret coefficients are not very reliable, but fairly accurate data are available in recent reports, particularly those by Snowdon and Turner.[2,3] These authors determined the Soret coefficients directly by the conductometric method for a number of electrolytes at 25°C. The Soret coefficients at higher concentrations were formerly given by Tanner[4] at a mean temperature of 32°C. Data for medium concentrations are lacking at present.

In the present work, we calculated the Soret coefficient for hydrochloric acid at 25°C by using known σ values for potassium chloride and the initial thermoelectric powers for system 1. The results are compared with the literature values in Table I, where the Sasaki values cited for comparison are those observed at the mean temperatures of 40°C[5] and 35°C[6]. Since the Soret coefficient is rather sensitive to the Soret coefficient is rather sensitive to the mean temperature at which it is measured, increasing with an increase in that temperature, it is inappropriate, strictly speaking, to make a direct comparison between Soret coefficients determined at different temperatures. However, as may be seen in Table I, the calculated values and the literature values were found to agree roughly in their magnitudes in a satisfactory manner, apart from details. Calculations for the medium concentrations could not be performed to yield correct values of the Soret coefficients for hydrochloric acid because of a lack of basic data on the Soret coefficients of potassium chloride in the corresponding region of concentration; therefore, tentative calculations were made by using the interpolated values of the Soret coefficients of potassium chloride for 0.1 and 0.5 M. No such peak as those reported by Chipman,[7] Hirota[8] and Sasaki[5] on the Soret coefficient of hydrochloric acid could be found here in the concentration range between 0.5 and 1.0 M. This might be either because the values of the Soret coefficients of potassium chloride used for the calculation were inadequate at higher concentrations, or becanse the basic conditions indicated in 4 can no longer hold at higher concentrations, or to both reasons. At any rate, the present method is likely to be applicable for determining the Soret coefficients at lower concentrations for any electrolyte that can form a thermocell with a convenient electrode system.

---

[2] P. N. Snowdon and J. C. R. Turner, *Trans. Faraday Soc.*, **56**, 1 (1960).

[3] P. N. Snowdon and J. C. R. Turner, ibid., **56**, 1409 (1960).

[4] C. C. Tanner, ibid., **23**, 75 (1927).

[5] K. Sasaki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 236 (1962).

[6] K. Sasaki, ibid., **83**, 368 (1962).

[7] J. Chipman, *J. Am. Chem. Soc.*, **48**, 2577 (1926).

[8] K. Hirota, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaisi*), **63**, 105, 999 (1942).

Summary

We have studied an electrolytic thermocouple formed by coupling two thermocells, consisting of electrodes of the same nature, and with different electrolytes, either hydrochloric acid or potassium chloride, but both of the same concentration; we have demonstrated that the Soret coefficient of hydrochloric acid relative to that of potassium chloride can be estimated from the initial thermoelectric powers of this electrolytic thermocouple, as long as the entropies as well as the heats of the transfer of the chloride ions may be assumed to be the same between these two electrolytes.

Agreements between calculations and observations have been roughly good in the range of concentration between 0.01 M and 1 M, though there are some uncertainties about the Soret coefficients of potassium chloride at higher concentrations. This method may have general applicability, particularly in the dilute region.

Department of Chemistry
Shizuoka University
Oiwa, Shizuoka