A Possibility for Determining the Entropies of Electrolytes from the Initial Thermoelectric Powers of Thermocells

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The partial molar entropy of a uni-univalent electrolyte (MX) in an aqueous *m* molal solution, can usually be calculated by the formal formula:

$$\left.\begin{aligned} S_{\mathrm{MX}}=S_{+}+S_{-}=S^{\circ}_{\mathrm{MX}}-2\boldsymbol{R}\ln m\gamma_{\pm} \\ -2\boldsymbol{R}T\mathrm{d}\ln\gamma_{\pm}/\mathrm{d}T \\ S^{\circ}_{\mathrm{MX}}=S^{\circ}_{+}+S^{\circ}_{-} \end{aligned}\right\} \tag{1}$$

where S_+ and S_- are the partial molar entropies of cations and anions respectively, and S°_{+} and S°_{-} refer to those at the standard state; $\gamma_{\pm}$ denotes the mean ion activity coefficient; $\boldsymbol{R}$ is the gas constant and T is the absolute temperature. The conventional values of the standard partial molar entropies of ions are available in Latimer's work[1] and also in NBS services.[2] Slight differences can be seen between them, however, and they are always worked up to yield the third-law molecular entropies (S°_{MX}) so as to be independent of the choice of the convention for the ion entropies. At any rate, it must be noted that most of these values have been determined from thermodynamic data on isothermal systems. The present writer will report a rather different basis for determining the partial molar entropies of electrolytes in aqueous solutions at the third-law convention from the thermoelectric data on non-isothermal systems without making any conventional assumptions.

Thermodynamic Relations. — In the case of thermocells with a single uni-univalent electrolyte, MX, which yields M^+ and X^- on dissociation, the initial thermoelectric power, ε_0, can be written as follows:[3]

$$\boldsymbol{F}\varepsilon_0^{\mathrm{C}}=-t_+S^*_+ + t_-S^*_- + \Delta S^{\circ\mathrm{C}}-(S^{\mathrm{C}}_{\mathrm{el}}+S^{*\mathrm{C}}_{\mathrm{el}})-S_+ \tag{2}$$

for thermocells with cation-reversible electrodes, whose characteristics are indicated by the superscript C, and

$$\boldsymbol{F}\varepsilon_0^{\mathrm{A}}=-t_+S^*_+ + t_-S^*_- + \Delta S^{\circ\mathrm{A}}-(S^{\mathrm{A}}_{\mathrm{el}}+S^{*\mathrm{A}}_{\mathrm{el}})+S_- \tag{3}$$

for thermocells with anion-reversible electrodes, whose characteristics are indicated by the superscript A. Here, $\boldsymbol{F}$ is the Faraday constant; t_+ and t_- are the transport numbers of cations and anions respectively, related in $t_+ + t_- = 1$ by difinition; S^*_+ and S^*_- are the partial molar Eastman entropies of the transfer of cations and anions respectively, the quantities defined by the ionic heats of transfer divided by the absolute temperature; S_{el} and S^*_{el} are the partial molar entropy and the entropy of the transfer of electrons in the metallic leads of the thermocell respectively; S_+ and S_- are the partial molar entropies of cations and anions respectively; ΔS°'s refer to the contributions from the changes in the standard molar entropies of the electrode materials of the thermocells for the electrode reactions per Faraday, differing according to the electrode

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[1] W. M. Latimer, K. S. Pitzer and W. V. Smith, *J. Am. Chem. Soc.*, **60**, 1829 (1938).

[2] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, U. S. Government Printing Office, Washington, D. C. (1952).

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

TABLE I. PARTIAL MOLAR ENTROPIES OF HYDROCHLORIC, HYDROBROMIC, AND HYDROIODIC ACIDS AT 25°C AND 0.01 M, AND AT THE STANDARD STATE

Case	a	b	c	d
HX	HCl	HCl	HBr	HI
Electrode system, A	Hg/HgCl	Ag/AgCl	Ag/AgBr	Ag/AgI
Leads for A	Pt	Ag	Ag	Ag
$\varepsilon_0^{\mathrm{A}}$ (μV./deg.)[a]	639	288*	435*	570
$\varepsilon_0^{\mathrm{C}}$ (μV./deg.)[a,b]	142	142	146	135
$\gamma_\pm$ (m=0.01)	0.904	0.904	0.906	0.908
$\mathrm{d}\ln\gamma_\pm/\mathrm{d}T$ (deg^{-1})	-7×10^{-5}	-7×10^{-5}	-7×10^{-5}	-7×10^{-5}
S_{HX}(e. u.) (m=0.01)[c]	32.2_9	31.5_9	37.5_3	42.8_7
S°_{HX}(e. u.),[d] this work	13.4_9	12.7_9	18.6_6	24.1_1
S°_{HX}(e. u.) Latimer[e]	13.5	13.5	19.7	25.3
S°_{HX}(e. u.) NBS[f]	13.17	13.17	19.29	26.14

a) Refs. 3 and 4.
b) Platinum leads are used for the electrodes C, $\mathrm{Pt/H_2}$.
c) Eq. 4.
d) S_{HX} (in Eq. 4) $+2\boldsymbol{R}\ln m\gamma_\pm+2\boldsymbol{R}T\mathrm{d}\ln\gamma_\pm/\mathrm{d}T$
e) Ref. 1.
f) Ref. 2.
* If an alternative value of $\varepsilon_0^{\mathrm{A}}=296$ μV./deg., which is given by interpolation of Sasaki's recent data on thermocell [Ag/AgCl, HCl (0.01 M)] at 25°C, is used, we get $S_{\mathrm{HCl}}=31.7_6$ e. u. or $S^\circ_{\mathrm{HCl}}=12.9_6$ e. u. (K. Sasaki, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **82**, 654 (1961); Haase and his co-worker gave 290 μV./deg. for [Ag/AgCl, HCl (0.01 M)] and 437.7 μV./deg. for [Ag/AgBr, HBr (0.01 M)] at 25°C (R. Haase and H. Schönert, *Z. physik. Chem. N. F.*, **25**, 193 (1960)).

systems (their practical forms are, for example, $\varDelta S^{\circ\mathrm{C}}=(1/2)S^\circ_{\mathrm{H_2}}$ for a hydrogen electrode; $\varDelta S^{\circ\mathrm{A}}=S^\circ_{\mathrm{Ag}}-S^\circ_{\mathrm{AgX}}$ for silver/silver halide electrodes, $S^\circ_{\mathrm{Hg}}-S^\circ_{\mathrm{HgCl}}$ for mercury/mercurous chloride electrodes, and so on). From Eqs. 2 and 3, the partial molar entropy of a uni-univalent electrolyte, MX, is derived as follows:

$$S_{\mathrm{MX}}=S_{+}+S_{-}=\boldsymbol{F}(\varepsilon_0^{\mathrm{A}}-\varepsilon_0^{\mathrm{C}})+\varDelta S^{\circ\mathrm{C}}-\varDelta S^{\circ\mathrm{A}}$$
$$-(S_{\mathrm{el}}^{\mathrm{C}}+S_{\mathrm{el}}^{*\mathrm{C}}-S_{\mathrm{el}}^{\mathrm{A}}-S_{\mathrm{el}}^{*\mathrm{A}}) \qquad (4)$$

Since the quantities on the right-hand-side of 4 are all measurable experimentally, the left-hand-side quantity can be determined.

Calculations. — In the literature, however, there are unexpectedly few examples to which the present method is applicable.[4,5] The only examples now available are the following combinations of thermocell systems;* (a) [Pt, $\mathrm{H_2}$/HCl] with [Hg/HgCl, HCl]; (b) [Pt, $\mathrm{H_2}$/HCl] with [Ag/AgCl, HCl]; (c) [Pt, $\mathrm{H_2}$/HBr] with [Ag/AgBr, HBr], and (d) [Pt, $\mathrm{H_2}$/HI] with [Ag/AgI, HI], all at 25°C and 0.01 M. The values of the initial thermoelectric powers which were used in our calculations are accurate to within 1.8 μV./deg. at worst, judging from the accuracy of other experiments we have performed along similar lines. Finally, the entropy terms regarding electrons in the metallic leads of two thermocells can be estimated from the thermoelectric power of a thermocouple composed of two metals of the same kinds as those used as the leads in these thermocells. The thermoelectric power, ε(C/A), of a metal C with respect to A can be defined as follows:[3]

$$\boldsymbol{F}\varepsilon(\mathrm{C/A})=-(S_{\mathrm{el}}^{\mathrm{C}}+S_{\mathrm{el}}^{*\mathrm{C}}-S_{\mathrm{el}}^{\mathrm{A}}-S_{\mathrm{el}}^{*\mathrm{A}}) \qquad (5)$$

Here the sign of ε(C/A) was taken, in accordance with the convention adopted by most authors, to be positive if the current so produced in the thermocouple flows at the cold junction from C to A. According to Temkin and Khoroshin,[6] we have ε(Pt/Cu) = −6.39 μV./deg. at 25°C, while ε(Ag/Cu) = +0.08±0.01 μV./deg. was observed by the present writer. Therefore, we have ε(Pt/Ag) = −6.47 μV./deg., or equivalent to −0.15 e.u.; it is ready to use in the cases of b, c and d. In the case of a, on the other hand, such an electronic contribution vanishes, because the electrode leads of these two thermocells are both made of the same platinum. By using the authorized values of the standard partial molar entropies ($S^\circ_{\mathrm{H_2}}$= 31.211 (±0.01) e. u.,[2] $S^\circ_{\mathrm{Hg(liq.)}}$=18.187 (±0.02) e. u.,[7] S°_{HgCl}=23.4 e. u.[2], S°_{Ag}=10.206 (±0.01)

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[4] Ref. 3, p. 285.

[5] T. Ikeda, *Rep. Liberal Arts Sci. Fac., Shizuoka Univ., Nat. Sci.*, **2**, 159 (1959).

* For example, [Ag/AgCl, HCl] represents a thermocell system, Ag/AgCl (T), HCl, AgCl/Ag ($T+\varDelta T$).

[6] M. I. Temkin and A. V. Khoroshin, *Zhur. Fiz. Khim.*, **26**, 500 (1952).

[7] R. H. Busey and W. F. Giauque, *J. Am. Chem. Soc.*, **75**, 806 (1953).

e. u.,[2,8] $S^{\circ}_{\mathrm{AgCl}}=22.97\pm0.10$ e. u.[2,9] $S^{\circ}_{\mathrm{AgBr}}=25.62\pm0.10$ e. u.[9] and $S^{\circ}_{\mathrm{AgI}}=27.59$ (±0.4) e. u.[10]), all at the third-law convention, the errors indicated in the brackets being estimated by us, taking into consideration the accuracy of the data given in the original papers), we can get from 4 the third-law partial molar entropies of three halide acids at 25°C and 0.01 M, as well as their standard values by the aid of 1. The results are listed in Table I. Here the calculated values of entropies are found to be lower than the accepted values[1,2] except for the case of a. Consequently, if the thermoelectric data on thermocells and the entropy data on the electrode materials are correct in our calculations, the current standard partial molar entropies of halide acids, particularly those of hydrobromic acid and hydroiodic acid, might have to be corrected considerably; our values may be accurate to within 0.2 e. u. in the cases of b and c, and may be within 0.5 e. u. in the case of d (the accuracy of the case of a can not be estimated because we do not know the probable error of $S^{\circ}_{\mathrm{HgCl}}$). The disagreement between the calculated values of S_{HCl} in the cases of a and b might be due to the use of an incorrect value of $S^{\circ}_{\mathrm{HgCl}}$ in the calculations.

Summary

An alternative method for determining the third-law partial molar entropies of electrolytes in aqueous solutions from the data on non-isothermal systems has been presented. They can be obtained from the difference between the initial thermoelectric powers of two different thermocells, the one being formed by cation-reversible electrodes and the other being formed by anion-reversible electrodes, both with common electrolytes of the same concentration. The partial molar entropies have been calculated to be 31.59, 37.53 and 42.87 e. u. for hydrochloric acid, hydrobromic acid, and hydroiodic acid respectively at 25°C and 0.01 M.

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[8] P. F. Meads, W. C. Forsythe and W. F. Giauque, ibid., 63, 1902 (1941).

[9] E. D. Eastman and R. T. Milner, *J. Chem. Phys.*, 1, 444 (1933).

[10] K. S. Pitzer, *J. Am. Chem. Soc.*, 63, 516 (1941).