# SHORT COMMUNICATIONS

## *Absolute Estimation of the Ionic Entropies of Transfer*

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The earlier attempts[1,2] of estimating the absolute ionic entropies of transfer are all based on an artificial assumption. Recently, the first absolute estimation has been carried out successfully by Agar and Breck[3]. The present report would give the second way of estimating these values exclusively from the observed data concerning the "Soret effect" and thermocells without making any assumption except the additivity of the ionic entropies of transfer, which was originally proposed by Eastman[1] and lately has been confirmed by Alexander[4] at low concentrations. For a thermocell of the system, $Ag|AgCl_s$, $MCl_{aq}$, $AgCl_s|Ag$, we can write, when the Soret effect is hindered, as follows:

$$\boldsymbol{F}\frac{d\varphi}{dT} = -t_+S_+^* + t_-S_-^* - S_{el}^* + S_{Ag} - S_{AgCl} + t_+S_{MCl} \qquad (1)$$

where $\boldsymbol{F}$ is Faraday's constant, $d\varphi$ is the thermopotential difference due to the temperature gradient $dT$, $t_+$ and $t_-$ are the transference numbers of positive and negative ions of the salt MCl (here uni-univalent) respectively, $S_+^*$, $S_-^*$ and $S_{el}^*$ are the entropies of transfer of hydrated positive and negative ions in solution phase and that of electron in metallic phase respectively, $S_{Ag}$ and $S_{AgCl}$ are the molar entropies of metallic silver and solid silver chloride respectively, and $S_{MCl}$ is the molar

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1) E. D. Eastman, *J. Am. Chem. Soc.*, **50**, 283, 292 (1928).

2) J. C. Goodrich, F. M. Goyan, E. E. Morse, R. G. Preston and M. B. Young, ibid., **72**, 4411 (1950).

3) J. N. Agar, and W. G. Breck, ***Trans. Faraday Soc.***, **53**, 167, 179 (1957).

4) K. F. Alexander, ***Z. physik. Chem.***, **203**, 213 (1954).

5) H. B. Callen, ***Phys. Rev.***, **73**, 1349 (1948); S. R. de Groot, "Thermodynamics of Irreversible processes", North Holland Publ. Co., Amsterdam and Intersc. Publ., New York., (1951).

TABLE I

IONIC ENTROPIES OF TRANSFER (cal./deg./mole) IN AQUEOUS $m$-MOLAL SOLUTION OF MCl AT 25°C. $\sigma$(deg.$^{-1}$), $d\varphi/dT$($\mu$V/deg.), $S_{Ag}=10.1$, $S_{AgCl}=23.0$, $S_{Hg}=18.3$, $S_{HgCl}=23.4$ cal./deg./mole.

| System MCl | Ag/AgCl, MCl($m$=0.05) | | | | | Ag/AgCl, MCl($m$=1.0) | | | | | Hg/HgCl,MCl($m$=1.0) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $t_+$[g] | $\sigma\times10^3$ | $d\varphi/dT$[b] | $S_+^*$ | $S_-^*$ | $t_+$[g] | $\sigma\times10^3$ | $d\varphi/dT$[b] | $S_+^*$ | $S_-^*$ | $d\varphi/dT$[e] | $S_+^*$ | $S_-^*$ |
| HCl | 0.829 | −1.76[c] | 145 | 10.4 | 18.4[f] | 0.845 | −7.3[a] | − 83 | 4.1 | $18._2$ | 330 | 3.5 | $19._9$ |
| LiCl | 0.321 | +0.31[a] | 511 | 6.5 | $24._5$ | 0.26 | 0. [d] | 289 | 0.2 | $19._6$ | 630 | 0.2 | $19._6$ |
| NaCl | 0.388 | −1.91[a] | 482 | 18.1 | 24.9 | 0.363 | −1.56[d] | 228 | 13.1 | 18.8 | 560 | 13.2 | 18.7 |
| KCl | 0.490 | −1.20[a] | 493 | 27.4 | 24.9 | 0.485 | −0.93[d] | 261 | $22._6$ | $19._4$ | 610 | $22._3$ | $19._7$ |
| $NH_4Cl$ | 0.491 | 0.0 [c] | 498 | $29._0$ | $24._4$ | — | — | — | — | — | — | — | — |

a, K. F. Alexander, *Z. physik. Chem.*, **203**, 213 (1954); b, H. A. Bernhardt and H. D. Crockford, *J. Phys. Chem.*, **46**, 473 (1942); c, J. Chipman, *J. Am. Chem. Soc.*, **48**, 2577 (1926); d, C. C. Tanner, *Trans. Faraday Soc.*, **23**, 75 (1927); e, Th. W. Richards, *Z. physik. Chem.*, **24**, 39 (1897); f, This anomalous value might be due to the fact that Chipman's value of $\sigma$ here used is incorrect, probably too low; g, I. C. T; B. E. Conway "Electrochemical Data", Elsevier Publ. Co., Amsterdam, (1952).

entropy of MCl in solution phase. Here $S_{MCl}=S_++S_-$, $S_+$ and $S_-$ being the partial molar entropies of hydrated positive and negative ions produced from one molecule of the salt MCl in solution phase.

Coupling the relations[5)], $S_+^*=Q_+^*/T+S_+$ and $S_-^*=Q_-^*/T+S_-$, with the approximation formula[6)] $\sigma=-(Q_+^*+Q_-^*)/2\boldsymbol{R}T^2$ for the Soret coefficient $\sigma$, one may yield the molecular entropy of transfer of the salt MCl as

$$S_+^*+S_-^*=-2\boldsymbol{R}T\sigma+S_{MCl} \qquad (2)$$

where $Q_+^*$ and $Q_-^*$ are the heat of transfer of hydrated positive and negative Ions of MCl in solution phase, and $\boldsymbol{R}$ is the gas constant.

Upon solving Eqs. 1 and 2 with respect to $S_+^*$ and $S_-^*$ by the aid of the relation of $t_++t_-=1$, one may yield

$$\left.\begin{aligned} S_-^* &= \boldsymbol{F}d\varphi/dT-S_{Ag}+S_{AgCl} \\ &\quad -2t_+\boldsymbol{R}T\sigma+S_{el}^* \\ S_+^* &= -\boldsymbol{F}d\varphi/dT+S_{Ag}-S_{AgCl} \\ &\quad -2t_-\boldsymbol{R}T\sigma-S_{el}^*+S_{MCl} \end{aligned}\right\} \qquad (3)$$

Since $S_{el}^*$ is very small as compared with the other terms in Eq. 3, sufficiently correct values of the ionic entropies of transfer may be obtained even by omitting term of $S_{el}^*$ from Eq. 3. Some of the values of $S_+^*$ and $S_-^*$ thus estimated for the 0.05 and 1 molal aqueous solutions of some electrolytes at 25°C are tabulated in Table I. There can be seen some remarkable facts: (1) the values of $S_+^*$ and $S_-^*$ persist their proper values, independent of what system they are originated from; (2) the value of $S_-^*$ is consistently the same, entirely independent of the nature of its conjugate cations present in the chloride solutions; (3) $S_i^*$ is a function of the concentration.

Finally it is very interesting to have a possibility of determing the heats of transfer for positive and negative ions separately, if only the individual ionic activity coefficients are known.

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6) S. R. de Groot, *J. Phys. Radium*, **8**, 129, 193 (1947).