Transported Entropies and Conventional Eastman Entropies of the Transfer of Some Univalent Ions in Aqueous Solutions at 25°C

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An absolute estimation of the transported entropies* of individual ions was carried out previously by the present writer.[1,2] However, recently Turner and his co-workers[3] have reported reliable, and perhaps final, values of the Soret coefficient for a number of 1 : 1-electrolytes by using a conductivity method, and since the data of the Soret coefficients used in our previous calculations were less reliable than Turner's values, and since much the same thing can be said of the data on initial thermoelectric powers used previously, it is worthwhile to recalculate the transported entropies of single ions by using the most accurate data now available.

General. — The transported entropy for a single ion can be calculated exclusively from the experimental data on the initial thermoelectric power of the thermocell and the Soret coefficient without making any conventional

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* The term "entropy of transfer" as defined by De Groot was used in the previous work and indicated with the symbol S^*, which is quite identical with the "transported entropy" used here with the symbol $\overline{\overline{S}}$. However, the usage of the former is undesirable, because such use causes confusion with the Eastman entropy of transfer, S^*, defined by Q^*/T, where Q^* is the heat of transfer at the absolute temperature, T.

[1] T. Ikeda, This Bulletin, **32**, 97 (1959).

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

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

TABLE I. ELECTROCHEMICAL DATA AT 25°C AND 0.01 M

t_+ =cationic transport number; $\gamma_\pm$ =mean activity coefficient; $\gamma' = -\boldsymbol{R}T\mathrm{d}\ln\gamma_\pm/\mathrm{d}T$ (in cal./deg.); $B=1+\mathrm{d}\ln\gamma_\pm/\mathrm{d}\ln m$; σ =Soret coefficient (in deg^{-1})

Electrolyte	t_+[a]	$\gamma_\pm$[b]	γ'	B	$-\sigma\times10^3$[c]
HCl	0.8251	0.904	0.04	0.958	9.01
LiCl	0.3289	0.906	0.10	0.969	−0.01
NaCl	0.3918	0.903	0.09	0.958	2.02
KCl	0.4902	0.902	0.10	0.956	1.43
RbCl	0.497	0.903	0.10	0.945	2.33
CsCl	0.504	0.896	0.11	0.942	2.44
LiBr	0.3226	0.909	0.05	0.962	0.05
NaBr	0.3853	0.9137	0.05	0.963	2.12
KBr	0.4833	0.9033	0.02	0.957	1.46
LiI	(0.235)	(0.908)	0.03	0.961	−1.47
NaI	(0.395)	0.917	0.02	0.958	0.54
KI	0.4884	0.905	0.02	0.960	−0.11
NaOH	0.1952	0.903	0.10	0.951	13.76
KOH	0.2658	0.901	0.07	0.954	13.31

a) B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., Amsterdam, Netherlands (1952).

b) Ref. 7.

c) Ref. 3.

assumption other than postulating the additivity for the partial molar ion entropies as well as for the ionic entropies (or heats) of transfer, though this property is now commonly acceptable, particularly in dilute solutions. The basic relations for calculating the transported entropies of individual ions are just the same as those used in the previous works.[1,2] In the simpler case, where the electrolyte contains a single salt giving two kinds of univalent ions, they are:[1,2,4]

$$\overline{\overline{S}}_+ = -\boldsymbol{F}\varepsilon_0 - \overline{\overline{S}}_{\mathrm{el}} + \Delta S^\circ{}_{\mathrm{M}} - 2t_-\boldsymbol{RT}B\sigma \tag{1}$$

and

$$\overline{\overline{S}}_- = \boldsymbol{F}\varepsilon_0 + \overline{\overline{S}}_{\mathrm{el}} - \Delta S^\circ{}_{\mathrm{M}} - 2t_+\boldsymbol{RT}B\sigma + (S_+ + S_-) \tag{2}$$

when the initial thermoelectric power for thermocells with cation-reversible electrodes is available, and

$$\overline{\overline{S}}_+ = -\boldsymbol{F}\varepsilon_0 - \overline{\overline{S}}_{\mathrm{el}} + \Delta S^\circ{}_{\mathrm{R}} - 2t_-\boldsymbol{RT}B\sigma + (S_+ + S_-) \tag{3}$$

and

$$\overline{\overline{S}}_- = \boldsymbol{F}\varepsilon_0 + \overline{\overline{S}}_{\mathrm{el}} - \Delta S^\circ{}_{\mathrm{R}} - 2t_+\boldsymbol{RT}B\sigma \tag{4}$$

when the ε_0 for thermocells with anion-reversible electrodes is available. Here, $\boldsymbol{F}$ is the Faraday constant. $\overline{\overline{S}}_{\mathrm{k}}$ represents the transported entropy of k ion species in an m molar solution; it is defined by $\overline{\overline{S}}_{\mathrm{k}} = S_{\mathrm{k}} + S_{\mathrm{k}}^*$, where S_{k} and S_{k}^* are the absolute partial molar entropy and the absolute molar Eastman entropy of the transfer of k ion species respectively. The latter S_{k}^*, the Eastman entropy of the transfer of k ion species, is related to the Soret coefficient, σ, as follows: for a 1 : 1-electrolyte it is

$$\sigma = -\frac{\mathrm{d}\ln m}{\mathrm{d}T} = -\frac{S_+{}^* + S_-{}^*}{2\boldsymbol{RT}B}, \quad B = \left(1 + \frac{\mathrm{d}\ln\gamma_\pm}{\mathrm{d}\ln m}\right)_T \tag{5}$$

where $\boldsymbol{R}$ is the gas constant; T is the absolute temperature and $\gamma_\pm$ is the mean ion activity coefficient on the molality scale at the molality of m. $\overline{\overline{S}}_{\mathrm{el}}$ denotes the transported entropy of electrons in the metallic leads of the thermocell concerned. t_+ and t_- are, respectively, the transport numbers of cations and anions. Finally, $\Delta S^\circ{}_{\mathrm{M}}$ and $\Delta S^\circ{}_{\mathrm{R}}$ 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. They differ with the electrode system; their practical forms are: $\Delta S^\circ{}_{\mathrm{M}} = 1/2\, S^\circ{}_{\mathrm{H_2}}$ for a hydrogen electrode; $\Delta S^\circ{}_{\mathrm{R}} = S^\circ{}_{\mathrm{Ag}} - S^\circ{}_{\mathrm{AgX}}$ for electrodes of silver/silver halide; $S^\circ{}_{\mathrm{Hg}} - S^\circ{}_{\mathrm{HgCl}}$ for mercury/calomel electrodes and $1/2(S^\circ{}_{\mathrm{Hg}} - S^\circ{}_{\mathrm{HgO}} - S^\circ{}_{\mathrm{H_2O}})$ for mercury/mercuric oxide electrodes when alkali hydroxide is used as an electrolyte.

Calculations. — The salt entropy, $(S_+ + S_-)$, was calculated in a formal manner by:

$$S_+ + S_- = S^\circ{}_+ + S^\circ{}_- - 2\boldsymbol{R}\ln m\gamma_\pm - 2\boldsymbol{RT}\,\mathrm{d}\ln\gamma_\pm/\mathrm{d}T$$

where $S^\circ{}_+$ and $S^\circ{}_-$ are, respectively, the

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[4] For example, H. J. V. Tyrrell, "Diffusion and Heat Flow in Liquids," Butterworths, London (1961).

TABLE II. TRANSPORTED ENTROPIES, $\overline{\overline{S}}_+$ AND $\overline{\overline{S}}_-$, AND "REDUCED" TRANSPORTED ENTROPIES, $\overline{\overline{S}}^\circ{}_+$ AND $\overline{\overline{S}}^\circ{}_-$, FOR CATION AND ANION SPECIES, RESPECTIVELY, AT 25°C AND 0.01 M

ε_0 = initial thermoelectric power

Electrolyte	Thermocell electrodes	ε_0 μV./deg.	$\overline{\overline{S}}_+$ e. u.	$\overline{\overline{S}}_-$ e. u.	$\overline{\overline{S}}^\circ{}_+$ e. u.	$\overline{\overline{S}}^\circ{}_-$ e. u.
HCl	Pt/H_2	142[a]	14.07	28.45	4.67	19.05
	Ag/AgCl	288[b]	14.67	27.90	5.23	18.50
	Hg/HgCl	636[c]	14.51	28.06	5.07	18.61
	Hg/HgCl	639[d]	14.44	28.12	5.00	18.72
LiCl	Ag/AgCl	669[b]	8.85	28.24	−0.60	18.79
	Hg/HgCl	1006[d]	8.94	28.15	−0.51	18.70
NaCl	Ag/AgCl	631[b]	20.44	28.27	10.98	18.81
	Hg/HgCl	963[d]	20.65	28.06	11.19	18.60
KCl	Ag/AgCl	640[b]	29.88	28.37	20.42	18.90
	Hg/HgCl	972[d]	30.09	28.16	20.63	18.69
RbCl	Ag/AgCl	614[a]	35.47	28.27	26.00	18.81
CsCl	Ag/AgCl	607[a]	38.82	28.19	29.33	18.70
LiBr	Ag/AgBr	831.3[c]	8.65	34.63	−0.75	25.20
NaBr	Ag/AgBr	788.8[c]	20.36	34.56	10.98	25.14
KBr	Ag/AgBr	794.6[c]	29.78	34.35	20.41	25.14
LiI	Ag/AgI	946[e]	8.50	38.57	−0.87	29.19
NaI	Ag/AgI	902[e]	20.44	38.19	11.08	28.83
KI	Ag/AgI	918[e]	29.87	38.25	20.50	28.88
NaOH	Hg/HgO	661.0[c]	19.92	26.03	10.46	16.56
KOH	Hg/HgO	617.0[c]	29.64	25.99	20.21	16.55

a) F. M. Goyan, Thesis, Univ. of California (1937).
b) J. C. Goodrich, Thesis, Univ. of California (1941).
c) J. C. Goodrich, F. M. Goyan, E. E. Morse, R. G. Preston and M. B. Young, *J. Am. Chem. Soc.*, **72**, 4411 (1950).
d) M. B. Young, Thesis, Univ. of California (1935).
e) R. G. Preston, Thesis, Univ. of California (1941).

standard partial molar entropies of cations and anions; their conventional values are given by Latimer and his co-workers.[5] The salt entropy is independent of the convention adopted in assigning its ion constituents; its absolute value is given on the basis of the third law. The other values of the standard entropies may be available in NBS service.[6] The values of B in 5 were obtained graphically from the mean ion activity coefficients.[7] The temperature coefficients of the mean ion activity coefficients can rarely be obtained by direct observation, so in most cases they were estimated by differentiating the Debye-Hückel equation. The transported entropy of electrons, $\overline{\overline{S}}_{el}$, in the metallic leads of thermocelles was approximated by the entropy of electrons; e. g., 0.04 e. u. for copper, and 0.05 e. u. for silver.[2] The other numerical data necessary for the calculations are listed in Table I, except for the ε_0 values, which are listed in Table II. All the data cited in the tables were taken at 25°C and 0.01 M. The σ values listed in Table I are those of Snowdon-Turner, but they have been corrected to 25°C at a rate[8] of $0.01\times10^{-3}\cdot\text{deg}^{-1}$ per degree of deviation in the mean temperature, at which the Soret coefficients were measured, from 25°C, since their original values were determined at mean temperatures slightly different from 25°C, ranging from 24.8°C to 25.4°C.

Upon applying these new data regarding σ and ε_0 as listed in Tables I and II to Eqs. 1—4, we get the transported entropies of individual ion species, i. e., $\overline{\overline{S}}_+$ and $\overline{\overline{S}}_-$. The results are listed in Table II. The single-ion transported entropies, $\overline{\overline{S}}_+$ and $\overline{\overline{S}}_-$, here obtained have been found to have their proper values characteristic of the nature of ions; they are nearly independent of the other ions present in the solution and of the type of the thermocells participating. This consequence is very important in yielding the transported entropies

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

[6] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, U. S. Government Printing Office, Washington, D. C. (1952).

[7] Landolt-Börnstein, "Physik. Chem. Tabellen," Erg. Bd. II (1931), III (1936).

[8] J. N. Agar and J. C. R. Turner, *Proc. Roy. Soc.*, **A255**, 307 (1960).

TABLE III. MEAN AND SELF-CONSISTENT VALUES OF "REDUCED" TRANPORTED ENTROPIES, $\bar{\bar{S}}^\circ_k$, AND CONVENTIONAL EASTMAN ENTROPIES OF TRANSFER, S_k^*, (IN cal./deg./mol.), AND HEATS OF TRANSFER, Q_k^*, (IN cal./mol.) FOR INDIVIDUAL IONS AT 25°C AND 0.01 M

The value in parentheses was adopted as the standard for estimating the self-consistent values of $\bar{\bar{S}}^\circ_k$.

Ion	$\bar{\bar{S}}^\circ_k$ mean	$\bar{\bar{S}}^\circ_k$ selfcon.	S°_k(con) Ref. 5	S_k^*(con) Eq. 8	Q_k^*(con)
H^+	4.99 ± 0.15	5.00	0	5.00	1490
Li^+	-0.68 ± 0.11	-0.54	4.7	-5.24	-1562
Na^+	10.98 ± 0.18	11.06	14.0	-2.94	-878
K^+	20.43 ± 0.10	20.59	24.2	-3.61	-1077
Rb^+	26.00	26.08	28.7	-2.62	-782
Cs^+	29.33	29.30	31.8	-2.50	-745
OH^-	16.56 ± 0.01	16.06	-2.49	18.55	5530
Cl^-	18.73 ± 0.10	(18.73)	13.5	5.23	1560
Br^-	25.16 ± 0.02	25.01	19.7	5.31	1584
I^-	28.97 ± 0.13	28.83	25.3	3.53	1052

as an absolute (not conventional) partial molar quantity without making any conventional assumptions. It would be desirable, if possible, to split $\bar{\bar{S}}_k$ into its two constituents, the absolute partial molar entropy, S_k, and the absolute molar Eastman entropy of transfer, S_k^*; however, we have no basis for doing so as yet.

On the other hand, it would be convenient to use a "reduced" quantity defined by $(\bar{\bar{S}}^\circ_k \equiv S^\circ_k + S_k^*)$, which is equivalent to $(\bar{\bar{S}}_k - \boldsymbol{R}\ln m\gamma_k - \boldsymbol{R}T\mathrm{d}\ln\gamma_k/\mathrm{d}T)$, in comparing $\bar{\bar{S}}_k$ values given at different concentrations, since $\bar{\bar{S}}_k$ depends greatly upon the concentration. To do this, $\gamma_+ = \gamma_- = \gamma_\pm$ was assumed for uni-univalent electrolytes. Calculated values of $\bar{\bar{S}}^\circ_k$ for cation and anion species are listed on the last two columns in Table II.

By using the calculated values of $\bar{\bar{S}}^\circ_k$ in Table II we have determined self-consistent values of $\bar{\bar{S}}^\circ_k$ for individual ion species by the following process: the most probable value of the "reduced" transported entropy of one ion species, for example, of the chloride ion (because so much data on it is available in the present case), was used as the standard for the estimation of the "reduced" transported entropies of its conjugate cations by subtracting it from $\bar{\bar{S}}^\circ_{MCl}$, the "reduced" transported entropy of any chloride MCl, which is calculable as the sum of the standard entropy and the Eastman entropy of transfer for one mole of the chloride MCl. Then the value of $\bar{\bar{S}}^\circ_{M^+}$, the "reduced" transported entropy of the cation, M^+, here determined was subtracted from $\bar{\bar{S}}^\circ_{MX}$, the "reduced" transported entropy of the other electrolyte, MX, with a common cation, M^+, to yield a self-consistent value of $\bar{\bar{S}}^\circ_{X^-}$ for any anion species, X^-. The process may then be extended.

The agreements between the self-consistent values thus determined and the simple average of $\bar{\bar{S}}^\circ_k$ for individual ion species from Table II are found in Table III to be fairly good, except for the hydroxide ion; the lack of agreement here may be due to the fact that the Soret coefficients of the hydroxides observed by Snowdon and Turner were somewhat lower. At any rate, the fact that such a good harmony was found might indicate, in other words, that the values of the Soret coefficient measured by Snowdon and Turner were quite proper.

Entropies of Transfer Based on the Convention of $\bar{\bar{S}}^\circ_{H^+}(con)\equiv$0. — The relation between the absolute (abs) and the conventional (con) standard molar entropies for k ion species of the ionic valency z_k can be written as follows:

$$\left.\begin{aligned} &S^\circ_{H^+}(\mathrm{con}) \equiv 0 \\ &S^\circ_k(\mathrm{con}) = S^\circ_k(\mathrm{abs}) - z_k S^\circ_{H^+}(\mathrm{abs}) \end{aligned}\right\} \tag{6}$$

We may define further the absolute and the conventional molar Eastman entropies of transfer respectively by the following equations:

$$S_k^*(\mathrm{abs}) = \bar{\bar{S}}^\circ_k - S^\circ_k(\mathrm{abs}) \tag{7}$$

and

$$S_k^*(\mathrm{con}) = \bar{\bar{S}}^\circ_k - S^\circ_k(\mathrm{con}) \tag{8}$$

By taking 6 into account, we have the alternative expression for S_k^*(con) as follows:

$$S_k^*(\mathrm{con}) = S_k^*(\mathrm{abs}) + z_k S^\circ_{H^+}(\mathrm{abs}) \tag{9}$$

or

$$Q_k{}^*(\mathrm{con}) = Q_k{}^*(\mathrm{abs}) + z_k T S^\circ{}_{\mathrm{H}^+}(\mathrm{abs}) \qquad (10)$$

Equation 9 gives a definite basis for the conventional Eastman entropy of transfer as defined by 8 to be based on the same convention as that adopted in assigning the ion entropy: the convention of $S^\circ{}_{\mathrm{H}^+}(\mathrm{con}) \equiv 0$ for an aqueous hydrogen ion of one molal activity at 25°C and 1 atm.

Now, if only $S^\circ{}_{\mathrm{H}^+}(\mathrm{abs})$ were known, all the absolute values of $S_k{}^*$ could be known from Eq. 9; however, the absolute values of $S^\circ{}_{\mathrm{H}^+}$ estimated so far by some authors[9-12] are not sufficient as yet to realize such a purpose. Consequently, only the conventional values of $S_k{}^*$ and $Q_k{}^*$ (as based on the convention of zero for the hydrogen ion, not for the chloride ion as adopted by most authors) were calculated; they are listed in the last two columns in Table III. These conventional values may be converted easily into absolute ones by the aid of Eq. 9 or 10, when $S^\circ{}_{\mathrm{H}^+}(\mathrm{abs})$ is available. The values of $S_k{}^*(\mathrm{con})$ or $Q_k{}^*(\mathrm{con})$ in Table III may be used conveniently for predicting unknown Soret coefficients by means of a combination of the ions indicated in the table.

Summary

Absolute ionic transported entropies, conventional ionic Eastman entropies of transfer, and conventional ionic heats of transfer, using the same convention ($S^\circ{}_{\mathrm{H}^+} \equiv 0$) as that adopted in assigning conventional standard ionic entropies, have been recalculated for ten univalent ions from the most accurate data now available on the initial thermoelectric powers and the Soret coefficients.

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[9] J. C. Goodrich, F. M. Goyan, E. E. Morse, R. G. Preston and M. B. Young, *J. Am. Chem. Soc.*, **72**, 4411 (1950).

[10] D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).

[11] W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

[12] R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).