

Entropies of Aqueous Ions

BY W. G. BRECK AND J. LIN

Dept. of Chemistry, Queen's University, Kingston, Canada

Received 5th February, 1965

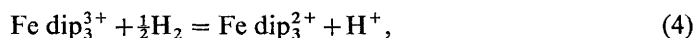
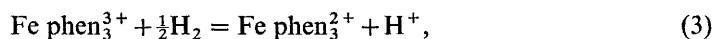
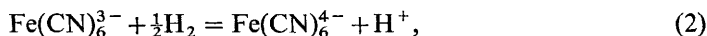
From a study of entropy changes for complex ions support has been found for Gurney's result that the standard partial molar entropy of the hydrogen ion ($S_{\text{H}^+}^\circ$) has an absolute value of -5.5 cal/g ion deg. On this basis, other absolute ionic values can be deduced for standard partial molar entropies S° , entropies of transport $S^{*\circ}$, and transported entropies \bar{S}° . A plot of \bar{S}° against S° for a variety of ions indicates that $S^{*\circ}$ and \bar{S}° increase stepwise with numerical charge and that, on the basis of the above datum for $S_{\text{H}^+}^\circ$, such plots for cations and anions (with the same numerical charge) are colinear. The transported entropies $\Delta\bar{S}_h$ of hydration of ions are evaluated and found to conform to the Born relation better than do the usual entropies of hydration ΔS_h .

EVALUATION OF STANDARD ENTROPIES OF IONS

In previous work ¹ the standard entropy changes,

$$\Delta S^\circ = S_1^\circ - S_2^\circ - \frac{1}{2}S_{\text{H}_2}^\circ + S_{\text{H}^+}^\circ, \quad (1)$$

for such reactions as :



have been considered. The subscripts 1 and 2 refer respectively to the reduced and oxidized forms of such pairs of complex ions, and the terms phen and dip signify respectively o-phenanthroline and dipyridyl ligands. It has been postulated ¹ that for the trichelated species the reduced and oxidized forms (1 and 2) are respectively isentropic, i.e., $S_1^\circ = S_2^\circ$. Accordingly, and by use of eqn. (1) and the third law value for $S_{\text{H}_2}^\circ$, $S_{\text{H}^+}^\circ$ has been estimated at -5.7 cal/g ion deg. If this proposal is sound it lends support to Gurney's ² value of -5.5 for the same quantity. Since other pertinent work ³ has been reported on the latter (-5.5) basis, the assumption is made here that $S_{\text{H}^+}^\circ = -5.5$ cal/g ion deg. to put the ionic entropies on an absolute scale. Whether the foregoing is judged to be convincing at this stage is not crucial for it is possible to consider what follows solely on the assumption of Gurney's value. Further support for this value is to be found later in this paper.

For a thermocell containing equimolar solutions of $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ functioning with two gold or platinum electrodes at different temperatures (e.g., 20, 30°C), the following relation has been derived ⁴:

$$F\varepsilon_\infty^\circ = \bar{S}_1^\circ - \bar{S}_2^\circ - \bar{S}_e = S_1^{*\circ} - S_2^{*\circ} + S_1^\circ - S_2^\circ - \bar{S}_e. \quad (5)$$

Here F is the faraday; the \bar{S}° terms are standard transported entropies, each comprising the entropy of transport at infinite dilution $S^{*\circ}$, and the standard partial molar entropy S° (for ions, electrons, molecules as appropriate); and ε_∞° is the value of the thermoelectric power of the thermocell, measured at the steady state and extrapolated to zero ionic strength for equimolar concentrations of $\text{K}_4\text{Fe}(\text{CN})_6$

and $K_3Fe(CN)_6$. \bar{S}_e has been calculated^{3, 5} as -0.045 cal/mole deg. for non-isothermal copper leads.

For reaction (2), ΔS° has been determined⁴ as -64.6 ; taking⁶ $\frac{1}{2}S_{H_2}^\circ$ as 15.6 and $S_{H^+}^\circ$ as -5.5 , from eqn. (1)

$$S_1^\circ - S_2^\circ = -64.6 + 15.6 + 5.5 = -43.5 \text{ cal/mole deg.} \quad (6)$$

The value of ε_∞° is reported⁴ as -1.651 mV/deg., or $F\varepsilon_\infty^\circ$ becomes -38.08 cal/mole deg., so that from eqn. (5),

$$S_1^{*\circ} - S_2^{*\circ} = -38.08 + 43.5 - 0.045 = 5.4 \text{ cal/mole deg.} \quad (7)$$

The entropies of transport, per equivalent, for the complete electrolytes $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$, at infinite dilution have been determined⁴ by the addition of an electrolyte with known Soret data (such as KCl) as:

$$S_{K^+}^{*\circ} + S_1^{*\circ}/4 = 6.36; \quad (8)$$

$$S_{K^+}^{*\circ} + S_2^{*\circ}/3 = 6.19 \text{ cal/equiv. deg.} \quad (9)$$

Solution of eqn. (7), (8) and (9) yields:

$$S_{K^+}^{*\circ} = 1.5; \quad S_1^{*\circ} = 19.5; \quad S_2^{*\circ} = 14.1; \quad S_{Cl^-}^{*\circ} = 0.7 \text{ cal/g ion deg.} \quad (10)$$

It has been shown⁷ that the addition of other electrolytes and measurement of initial thermoelectric powers (ε_0) can lead to further values. Also, Agar³ has compiled a table of such ionic entropies of transport (or Eastman entropies) based on the same datum ($S_{H^+}^\circ = -5.5$) so that these may be directly transposed. Latimer's list⁶ of partial molar ionic entropies can be converted from the conventional ($S_{H^+}^\circ = 0$) to the present basis by the addition of the correction $-5.5z$ (with the valence z containing the sign).

The consistency of results may be judged by examining the data for a few ions. Agar³ has reported the heat of transport at infinite dilution for HCl as 3245 cal/mole which corresponds to an entropy, $S_{H^+}^{*\circ} + S_{Cl^-}^{*\circ}$, of 10.9 cal/mole deg. Using the

TABLE 1.—STANDARD ENTROPIES OF AQUEOUS IONS (cal/g ion deg. at 25°C)

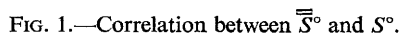
ion	S° conv. ⁶	S° abs.	$S^{*\circ}$ abs.	\bar{S}° , this work	\bar{S}° , ref. (3)	\bar{S}° , ref. (9)	\bar{S}° , ref. (5)	$\Delta\bar{S}_h$	ΔS_h	z^2/r^\dagger
H ⁺	0	-5.5	10.2	4.7	4.8	5.6	5.2	—	—	—
Li ⁺	3.4	-2.1	—	—	-2.0	-0.6	-1.4	-27.4	-27.5	1.67
Na ⁺	14.4	8.9	2.2	11.1	11.4	11.6	10.8	-17.8	-19.2	1.05
K ⁺	24.5	19.0	1.5	20.5	20.7	21.0	20.0	-10.0	-11.5	0.75
Rb ⁺	28.7	23.2	—	—	26.9	27.3	—	-5.9	-9.6	0.68
Cs ⁺	31.8	26.3	—	—	29.4	29.6	—	-4.8	-7.9	0.59
NH ⁺	27.0	21.5	—	—	—	—	21.4	—	—	—
Ag ⁺	17.7	12.2	—	—	16.9	—	—	-16.6	-21.3	0.79
Tl ⁺	30.4	24.9	2.9	27.8	27.8	—	—	-7.6	-10.5	0.69
Mg ²⁺	-28.2	-39.2	5.3	-33.9	-33.5	—	-36.3	-63.0	-68.3	6.15
Ca ²⁺	-13.2	-24.2	—	—	—	-15.8	-15.5	-46.4	-54.8	4.04
Sr ²⁺	-9.4	-20.4	—	—	—	-10.6	-9.9	-43.5	-53.3	3.54
Ba ²⁺	3	-8	7.6	-0.4	0	2.7	-0.3	-34.6	-42.2	2.96
Zn ²⁺	-25.5	-36.5	—	—	—	—	-31.9	-63.9	-68.5	5.41
Cd ²⁺	-14.6	-25.6	6.1	-19.5	-19.5	—	—	-53.1	-59.2	4.12
La ³⁺	-39	-55.5	12.4	-43.1	-42.6	—	—	-77.4	-89.8	7.82
F ⁻	-2.3	3.2	—	—	6.5	—	—	-21.9	-25.2	0.74
Cl ⁻	13.2	18.7	0.7	19.4	19.2	19.3	19.5	-10.8	-11.5	0.55
Br ⁻	19.3	24.8	0.6	25.4	25.4	25.3	23.4	-7.3	-7.8	0.51
I ⁻	26.1	31.6	-0.9	30.7	30.4	28.4	—	-3.3	-2.4	0.46
OH ⁻	-2.5	3.0	14.2	16.5	16.9	—	—	—	—	—
SO ₄ ²⁻	4.1	15.1	7.8	22.9	—	—	—	—	—	—
Fe(CN) ₆ ⁴⁻	(133.5)	(133.5)	14.1	(147.6)	—	—	—	—	—	—
Fe(CN) ₆ ³⁻	(68)*	(90)	19.5	(109.5)	—	—	—	—	—	—

* This figure is doubtful and consequently so are the other values (in parentheses) derived from it; however, for the purpose of the plot in fig. 1 this does not matter providing that for these ions the $S^{*\circ}$ values (absolute) are taken as 14.1 and 19.5 cal/g ion deg. respectively.

† Pauling radii in Å.

$S_{\text{Cl}^-}^{\circ}$ is assigned an absolute value of 18.7 (conventionally 13.2); this, coupled with $S_{\text{Cl}^-}^{\circ} = 0.7$, gives $\bar{S}_{\text{Cl}^-}^{\circ} = 19.4$, which can be compared with the results of other work,^{3, 9, 5} respectively 19.16, 19.3, 19.5 cal/g ion deg. Similarly, $S_{\text{K}^+}^{\circ} = 24.5 - 5.5 = 19.0$; $S_{\text{K}^+}^{\circ} = 1.5$; $\bar{S}_{\text{K}^+}^{\circ} = 20.5$ cal/g ion. Proceeding in this way it is possible to accumulate data for a variety of ions as in table 1.

Using the data of table 1, a plot is given in fig. 1 of the transported entropies \bar{S}° against the absolute partial molar entropies S° . Since the agreement in \bar{S}° values is good, it makes little difference for this purpose whose values are used. Generally, values from this work are plotted and where these are lacking, others taken. Agar's values³ of $S^{*\circ}$ are also used as required.



The particular datum chosen here for separation of absolute ionic entropies in general puts values of \bar{S}° close to those of S° , with the small difference consisting of S^{*0} . If all entropies of transport were zero, corresponding values of \bar{S}° and S° would be identical and the plot would consist of a straight line through the

origin at a slope of 45° . Vertical deviation from this solid line on the figure is therefore a measure of $S^{*\circ}$. If all univalent ions had small positive, more or less uniform, values of $S^{*\circ}$, their plot should lie slightly above and parallel to the above 45° line. Inspection of the plot shows that this is approximately the case, with notable exceptions (H^+ , OH^-). Divalent ions have larger, but uniform values of $S^{*\circ}$, as judged by their plot which lies higher but again parallel. Data for trivalent and quadrivalent ions are too few, but the values plotted do conform to the same pattern. The dashed lines in fig. 1 have been drawn at a slope of 45° , in each case to best fit points for ions of the same numerical charge. According to the above results it would be reasonable to assign increments in $S^{*\circ}$ (or \bar{S}°) on the basis of some function of charge.

It is not fortuitous that points for cations and anions (with the same numerical charge) fall on the same line; this result depends on the choice of absolute value of $S_{H^+}^\circ$. If chosen much different from -5.5 cal/g ion deg. this would not happen. For example, Ikeda¹⁰ has given a similar plot of \bar{S}° against S° but the values used are conventional ($S_{H^+}^\circ = 0$), so that lines through the points for cations and anions do not coincide. The correlation shown here resembles that of Gurney² wherein by assuming that $S_{H^+}^\circ = -5.5$ he was able to draw a common line for cations and anions on plotting the resulting values of S° against viscosity B -coefficients, which in turn he correlated with values of a measurable ionic property, the conductance. In this work $S_{H^+}^\circ$ is taken by argument (and not *a priori*) to be -5.7 (or -5.5) and a common line for cations and anions obtained on correlating resulting values of S° with another measurable ionic property, the transported entropy. This suggests that there might be some relationship between the transported entropy and the conductance of an ion; indeed the contribution to the entropy by the moving ion in its function in the electrode process along with its function in migration is analogous to the mechanism of a Hittorf transport experiment, wherein a single ion property is isolated.

The marked exceptions in fig. 1 deserve comment. Values of $S^{*\circ}$ for H^+ and OH^- are exceptionally large for univalent ions, recalling their exceptional mobilities and chain-transfer mechanism of conductance in aqueous solution. The fact that both of these ions bear such a unique relation to the solvent suggests that their behaviour might be exceptional. For example, as one of these ions approaches a water chain and another leaves the other end of the chain, a transport of entropy may arise not only from the alternate ordering and disordering effects of the ionic field on the water structure, but more significantly as transport of entropies of reaction as hydrogen bonds are alternately made and broken. The heats of transport involved here are 3-4 kcal/mole while experimental values of the hydrogen bond energy in water range from 4 to 5 kcal.

DEPENDENCE OF \bar{S}° AND $\Delta\bar{S}_h$ ON RADIUS

Other ions show less drastic deviations. To account for the characteristic behaviour of individual ions, the ionic radius should be taken into account. Khoroshin and Temkin⁵ write the transported entropy of an ion (or "entropy of the moving ion") as composed of the following contributions,

$$\bar{S}^\circ = S_g + \Delta S_h + S^{*\circ}, \quad (11)$$

where ΔS_h is the entropy change on hydration of a gaseous ion and S_g is the contribution by the gaseous ion, calculated according to

$$S_g = 19.6 + \frac{3}{2}R \ln M. \quad (12)$$

Here M is the atomic mass and the constant term (19.6) depends on the concentration considered (1 mole/l.) but its actual value here is unimportant since it is taken the same for all ions. They eliminate S_g and hence mass dependence by defining the "entropy of hydration of the moving ion" or transported entropy of hydration $\Delta\bar{S}_h$ by

$$\Delta\bar{S}_h = \Delta S_h + S^{*\circ} = \bar{S}^\circ - S_g, \quad (13)$$

in order to assess the dependence on radius r . The quantities obtained on multiplying values of $\Delta\bar{S}_h$ by values of Pauling's radii in Å they show to be quite constant for a given valence, the averages being -15.9 for univalent cations and -46.9 for divalent cations. They conclude that $\Delta\bar{S}_h$ is related to r by

$$\Delta\bar{S}_h = A/r, \quad (14)$$

where A is a constant for cations of a given valence (-15.9 , -46.9). Whether the above relation is true for both $S^{*\circ}$ and ΔS_h , of which $\Delta\bar{S}_h$ is composed, is difficult to say since in most cases $\Delta\bar{S}_h$ consists mainly of ΔS_h and $S^{*\circ}$ is usually small.

DEPENDENCE OF \bar{S}° AND $\Delta\bar{S}_h$ ON VALENCE

Laidler and Pegis^{11, 12} have correlated ΔS_h (based on $S_{H^+}^\circ = -5.5$) with z^2/r following the Born relation which for aqueous solution at 25°C predicts that the electrostatic contribution to the entropy of the ion be given by $-9.42 z^2/r$. Others

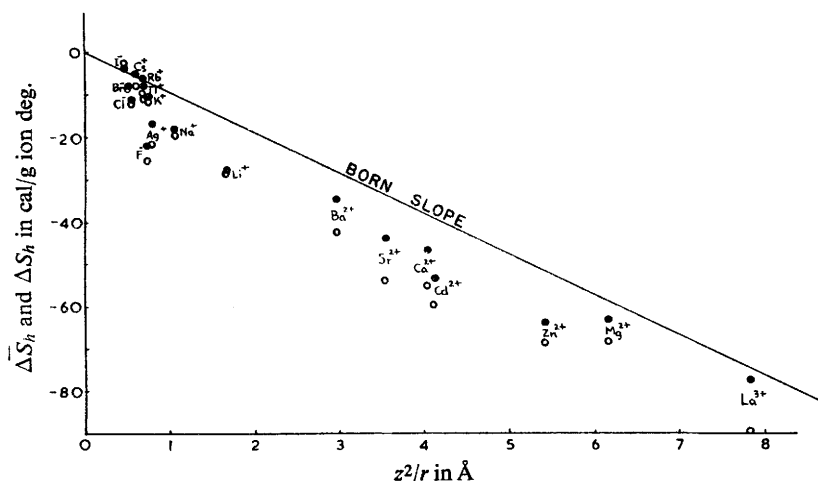


FIG. 2.—Born plot of $\Delta\bar{S}_h$ (black circles) and ΔS_h (white circles).

have obtained correlations with z/r^2 but without the support of the Born relation and by the use of conventional partial molar entropies which cannot produce a coincidence for cationic and anionic values unless $S_{H^+}^\circ$ is close to zero, or some bias is introduced in the treatment.

Assuming that $\Delta\bar{S}_h$ does follow $1/r$ as indicated, it is of interest to pursue the dependence of $\Delta\bar{S}_h$ (which includes $S^{*\circ}$) on valence. Following Khoroshin and Temkin, values of $\Delta\bar{S}_h = \bar{S}^\circ - 19.6 - \frac{3}{2}R \ln M$ as well as of $\Delta S_h = S^\circ - 19.6 - \frac{3}{2}R \ln M$ have been calculated for monatomic ions and entered in table 1 along with values of z^2/r . Both $\Delta\bar{S}_h$ and ΔS_h are plotted against z^2/r in fig. 2 and a line of the Born slope of -9.42 has been drawn for comparison. In some cases, the values of $\Delta\bar{S}_h$

and ΔS_h are not significantly different; in others, the addition of $S^{*\circ}$ to ΔS_h to give $\Delta \bar{S}_h$ tends to improve the agreement. For example, ΔS_h for I^- is too high and $S^{*\circ}$ for I^- is negative. In most other cases, the values of ΔS_h are too low and are raised by the addition of positive values of $S^{*\circ}$. As a result the correlation of $\Delta \bar{S}_h$ with z^2/r is better than that of ΔS_h ; or the Born relation is more applicable to \bar{S}° and $\Delta \bar{S}_h$ than to S° and ΔS_h . Standard deviations from the Born line as drawn in fig. 2 are for $\Delta \bar{S}_h$ and ΔS_h respectively 7.9 and 12.2 cal/g ion deg.; both values could be lowered by a different choice of intercept for the Born line.

In any attempt at further improvement in the plot the approximate nature of the Born model should be recognized, particularly with respect to the dielectric medium which is considered continuous. Such a model should be satisfactory when the charged particles are large compared with the water molecules, but not for the monatomic ions studied here. Refinement by a more detailed treatment of the dielectric effects considerable improvement in the plot for ΔS_h as shown by Laidler and Pegis¹² and Glueckauf.¹³

We are indebted to the National Research Council of Canada for assistance in the form of grants and to the Provincial Government of Ontario for the provision of a fellowship (held by J. L.).

¹ Lin and Breck, *Can. J. Chem.*, 1965, **43**, 766.

² Gurney, *Ionic Processes in Solution*, (McGraw-Hill, New York, 1953).

³ Agar, *Thermogalvanic Cells in Adv. Electrochem. Electrochem. Eng.*, Vol. 3, ed. Delahay. (Interscience, New York, 1963).

⁴ Breck and Lin, *Trans. Faraday Soc.*, 1965, **61**, 1511.

⁵ Khoroshin and Temkin, *Zhur. Fiz. Khim.*, 1952, **26**, 773.

⁶ Latimer, *Oxidation Potentials*, 2nd ed., (Prentice-Hall, New Jersey, 1952).

⁷ Breck and Lin, *Trans. Faraday Soc.*, 1965, **61**, 744.

⁸ Breck, Cadenhead and Hammerli, *Trans. Faraday Soc.*, 1965, **61**, 37.

⁹ Haase, Hoch and Schönert, *Z. Physik. Chem.*, 1960, **25**, 193.

¹⁰ Ikeda, *J. Chem. Physics*, 1959, **30**, 345.

¹¹ Laidler, *Can. J. Chem.*, 1956, **34**, 1107.

¹² Laidler and Pegis, *Proc. Roy. Soc. A*, 1957, **241**, 80.

¹³ Glueckauf, *Trans. Faraday Soc.*, 1964, **60**, 572.