expected since much of the $\overline{C_{p_2}}^\circ$ data on ionic solutes pass through a maximum near this temperature. By this emperical extrapolation, entropy constants have been estimated up to 200° (Table III). The validity of such extrapolations can be tested in a limited way by comparison of the predicted and experimental entropies for the few solutes known at 200° (Table IV).

The agreement between the predicted and observed values of $\overline{S_2}^\circ$ at 200° is quite satisfactory and suggests that the general validity of the correspondence principle holds up to at least 200°.

It is to be noted that once the extrapolation method has been decided upon, values for the constants $a_{(t)}$ and $b_{(t)}$ above 150° are fixed and are not arbitrarily defined. Consequently, the test given in Table IV is rigorous for the species listed, although necessarily limited.

TABLE IV

COMPARISON OF PREDICTED AND OBSERVED ENTROPIES AT 200°

Ions	$\overline{S_2}^\circ$ (obsd),[a] cal. mole^{-1} deg.$^{-1}$	$\overline{S_2}^\circ$(calcd),[b] cal. mole^{-1} deg.$^{-1}$
H^+, CO_3^{-2}	-54 ± 6	-61
H^+, Cl^-	-1 ± 2	-1.3
H^+, Br^-	5 ± 2	4.7
H^+, OH^-	-16 ± 4	-16.7
$2Ag^+, SO_4^{-2}$	20 ± 4	21.7
H^+, HCO_3^-	24 ± 4	23.1
Ca^{+2}, SO_4^{-2}	-32	-31.7

[a] From Table I; some data are available in the literature on the solubility of AgCl up to 200°. However, at the present time it is almost impossible to account quantitatively for the hydrolysis of Ag^+ at these high temperatures under the conditions of the experiments. [b] Calculated from eq. 7 using the constants given in Table III.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

The Thermodynamic Properties of High Temperature Aqueous Solutions. V. The Calculation of Ionic Heat Capacities up to 200°. Entropies and Heat Capacities above 200°[1]

BY CECIL M. CRISS[2] AND J. W. COBBLE

Equations are given for calculating heat capacities at 25° and at elevated temperatures from the correspondence principle for entropies previously developed.

Introduction

Probably the most useful function for predicting the thermodynamic properties of electrolyte solutions at higher temperatures is the partial molal heat capacity, $\overline{C_{p_2}}^\circ$, as a function of temperature. Consider the situation when it is desirable to know the free energy of a reaction at some elevated temperature, t_2, when it is known at t_1

$$\Delta F^\circ_{(t_2)} = \Delta F^\circ_{(t_1)} + \overline{\Delta C_p^\circ}\Big]_{t_1}^{t_2} \times$$
$$\Delta T - \Delta S^\circ_{(t_1)}\Delta T - T_2\overline{\Delta C_p^\circ}\Big]_{t_1}^{t_2} \ln\frac{T_2}{T_1} \quad (1)$$

or combining terms

$$\Delta(\Delta F^\circ) = -\Delta S^\circ_{(t_1)}\Delta T + \overline{\Delta C_p^\circ}\Big]_{t_1}^{t_2} \times$$
$$\left[\Delta T - T_2 \ln\frac{T_2}{T_1}\right] \quad (2)$$

where $\overline{\Delta C_p^\circ}\Big]_{t_2}^{t_1}$ is the average value of ΔC_p° between t_1 and t_2.

The knowledge of ΔF° and ΔS° at one temperature and a value of the average heat capacity change between the two temperatures are sufficient to calculate $\Delta F^\circ_{(t_2)}$.[3] However, there are so few data at present on $\overline{C_{p_2}}^\circ$ as a function of temperature that the method cannot be used for any significant number of electro-

lytes. Furthermore, although a greater number of $\overline{C_{p_2}}^\circ$ values are known at just one temperature, 25°, such data cannot be reliably used at other temperatures since in general $\overline{C_{p_2}}^\circ$ varies considerably with temperature.

In a previous communication, a correspondence principle for entropies for higher temperature solutions was developed.[4] It immediately follows that whenever the entropy of an ion is known or can be accurately predicted at two temperatures, the *average* value of the heat capacity $\overline{C_{p_2}}^\circ\Big]_{t_1}^{t_2}$ between those temperatures can be calculated. The purpose of this communication is to extend the entropy correspondence principle to the calculation and prediction of $\overline{C_{p_2}}^\circ$ and $\overline{C_{p_2}}^\circ\Big]_{t_1}^{t_2}$ for electrolytes over extended temperature ranges.

The Correspondence Principle and Heat Capacity Equations

The linear correspondence of entropy for ions between 25° and t_2 can be written as[4]

$$S^\circ_{(t_2)} = a_{(t_2)} + b_{(t_2)}S^\circ_{25}(\text{abs.}) \quad (3)$$

S°_{25}(abs.) refers to the ionic entropies on the "absolute" scale; S°_{25}(abs.) $= S^\circ_{25}$(conventional) $- 5.0Z$, where Z is the ionic charge.[5] The average value of the partial molal heat capacity between 25° and t_2 is

$$\overline{C_{p_2}}^\circ\Big]_{25}^{t_2} = \frac{S^\circ_{(t_2)} - S^\circ_{(25)}}{\ln T_2/298.2} \quad (4)$$

(1) Supported by a grant from the National Science Foundation.

(2) Partly from the Ph.D. Thesis of Cecil M. Criss, Purdue University, 1961.

(3) Strictly speaking, $\overline{\Delta C_p}^\circ$ in the linear temperature term will be somewhat different from the value of the function in the ln T term. In practice, this difference is not significant between 25 and 200°, and in 50° steps at temperatures above 200°.

(4) C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.*, **86**, 5385 (1964).

(5) Hereafter, entropies will be considered as being on an "absolute" scale unless specifically noted otherwise.

TABLE I

HEAT CAPACITY PARAMETERS (EQ. 6)[a]

t, °C.	Cations		OH⁻ and anions		Oxy anions		Acid oxy anions		H⁺[b] $\overline{C_p}°\Big]_{25}^{t_2}$
	$\alpha_{(t)}$	$\beta_{(t)}$	$\alpha_{(t)}$	$\beta_{(t)}$	$\alpha_{(t)}$	$\beta_{(t)}$	$\alpha_{(t)}$	$\beta_{(t)}$	
60	35	−0.41	−46	−0.28	−127	1.96	−122	3.44	23
100	46	−0.55	−58	0.000	−138	2.24	−135	3.97	31
150	46	−0.59	−61	−0.03	−133	2.27	(−143)	(3.95)	33
200	(50)	(−0.63)	(−65)	(−0.04)	(−145)	(2.53)	(−152)	(4.24)	(35)

[a] Parenthetical values are derived from extrapolated values of the corresponding entropy terms from lower temperatures and are thus subject to greater error. [b] Entries in this column refer to the average value of the heat capacity for H⁺(aq) as derived from fixing the entropy of H⁺(aq) at each temperature. Units are cal. mole⁻¹ deg.⁻¹

From eq. 3 and 4 it follows that

$$\overline{C_{p_2}}°\Big]_{25}^{t_2} = \frac{a_{(t_2)} - \overline{S}°_{25}[1.000 - b_{(t_2)}]}{\ln T_2/298.2} \quad (5)$$

which can be rewritten as[5,6]

$$\overline{C_{p_2}}°\Big]_{25}^{t_2} = \alpha_{(t_2)} + \beta_{(t_2)}\overline{S}°_{25} \quad (6)$$

where $\alpha_{(t_2)} = a_{(t_2)}/(\ln T_2/298.2)$ and $\beta_{(t_2)} = -[1.000 - b_{(t_2)}]/(\ln T_2/298.2)$. Values of $a_{(t)}$ and $b_{(t)}$ have been evaluated previously[4] up to 200°, and the corresponding heat capacity constants, $\alpha_{(t)}$ and $\beta_{(t)}$, are given in Table I.

From eq. 6 and the parameters given in Table I, combined with the heat capacities for pure substances,[7] the average value of the heat capacity change for a reaction over the temperature range 25° to t_2 can be calculated up to 200°, and $\Delta F°$ evaluated from eq. 1 over the same range. The only additionally required thermochemical information are $\Delta S°_{25}$ and $\Delta F°_{25}$. In many cases, reliable estimates can even be made in lieu of experimental values of the entropy at 25°. The reader is referred elsewhere for these previously published methods of estimating $\overline{S}_2°$.[8-12] The great usefulness of this extension of the entropy correspondence principle is that it does not require any direct information on $\overline{C_{p_2}}°$ for electrolytes at any temperature.

For convenience, values of $\overline{C_{p_2}}°\Big]_{25}^{t_2}$ up to 200° have been estimated and tabulated for some common ions in Table II.

Ionic Heat Capacities at 25°

The correspondence relationship can also be used in estimating point values of the ionic heat capacity, $\overline{C_{p_i}}°$, at a given temperature. Equation 6 suggests that as the average heat capacity is taken over smaller and smaller temperature intervals, $\overline{C_{p_2}}°\Big]_{t_1}^{t_2}$ will approach $\overline{C_{p_2}}°$ at that mean temperature, and

$$\overline{C_{p_2}}°_{(t)} \approx A_{(t)} + B_{(t)}\overline{S}°_{25} \quad (7)$$

It is of interest to test this relationship at 25° where sufficient data exist over a wide variety of ions. How-

(6) For reasons already discussed in ref. 4, eq. 6 contains only an apparent error in explicitly omitting considerations of the mass and symmetry of the ions.

(7) K. K. Kelley, U. S. Bureau of Mines Bulletin 476, U. S. Government Printing Office, Washington, D. C., 1949.

(8) R. E. Powell and W. M. Latimer, J. Chem. Phys., 19, 1139 (1951).

(9) K. J. Laidler and C. Pegis, Proc. Roy. Soc. (London), A241, 80 (1957); K. J. Laidler, Can. J. Chem., 34, 1107 (1956).

(10) R. E. Connick and R. E. Powell, J. Chem. Phys., 21, 2206 (1953).

(11) J. W. Cobble, ibid., 21, 1443, 1446, 1451 (1953).

(12) A. M. Couture and K. J. Laidler, Can. J. Chem., 35, 202 (1957).

TABLE II
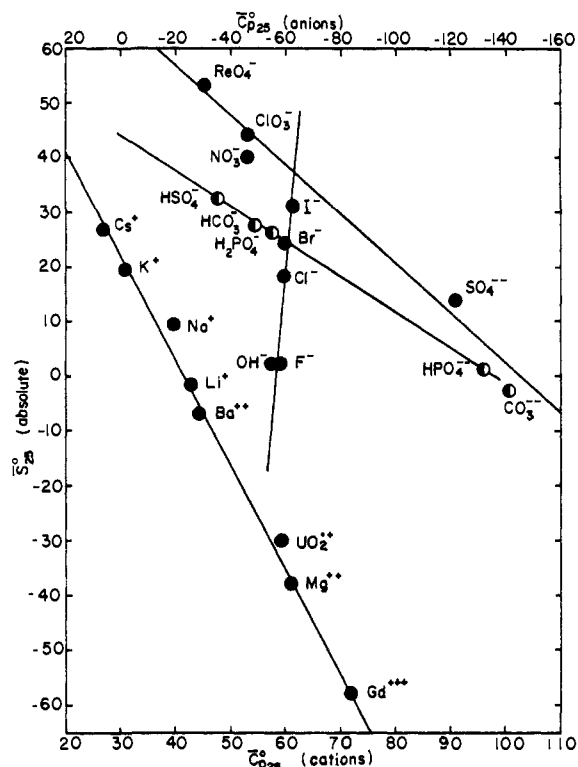
BEST VALUES OF IONIC PARTIAL MOLAL HEAT CAPACITIES[a] FOR SOME COMMON IONS (CAL. MOLE⁻¹ DEG.⁻¹)

Ion	$\overline{C_p}°_{25}$	$\overline{C_p}°\Big]_{25}^{60}$	$\overline{C_p}°\Big]_{25}^{100}$	$\overline{C_p}°\Big]_{25}^{150}$	$\overline{C_p}°\Big]_{25}^{200}$
H⁺	28	23	31	33	35
Li⁺	41	36	47	47	52
Na⁺	37	35	41	41	45
K⁺	31	27	35	35	39
Rb⁺	30	25	32	31	35
Cs⁺	26	24	31	30	34
Tl⁺	28	25	32	31	35
Ag⁺	35	30	39	39	43
Be⁺²	76	62	82	84	92
Mg⁺²	62	51	67	69	75
Ca⁺²	54	45	59	60	66
Sr⁺²	52	43	57	57	63
Ba⁺²	44	38	50	50	55
Ra⁺²	40	34	44	44	49
Cu⁺²	59	49	64	66	72
Mn⁺²	57	47	63	64	70
Cd⁺²	54	45	60	61	67
Pb⁺²	44	37	49	49	54
Al⁺³	89	72	95	99	108
Cr⁺³	88	71	95	98	107
Fe⁺³	86	70	93	96	105
Gd⁺³	72	59	78	80	88
Sc⁺³	79	64	85	88	96
Zr⁺⁴	98	78	104	108	117
U⁺⁴	93	75	100	104	113
UO₂⁺²	56	47	63	64	69
Fe(OH)⁺²	59	49	64	66	72
F⁻	−57	−47	−58	−61	−65
Cl⁻	−59	−51	−58	−62	−66
Br⁻	−61	−53	−58	−61	−65
I⁻	−62	−55	−58	−61	−64
OH⁻	−57	−47	−58	−61	−65
SH⁻	−60	−52	−58	−62	−66
ReO₄⁻	−30	−23	−25	−25	−25
ClO₄⁻	−40	−33	−36	−39	−39
NO₃⁻	−56	−49	−63	−55	−57
SO₄⁻²	−115	−99	−108	−105	−114
SO₃⁻²	−139	−121	−132	−127	−138
PO₄⁻³	−226	−200	−216	−205	−227
CO₃⁻²	−151	−132	−146	−138	−151
HSO₄⁻	−35[b]	−13	−10	−18	−18
HSO₃⁻	−43[b]	−16	−11	−21	−21
HCO₃⁻	−48[b]	−27	−25	−34	−35
H₂PO₄⁻	−55[b]	−31	−23	−39	−41
HPO₄⁻²	−132[b]	−118	−129	−138	−146

[a] Calculated from eq. 6 and Table I; in some cases minor adjustments of a few cal. mole⁻¹ deg.⁻¹ in the heat capacities have been made to agree better with direct experimental determinations and to smooth out the variation of heat capacity with temperature. [b] These 25° values are simply recorded from temperature coefficient measurements of cell potentials alone and are subject to large errors.

Fig. 1.—Correlation diagram of $\overline{C_p}°_{25}$ for ions with the absolute entropy. $\overline{C_{p_{25}}}°_{(H^+, aq)} = 28$ cal. mole^{-1} deg.$^{-1}$; $\overline{S}°_{25(H^+, aq)} = -5.0$ cal. mole^{-1} deg.$^{-1}$. Half-filled circles represent values based solely upon equilibrium constant data and are to be considered as preliminary estimates.

ever, some further choice must first be made in order to separate the experimental heat capacities into ionic values. The previous assignment of the entropy of H$^+$ at each temperature can be used to define the ionic heat capacity at a given temperature. This can be done by noting that

$$\int_{t_1}^{t_2} d\overline{S}_2° = \int_{t_1}^{t_2} \overline{C_{p_2}}° \frac{dt}{T} \qquad (8)$$

If the absolute entropy of H$^+$(aq) is plotted against temperature, the slope of the resulting curve at some temperature t is

$$\frac{d}{dt}\int_{t_1}^{t_2} d\overline{S}_2° = \frac{d}{dt}\int_{t_1}^{t_2} \overline{C_{p_2}}° \frac{dt}{T} \qquad (9)$$

In the limit, as $t_1 \rightarrow t_2$

$$\left(\frac{d\overline{S}_2°}{dt}\right)T = \overline{C_{p_2}}° \qquad (10)$$

(dS/dt) was evaluated[13] from the previously[4] assigned ionic entropies of H$^+$(aq) as 0.0922; at 25°, the "absolute" ionic heat capacity of H$^+$(aq) from eq. 10 then becomes 28 cal. mole^{-1} deg^{-1}.

In Fig. 1, the known[14] ionic heat capacity data on.this

(13) The graph of the entropy of the hydrogen ion against temperature is actually sigmoid in nature; the curvature is particularly marked in the vicinity of 60° where most electrolyte heat capacities show maxima, and below 25° where $\overline{C_{p_2}}°$ changes rapidly with temperature. The curvature may, however, be an artifact arising from errors involved in evaluation of the absolute ionic entropy at each temperature. The best that can be done at present is to obtain only an approximate value for the slope at 25°. Fortunately, the test under discussion is not very sensitive to the exact value of (dS/dt).

(14) Partial molal heat capacity data at 25° are from previously summarized values and from newer data collected in these laboratories as fol-

"absolute" scale at 25° are plotted against the "absolute" ionic entropies. The predicted linearity probably is as good as the errors in the heat capacity data, considering that there are only a few salts for which the values of $\overline{C_{p_2}}°$ were obtained calorimetrically at dilutions below 0.1 M.[14,15] The parameters of eq. 7 are tabulated in Table III for the ion types known at 25° and are useful in the estimation of $\overline{C_p}°_{25}$.

TABLE III

HEAT CAPACITY PARAMETERS AT 25° (EQ. 7)

$\overline{C_{p_2}}°_{(H^+, aq.)} \equiv 28$ cal. mole^{-1} deg.$^{-1}$

Ion	A	B
Cations	41.6	−0.523
OH$^-$, anions	−56.5	0.179
Oxy anions	−145	2.20
Acid oxy anions	−136	3.07

Estimation of Ionic Entropies and Heat Capacities above 200°

The estimation of heat capacities for ionic solutes above 200° must be based at the present time purely on some method of extrapolation from lower temperatures. There are a number of ways this can be done, although it should be emphasized that all are subject to greater errors than at temperatures below 200°.

The first most obvious method is to calculate $\Delta C_p \Big]_{25}^{t}$ for a given reaction at 100, 150, and 200° and, by inspection, extrapolate this function to higher temperatures. If there are ions present on both sides of the reaction, then ΔC_p will tend to change more slowly than the individual $\overline{C_{p_2}}° \Big]_{25}^{t}$ values.

A better method is to extrapolate the entropy parameters[4] of eq. 3 to higher temperatures. It had been found previously that these parameters vary *approximately* linearly with temperature[16] over the 100–200°

lows: NaCl, −18.9; BaCl$_2$, −72.6 (ref. 15); HCl, −30.5; NaReO$_4$, 8.8 [J. C. Ahluwalia and J. W. Cobble, J. Am. Chem. Soc., 86, 5377 (1964)]; CsI, −36.6 [R. E. Mitchell and J. W. Cobble, ibid. 86, 5401 (1964)]; GdCl$_3$, −105 [E. C. Jekel, C. M. Criss, and J. W. Cobble, ibid., 86, 5404 (1964)]; KCl, −27.7; NaI, −23.4; LiCl, −15.8; KOH, −25; KBr, −28.9; KNO$_3$, −15.5 [G. N. Lewis and M. Randall, "Thermodynamics," 2nd Ed., revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Co., New York, N. Y., 1961, p. 652]. Further ionic values, based upon $\overline{C_p}°_{25}$ for H$^+$ $\equiv$ 0, are given in the Lewis and Randall text, p. 400, as follows: Mg^{+2}, 59; F$^-$, −57.5; SO$_4^{-2}$, −122; ClO$_3^-$, −46. These values were converted to the present scale of $\overline{C_p}°_{25}$ for H$^+$ $\equiv$ 28 before they were entered on Fig. 1. The heat capacity of UO$_2^{+2}$ is from the UO$_2$Cl$_2$(aq) data of A. F. Kapustinskii and I. I. Lipilina, Dokl. Akad. Nauk SSSR (Engl. Transl.), 104, 264 (1955); the revised entropy of UO$_2^{+2}$ given by M. H. Rand and O. Kubaschewski, "The Thermochemical Properties of Uranium Compounds," Oliver and Boyd. Ltd., London, 1963, p. 12. It is perhaps worth noting that it is difficult to find a complete and consistent set of ionic heat capacities involving both newer and older data. Indeed, in the text referred to above, there are two sets of entries for both NO$_3^-$ and OH$^-$. Newer values and more recent concentration extrapolations of older data have been given preference in Fig. 1. However, part of the scatter may be due to this unavoidable use of the data. Consequently, errors of up to five heat capacity units may be involved in some cases.

Data on CO$_3^{-2}$ and the acid oxy anions are from potentiometric determinations of the respective dissociation constants and their temperature coefficients as follows: H$_2$PO$_4^-$ (from H$_3$PO$_4$), HPO$_4^{-2}$ (from H$_2$PO$_4^-$), and HSO$_4^-$ (from SO$_4^{-2}$) [H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Co., New York, N. Y., 1958, p. 667]. The required $\overline{C_{p_2}}°$ for H$_3$PO$_4$(aq) was estimated at 25° to be 24 cal. mole^{-1} deg.$^{-1}$ from the data of E. P. Egan, Jr., B. B. Luff, and Z. T. Wakefield, J. Phys. Chem., 62, 1091 (1958). The CO$_3^{-2}$ and HCO$_3^-$ values are from the Harned and Owen reference, pp. 692 and 758. Heat capacities from temperature coefficient studies of equilibrium constants are, of course, subject to even much greater errors than the calorimetric data.

(15) C. M. Criss and J. W. Cobble, J. Am. Chem. Soc., 83, 3223 (1961).

(16) It should perhaps be emphasized that this functional dependence of $a_{(t)}$ and $b_{(t)}$ at higher temperatures implies an ionic heat capacity propor-

Table IV

Estimated Entropy Parameters above 150°[a]

t, °C.	$\bar{S}°_{H^+}$	Cations		Anions and OH⁻		Oxy anions		Acid oxy anions	
		$a_{(t)}$	$b_{(t)}$	$a_{(t)}$	$b_{(t)}$	$a_{(t)}$	$b_{(t)}$	$a_{(t)}$	$b_{(t)}$
200	11.1	23.3	0.711	−30.2	0.981	−67.0	2.020	−70.0	2.960
250	16.1	29.9	0.630	−38.7	0.978	−86.5	2.320	−90.0	3.530
300	20.7	36.6	0.548	−49.2	0.972	−106	2.618	...	...

[a] For eq. 3, in cal. mole⁻¹ deg.⁻¹.

range. If one is willing to risk assuming that this approximate linearity will continue above 200°, then the entropy parameters given in Table IV can be estimated. Because of the fact that the linear ΔT and $\Delta \log T$ averages of $\bar{C}_p°$ in eq. 1 are not the same over too great a temperature interval, calculations of the free energy above 200° should be carried out in 50° intervals.[17] Values of the entropies for the ions involved in a given reaction can be calculated at 200, 250, and 300°. These values can then be used in turn to generate the corresponding ionic heat capacities over 50° intervals.

$$\bar{C}_{p_1}°\bigg]_{t_1}^{t_2} = \frac{\bar{S}°_{(t_2)} - \bar{S}°_{(t_1)}}{\ln T_2/T_1} \qquad (11)$$

The resulting series of $\Delta C_p\bigg]_{t_1}^{t_2}$ above 200° can finally be used to estimate $\Delta F_{(t_2)}$ using eq 1.

Discussion

It is of interest to inquire into the assignment of ionic heat capacities which have resulted from the treatment just presented. The general correspondence principle itself does not provide any direct indication of either the method or validity of assigning ionic entropies from solute entropies. While it is true that the entropy (and thus heat capacity) of $H^+(aq)$ is fixed by trial and error at each temperature in order to obtain a linear correspondence in accordance with eq. 3, this is not necessarily a unique assignment. Indeed, as originally formulated,

tional to the absolute temperature. However, this approximation does not follow from the correspondence principle. The latter is perfectly general and can accommodate almost any functional heat capacity variation with temperature. Indeed, the values given in Table I correctly reflect the maximum in $\bar{C}_{p_2}°$ that salts show near 60°, and the evidence clearly indicates that over large temperature intervals the ionic heat capacities will be a complex function of temperature.

(17) Still another source of error can arise from not considering the effect of solvent pressure on ΔF at the highest temperatures. Fortunately, in most cases this will probably not be significant below 300° and will be discussed further in the communication following this paper.

the entropies could be related through some other, nonlinear type of function, in which case the entropy of $H^+(aq)$ would probably take on different values at the elevated temperatures.

Nevertheless, one can still inquire into possible reasons that might give cations positive heat capacities and anions negative values. In the entropy expression which results from the Born equation there is always a dielectric term, $(1/D^2)(\partial D/\partial t)$. In the near vicinity of an ion there is question even with regard to the sign of this term. Because of the different orientation of solvent water molecules around cations and anions, it may be possible for the dielectric term to be either positive or negative. As the temperature changes, the contribution of the dielectric term may thus be of different sign, and the resulting heat capacities could also be of different sign. Another factor which is always present is a change in hydration of the ions. Because the entropy of unbound water molecules probably increases with temperature faster than for the bound species, ions of even constant hydration number will have decreasing entropies (negative heat capacities) with increasing temperature. Thus different temperature hydration effects of cations and anions may also give rise to differing signs for the anion and cation heat capacities. It may be noted that the present ionic heat capacity divisions are in qualitative agreement with those obtained from purely theoretical reasons by others.[18] The question can probably be resolved by repetition of thermocell experiments at higher temperatures. Although there is no satisfactory means of separating the absolute ionic entropy and ionic entropy of transfer which results from such experiments, the entropy of transfer might not be very temperature sensitive. Consequently, the trend of the absolute entropy of an ion with temperature could possibly be discerned and would be of great help in making proper assignments of absolute ionic entropies at higher temperatures.

(18) M. Eigen and E. Wicke, Z. Elektrochem., 55, 354 (1951).