Standard state heat capacities of aqueous electrolytes and some related undissociated species[1]

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Abstract: Uses of heat capacities of solutions of electrolytes are reviewed, with a particular emphasis on the standard state partial molar heat capacities and their applications to calculations of the effects of temperature on equilibrium constants, electrode potentials, enthalpies, and entropies. Methods of obtaining these standard partial molar heat capacities are summarized, followed by comparisons of values obtained in different ways. Many of the "best" such heat capacities are collected and then used as the basis for establishing single-ion heat capacities based on the convention that $C_p^{\circ}(H^+) = 0$, followed by illustrations of the convenient use of these quantities. Finally, there is brief discussion of theoretical analysis of these standard partial molar heat capacities in relation to ion–solvent interactions.

Key words: heat capacities, electrolytes; aqueous solutions, heat capacities; thermodynamics, electrolytes.

Résumé : On présente une revue de l'utilisation des capacités calorifiques de solutions d'électrolytes en insistant d'une façon particulière sur les capacités calorifiques molaires partielles dans l'état standard et leurs applications aux calculs des effets de la température sur les constantes d'équilibre, les potentiels d'électrode, les enthalpies et les entropies. On résume les méthodes d'obtenir ces capacités calorifiques molaires partielles standard et on présente ensuite un comparaison des diverses valeurs obtenues d'après les diverses manières. Plusieurs des «meilleures» propriétés, comme les capacités calorifiques, ont été rassemblées et ont ensuite été utilisées comme base pour l'établissement des capacités calorifiques d'un seul ion en se basant sur la convention que $C_p^{\circ}(H^+) = 0$; elles sont suivies par des illustrations sur l'utilisation commode de ces quantités. Enfin, on présente une brève discussion de l'analyse théorique de ces capacités calorifiques molaires partielles standard en relation avec les interactions ion–solvant.

Mots clés : capacités calorifiques, électrolytes, solutions aqueuses; thermodynamique.

[Traduit par la rédaction]

Introduction

Knowledge of heat capacities of pure substances is useful because such heat capacities can be used in a wide variety of thermodynamic calculations, many of which involve the effects of changing temperature on other thermodynamic properties such as Gibbs energies and related equilibrium constants, enthalpies, and entropies. The principle of these calculations and methods of carrying them out have been reviewed in many texts dealing with chemical thermodynamics.

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[1] This paper, part of which was presented by L.G.H. at the *"Taube Fest"* on 7 October 1995 at the University of Saskatchewan, is dedicated to Henry Taube.

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Although it has been known for a long time that similar calculations for aqueous solutions of electrolytes could be useful, the general paucity of required experimental results severely limited these kinds of applications. In recent years, however, advances in calorimetry have made it practical to obtain reliable and accurate heat capacities of dilute aqueous solutions, thereby leading to the partial molar heat capacities needed for the kinds of calculations mentioned above.

In the remainder of this Introduction, we will provide words and equations (to be used later) to call attention to some of the uses of partial molar heat capacities: (*i*) We provide a review of experimental methods and illustrate methods of calculating the standard state partial molar heat capacities that will form the principal part of the rest of this paper. (*ii*) We provide a critical review of standard state partial molar heat capacities of aqueous inorganic electrolytes (also acetate ion, Ac^-) and a few non-ions such as $HAc(aq)$, $NH_3(aq)$, $CO_2(aq)$, $SO_2(aq)$, $H_2S(aq)$, and $H_3PO_4(aq, undissociated)$. (*iii*) We select "best" values of standard state partial molar heat capacities and provide specific illustrations of some of their uses. (*iv*) We refer briefly to uses of heat capacities in connection with theoretical attempts to improve or extend knowledge of ion–solvent interactions.

To introduce the need for the heat capacities that are the focus of this paper, we begin with the van't Hoff equation:

[1] $(\partial \ln K/\partial T)_p = \Delta_r H^\circ/RT^2$

Making the approximation that the standard state enthalpy of reaction, $\Delta_r H^\circ$, is a constant (independent of temperature), integration of eq. [1] leads to

[2] $\ln K = -(\Delta_r H^\circ/RT) + I$

in which I is a constant of integration.

Equation [2] is often useful over small ranges of temperature, but is generally inadequate for wide or even moderate ranges of temperature. One illustration of the inadequacy of this equation is provided by the observation that $\ln K$ is (for temperature-independent $\Delta_r H^\circ$) predicted to be a linear function of $1/T$, increasing or decreasing forever as the temperature increases or decreases, which is contrary to the reality that values of K and thence $\ln K$ for many reactions involving aqueous electrolytes pass through a minimum or maximum with changing temperature. The explanation for this kind of failure of eq. [2] is that $\Delta_r H^\circ$ is not generally a constant (independent of temperature), but depends on temperature as shown below.

Effects of temperature on $\Delta_r H^\circ$ and also on $\Delta_r S^\circ$ are described by the following equations:

[3] $(\partial \Delta_r H^\circ/\partial T)_p = \Delta_r C_p{}^\circ$

[4] $(\partial \Delta_r S^\circ/\partial T)_p = \Delta_r C_p{}^\circ/T$

Here we have used $\Delta_r C_p{}^\circ$ to represent the change in heat capacity for a chemical reaction, which is related to the heat capacities of the reactants and products of reaction by

[5] $\Delta_r C_p{}^\circ = \Sigma C_p{}^\circ(\text{products}) - \Sigma C_p{}^\circ(\text{reactants})$

For aqueous solutes, the relevant heat capacity denoted by $C_p{}^\circ$ is the standard state partial molar heat capacity.

Equations [3] and [4] shows that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are independent of temperature only in the special (unusual!) case in which $\Delta_r C_p - 0$. Because heat capacities generally depend on temperature, consider various approaches to making use of eq. [3] in combination with eq. [1]. One approach (others are discussed later) is to express the heat capacity of each substance or ion in terms of an empirical power series, such as

[6] $C_p{}^\circ = a + bT + cT^2 + \dots$

Combination of equations [5] and [6] leads to

[7] $\Delta_r C_p{}^\circ = \Delta a + (\Delta b)T + (\Delta c)T^2 + \dots$

We now illustrate the principle of making use of heat capacities by cutting off eq. [7] after the Δa term, which means that we are (for now) considering $\Delta_r C_p{}^\circ$ to be independent of temperature. In this case, integration of eq. [3] leads to

[8] $\Delta_r H^\circ = \Delta H_i + (\Delta a)T$

in which ΔH_i is a constant of integration. Insertion of eq. [8] in eq. [1] and integration leads to

[9] $\ln K = -(\Delta H_i/RT) + [(\Delta a)(\ln T)/R] + I$

in which I is another constant of integration.

Equation [9] corresponds to a nonlinear dependence of $\ln K$ on $1/T$. Further, it can be shown by differentiating eq. [9] with respect to temperature and setting the resulting derivative equal to zero that there is some temperature at which $\ln K$ is either a minimum or a maximum, which is a very substantial improvement over eq. [2]. It will be shown later that using a constant (independent of temperature) value of $\Delta_r C_p{}^\circ$ leads to remarkably accurate calculations of equilibrium constants over wide ranges of temperature, which justifies part of our focus on heat capacities at just one temperature (298.15 K). It will also be shown that such calculations can be extended to much wider ranges of temperature by making use of heat capacities that have been measured over relatively small ranges of temperature.

Rather than carry out the differentiation of eq. [9] as mentioned above to obtain the temperature at which the value of K passes through a maximum or minimum, we proceed in another way. Integrating eq. [3] between limits of $T = 298$ K and some T_m at which the value of K goes through a maximum or minimum, we obtain

[10] $\Delta_r H^\circ(\text{at } T_m) - \Delta_r H^\circ(\text{at } T = 298 \text{ K}) = \Delta_r C_p{}^\circ(T_m - 298)$

Setting $\Delta_r H^\circ(\text{at } T_m) = 0$ (because this corresponds to a maximum or minimum in $\ln K$ vs. $1/T$), we obtain the following simple equation that relates the temperature at which the value of K passes through a maximum or minimum to the values of $\Delta_r H^\circ$ and $\Delta_r C_p{}^\circ$ at just one temperature (298 K):

[11] $T_m = -[\Delta_r H^\circ(\text{at } T = 298 \text{ K})/\Delta_r C_p{}^\circ] + 298 \text{ K}$

Much of the rest of this paper is devoted to collection of $C_p{}^\circ$ values for $T = 298.15$ K, with a few illustrations of their uses; we will also cite measurements leading to $C_p{}^\circ$ values at other temperatures and their uses.

Although the focus in this paper is on the standard state partial molar heat capacities represented here by $C_p{}^\circ$, non-standard state (for $m > 0$) partial molar heat capacities are also useful. Here we only mention that these non-standard state partial molar heat capacities are related to the temperature dependence of enthalpies of dilution and thence to the temperature dependence of activity coefficients and osmotic coefficients, as reviewed by Millero (1).

Experimental and calculation methods

One approach to obtaining standard state partial molar heat capacities is to solve eq. [1] for $\Delta_r H^\circ$, differentiate with respect to temperature, and combine with eq. [2] to obtain

[12] $\Delta_r C_p{}^\circ = R[2T(\partial \ln K/\partial T)_p + T^2(\partial^2 \ln K/\partial T^2)_p]$

Because of the magnification of uncertainties and errors associated with two differentiations, this approach is useful only when there are very accurate values for the equilibrium constant over a wide range of temperature. Our focus here is on other methods of obtaining standard state partial molar heat capacities of solutes.

Most of the standard state partial molar heat capacities that we will be considering have been derived from calorimetric

results expressed in terms of apparent molar heat capacities, $C_{p,\phi}$, which are defined in terms of measured quantities as

[13] $\quad C_{p,\phi} = [C_p(\text{soln}) - n_1 C_{p,1}{}^*]/n_2$

In this defining equation, $C_p(\text{soln})$ represents the heat capacity of a solution containing n_1 moles of water and n_2 moles of solute and $C_{p,1}{}^*$ represents the molar heat capacity of water. The apparent molar heat capacity is related to the partial molar heat capacity of solute (C_p) by

[14] $\quad C_p = C_{p,\phi} + n_2(\partial C_{p,\phi}/\partial n_2)$

At infinite dilution we have $n_2 = 0$ and thence the important relationship

[15] $\quad C_p{}^\circ = C_{p,\phi}{}^\circ$

in which $C_p{}^\circ$ represents the standard state partial molar heat capacity of solute and $C_{p,\phi}{}^\circ$ represents the value of the apparent molar heat capacity that is obtained on extrapolation to $n_2 = 0$, corresponding to extrapolation to a composition of zero molality.

Apparent molar heat capacities of dilute solutions of strong electrolytes are represented accurately by equations of the form

[16] $\quad C_{p,\phi} = C_p{}^\circ + (\omega)^{3/2} A_C(\rho_1{}^\circ)^{1/2}(m)^{1/2} + B_C\omega m$

in which $C_p{}^\circ$ represents the value of $C_{p,\phi}$ at $m = 0$ (see eq. [15]), A_C is derived from the Debye–Hückel theory and the dielectric constant of water, $\rho_1{}^\circ$ represents the density of water, m represents the molality, B_C is an adjustable parameter, and ω is defined by

[17] $\quad \omega = 0.5\Sigma \nu_i(z_i)^2$

in which the ν_i are the subscripts in the chemical formula $A_{\nu+}B_{\nu-}$ and the z_i are the formal charges of the ions.

The experimental problems associated with obtaining accurate values of $C_{p,\phi}$ for dilute solutions are formidable because the difference between $C_p(\text{soln})$ and $n_1 C_{p,1}{}^*$ is very small compared with either $C_p(\text{soln})$ or $n_1 C_{p,1}{}^*$. It follows that accurate values of $C_{p,\phi}$ for dilute solutions can be obtained only from the results of extremely accurate measurements or from results of accurate measurements that lead reasonably directly to values of the difference represented by $[C_p(\text{soln}) - n_1 C_{p,1}{}^*]$ in the numerator of eq. [13]. The twin calorimeters designed, built, and used by Randall, Rossini, Gucker, and a few others, as reviewed by Parker (2), provided data of this kind and permitted the evaluation of the first reasonably accurate values of $C_{p,\phi}{}^\circ$ for aqueous electrolytes.

More recently, however, the Picker flow calorimeter (3) has permitted more accurate measurements to be made more rapidly, leading to most of the $C_{p,\phi}$ and derived $C_p{}^\circ$ values to be considered here. The clever principle of the original Picker calorimeter that was designed and built for measurements at or near 25°C has been adapted by Picker for measurements up to about 150°C and by Smith-Magowan and Wood (4) and others to permit measurements to much higher temperatures (and pressures).

Several publications (5–8) have reported consideration of and remedies for small systematic errors that may be present in flow calorimeters. In one of these papers Desnoyers et al. (5) also provide a useful summary of $C_p{}^\circ$ values that were obtained during the first few years of use of the Picker calorimeter in Desnoyers' laboratory.

Use of eq. [16] for evaluation of $C_p{}^\circ$ from measured values of $C_{p,\phi}$ at several molalities requires that we know the value of A_C from the Debye–Hückel theory. Because A_C depends on the second derivative of the dielectric constant of water with respect to temperature, there have been some uncertainties in choosing a "best" value. We therefore review briefly the results of several recent calculations.

Before going on to consider specific results, it is well to point out that some previous authors have written another version of eq. [16] in terms of $A_C(c)^{1/2}$ in which c represents concentration (molarity) rather than in terms of molality and $A_C(\rho_1{}^\circ)^{1/2}(m)^{1/2}$ as in our eq. [16]. Further, some authors have derived Debye–Hückel parameters that are appropriate to partial molar properties, while others have derived these parameters to be appropriate to apparent molar properties as in our eq. [16]. It is necessary to consider these complications and also lack of uniformity in symbols used to represent various quantities in making use of results of different authors. Because our eq. [16] contains the product $A_C(\rho_1{}^\circ)^{1/2}$, we will express results of various calculations in terms of this product.

Leduc et al. (9) have used published dielectric constants and densities of water to obtain values of $A_C(\rho_1{}^\circ)^{1/2}$ for several temperatures, including the value 28.95 J K^{-1} mol$^{-3/2}$ kg$^{1/2}$ for 25°C. Similar calculations have been reported by Perron et al. (10) for several temperatures; they have reported nearly the same value as above for 25°C. More recently, Pitzer and coworkers (11), Ananthaswamy and Atkinson (12), Archer and Wang (13), and Spitzer et al. (14) have reconsidered the temperature dependence of the dielectric constant of water and have carried out calculations of the various parameters to be used in Debye–Hückel equations for heat capacities and also other thermodynamic properties for wide ranges of temperatures. Results of all of these later calculations (11–14) are consistent with a "best" value of $A_C(\rho_1{}^\circ)^{1/2}$ from about 12–23% larger than the value from Desnoyers and colleagues (9, 10) that is given above.

In the favourable cases of electrolytes of 1:1 charge type for which we have accurate values of $C_{p,\phi}$ for sufficiently dilute solutions, choosing different reasonable (in the range cited above) values of $A_C(\rho_1{}^\circ)^{1/2}$ leads to very small differences in calculated values of $C_p{}^\circ$, but for higher charge type electrolytes (14) or when results of accurate measurements are not available for sufficiently dilute electrolytes, choice of value for the Debye–Hückel parameter can have a significant effect on the value of the derived $C_p{}^\circ$.

As will be seen later, most of the $C_p{}^\circ$ values that are selected as "best" for $T = 298.15$ K are based on measurements with Picker-type calorimeters and data analysis based on eq. [16] or similar equations. A simple and commonly adopted procedure for using eq. [16] is based on rearranging to obtain

[18] $\quad C_{p,\phi} - (\omega^{3/2} A_C(\rho_1{}^\circ)^{1/2}(m^{1/2})) = C_p{}^\circ + B_C\omega m$

A graph of the quantity represented by the left side of eq. [18]

against m leads to a straight line, with the intercept at $m = 0$ being the value of $C_p{}^\circ$.

Another approach that has proven useful is based on eq. [3] and enthalpies of reaction that have been measured at several temperatures. Early applications (15, 16) of this method involved calorimetric measurements leading to the standard enthalpies of ionization of aqueous benzoic acid at several temperatures (10–40°C). More recently and of more importance for our present purpose, Cobble, Criss, and others have used a method based on eq. [3] to obtain useful values of $C_p{}^\circ$ for several electrolytes over wide ranges of temperature, as first reported by Criss and Cobble (17). Their calorimetric measurements led to values of the standard state enthalpy of solution, $\Delta_S H^\circ$, of sodium chloride in water as represented by

[19] $NaCl(cr) = Na^+(aq) + Cl^-(aq)$
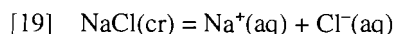
at 13 temperatures ranging from 0.02°C to 95.18°C. The values of $\Delta_S C_p{}^\circ$ obtained as the derivative of $\Delta_S H^\circ$ with respect to temperature (see eq. [3]) can be expressed as

[20] $\Delta_S C_p{}^\circ = C_p{}^\circ(Na^+,Cl^-) = C_p{}^\circ(NaCl)$

in which $C_p{}^\circ(Na^+,Cl^-)$ and $C_p{}^\circ(NaCl)$ represent the standard state partial molar heat capacity of aqueous sodium chloride and the molar heat capacity of $NaCl(cr)$ at the temperature of interest. Because values of $C_p{}^\circ$ for $NaCl(cr)$ were already known, Criss and Cobble (17) were able to obtain values of $C_p{}^\circ(Na^+,Cl^-)$ that were reported over the temperature range from 0 to 100°C. Gardner et al. (18) have carried out similar measurements at 114.25, 149.90, and 199.50°C and have combined these results with those from Criss and Cobble (17) to obtain values of $C_p{}^\circ(Na^+,Cl^-)$ that are reported over the 0–200°C range of temperatures. The method used in these two investigations (17, 180 and also others to be cited later has been called the "integral heat" method.

Bernarducci et al. (19) used still another method of obtaining a value for $C_p{}^\circ$, based on combining a value of $C_{p,\phi}$ for a concentrated solution (relatively easy to measure) with the temperature dependence of the enthalpy of dilution to $m = 0$ for this same concentrated solution. They have applied this method to $FeCl_2(aq)$. Although their reported uncertainty (± 30 J K^{-1} mol^{-f}) in $C_p{}^\circ$ for 25°C is considerably larger than uncertainties attributed to values of $C_p{}^\circ$ for many electrolytes based on results of measurements with the Picker calorimeter or as derived from several applications of the "integral heat" method, it is likely that the method used by Bernaducci et al. (19) can also be applied usefully to some systems.

Analysis of heat capacity data for systems in which there is an identifiable chemical equilibrium requires consideration of what is now often called the "relaxation" contribution to the total heat capacity. An early example was provided by McCollum (20), who measured heat capacities of the system in which the equilibrium represented by $N_2O_4(g) = 2\ NO_2(g)$ contributes to the total measured heat capacity. Later, Randall and Taylor (21) wrote "If a reaction — for example, the dissociation of bisulfate ion into hydrogen and sulfate ions — is more complete at a higher temperature than at a lower, then the heat corresponding to the additional fraction of bisulfate dissociated at the higher temperature will be measured as though it were a part of the heat capacity of the solution." They (21)

had recognized an important problem, but did not continue with any detailed thermodynamic calculations.

The first specific considerations and applications (22, 23) of relaxation contributions to the measured heat capacities of aqueous solutions were followed by many more, which will be cited later in connection with specific electrolytes. Here we call attention to general treatments by Mains et al. (24) and Blandamer et al. (25).

The principle of a relaxation contribution to a measured heat capacity can be illustrated by consideration of a simple imaginary system in which there is a temperature-dependent equilibrium between two isomeric forms of the same "substance," with these two isomeric forms mixing to form an ideal solution so that we need not be concerned here with such complications as activity coefficients, enthalpies of dilution, or the difference between $\Delta_r H$ and $\Delta_r H^\circ$. The chemical equilibrium in this imaginary system is represented by

[21] $A = B$ $K = f/(1 - f)$
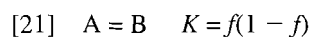
in which f represents the fraction of total substance that is in the B isomer form. The measured heat capacity of a system containing one mole is

[22] $C_{p,meas} = (Q/\Delta T) = (1 - f)C_{p,A}{}^* + fC_{p,B}{}^* + (\Delta f/\Delta T)\Delta_r H$

in which $C_{p,A}{}^*$ and $C_{p,B}{}^*$ represent the heat capacities of the pure isomeric forms A and B, respectively. Because the changes in temperature in most measurements of heat capacities of solutions are small, it is common to replace $(\Delta f/\Delta T)$ with the differential equivalent, (df/dT), and thence obtain an analytical (rather than an equally useful and correct numerical) representation of the relaxation contribution to the total heat capacity. There is also the intangible matter of scientific beauty, which some of us see in an analytical representation. To evaluate the relaxation contribution, which is the last term on the right side of eq. [22], we begin by solving eq. [21] for f and then differentiating with respect to temperature to obtain

[23] $df/dT = (dK/dT)/(1 + K)^2 = (K/K)(dK/dT)/(1 + K)^2$
          $= K(d \ln K/dT)/(1 + K)^2 = K\Delta_r H^\circ/RT^2(1 + K)^2$

Using this last expression with the last term in eq. [22] and recognizing that $\Delta_r H^\circ = \Delta_r H$ for this ideal solution system, we obtain

[24] $C_p{}^{rel} = K(\Delta_r H^\circ)^2/RT^2(1 + K)^2$

for the (always positive) relaxation contribution to the heat capacity.

Evaluation of $C_p{}^{rel}$ for systems of nonideal electrolytes must include considerations of activity coefficients and their dependence on temperature (related to enthalpies of dilution) and to the distinction between $\Delta_r H$ and $\Delta_r H^\circ$ (also related to enthalpies of dilution), but the general principle is the same as outlined here for our simple imaginary ideal system. After values of $C_p{}^{rel}$ have been calculated for an electrolyte system, these values are then subtracted from the experimental values of $C_{p,\phi}$ to obtain the $C_{p,\phi}$(species) values that are then combined with some version of the Debye–Hückel theory (such as eq. [16]) to obtain the standard state partial molar heat capacities

represented by C_p° to be used in various thermodynamic calculations of equilibrium constants, etc.

Because the details of calculation of C_p^{rel} are different for nearly every system that has been investigated, we do not try to illustrate any "typical" calculation. Instead, each reference cited here that involves any specific calculation of C_p^{rel} is followed by the symbol (C_p^{rel}) in the list of references.

Values of standard state partial molar heat capacities of aqueous solutes for $T = 298.15$ K and some of their uses

As background for our selection of "best" values for C_p° of aqueous solutes for 298.15 K, we begin by considering probable accuracies and uncertainties in values obtained in different ways.

It is now clear from experimental results and analysis reported in several publications already cited, in a recent analysis by Criss and Millero (26), and in other publications to be cited later that nearly all of the C_p° values derived from results of measurements with the Picker calorimeter have smaller uncertainties than do C_p° values derived from earlier measurements cited by Parker (2). Although we are not making use of the heat capacities for dilute solutions that have been cited by Parker (2), it is worth emphasizing that many of the results she has cited for more concentrated solution are still quite useful for other purposes.

Our considerations of the differences between C_p° values for the same solute reported by different users of Picker calorimeters and for a few solutes by the same users at different times provide one basis for estimating the experimental uncertainties to be associated with these values. Another contribution to the total uncertainty of C_p° values comes from the method of extrapolation to $m = 0$. As stated earlier in this paper, one common method for doing this extrapolation is based on eqs. [16] and [18]. But it should be recognized that other extrapolations that are consistent with the Debye–Hückel limiting law can also be justified; one such method of extrapolation, based on equations developed by Pitzer, has been used by Criss and Millero (26) because that formulation is well suited to combination with other thermodynamic quantities for calculation of the effect of temperature on activity coefficients. The difference in values of C_p° obtained by way of different extrapolation procedures is very small when there are values of $C_{p,\phi}$ for sufficiently dilute solutions, but becomes larger when such values are unavailable and extrapolations must be based on experimental results for less dilute solutions. All of these considerations lead us to suggest that total uncertainties in a few values of C_p° based on measurements with the Picker calorimeter may be as small as ± 1 J K^{-1} mol^{-1}, but most of these total uncertainties are in the range ± 2 to ± 4 J K^{-1} mol^{-1} for temperatures close to 25°C. For those systems for which it is necessary to make measurements on solutions of mixed electrolytes or for which C_p^{rel} is large, total uncertainties may be larger than ± 4 J K^{-1} mol^{-1}.

An illustration that provides partial justification for the uncertainty estimates above and that also leads to an estimate of uncertainties to be associated with values of C_p° obtained by application of the "integral heat" method can be based on consideration of values of C_p° for NaCl(aq) at 25°C.

The enthalpies of solution at several temperatures measured by Criss and Cobble (17) led them to $C_p^{\circ} = -79.1$ J K^{-1} mol^{-1} for NaCl(aq) at 25°C. The compilation by Desnoyers et al. (5), based only on measurements in their laboratory, lists $C_p^{\circ} = -84.4$ J K^{-1} mol^{-1} for NaCl(aq); their tabulated conventional single ion heat capacities lead to a calculated $C_p^{\circ} = -84$ J K^{-1} mol^{-1}. Criss and Millero (26) have analyzed several sets of reported values of $C_{p,\phi}$ and have obtained $C_p^{\circ} = -82.85$ J K^{-1} mol^{-1}; their tabulated single ion heat capacities lead to a calculated $C_p^{\circ} = -83.31$ J K^{-1} mol^{-1}. Hovey (27) has cited five values of C_p° ranging from -83.7 to -85.5 J K^{-1} mol^{-1}, with an average $C_p^{\circ} = -84.3$ J K^{-1} mol^{-1}; his tabulated single ion heat capacities lead to a calculated $C_p^{\circ} = -84.4$ J K^{-1} mol^{-1}. Clarke and Glew (28) have reviewed heat capacities and also other thermodynamic properties of NaCl(aq) over a range of temperatures and have selected $C_p^{\circ} = -83.94$ J K^{-1} mol^{-1} for NaCl(aq) at 298.15 K as the best value for overall consistency. Altogether, it now seems reasonable to select $C_p^{\circ} = -84$ J K^{-1} mol^{-1} as a "best" value for NaCl(aq) at 25°C, with a total uncertainty ± 1 J K^{-1} mol^{-1}. It therefore follows that the total uncertainty in the $C_p^{\circ} = -79.1$ J K^{-1} mol^{-1} reported by Criss and Cobble (17) is at least ± 4 J K^{-1} mol^{-1}. Further consideration of the calculations reported by Clarke and Glew (28) lead to the more specific estimate that the C_p° values from Criss and Cobble (17) for NaCl(aq) at temperatures up to about 100°C have probable uncertainties larger than ± 5 J K^{-1} mol^{-1} but smaller than ± 10 J K^{-1} mol^{-1}. Although these estimated uncertainties for C_p° values obtained by the integral heat method are larger than estimated uncertainties in C_p° values based on results of modern flow calorimetry, it is clear that C_p° values based on the integral heat method are accurate enough to be very useful.

Further support for the estimated uncertainty range for values of C_p° based on the integral heat method is provided by comparison of C_p° values for CsI(aq), for which we have -153.1 J K^{-1} mol^{-1} from Mitchell and Cobble's (29) application of the integral heat method and the probably more accurate -145.0 J K^{-1} mol^{-1} from flow calorimetry (5).

The comparisons of values of C_p° from the integral heat method with values of C_p° from modern flow calorimetry that we have cited have been chosen partly because of the importance of NaCl(aq) and partly to provide illustrations to support our estimates of uncertainties; it should not be assumed that these reasonable estimates of uncertainties represent established or even probable errors in the values of C_p° based on the integral heat method. For example, Mastroianni and Criss (30) have applied the integral heat method to obtain values of C_p° for NaClO$_4$(aq) over the range 0–95°C, including $C_p^{\circ} = 17.6$ J K^{-1} mol^{-1} for 25°C, which is in good agreement with $C_p^{\circ} = 15.2$ and 16.6 J K^{-1} mol^{-1} from two sets of measurements (31, 32) with Picker flow calorimeters.

Jekel et al. (33) measured enthalpies of solution of GdCl$_3$(cr) at several temperatures and used these results to calculate $C_p^{\circ} = -435$ J K^{-1} mol^{-1} for GdCl$_3$(aq) at 25°C. Xiao and Tremaine (34) have made measurements with a flow calorimeter, leading to C_p° values for Gd(ClO$_4$)$_3$(aq), La(ClO$_4$)$_3$(aq), and LaCl$_3$(aq), which in turn lead to a calculated $C_p^{\circ} = -452$ J K^{-1} mol^{-1} for GdCl$_3$(aq) at 25°C. The difference (17 J K^{-1} mol^{-1}) between these two values of C_p° for GdCl$_3$(aq) that have been obtained in different ways is consistent with estimates of uncertainties already given here for 1:1

electrolytes because of the larger uncertainties in extrapolating to $m = 0$ for 3:1 electrolytes than for 1:1 electrolytes.

One use of standard state partial molar heat capacities is illustrated by beginning with calculation of $\Delta_r C_p^\circ$ for ionization of water as in

[25] $H_2O(liq) = H^+(aq) + OH^-(aq)$
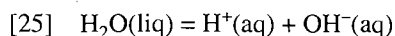
For this calculation we use

[26] $\Delta_r C_p^\circ = C_p^\circ(H^+,X^-) + C_p^\circ(M^+,OH^-)$
$$- C_p^\circ(Na^+,X^-) - C_p^*(H_2O)$$

Singh et al. (35) have applied eq. [26] by using their C_p° values for the electrolytes (HCl, NaCl, NaOH), (HBr, NaBr, NaOH), (HCl, KCl, KOH), and (HBr, KBr, KOH) to obtain $\Delta_r C_p^\circ = -214.1, -215.7, -215.4,$ and -215.8 J K^{-1} mol^{-1}. Later C_p° values from Singh et al. (31) for aqueous HClO$_4$ and NaClO$_4$ led to $\Delta_r C_p^\circ = -213.8$ J K^{-1} mol^{-1}. Also, C_p° values from Enea et al. (36) for aqueous HNO$_3$, NaNO$_3$, and KNO$_3$ led to $\Delta_r C_p^\circ = -214.7$ and -214.6 J K^{-1} mol^{-1}. The average of all seven of these values is $\Delta_r C_p^\circ = -214.9$ J K^{-1} mol^{-1}. Because all of the heat capacities used in these calculations were obtained in the same laboratory, using the same flow calorimeter and the same experimental procedures, followed by the same kind of extrapolations to $m = 0$, some of whatever systematic errors were present have been cancelled in the subtraction of C_p° values shown in eq. [26].

It should also be mentioned that Allred and Woolley (7) have made flow calorimetric measurements in another laboratory, leading to values of C_p° for HCl(aq), NaCl(aq), and NaOH(aq) at 25°C (also two other temperatures). Their values of C_p° lead to $\Delta_r C_p^\circ = -216.8$ J K^{-1} mol^{-1} for ionization of water at 25°C, in satisfactory agreement with the values listed in the preceding paragraph.

On the basis of the eight value for $\Delta_r C_p^\circ$ of ionization of water cited (7, 31, 35, 36) in the two preceding paragraphs, we choose $\Delta_r C_p^\circ = -215$ J K^{-1} mol^{-1} as the best available value for ionization of water at 298 K. Because conventional single-ion heat capacities are based on $C_p^\circ(H^+) = 0$ and the molar heat capacity of pure water is known with excellent accuracy, this chosen best value for $\Delta_r C_p^\circ$ leads directly to a "best" conventional value for $C_p^\circ(OH^-)$ and is therefore a helpful start on compiling a useful collection of these single-ion heat capacities, to which we turn after one illustration of a use of heat capacities.

Earlier, we derived eq. [9] for the dependence of the equilibrium constant on temperature when $\Delta_r C_p^\circ$ is taken to be a constant, independent of temperature. Using the known value of $\Delta_r H^\circ$ at 298.15 K in eq. [8] permits evaluation of the constant of integration ΔH_i. Using the chosen value of $\Delta_r C_p^\circ = \Delta a$ with the known value of the equilibrium constant K at T = 298.15 K permits evaluation of the other constant of integration (I) and thence yields an equation that permits calculation of a value for the equilibrium constant at any temperature T. We carried out these calculations for several temperatures in the range 273–573 K (0–300°C) and found that the values of pK(calculated) differ by less than 0.02 from the best experimental values previously selected (37) for this temperature range. We also use our selected value of $\Delta_r C_p^\circ = -215$ J K^{-1} mol^{-1} and $\Delta_r H^\circ = 55\ 815$ J mol^{-1} (37, 38) in eq. [11] to cal-

culate $T_m = 557$ K (250°C) as the temperature where the equilibrium constant for ionization of water passes through a maximum. This calculated temperature is about 35° higher than the actual temperature (37) at which K passes through a maximum. Here we are not concerned with the small effect of the difference between $p = 1$ atm (or 1 bar) and the saturation pressure for $t > 100°C$, which has been discussed elsewhere (37).

It is possible to improve on the calculations summarized above by recognizing that C_p° values for electrolytes do depend on temperature and that $\Delta_r C_p^\circ$ also depends on temperature. Using $\Delta_r C_p^\circ = f(T)$ in eq. [3] leads to a more complicated version of eq. [8], which is then substituted in eq. [1] to obtain a more complicated version of eq. [9]. Later in this paper we cite some examples of such calculations, but it is worth emphasizing now that the simpler calculations described here, which are based on a constant (independent of temperature) $\Delta_r C_p^\circ$, are accurate enough over wide ranges of temperature to be useful for many purposes.

Tables 1–4 contain our selections of what we regard as "best" values for standard state partial molar heat capacities (C_p°) for $T = 298.15$ K for a large number of inorganic electrolytes and for a few "neutrals" (undissociated H$_3$PO$_4$, CO$_2$, SO$_2$, H$_2$S, NH$_3$) and one organic (acetic acid) that are related to electrolytes under consideration in this paper. All of the heat capacities listed in these tables are based on heat capacities of solutions that have been measured relative to the heat capacity of pure water, using modern flow calorimeters of the type developed by Picker et al. (3). Although we believe there are good reasons for basing our selections of best standard state partial molar heat capacities on heat capacities measured with flow calorimeters, we emphasize that heat capacities obtained in other ways are also useful. Some illustrations of such alternative heat capacities are provided in the following paragraphs.

Allred and Woolley (44) have used flow calorimetry to obtain standard state partial molar heat capacities of NH$_4^+$Cl$^-$(aq) and NH$_3$(aq); their results have been heavily weighted in selecting the values for these solutes that are listed in Tables 1 and 4, respectively. Allred and Woolley (44) have used their heat capacities in obtaining $\Delta_r C_p^\circ$ for

[27] $NH_4^+(aq) = H^+(aq) + NH_3(aq)$
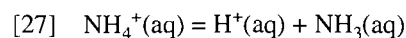
at three temperatures. We select $\Delta_r C_p^\circ = 9$ J K^{-1} mol^{-1} as the best value (independent of temperature near 298 K) that can be derived from their results. We also note that Oloffson (65) has made calorimetric measurements leading to $\Delta_r H^\circ$ for reaction [27] at seven temperatures in the range 278–418 K and has derived (using eq. [3]) a temperature-independent $\Delta_r C_p^\circ = 11$ J K^{-1} P. Although it is likely that the uncertainty in the $\Delta_r C_p^\circ$ from measured heat capacities is slightly smaller than the uncertainty in the value derived by application of eq. [3] to enthalpies of reaction at several temperatures, the comparison cited here provides convincing evidence that the "integral heat" method based on eq. [3] can provide first-rate results.

Allred and Woolley (44) also used flow calorimetry to obtain standard state partial molar heat capacities of Na$^+$,Ac$^-$(aq) and HAc(aq). On the basis of their results, we have selected (Table 4) C_p(HAc) = 170 J K^{-1} mol^{-1} as the best available value for 298.15 K. Two earlier calorimetric investi-

Table 1. Standard state partial molar heat capacities $(C_p{}^\circ)^a$ of 1:1 aqueous electrolytes at 298.15 K.

Solute	$C_p{}^\circ$	References	Solute	$C_p{}^\circ$	References
H^+,Cl^-	−126	5, 7, 26, 35, 39	K^+,Cl^-	−114	5, 6, 26, 35
H^+,Br^-	−132	26, 35	K^+,Br^-	−119	5, 6, 35
H^+,NO_3^-	−71	36, 40, 41	K^+,I^-	−109	5
H^+,ClO_4^-	−26	31, 40, 41	K^+,OH^-	−127	35, 45
H^+,HSO_4^-	−18	55	K^+,NO_3^-	−60	36
Li^+,Cl^-	−65	5	K^+,ClO_3^-	−43	32
Li^+,Br^-	−69	5	K^+,BrO_3^-	−77	32
Li^+,OH^-	−77	45	K^+,IO_3^-	−59	32, 36
Na^+,F^-	−75	5	K^+,MnO_4^-	+1	47
Na^+Cl^-	−84	5, 7, 28, 35, 46	K^+,HCO_3^-	−38	52
Na^+,Br^-	−88	5, 35	K^+,HSO_3^-	+2	52
Na^+,I^-	−77	5	$K^+,HCrO_4^-$	+15	52
Na^+OH^-	−97	5, 7, 35, 45	Rb^+,F^-	−125	5
Na^+,NO_3^-	−29	32, 36	Rb^+,Cl^-	−136	5
Na^+,ClO_3^-	−17	32	Rb^+,Br^-	−139	5
Na^+,ClO_4^-	+16	31, 32	Rb^+,I^-	−132	5
Na^+,BrO_3^-	−50	32	Cs^+,F^-	−139	5
Na^+,IO_3^-	−30	47	Cs^+,Cl^-	−149	5
Na^+,TcO_4^-	+28	48	Cs^+,Br^-	−155	5
Na^+,ReO_4^-	+28	48	Cs^+,I^-	−145	5
Na^+,HCO_3^-	−11	50–52	NH_4^+,Cl^-	−56	5, 32, 44
Na^+,HSO_3^-	+40	52, 54	NH_4^+,Br^-	−67	5
$Na^+,Al(OH)_4^-$	+139	49	NH_4^+,ClO_4^-	+47	32
$Na^+,H_2PO_4^-$	+8	50, 53	NH_4^+,NO_3^-	−2	32
Na^+,HS^-	−51	43	Ag^+,NO_3^-	−37	57
Na^+,Ac^-	+68	5, 44	Ag^+,ClO_4^-	+11	57
K^+,F^-	−104	5			

^{a}Units for $C_p{}^\circ$ are J K^{-1} mol^{-1}.

gations (66, 67) led to $C_p{}^\circ(HAc) = 165$ and 167 J K^{-1} mol^{-1}, each with larger uncertainty than the value we have selected, but in satisfactory agreement with the selected value. Allred and Woolley (44) used their heat capacities in calculating $\Delta_r C_p{}^\circ = (−143 \pm 3)$ J K^{-1} mol^{-1} for the reaction represented by

[28] $HAc(aq) = H^+(aq) + Ac^-(aq)$
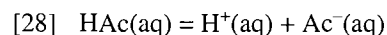
Olofsson (68) made calorimetric measurements leading to values of $\Delta_r H^\circ$ at five temperatures in the range 274–373 K and used eq. [3] to derive $\Delta_r C_p{}^\circ = (−143 \pm 5)$ J K^{-1} mol^{-1} for reaction [28]. Once again a comparison shows that calorimetrically measured heat capacities and calorimetrically measured enthalpies at several temperatures can lead to results that are in excellent agreement with each other, it being probable that the uncertainties are smaller for directly measured heat capacities than for heat capacities derived by way of eq. [3].

Table 5 contains our selections of "best" standard state partial molar heat capacities for single ions, all based on the common convention that sets $C_p{}^\circ(H^+) = 0$. Using our previously selected $\Delta_r C_p{}^\circ = −215$ J K^{-1} mol^{-1} for ionization of water with this convention and the accurately known molar heat capacity of water leads to $C_p{}^\circ(OH^-) = −140$ J K^{-1} mol^{-1}. Then the value for $C_p{}^\circ(Na^+,OH^-)$ listed in Table 1 leads to a value for $C_p{}^\circ(Na^+)$. A further step is to use this value for $C_p{}^\circ(Na^+)$ with

the $C_p{}^\circ(Na^+,Cl^-)$ listed in Table 1 to calculate a value for $C_p(Cl^-)$. There are, however, other routes to obtain these $C_p{}^\circ(ion)$ values. For example, the value for $C_p{}^\circ(H^+,Cl^-)$ leads directly to a value for $C_p{}^\circ(Cl^-)$, which can then be used with $C_p{}^\circ(Na^+,Cl^-)$ to obtain a value for $C_p{}^\circ(Na^+)$. We have considered a large number of these alternative routes to values for various $C_p{}^\circ(ion)$ and have selected those values that give the best overall fits to the $C_p{}^\circ$ values listed in Tables 1–3, with allowance made for estimated uncertainties in the $C_p{}^\circ$ values.

We have already illustrated how $C_p{}^\circ$ values (only for $T = 298.15$ K) can be used in calculating the equilibrium constant for ionization of water over a wide range of temperatures. Similar calculations, using only $C_p{}^\circ$ values for $T = 298.15$ K, have been carried out for other equilibria in several of the references (for examples see refs. 43, 50, 54, and 56) already cited.

Although we have chosen here to carry out calculations of equilibrium constants over a wide range of temperature by combining eqs. [1], [3], and [8] to obtain eq. [9], this same calculation can be done by combining eq. [8] with

[29] $\Delta_r S^\circ = \Delta S_i + \Delta_r C_p{}^\circ \ln T$

that is based on integration of eq. [4], to obtain $\Delta_r G^\circ = \Delta_r H^\circ − T\Delta_r S^\circ$. Further use of this $\Delta_r G^\circ$ in $\Delta_r G^\circ = −RT \ln K$ permits

Table 2. Standard state partial molar heat capacities $(C_p{}^\circ)^a$ of 1:2 and 2:1 aqueous electrolytes at 298.15 K.

Solute	$C_p{}^\circ$	References	Solute	$C_p{}^\circ$	References
$2Na^+,SO_4^{2-}$	−190	5, 62	$Mn^{2+},2Cl^-$	−259	47
$2Na^+,S_2O_3^{2-}$	−164	62	$Mn^{2+},2NO_3^-$	−156	60
$2Na^+,S_2O_8^{2-}$	−29	62	$Mn^{2+},2ClO_4^-$	−62	59
$2Na^+,MoO_4^-$	−123	62	$Fe^{2+},2ClO_4^-$	−78	27
$2Na^+,WO_4^{2-}$	−110	62	$Co^{2+},2Cl^-$	−279	58
$2Na^+,SO_3^{2-}$	−178	54	$Co^{2+},2NO_3^-$	−170	60
$2Na^+,CO_3^{2-}$	−216	50	$C^{2+},2ClO_4^-$	−81	59
$2Na^+,HPO_4^{2-}$	−168	50, 53	$Ni^{2+},2Cl^-$	−294	57
$2K^+,SO_4^{2-}$	−254	5, 40, 62	$Ni^{2+},2NO_3^-$	−186	60
$2K^+,S_2O_8^{2-}$	−84	62	$Ni^{2+},2ClO_4^{2-}$	−93	59
$2K^+,CrO_4^{2-}$	−244	56, 62	$Cu^{2+},2NO_3^-$	−161	60
$2K^+,Cr_2O_7^{2-}$	−105	56	$Cu^{2+},2ClO_4^-$	−72	58
$Mg^{2+},2Cl^-$	−268	5	$Zn^{2+},2NO_3^-$	−165	60
$Mg^{2+},2ClO_4^-$	−66	58	Zn^{2+},ClO_4^-	−73	59
$Mg^{2+},2NO_3^-$	−160	60	$Cd^{2+},2NO_3^-$	−152	58
$Ca^{2+},2Cl^-$	−281	5, 46, 58	$Cd^{2+},2ClO_4^-$	−57	59
$Ca^{2+},2ClO_4^-$	−77	59	$Hg^{2+},2ClO_4^-$	−67	61
$Ca^{2+},2NO_3^-$	−170	60	$Pb^{2+},2ClO_4^-$	−107	61
$Sr^{2+},2Cl^-$	−289	5	$UO_2^{2+},2ClO_4^-$	−8	42
$Ba^{2+},2Cl^-$	−300	5			

^{a}Units for $C_p{}^\circ$ are J K^{-1} mol^{-1}.

Table 3. Standard state partial molar heat capacities $(C_p{}^\circ)^a$ of 1:3, 1:4, and 3:1 aqueous electrolytes at $T = 298.15$ K.

Solute	$C_p{}^\circ$	References
$3Na^+,PO_4^{3-}$	−369	50, 53
$3K^+,Fe(CN)_6^{3-}$	−215	14
$4K^+,Fe(CN)_6^{4-}$	−475	14
$Al^{3+},3Cl^-$	−497	63,^{b} 64
$Al^{3+},3NO_3^-$	−331	63,^{b} 64
$Cr^{3+},3NO_3^-$	−240	14
$La^{3+},3Cl^-$	−477	14, 34
$La^{3+},3ClO_4^-$	−177	34
$Gd^{3+},3ClO_4^-$	−148	34

^{a}Units for $C_p{}^\circ$ are J K^{-1} mol^{-1}.
^{b}The calculations of $C_p{}^\circ$ reported in this paper were based on measured heat capacities that were reported by Hovey and Tremaine in ref. 64.

Table 4. Standard state partial molar heat capacities $(C_p{}^\circ)^a$ of "neutrals" in aqueous solution at $T = 298.15$ K.

Solute	$C_p{}^\circ$	References
H_3PO_4(aq, undissoc.)	+94	50
CO_2(aq)	+243	52
SO_2(aq)	+195	52
H_2S(aq)	+178	43
NH_3(aq)	+75	44
HAc(aq)	+170	44

^{a}Units for $C_p{}^\circ$ are J K^{-1} mol^{-1}.

calculation of $K = f(T)$ as already done in another way. Similarly, combination of $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$ for a cell reaction with $\Delta_r G^\circ = -nFE^\circ$ permits convenient calculations of standard state cell potentials (E°) over wide ranges of temperatures.

Heat capacities of aqueous solutions at temperatures other than *T* = 298.15 K

Heat capacities of solutions of several electrolytes have been measured over temperature ranges from 10 to 55°C. Results of

such measurements permit evaluation of the parameters in various equations for $C_p{}^\circ = f(T)$, which then permit extrapolation to much higher temperatures. The Helgeson–Kirkham–Flowers (69) and Holmes–Mesmer (70) equations have been used many times for this purpose. An example of this kind of calculation using $C_p{}^\circ$ values for the temperature range 10–55°C for calculations that extend to 350°C is provided by Hovey et al. (55) for the second dissociation constant of sulfuric acid.

A clear illustration of the predictive power of the Helgeson–Kirkham–Flowers (HKF) and Holmes–Mesmer (HM) equations mentioned above is provided by consideration of values of $C_p{}^\circ[Na^+,Al(OH)_4^-]$. Hovey et al. (49) measured these heat capacities at four temperatures in the range 10–55°C and used the HKF equation to estimate heat capacities at much higher temperatures. Then Caiani et al. (71) measured these heat capacities at five temperatures in the range 53–245°C. Still

Table 5. Conventional[a] standard state partial molar heat capacities[b] of aqueous ions at $T = 298.15$ K.

Ion	C_p°	Ion	C_p°	Ion	C_p°
H^+	0	Pb^{2+}	−55	Ac^-	+26
Li^+	+62	UO_2^{2+}	+44	MnO_4^-	−11
Na^+	+42	Al^{3+}	−119	TcO_4^-	−14
K^+	+12	Cr^{3+}	−27	ReO_4^-	−14
Rb^+	−9	La^{3+}	−99	$Al(OH)_4^-$	+97
Cs^+	−23	Gd^{3+}	−70	$HCrO_4^-$	+3
NH_4^+	+69	OH^-	−140	$H_2PO_4^-$	−34
Ag^+	+35	F^-	−116	CO_3^{2-}	−300
Mg^{2+}	−16	Cl^-	−126	SO_3^{2-}	−262
Ca^{2+}	−27	Br^-	−132	SO_4^{2-}	−276
Sr^{2+}	−37	I^-	−121	$S_2O_3^{2-}$	−248
Ba^{2+}	−48	NO_3^-	−71	$S_2O_8^{2-}$	−110
Mn^{2+}	−10	ClO_4^-	−26	CrO_4^{2-}	−268
Fe^{2+}	−26	ClO_3^-	−57	$Cr_2O_7^{2-}$	−129
Co^{2+}	−28	BrO_3^-	−90	MoO_4^{2-}	−207
Ni^{2+}	−42	IO_3^-	−71	WO_4^{2-}	−194
Cu^{2+}	−20	HCO_3^-	−52	HPO_4^{2-}	−253
Zn^{2+}	−22	HSO_3^-	−4	PO_4^{3-}	−495
Cd^{2+}	−8	HSO_4^-	−18	$Fe(CN)_6^{3-}$	−251
Hg^{2+}	−15	HS^-	−93	$Fe(CN)_6^{4-}$	−523

[a]Based on $C_p^\circ(H^+) = 0$.
[b]Units for C_p° are J K^{-1} mol^{-1}.

more recently, Chen et al. (72) have measured $\Delta_r H^\circ$ at five temperatures in the range 100–150°C for the reaction represented by

[30] $Al(OH)_3(cr) + OH^-(aq) = Al(OH)_4^-(aq)$
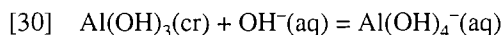
and applied eq. [3] to obtain values of $\Delta_r C_p^\circ$ and thence values of $C_p^\circ[Na^+, Al(OH)_4^-)]$. Although the complete collection of C_p° values based on these three sets of calorimetric measurements leads to the most accurate representation of the thermodynamic properties of this system, it is important to note that the high-temperature heat capacities predicted (49) on the basis of measurements over the relatively narrow range 10–55°C are in good agreement with the heat capacities that were measured or calculated via eq. [3] later.

As previously mentioned, we have not tabulated C_p° values from Criss, Cobble, and colleagues obtained by way of the integral heat method in selecting the "best" values for $T = 298.15$ K because we believe that values based on modern flow calorimetry are more accurate. But it should be recognized that their values for C_p° for several electrolytes are the best values available for $T > 298$ K and can be used for various calculations of the sort already described here and that have been described by Criss, Cobble, and colleagues.

Wood and colleagues at the University of Delaware have used a flow calorimeter of the type described in 1981 (4) for measurement of many heat capacities at high temperatures and also at various pressures, including measurements at temperatures above the critical temperature of water. Many of their results have been cited by Wood et al. (73). Other measurements have been reported for (H^+, Cl^-) to 140°C by Tremaine et al. (39), for [Na^+, OH^-] to 250°C by Simonson et al. (74), and

for hydrolyzed and unhydrolyzed solutions of aluminum chloride by Conti et al. (75). We also mention that researchers at Brigham Young University have made calorimetric measurements leading to values of $\Delta_r H^\circ$ for several reactions at high temperatures and thence to useful values of $\Delta_r C_p^\circ$ for these high temperatures. All of these (and other) heat capacities for high temperatures are now sufficient in number and quality to justify a detailed review that cannot be included here.

Theoretical considerations of heat capacities of aqueous electrolytes

Theoretical analysis of C_p° values for aqueous electrolytes can contribute to our knowledge of ion–water interactions. Early efforts in this direction were reported by Zwicky (76) and by Everett and Coulson (77). More recent reports by Leyendekkers (78) and by Sen (79) illustrate two other approaches. Wood et al. (new work and a review are included in ref. 73) have worked on both theory and measurements to obtain information about partial molar heat capacities (also other thermodynamic properties) for aqueous electrolytes over a range of temperatures and pressures, including near and above the critical conditions for water. One theoretical prediction and experimental verification (80) is that the partial molar heat capacities of electrolytes approach $-\infty$ as T_c is approached from lower temperatures and approach $+\infty$ as T_c is approached from higher temperatures. We also mention that Oelkers et al. (81) have reviewed and extended earlier work by Helgeson and colleagues, such as that leading to the HKF equation (69).

Jolicoeur and Mercier (82), Conway (83) Tremaine et al. (84), French and Criss (85), and Abraham and Marcus (86) have reported methods of estimating "absolute" (rather than conventional) values of single ion heat capacities. It has been pointed out clearly and correctly in several of these papers that it may be appropriate to consider conventional ionic heat capacities when only ions of these same charge are being compared with each other (for example, to learn about the effects of ionic size on heat capacity), but it is necessary to consider "absolute" ionic heat capacities when comparing ions having different charges or when one is concerned with any quantitative theoretical analysis of heat capacities of hydration.

We also mention that Abraham and Marcus (86) and Criss and Millero (26) have provided useful reviews of standard state partial molar heat capacities of aqueous electrolytes. The first of these reviews (86) that was published in 1986 was concerned with both inorganic and organic electrolytes. Although parts of this review are now out of date because of research done in the past decade, the part that is devoted to organic electrolytes is still the best available review. In addition, there is a detailed discussion of the effects of ion–water interactions (hydration) on heat capacities. The more recent report by Criss and Millero (26) was concerned only with 1:1 electrolytes and is focussed on using heat capacities over a range of compositions as part of the evaluation of activity coefficients and osmotic coefficients as a function of both temperature and composition.

Acknowledgements

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