Extrapolation of Enthalpies of Reaction in Electrolyte Systems to Infinite Dilution

Andrey V. Plyasunov[a] and Ingmar Grenthe[b],*

[a] Institute of Experimental Mineralogy, Chernogolovka, Moscow 142432, Russia and [b] Department of Chemistry, Inorganic Chemistry, Royal Institute of Technology (KTH), S-10044 Stockholm, Sweden

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The use of theory-based equations for the calculation of standard enthalpies of reaction from experimental data is discussed. The reactions used as examples have been studied in the presence of an ionic medium, or in the presence of a large excess of one reactant, which then serves as the ionic medium. The results show that precise estimates of the standard enthalpies of reaction may be obtained, by using both the Pitzer and the Brønsted–Guggenheim–Scatchard specific ionic interaction models. 'Empirical' equations based on a simple Debye–Hückel model should be avoided. The validity of the Vasil'ev–Yasinskii equation has also been tested. It is shown that this ignores the contribution of the enthalpies of mixing of the reaction participants and the ionic medium electrolyte to $\Delta_r H_m$. Published data obtained by using this procedure should therefore be revised. Literature data on the standard enthalpies of formation of $Al^{3+}(aq)$ and $Al(OH)_4^-(aq)$ at 298.15 K, have been revised, and new values $\Delta_f H_m°[Al^{3+}(aq)] = -539.2 \pm 1.0 \text{ kJ mol}^{-1}$ and $\Delta_f H_m°[Al(OH)_4^-(aq)] = -1502.7 \pm 1.0 \text{ kJ mol}^{-1}$, are proposed.

Determinations of standard enthalpy of reactions in aqueous solutions (i.e at infinite dilution) in general involve the determinations of enthalpy of reactions at finite concentrations and the relevant enthalpy of mixing and dilution of the components. A typical example is the papers of Berg and Vanderzee,[1,2] where the standard enthalpy of formation of aqueous zinc ion has been determined from the enthalpy of solution of $ZnO(cr)$ in $HClO_4$ solutions, the enthalpy of dilution of $Zn(ClO_4)_2$ (aq) and the enthalpy of mixing of $Zn(ClO_4)_2(aq)$ and $HClO_4(aq)$. The enthalpy of reaction are measured at finite concentrations, often in a solution with a large excess of one of the reactants (this will then function as an 'ionic medium' electrolyte), and then using some empirical or semi-empirical method to extrapolate the data to infinite dilution. The use of empirical methods might result in a loss of accuracy of the standard enthalpy of reaction, as compared to the accuracy of the experimental data. An example of such an empirical method is provided by the recent data of Zeng et al.[3,4] on the standard enthalpy of formation of $Al^{3+}(aq)$ and $Al(OH)_4^-(aq)$ at 298.15 K. These quantities were obtained from the heats of solution of $Al(cr)$ in aqueous HCl and aqueous NaOH, respectively. The extrapolation to infinite dilution was made by assuming that the heat

* To whom correspondence should be addressed.

of dilution of the ionic species is proportional to the square root of the ionic strength of the solution. According to Debye–Hückel theory (see Harned and Owen),[5] the enthalpy of dilution of an electrolyte to infinite dilutions (by definition equal to relative apparent molar enthalpy of the electrolyte with opposite sign) is strictly proportional to the square root of the ionic strength I, only in the concentration range of validity of the limiting Debye–Hückel law, i.e. at ionic strengths less than 0.01–0.10 m. At higher ionic strengths the enthalpy of dilution has a complex concentration dependence, which in general cannot be described by this simple function, cf. Fig. 1, where the relative apparent molar enthalpy of $NaOH^6$ and $NaCl^7$ solutions are plotted vs. $I^{1/2}$. Another important observation is that information on heats of dilution of the reaction participants in general does not provide sufficient information to calculate the enthalpy of reaction at infinite dilution, as will be discussed below. Therefore, a more satisfactory and more reliable extrapolation of the enthalpies of reaction to infinite dilution should use extrapolation equations based on theory. In the following section we will describe two such equations, both based on theoretical models for the concentration dependence of activity coefficients of solutes. The standard enthalpies of formation of $Al^{3+}(aq)$ and $Al(OH)_4^-(aq)$ at 298.15 K will then be discussed in some detail.
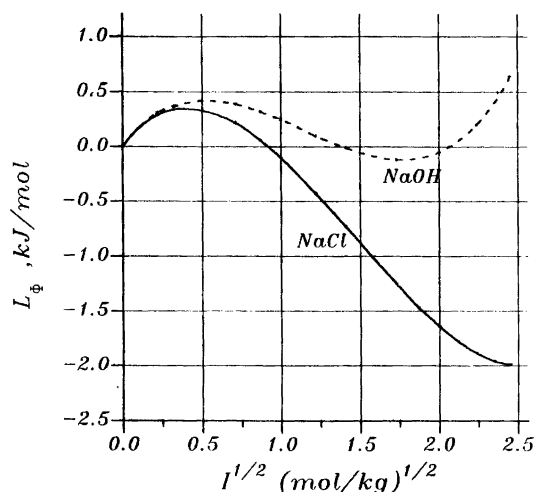
Fig. 1. The relative apparent molar enthalpies (equal to the heats of dilution with opposite sign) of NaOH[6] and NaCl[7] as a function of the square root of the ionic strength at 298.15 K.

Equations describing the concentration dependence of enthalpies of reaction

For a chemical reaction in the general form

$$\sum_i p_i Q_i + r\text{H}_2\text{O}(1) = 0 \tag{1}$$

the enthalpy of reaction at finite concentrations is equal to

$$\Delta_r H_m = \Delta_r H_m{}^\circ + \sum_i p_i L_{2,i} + rL_1 \tag{2}$$

where $\Delta_r H_m{}^\circ$ and $\Delta_r H_m$ are the enthalpies of reaction at infinite dilution (the usual standard state) and in a solution of finite concentration, respectively; $L_{2,i}$ and L_1 are the relative partial molar enthalpy of the solute and of water, respectively. Eqn. (2) follows from the fact that the change of any thermodynamic function (Gibbs energy, enthalpy etc.) of a reaction is the sum of corresponding partial molar thermodynamic characteristics of the reaction participants with their proper stoichiometric coefficients. Eqn. (2) can also be obtained from the statement for the concentration dependence of the equilibrium constant for the general reaction (1) and applying the Van't Hoff equation and the definitions of the relative partial molar enthalpies of water and solutes. Solution coordination chemists often perform equilibrium constant determinations and calorimetry in the presence of an ionic medium, chosen in such a way that the concentrations of reactants/products are much smaller than that of the ionic medium. In this way one can ensure that the activity coefficients of the reacting species remain essentially constant during the reaction. If an ionic medium is not used, one may have one reactant in large excess over the others, and this may then serve as an 'ionic medium'. In order to recalculate the measured enthalpies of reaction to the chosen standard state, usually the one where the ionic strength is zero, it is necessary to measure

the enthalpies of dilution of the reactants/products, or to use an analytical statement for the apparent relative molar enthalpy of the reaction participants. These must be consistent with the models used for the description of the concentration dependence of $\log K$ for the reaction (or the activity coefficients of the reaction participants). In this communication we will describe two such models based on the Pitzer and the Brønsted–Guggenheim–Scatchard (BGS) equations for activity coefficients. The first approach is used mainly for describing the thermodynamics of electrolyte solutions, both single and mixed,[8] while the latter is used mainly for description of the concentration dependence of equilibrium constants for reactions[9–11] in ionic media.

The Pitzer formalism. Using the Pitzer equations the following statement is obtained for the relative partial molar enthalpy of a cation M present in small concentration in a solution of a strong electrolyte NX, serving as the ionic medium. Assuming that all binary and ternary mixing parameters have vanishing temperature derivatives, we obtain

$$L_{2,\text{M}} = -RT^2 \left(\frac{\partial \ln \gamma_\text{M}}{\partial T} \right)_{P, m_j}$$

$$= \frac{Z_\text{M}{}^2 A_\text{L}}{4} \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right]$$

$$- RT^2 Z_\text{M}{}^2 m_\text{N} m_\text{X} \beta_\text{NX}{}^{(1)\text{L}} \frac{g'(\alpha I^{1/2})}{I}$$

$$- 2RT^2 m_\text{X} [\beta_\text{MX}{}^{(0)\text{L}} + \beta_\text{MX}{}^{(1)\text{L}} g(\alpha I^{1/2})]$$

$$- RT^2 m_\text{X} (m_\text{N} Z_\text{N} + m_\text{X} Z_\text{X}) C_\text{MX}{}^\text{L}$$

$$- RT^2 Z_\text{M} m_\text{N} m_\text{X} C_\text{NX}{}^\text{L} \tag{3}$$

where A_L is the Debye–Hückel parameter for the enthalpy, $A_\text{L} = 1.986 \text{ kJ kg}^{1/2} \text{ mol}^{-3/2}$ at 298.15 K and 1 atm;[8] Z_M, Z_N and Z_X stand for the charges of M, N and X, respectively; $b = 1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ is a universal parameter in the Pitzer model, and

$$g'(\alpha I^{1/2}) = -\frac{2}{\alpha^2 I} \left[1 - \left(1 + \alpha I^{1/2} + \frac{\alpha^2 I}{2} \right) \exp(-\alpha I^{1/2}) \right]$$

$$g(\alpha I^{1/2}) = \frac{2}{\alpha^2 I} [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})]$$

$\alpha = 2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ is another universal parameter in the model. The parameters $\beta^{(0)\text{L}}$, $\beta^{(1)\text{L}}$ and C^L are defined as follows

$$\beta^{(0)\text{L}} = \left(\frac{\partial \beta^{(0)}}{\partial T} \right)_P; \quad \beta^{(1)\text{L}} = \left(\frac{\partial \beta^{(1)}}{\partial T} \right)_P; \quad C^\text{L} = \left(\frac{\partial C}{\partial T} \right)_P$$

where $\beta^{(0)}$, $\beta^{(1)}$ and C are the parameters for the osmotic and activity coefficients in the Pitzer model.

The corresponding expression for relative partial molar enthalpy of the anion Y is obtained by changing the subscripts M and X for Y and N, respectively.

The relative partial molar enthalpy of water in the ionic mediun NX is equal to:

$$L_1 = \frac{M_w}{1000}\left[\frac{-A_L I^{3/2}}{2(1 + bI^{1/2})} + 2RT^2 v_M v_X m^2 (\beta_{NX}{}^{(0)L}\right.$$

$$\left. + \beta_{NX}{}^{(1)L}\exp(-\alpha I^{1/2}) + 2v_N Z_N m C_{NX}{}^L)\right] \qquad (4)$$

where M_w is the molar mass of water, and v_N and v_X are the stoichiometric coefficients of N and X in the ionic medium electrolyte (both equal to 1 for the 1:1 electrolyte NX).

The Pitzer model gives the following statement for the concentration dependence of the enthalpy of reaction studied at 'trace' concentrations of reactants/products, in a solution with a large excess of 1–1 ionic medium:

$$\Delta_r H_m - rL_1 = \Delta r H_m{}^\circ + \frac{\Delta Z^2 A_L}{4}$$

$$\times \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b}\ln(1 + bI^{1/2})\right]$$

$$- RT^2 \Delta Z^2 m^2 \beta_{NX}{}^{(1)L}\frac{g'(\alpha I^{1/2})}{I}$$

$$- RT^2 m^2 \Delta|Z| C_{NX}{}^L - 2RT^2 m \Delta\beta^{(0)L}$$

$$- 2RT^2 m \Delta\beta^{(1)L} g(\alpha I^{1/2}) - 2RT^2 m^2 \Delta C^L \qquad (5)$$

where

$$\Delta Z^2 = \sum_i p_i Z_i{}^2; \quad \Delta|Z| = \sum_i p_i |Z_i|;$$

$$\Delta\beta^{(0)L} = \sum_i p_i \beta_{ij}{}^{(0)L}; \quad \Delta\beta^{1(L)} = \sum_i p_i \beta_{ij}{}^{(1)L};$$

$$\Delta C^L = \sum_i p_i C_{ij}{}^L$$

The subscript i refers to a reaction participant, and j to a counter-ion of the ionic medium. Deriving eqn. (5) we neglected the contributions of binary and ternary mixing Pitzer parameters and higher-order electrostatic effects for unsymmetrical mixtures. However, they are not relevant for the extrapolation equation. It can be shown that in a 'constant ionic medium' the binary and ternary mixing terms appear in the extrapolation equation as terms proportional to m and m^2, respectively; therefore, they are included in the $\Delta\beta^{(0)L}$ and ΔC^L terms. The higher-order electrostatic terms are non-linear with the ionic strength only at low concentrations of the ionic medium; hence they will be accounted for mainly in the $\Delta\beta^{(0)L}$ value.

In order to describe the concentration dependence of the enthalpy of reaction using the Pitzer formalism, it is necessary to determine or estimate a number of parameters. This is no easy task, as the parameters often have to be determined by a regression analysis based on a fairly small number of measured enthalpies of reaction. The precision in the measured enthalpy values is seldom better than 0.2–0.5 kJ mol^{-1}, which results in an addi-

tional uncertainty in the evaluated Pitzer parameters. The main problem is a reliable estimation of $\Delta\beta^{(1)L}$, which determines the concentration dependence of the second virial coefficient in the Pitzer approach, and therefore has a substantial influence on the estimated value of $\Delta_r H_m{}^\circ$ for the reaction. For a reliable determination of this parameter it is necessary to have precise experimental data at low ionic strengths (<0.5–1.0 m), where the relative contribution of this parameter to the value of ΔB^L is largest. The same problem is encountered when using the Pitzer model to estimate the ionic medium dependence of concentration equilibrium constants.

The Brønsted–Guggenheim–Scatchard equation. The BGS ion-interaction equation for the estimation of activity coefficient of ions[11] is:

$$\ln \gamma_i = -\frac{AZ_i{}^2 I^{1/2}}{1 + 1.5I^{1/2}} + \sum_j \varepsilon(i, j)m_j \qquad (6)$$

where $\varepsilon(i, j)$ is the specific ion interaction parameter between ions i and j, the index j stands for ions having a charge sign opposite to that of ion i (or for neutral species). The corresponding equations for the concentration dependence of the relative partial molar enthalpy of a cation M present at low ('trace') concentration in an ionic medium NX, and for the relative partial molar enthalpy of water (L_1) are given below (assuming the numerical factor 1.5 kg$^{1/2}$ mol$^{-1/2}$ to be a constant, independent of temperature)

$$L_{2,M} = -RT^2\left(\frac{\partial \ln \gamma_M}{\partial T}\right)_{P,m_j}$$

$$= \frac{3}{4}\frac{A_L Z_m{}^2 I^{1/2}}{1 + 1.5I^{1/2}} - RT^2 \varepsilon_L(M, X)m_X \qquad (7)$$

$$L_1 = \frac{M_w}{1000}\left[-\frac{3}{2}\frac{A_L}{1.5^3}\left((1 + 1.5I^{1/2}) - 2\ln(1 + 1.5I^{1/2})\right.\right.$$

$$\left.\left. - \frac{1}{(1 + 1.5I^{1/2})}\right) + RT^2 v_N Z_N m^2 \varepsilon_L(N, X)\right] \qquad (8)$$

where

$$\varepsilon_L(M, X) = \left(\frac{\partial \varepsilon(M, X)}{\partial T}\right)_P$$

The BGS model results in the following equation for the concentration dependence of the enthalpy of reaction, studied at trace concentrations of reactants/products in a solution with a large excess of an 1–1 electrode:

$$\Delta_r H_m - rL_1 = \Delta_r H_m{}^\circ + \frac{3}{4}\frac{A_L \Delta Z^2 I^{1/2}}{1 + 1.5I^{1/2}} - RT^2 m \Delta\varepsilon_L \qquad (9)$$

where

$$\Delta\varepsilon_L = \sum_i p_i \varepsilon_L(i, j)$$

where the subscript i refers to a reaction participant and j to a counter-ion from the ionic medium electrolyte.

Comparison of the experimental concentration dependence of enthalpies of reaction with the predictions of the Pitzer and BGS models

In order to test the equations describing the concentration dependence of $\Delta_r H_m$ and the determination of $\Delta_r H_m{}^\circ$ at infinite dilution, we have used data for the reaction $H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$ in different ionic media. The value of $\Delta_r H_m{}^\circ$ for this reaction has been recommended by CODATA,[12] but we have treated it as an unknown quantity in the regression analysis in order to demonstrate the numerical problems with this type of data. The Pitzer parameters for the different ionic species are also known for this system, which makes it possible to estimate the accuracy of $\Delta\beta^{(0)L}$ and $\Delta\beta^{(1)L}$ (cf. Table 1).

The experimental calorimetric data in $NaClO_4$ media at 298.15 K have been obtained in two laboratories (Arnek and Kakolowicz;[13] Lobanov et al.[14]), the results at the same ionic medium concentration, 3.50 mol kg^{-1}, agree within ± 0.25 kJ mol^{-1}. The reaction has also been studied in NaCl solutions, where experimental calorimetric data have been obtained by Lobanov and Vasil'ev[14] at 298.15 K. These data agree within ± 0.12 kJ mol^{-1}

with the values given by Harned and Mannweiler,[15] based on a precise potentiometric study of the thermodynamics of water ionization in NaCl solutions at 0-60°C, over a wide range of sodium chloride concentrations. The data on $\Delta_r H_m$ have been corrected with the value of L_1 and fitted using both the Pitzer and the BGS models. In addition, we tested the empirical 'Debye–Hückel' equation

$$\Delta_r H_m = \Delta_r H_m{}^\circ + WI^{1/2} \tag{10}$$

used by Zeng et al.,[3] i.e. assuming that the enthalpies of dilution are proportional to the square root of the ionic strength of solution over the whole concentration range studied; W is a fitting parameter. The regression analysis was made by using a linear least-squares method, with uncertainty estimates in $\Delta_r H_m$ equal to ± 0.3 kJ mol^{-1} and ± 0.2 kJ mol^{-1}, for the data in $NaClO_4$ and NaCl media, respectively.

The values of the unknown parameters in the various model equations are given in Table 1; the estimated uncertainties are equal to 3σ, where σ is the mean-square error of the unknowns. Using the Pitzer equation only

Table 1. The results of the least-squares determination of the standard enthalpy of reaction, and interaction parameters in fitting equations for the reaction $H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$ in $NaClO_4$ and NaCl media by using theory based equation (the Pitzer and BGS models), and one ad hoc equation, based on a simplistic Debye–Hückel model.[a]

Fitting equation	$\Delta_r H_m{}^\circ$/kJ mol^{-1}	Concentration parameters	Mean square error per unit weight, $\sigma_0{}^b$
NaClO$_4$ ionic medium			
Pitzer[c]	55.51 ± 0.36	$\Delta\beta^{0(L)} = (1.12 \pm 0.10) \times 10^{-3d}$ $\Delta\beta^{(0)L} = 1.19 \times 10^{-3}$ from tabulated Pitzer parameters	0.448
Pitzer[e]	55.86 ± 1.68	$\Delta\beta^{(0)L} = (1.04 \pm 0.39) \times 10^{-3d}$ $\Delta\beta^{(1)L} = (1.15 \pm 5.32) \times 10^{-3d}$ $\Delta\beta^{(1)L} = 2.07 \times 10^{-3}$ from tabulated Pitzer parameters	0.499
Brønsted–Guggenheim–Scatchard	55.70 ± 0.35	$\Delta\varepsilon_L = (0.87 \pm 0.19) \times 10^{-3d}$	0.425
Zeng et al. [eqn. (10)]	57.49 ± 0.57	$W = -1.34 \pm 0.39^f$	0.450
NaCl ionic medium			
Pitzer[c]	55.84 ± 0.14	$\Delta\beta^{(0)L} = (0.21 \pm 0.05) \times 10^{-3d}$ $\Delta\beta^{(0)L} = 0.39 \times 10^{-3}$ from tabulated Pitzer parameters	0.235
Pitzer[d]	56.11 ± 0.25	$\Delta\beta^{(0)L} = (0.13 \pm 0.07) \times 10^{-3d}$ $\Delta\beta^{(1)L} = (0.95 \pm 0.85) \times 10^{-3d}$ $\Delta\beta^{(1)L} = 0.42 \times 10^{-3}$ from tabulated Pitzer parameters	0.095
Brønsted–Guggenheim–Scatchard	56.01 ± 0.14	$\Delta\varepsilon_L = -(0.42 \pm 0.09) \times 10^{-3d}$	0.238
Zeng et al. [eqn. (10)]	56.37 ± 0.33	$W = 1.15 \pm 0.25^f$	0.346
CODATA	55.82 ± 0.06		

[a] All uncertainties are given as 3σ. [b] The mean square error per unit weight σ_0 is defined as $\sigma_0{}^2 = \Sigma w(\Delta_r H_m - \Delta_r H_{m,calc})^2/(n - m)$, where w is the weighting factor determined as the reciprocal square of the estimated uncertainty in $\Delta_r H_m$ value; $\Delta_r H_{m,calc}$ is the value of the enthalpy of reaction calculated using the obtained regression parameters; n is the number of experimental data; m is the number of variables. [c] Neglecting the contribution of $\Delta\beta^{(1)L}$ and ΔC^L terms. [d] Units: kg mol^{-1} K^{-1}. [e] Neglecting the contribution of the ΔC^L term. [f] Units: kg$^{-1/2}$ mol$^{-3/2}$ kJ. [g] The following Pitzer parameters were used: $\beta_{H,Cl}{}^{(0)L} = -3.081 \times 10^{-4}$, $\beta_{Na,OH}{}^{(0)L} = 7.000 \times 10^{-4}$, $\beta_{H,ClO_4}{}^{(0)L} = 4.905 \times 10^{-4}$, $\beta_{H,Cl}{}^{(1)L} = 1.419 \times 10^{-4}$, $\beta_{Na,OH}{}^{(1)L} = 1.34 \times 10^{-4}$, $\beta_{H,ClO_4}{}^{(1)L} = 19.31 \times 10^{-4}$.

$\Delta_r H_m^\circ$ and $\Delta\beta^{(0)L}$ could be determined with sufficient precision: attempts to estimate the parameters $\Delta\beta^{(1)L}$ and ΔC^L simultaneously with $\Delta_r H_m^\circ$ and $\Delta\beta^{(0)L}$ resulted in large errors in the estimated parameters (cf. Table 1). It is seldom possible to determine the parameter $\Delta\beta^{(1)L}$ from the regression; however, it might be essential for the accuracy of $\Delta_r H_m^\circ$, cf. Table 2. Note that the Pitzer equation with only the parameter $\Delta\beta^{(0)L}$ is not identical to the BGS equation due to the different analytical expressions for the Debye–Hückel term.

All theory-based equations give reasonable estimates of $\Delta_r H_m^\circ$ for the water dissociation reaction. With the exception of the 'Debye–Hückel' model of Zeng et al., all estimates are, within the given uncertainty estimates, in agreement with the CODATA recommendation. The value of $\Delta_r H_m^\circ$ obtained from the NaCl data are also in excellent agreement with the CODATA recommendation (in our view the agreement for the 'Debye–Hückel' model is accidental). We have plotted the experimental data (symbols) and the results of the regression using the BGS and the 'Debye–Hückel' (ZCC) equations in Figs. 2a and 2b. The Pitzer equation in both variants (Table 1) gives results close to BGS equation, and the corresponding lines are not given for clarity.

The determination of the standard enthalpy of formation of Al^{3+} (aq). In a recent paper by Zeng et al.[4] the results of experimental calorimetric determinations of the enthalpies of reaction at 298.15 K for the reaction

$$Al(cr) + 3H^+(aq) \rightarrow Al^{3+}(aq) + \tfrac{3}{2}H_2(g) \tag{11}$$
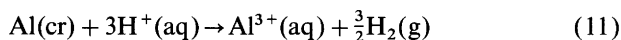
in concentrated solutions of HCl are presented. In all there are eight determinations of the heats of reaction (11) in a range of HCl concentration between 0.2838 and 6.0598 mol kg^{-1}. For the evaluation of $\Delta_r H_m^\circ$ of Al^{3+}(aq), Zeng et al. assumed that the enthalpies of dilution were proportional to the square root of ionic strength of solution. The following equation was employed for the experimental data regression

$$\Delta_r H_m = \Delta_r H_m^\circ + A_1 I_1^{1/2} - A_2 I_2^{1/2} \tag{12}$$

where I_1 is the ionic strength of the initial solution and I_2 that of the final solution after complete reaction of a
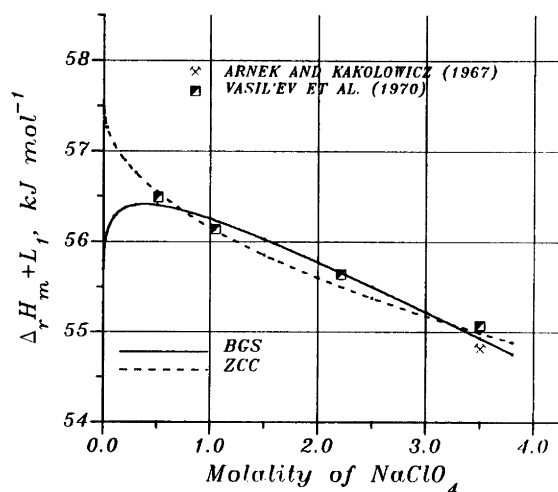
(a)
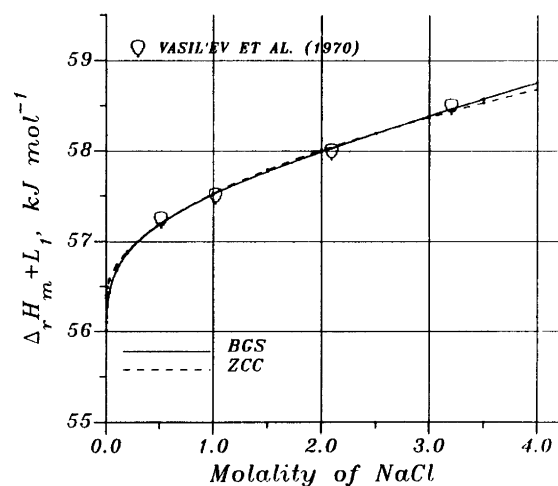
(b)

Fig. 2. The concentration dependence of the enthalpy of reaction for $H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$ in NaClO$_4$ (a) and NaCl (b) media. Symbols are the experimental data, the lines are the results from regression using different equations: Brønsted–Guggenheim–Scatchard (BGS) and Zeng–Chen–Chen (ZCC).

Table 2. The results of the linear least-square determination of unknowns using the Pitzer and BGS equations for the reaction $Al(cr) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3/2H_2(g)$ in HCl media (all uncertainties are given as 3σ).

Fitting equations	$-\Delta_r H_m^\circ$/kJ mol^{-1}	Interaction parameters	Mean square error per unit weight, σ_0
Pitzer[a]	540.73 ± 0.77	$\Delta\beta^{(0)L} = -(0.16 \pm 0.16) \times 10^{-3b}$	1.22
Pitzer[c]	539.67 ± 1.35	$\Delta\beta^{(0)L} = -(0.35 \pm 0.25) \times 10^{-3b}$ $\Delta\beta^{(1)L} = (3.6 \pm 4.2) \times 10^{-3b}$	0.87
Pitzer[d]	538.46 ± 0.80	$\Delta\beta^{(0)L} = -(0.56 \pm 0.16) \times 10^{-3b}$ $\Delta\beta^{(1)L} = 7.7 \times 10^{-3}$ (fixed)[b]	1.26
Brønsted–Guggenheim–Scatchard	539.72 ± 0.50	$\Delta\varepsilon_L = -(1.08 \pm 0.20) \times 10^{-3b}$	0.79

[a] Neglecting the contribution of the $\Delta\beta^{(1)L}$ and ΔC^L terms. [b] Units: kg mol^{-1} K^{-1}. [c] Neglecting the contribution of the ΔC^L term. [d] Neglecting the contribution of the ΔC^L term and with a fixed value of $\Delta\beta^{(1)L}$ (see text).

given (small) mass of aluminium with the aqueous HCl solution $[I_2 = I_1 + 3\Delta n_{Al}/m(H_2O)$, where Δn_{Al} is the number of moles of Al, $m(H_2O)$ is the mass (in kg) of water], and A_1 and A_2 are fitting constants. The value $\Delta_r H_m^\circ = \Delta_f H_m^\circ[Al^{3+}(aq)$, 298.15 K] = -538.25 kJ mol^{-1}, obtained in this way, is in excellent agreement with the CODATA recommended value -538.4 ± 1.5 kJ mol^{-1}.

We used the theory-based equations to determine the values of $\Delta_r H_m^\circ$ from the experimental data of Zeng et al.[4] All experimental results were assumed to have the same uncertainty, 0.4 kJ mol^{-1}. The results are shown in Table 2, where the uncertainty in the fitting parameters are given as 3σ. For the Pitzer equation we considered three fitting variants, using the following parameters: (1) $\Delta_r H_m^\circ$, $\Delta\beta^{(0)L}$, $\Delta\beta^{(1)L}$; (2) $\Delta_r H_m^\circ$, $\Delta\beta^{(0)L}$, i.e. assuming $\Delta\beta^{(1)L} = 0$; (3) $\Delta_r H_m^\circ$, $\Delta\beta^{(0)L}$, and a fixed value of $\Delta\beta^{(1)L}$ equal to 7.7×10^{-3} kg mol^{-1} K^{-1}, obtained by assuming the same interaction parameter $\beta^{(1)L} = 8 \times 10^{-3}$ kg mol^{-1} K^{-1} for $Al^{3+}-Cl^-$ as for $La^{3+}-Cl^-$.[8] The results in Table 2 show that the value of $\Delta_r H_m^\circ$ is sensitive to the value of $\Delta\beta^{(1)L}$; however, the number of data and their precision are not sufficient to obtain the reliable determination of all relevant parameters in the Pitzer equations. By using the results obtained from the different approximations of these equations we can estimate the range in which the 'true' value of $\Delta_r H_m^\circ$ is located. The value of $\Delta_r H_m^\circ$ obtained on the basis of the BGS equation, -539.72 ± 0.50 kJ mol^{-1}, is consistent with all estimates based on the Pitzer equation; hence we accept $\Delta_r H_m^\circ = -539.7 \pm 1.0$ kJ mol^{-1} for the reaction (11). The uncertainty has been increased to take into account the possible errors of both experiment and extrapolation, e.g. the neglect of the possible dependence of the enthalpy of reaction on the initial quanity of Al used. The value proposed is, within the estimated uncertainty, in agreement with that of Zeng et al.,[4] -538.25 ± 1.0 kJ mol^{-1}. However, this is probably accidental, because the extrapolation procedure used by Zeng et al. has no theoretical foundation. The concentration dependence of the enthalpy of reaction (11) as a function of the HCl molality is shown in Fig. 3.

The following values for the standard enthalpy of formation of $Al^{3+}(aq)$ have been proposed: -539.7 ± 1.0 kJ mol^{-1} from experimental data of Zeng et al.;[4] -538.3 ± 2.0 kJ mol^{-1}; -538.5 ± 1.3 kJ mol^{-1}, from the CODATA compilation and based on the standard enthalpy of formation and enthalpy of dilution of $AlCl_3(cr)$ and $AlCl_3 \cdot 6H_2O(cr)$, respectively, cf. Ref. 12, p. 46; and -540.9 ± 4.1 kJ mol^{-1} from the temperature dependence of the solubility of gibbsite in acidic solutions by Palmer and Wesolowski.[16] As the 'best' value we have selected the mean weighted value $\Delta_f H_m^\circ[Al^{3+}(aq)$, 298.15 K] = -539.2 ± 1.0 kJ mol^{-1}.

Determination of the standard enthalpy of formation of $Al(OH)_4^-$ (aq). Zeng et al.[3] determined the standard enthalpy of formation of $Al(OH)_4^-(aq)$ at 298.15 $\pm$
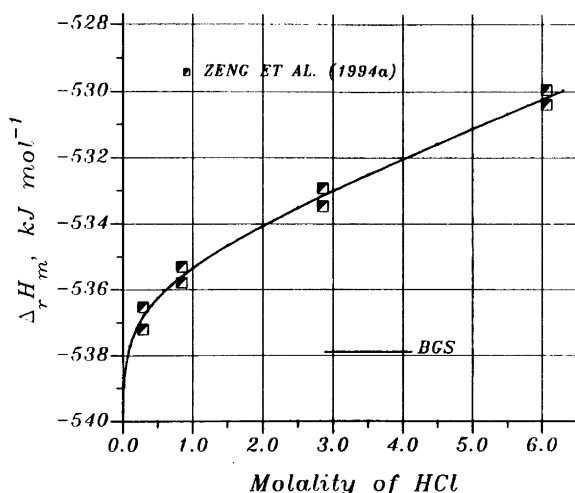
Fig. 3. The concentration dependence of the enthalpy of reaction $Al(cr) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3/2H_2(g)$ in HCl media. The symbols are the experimental data, the line is the results from regression using the Brønsted–Guggenheim–Scatchard (BGS) equations. The size of symbols is approximately equal to the experimental uncertainty (± 0.4 kJ mol^{-1}).

0.50 K from calorimetric measurements of the enthalpy of reaction of Al(cr) with NaOH(aq)

$$Al(cr) + OH^-(aq) + 3H_2O(l)$$
$$= Al(OH)_4^-(aq) + \tfrac{3}{2}H_2(g) \qquad (13)$$
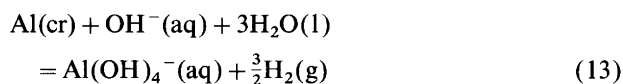
The experimental results have been obtained at different NaOH concentrations ranging from 0.2511 to 4.5138 mol kg^{-1}. The estimated uncertainty in the determinations is within 0.3 kJ mol^{-1}. In order to obtain the value of $\Delta_r H_m^\circ$, the authors used eqn. (10) to obtain $\Delta_r H_m^\circ = -416.96$ kJ mol^{-1}. By combining this value with the standard enthalpies of formation of $OH^-(aq)$ and $H_2O(l)$ from the CODATA compilation the authors obtained $\Delta_f H_m^\circ[Al(OH)_4^-(aq)$, 298.15 K] = -1504.46 ± 1.0 kJ mol^{-1}. The results obtained in previous investigations are: -1499.8 kJ mol^{-1} from the temperature dependence of the solubility of boehmite;[17] -1502.8 ± 1.5 kJ mol^{-1} from calorimetric determinations of the enthalpy of dissolution of gibbsite in NaOH solutions at different temperatures;[18] and -1496.0 ± 1.3 kJ mol^{-1} from solution equilibria of gibbsite, diaspore, and boehmite.[19] Since the publication of Zeng et al.[4] a more recent value, -1500.6 ± 1.5 kJ mol^{-1}, based on solubility data of gibbsite, has been reported by Wesolowski.[20] For the isocoulombic reaction (13) the value of ΔZ^2 is equal to zero, i.e. from theory one does not have a square root, but rather a linear dependence of $\Delta_r H_m$ on the ionic strength. We therefore used the Pitzer and BGS equations to fit the experimental data of Zeng et al.,[3] assuming the uncertainties of the data to be ± 0.3 kJ mol^{-1}. The results are shown in Fig. 4 and in Table 3, all uncertainties in the regression parameters are given as 3σ. For the isocoulombic reaction (13), the BGS and the reduced Pitzer equation with $\Delta\beta^{(1)L}$ and
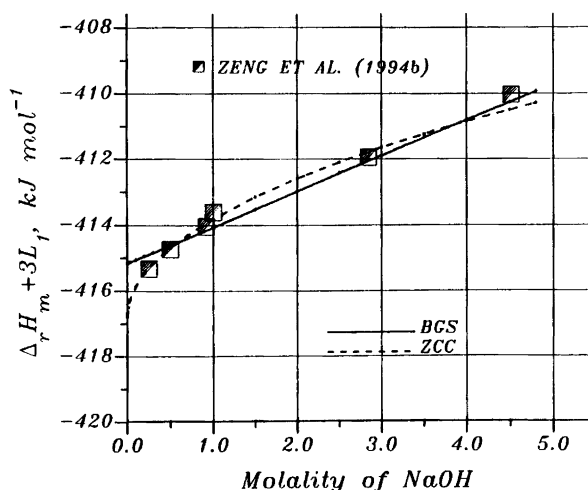
Fig. 4. The concentration dependence of the enthalpy of reaction $Al(cr) + OH^-(aq) + 3H_2O(l) \rightarrow Al(OH)_4^-(aq) + 3/2H_2(g)$ in NaOH media. The symbols are the experimental data, the lines are the results from regression using the Brønsted–Guggenheim–Scatchard (BGS) and Zeng–Chen–Chen (ZCC) equations. The size of symbols is approximately equal to the experimental uncertainty (± 0.3 kJ mol^{-1}).

ΔC^L both equal to zero gave identical results. The Pitzer equation, including the $\Delta\beta^{(0)L}$ and $\Delta\beta^{(1)L}$ terms, gives a slightly different value of $\Delta_r H_m{}^\circ$, although the difference is within the uncertainty interval for both estimates. With the experimental data available we consider the approximation $\Delta\beta^{(1)L} = 0$ to be the most reasonable, because the individual $\beta^{(1)L}$ values are expected to be rather close for the reactants and products with the same charge. We have selected $\Delta_r H_m{}^\circ = -415.16 \pm 1.0$ kJ mol^{-1} as the 'best' value, the uncertainty includes the estimated experimental and extrapolation errors. This value differs by more than 1.7 kJ mol^{-1} from the one obtained by Zeng *et al.*[3] using eqn. (10). Using the CODATA enthalpies of formation of $H_2O(l)$ and $OH^-(aq)$ we obtain $\Delta_f H_m{}^\circ[Al(OH)_4^-(aq)$, 298.15 K$] = -1502.67 \pm 1.00$ kJ mol^{-1}, in excellent agreement with the only previous calorimetric determination -1502.8 ± 1.5 kJ mol^{-1} (Chen *et al.*[18]).

Even though all the different model functions are comparable in accuracy for interpolations (cf. Figs. 2–4), they give different values on extrapolation to zero concentration. For the reliable determination of $\Delta_r H_m{}^\circ$ from

experimental data one should use methods based on well established theory, rather than 'empirical' equations. The choice between the Pitzer model and the BGS model must be based on the number of data available, the ionic strength used and the precision of experimental results. In our experience, the existing data on heats of reaction do not allow the use of equations containing more than one interaction parameter.

Use of the Vasil'ev–Yasinskii equation

Vasil'ev and Yasinskii[21] starting from the following equation for the activity coefficient of an ion i:

$$\ln \gamma_i = -\frac{AZ^2I^{1/2}}{1 + 4.9BI^{1/2}} + bI \tag{14}$$

where A and B stand for the Debye–Hückel parameters and the numerical factor 4.9 is the 'distance of closest approach' in the Debye–Hückel model, deduced an analytical equation for the extrapolation of enthalpies of reaction to infinite dilution:

$$\Delta_r H_m = \Delta_r H_m{}^\circ + \Delta Z^2 \psi + \Delta b_L I \tag{15}$$

where

$$\psi = \frac{3A_L}{4(4.9B)^3}\psi_1 + \frac{B_L}{(4.9B)^4}\psi_2$$

A_L and B_L are the Debye–Hückel parameters for the enthalpy, and A_L has the same numerical value as in the Pitzer equation, $B_L = -0.665 \times 10^8$ kJ kg$^{1/2}$ mol$^{-3/2}$ cm^{-1} and $B = 0.3287 \times 10^8$ kg$^{1/2}$ mol$^{-1/2}$ cm^{-1} (Vasil'ev and Yasinskii[21]) at 298.15 K and 1 atm. Ψ_1 and Ψ_2 are equal to

$$\psi_1 = \frac{1}{I}(\chi^2 - 4\chi + 2\ln\chi + 3)$$

$$\psi_2 = \frac{1}{I}\left(\chi^2 - 6\chi + 6\ln\chi + \frac{2}{\chi} + 3\right)$$

where $\chi = 1 + 4.9BI^{1/2}$. This equation results in a somewhat higher value of $\Delta_r H_m{}^\circ$ for the enthalpy of dissociation of water, equal to $\Delta_r H_m{}^\circ = 56.08 \pm 0.31$ kJ mol^{-1}, and $\Delta_r H_m{}^\circ = 56.37 \pm 0.07$ kJ mol^{-1}, respectively, from data in NaClO$_4$ and NaCl media. The corresponding BGS values are 55.70 ± 0.35 kJ mol^{-1} and 56.01 ± 0.14 kJ mol^{-1}, respectively .

Table 3. The results of the least-squares determination of unknowns using the Pitzer and BGS equations for the reaction $Al(cr) + OH^-(aq) \rightarrow 3H_2O(l) \rightarrow Al(OH)_4^-(aq) + 3/2H_2(g)$ in NaOH media (all uncertainties given as 3σ).

Fitting equations	$-\Delta_r H_m{}^\circ$/kJ mol^{-1}	Interaction parameters	Mean square error per unit weight, σ_0
Pitzer[a]	415.16 ± 0.63	$\Delta\beta^{(0)L} = -(0.73 \pm 0.19) \times 10^{-3c}$	1.16
Pitzer[b]	416.21 ± 0.88	$\Delta\beta^{(0)L} = -(0.47 \pm 0.23) \times 10^{-3c}$ $\Delta\beta^{(1)L} = -(3.8 \pm 3.0) \times 10^{-3c}$	0.55
Brønsted–Guggenheim–Scatchard	415.16 ± 0.63	$\Delta\varepsilon_L = -(1.47 \pm 0.38) \times 10^{-3c}$	1.16

[a] Neglecting the contribution of the $\Delta\beta^{(1)L}$ and ΔC^L terms. [b] Neglecting the contribution of the ΔC^L term. [c] Units: kg mol^{-1} K^{-1}.

The Vasil'ev–Yasinskii (V–Y) equation has been derived using the following relations, where $L_{\phi,i}$ stands for the relative apparent molal enthalpy of reaction participant i.

$$\Delta_r H_m(I) = \Delta_r H_m{}^\circ + \sum_i p_i L_{\phi,i}(I) \qquad (16)$$

$$L_2 = L_\phi + I\left(\frac{\partial L_\phi}{\partial I}\right)$$

$$L_2 = -RT^2\left(\frac{\partial \ln \gamma}{\partial T}\right)$$

Eqn. (16) was postulated; no attempts to deduce this formula from more general thermodynamic relations have been undertaken. It is obvious that eqns. (2) and (16) are not consistent with one another. The reason is than eqn. (16) is based on the wrong assumption $H_{2,i} = H_{2,i}{}^\circ + \phi_{L,i}$ [see eqn. (5) in the paper by Vasil'ev and Yasinskii],[21] which is in contradiction to the strict thermodynamic relation $H_{2,i} - H_{2,i}{}^\circ = L_{2,i}$.
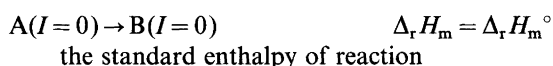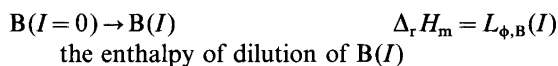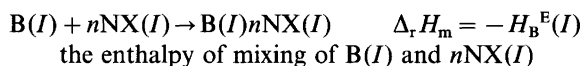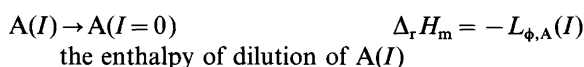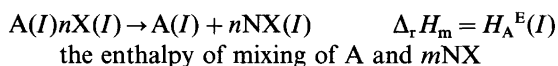
The V–Y equation has often been used to deduce standard enthalpies of reaction at zero ionic strength from calorimetric experiments in ionic media, especially by Russian scientists. It is therefore of interest to find the relationship between the apparent molar enthalpies of the reaction participants and the enthalpy of reaction. We will do this by using the following simple reaction as an example:

$$A \to B \qquad (17)$$
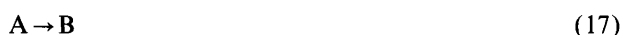
in a NX ionic medium, with ionic strength I. The thermochemical equation for this reaction is usually written as

$$A(I) \times nNX(I) \to B(I) \times nNX(I) \qquad (18)$$

where n is the mol ratio $NX/A = NX/B$. The reaction may also be represented as the sum of the following reactions:

$A(I)nX(I) \to A(I) + nNX(I) \qquad \Delta_r H_m = H_A{}^E(I)$
the enthalpy of mixing of A and mNX

$A(I) \to A(I = 0) \qquad \Delta_r H_m = -L_{\phi,A}(I)$
the enthalpy of dilution of A(I)

$B(I) + nNX(I) \to B(I)nNX(I) \qquad \Delta_r H_m = -H_B{}^E(I)$
the enthalpy of mixing of B(I) and nNX(I)

$B(I = 0) \to B(I) \qquad \Delta_r H_m = L_{\phi,B}(I)$
the enthalpy of dilution of B(I)

$A(I = 0) \to B(I = 0) \qquad \Delta_r H_m = \Delta_r H_m{}^\circ$
the standard enthalpy of reaction

$H_A{}^E(I)$ is the difference between the enthalpy of a solution of composition $A(I)nNX(I)$ and the sum of the enthalpies of solutions of compositions $A(I)$ and $nNX(I)$, all of the same ionic strength I, the other quantities are defined

by the equations above. The enthalpy change for reaction (17) is then equal to

$$\Delta_r H_m(17) = \Delta_r H_m{}^\circ(17) - L_{\phi,A}(I) + L_{\phi,B}(I)$$
$$+ H_A{}^E(I) - H_B{}^E(I) \qquad (19)$$

which differs from the V–Y equation by the term $H_A{}^E(I) - H_B{}^E(I)$. The value of $H_A{}^E(I)$ can be calculated from the experimental data on excess enthalpies of mixing of solutions A and NX at constant total ionic strengths, if available. By using the system HCl–NaCl at trace concentrations of HCl as an example, we obtain the following values of $H_{HCl}{}^E$ at different ionic strengths: 0.54 kJ mol^{-1} at $I = 1$ m, 1.87 kJ mol^{-1} at $I = 2$ m, 3.13 kJ mol^{-1} at $I = 3$ m.[22] These examples indicate the possible magnitude of the corrections required for data that have been treated using the Vasil'ev–Yasinskii equation. The excess enthalpies of mixing usually decreases with decreasing ionic strength/ionic medium concentration (cf. the HCl–NaCl system above); hence, we do not expect large changes in the resulting enthalpy of reaction at infinite dilution. Nevertheless, a revision of the $\Delta_r H_m{}^\circ$ values obtained using the V–Y equation should be undertaken to check this. Finally, we want to emphasize that at trace concentrations of the solute i, in the NX ionic medium, the sum of $L_{\phi,i}(I) - H_i{}^E(I)$ is equal to the partial molar enthalpy of $i, L_{2,i}$, because this reflects all changes in the heat content of the solution of NX, when adding 1 mol of the species i to an infinite amount of the NX solution.

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