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TDB-4

TEMPERATURE CORRECTIONS TO THERMODYNAMIC DATA AND ENTHALPY CALCULATIONS

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This guideline consists of the extracted Chapter X from [97ALL/BAN].

Temperature Corrections to Thermodynamic data and Enthalpy Calculations

The thermodynamic data selected in the critical reviews carried out within the NEA Thermochemical Data Base Project (TDB) consistently refer to a temperature of $T_0 = 298.15$ K ($t_0 = 25.00^\circ\text{C}$) [98WAN/ÖST]. When available, heat capacity functions may be selected for a specified temperature range, usually up to 600 K if possible, as this temperature is considered to represent the upper limit relevant for radioactive waste disposal purposes. In the data base of the NEA–TDB project, the following general form of the temperature dependencies of the heat capacity is used for temperature intervals that do not involve any phase transitions:

$$C_{p,m}^\circ(T) = a + bT + cT^2 + jT^3 + dT^{-1} + eT^{-2} + kT^{-3} + f \ln T + gT \ln T + h\sqrt{T} + i \frac{1}{\sqrt{T}}. \quad (1)$$

For any specific system, only a few of these coefficients will be required (frequently a , b and e). The conversion of thermodynamic data at 298.15 K to temperatures other than 298.15 K is often necessary for both their critical evaluation and their application. The need for such corrections can be a problem in cases where experimental heat capacity functions are unavailable, which is true for a large number of the aqueous species. For the reanalysis of equilibrium constants, the corrections of experimental results from other temperatures to 298.15 K can often be done with a sufficient degree of confidence by assuming constant enthalpy values, either from experimental investigations or from estimations by analogy, since the temperature differences are usually small, in many cases less than 10 K. For this reason, the heat capacity change of the reaction, $\Delta_r C_{p,m}^\circ$, unless experimentally known, is set equal to zero in the NEA–TDB reviews for temperature intervals $\Delta T \leq 10$ K.

On the other hand, the user of the data sets selected in the TDB reviews may want to use them at temperatures significantly different from 298.15 K. As experimental information on wider temperature ranges is not available for many aqueous systems, it may become necessary to estimate the temperature dependency of the thermodynamic properties. One main purpose of this document is to present procedures that allow the estimation of such temperature dependencies.

The rest of this document is a reproduction of Chapter X of the book “Modelling in Aquatic Chemistry” [97ALL/BAN], which in turn was built on an earlier

version of this guideline.

1 Introduction

Recalculation of chemical equilibrium data from the reference temperature of 298.15 K (25.00°C) to any desired temperature is made by using the relationships provided by thermodynamics. The procedures are straight-forward provided that information is available for $\Delta_r H_m^\circ$ or $\Delta_r S_m^\circ$ at the reference temperature and for their temperature dependencies. Complete information of this kind is rarely available for formation reactions of chemical complexes in aqueous solution and it is therefore necessary to rely on approximation methods of various kinds. These methods will be described in some detail in this guideline.

Experimental thermodynamic information about the chemical species (chemical speciation) in a particular system forms the basis of thermodynamic databases. However, experiments only provide information about the species that are present in noticeable amounts in the laboratory systems (and thus are detectable in the experiments). A complication in the modelling of the properties of systems at different temperatures is the possibility of a change in speciation with temperature, since even a temperature change as small as from 298 to 323 K may result in the appearance of new species [76BAE/MES, 87CIA/IUL]. The modelling in such situations can only be made using general principles of chemistry (see Chapter III of [97ALL/BAN]). One may also have to make experimental determinations in situations where one is reasonably confident that a change in speciation is of critical importance for the understanding of the system at higher temperatures.

There are some general considerations that can be used as guidelines:

- The dielectric constant of liquid water decreases strongly with increasing temperature (*cf.* Figure 2 on p.16), hence, complexes of low or zero charge are favoured at higher temperatures.
- Hydrolysis of metal ions increases with increasing temperature, in keeping with the general increase of acidity of water with increasing temperature.
- The relative amounts of polynuclear complexes and other complexes with high charges decrease with increasing temperature [94PLY/GRE]. This effect can be correlated with the decrease in the dielectric constant of the solvent water with increasing temperature (*cf.* Figure 2). Even surprisingly simple electrostatic models are able to describe this feature with fair accuracy. In the final section of this guideline we will describe the characteristic features of one such model and its predictive properties.

Thermodynamic data may also need to be corrected for ionic strength effects both at 298.15 K and at other temperatures. This is not a straight-forward problem at $T \neq 298.15$ K as discussed in Chapter IX of [97ALL/BAN].

As will be seen from the following text the approximation methods used to describe the temperature dependencies of chemical equilibria rely heavily on simple electrostatic models which treat the participating ionic species as point-charges and the solvent as a homogeneous dielectric continuum; both assumptions are oversimplifications.

The extrapolation of experimental values of $\Delta_r G_m^\circ(T)$ (or, conversely, equilibrium constants) to a reference temperature, generally 298.15 K, is usually done by using various modifications of the so-called second- and third-law methods. The third-law extrapolations require free energy functions and are generally the preferred method of calculation when long temperature extrapolations are required, particularly where the reactants and products are pure phases for which experimental heat capacities or relative enthalpies are available or can be accurately estimated. That is, third-law extrapolations should generally be used for equilibria between different phases at high temperatures. When extrapolations over relatively small temperature ranges are made, then second-law extrapolations can be used for accurate calculations, but this method requires experimental or estimated heat capacities around the temperature of interest. Second-law extrapolations should generally be used for aqueous equilibria.

2 Second-law extrapolations

The standard molar Gibbs energy change for a reaction at any given temperature is given by

$$\Delta_r G_m^\circ = \Delta_r H_m^\circ - T \Delta_r S_m^\circ, \quad (2)$$

and the temperature dependence of the Gibbs energy is:

$$\left(\frac{\partial \Delta_r G_m^\circ}{\partial T} \right)_p = -\Delta_r S_m^\circ.$$

The *Gibbs-Helmholtz equation* is:

$$\left(\frac{\partial \Delta_r G_m^\circ / T}{\partial T} \right)_p = \frac{-\Delta_r H_m^\circ(T)}{T^2}, \quad (3)$$

which has the integrated form*:

$$\int_{T_0}^T d \left(\frac{\Delta_r G_m^\circ(T)}{T} \right) = - \int_{T_0}^T \left(\frac{\Delta_r H_m^\circ(T)}{T^2} \right) dT. \quad (4)$$

* T_0 stands for the reference temperature (= 298.15 K).

From the integration of this equation, and from using the temperature derivatives of the enthalpy and entropy,

$$\left(\frac{\partial \Delta_r H_m^\circ}{\partial T}\right)_p = \Delta_r C_{p,m}^\circ, \quad (5)$$

$$\left(\frac{\partial \Delta_r S_m^\circ}{\partial T}\right)_p = \frac{\Delta_r C_{p,m}^\circ}{T}, \quad (6)$$

it is possible to write the temperature dependence of the Gibbs energy as a function of the entropy at the reference temperature ($T_0 = 298.15$ K), as well as the heat capacity function. It is, however, also possible [86NOR/MUN, Eq. (4-14)], and simpler to use Eqs. (2), (5) and (6) to write

$$\begin{aligned} \Delta_r G_m^\circ(T) &= \Delta_r H_m^\circ(T_0) + \int_{T_0}^T \Delta_r C_{p,m}^\circ dT \\ &\quad - T \left(\Delta_r S_m^\circ(T_0) + \int_{T_0}^T \frac{\Delta_r C_{p,m}^\circ}{T} dT \right). \end{aligned}$$

This equation is usually recast in terms of only one thermodynamic function other than Gibbs energy and heat capacity, *e.g.*, if the choice is entropy,

$$\begin{aligned} \Delta_r G_m^\circ(T) &= \Delta_r G_m^\circ(T_0) - (T - T_0) \Delta_r S_m^\circ(T_0) \\ &\quad + \int_{T_0}^T \Delta_r C_{p,m}^\circ dT - T \int_{T_0}^T \frac{\Delta_r C_{p,m}^\circ}{T} dT. \end{aligned} \quad (7)$$

Alternatively, one may write the temperature dependence of the equilibrium constant as a function of the standard enthalpy and the standard heat capacity,

$$\begin{aligned} \log_{10} K^\circ(T) &= \log_{10} K^\circ(T_0) - \frac{\Delta_r H_m^\circ(T_0)}{R \ln(10)} \left(\frac{1}{T} - \frac{1}{T_0} \right) \\ &\quad - \frac{1}{RT \ln(10)} \int_{T_0}^T \Delta_r C_{p,m}^\circ dT + \frac{1}{R \ln(10)} \int_{T_0}^T \frac{\Delta_r C_{p,m}^\circ}{T} dT, \end{aligned} \quad (8)$$

where R is the gas constant ($8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). Either Eq. (7) or (8) may be used to calculate equilibrium constants at a temperature T if:

1. the equilibrium constant at 298.15 K is known;
2. the temperature dependence of $\Delta_r C_{p,m}^\circ$ is known, or the temperature interval is small enough that $\Delta_r C_{p,m}^\circ$ can be assumed to be constant;
3. either $\Delta_r H_m^\circ(T_0)$ or $\Delta_r S_m^\circ(T_0)$ are known.

Unfortunately, experimentally derived heat capacity data have not been measured for most aqueous species and for many solid phases. Therefore, in order to use Eqs. (7) or (8), one will have to make either approximations (as discussed below) or estimations (*cf.* Section 4).

If the reaction of interest involves only species for which the pertinent coefficients in the following equation for the heat capacity[†]

$$C_{p,m}^{\circ}(T) = a + bT + cT^2 + jT^3 + dT^{-1} + eT^{-2} + kT^{-3} + f \ln T + gT \ln T + h\sqrt{T} + i \frac{1}{\sqrt{T}} \quad (9)$$

are available (which is seldom the case), then the approximation methods given below are not needed, and the integrals in Eqs. (7) and (8) can be performed analytically and will take the following form:

$$\begin{aligned} \int_{T_0}^T \Delta_r C_{p,m}^{\circ} dT &= \Delta a (T - T_0) + \frac{\Delta b}{2} (T^2 - T_0^2) \\ &+ \frac{\Delta c}{3} (T^3 - T_0^3) + \frac{\Delta j}{4} (T^4 - T_0^4) + \Delta d \ln \left(\frac{T}{T_0} \right) \\ &- \Delta e \left(\frac{1}{T} - \frac{1}{T_0} \right) - \frac{\Delta k}{2} (T^{-2} - T_0^{-2}) \\ &- \Delta f [T(1 - \ln T) - T_0(1 - \ln T_0)] \\ &- \frac{\Delta g}{2} [T^2(0.5 - \ln T) - T_0^2(0.5 - \ln T_0)] \\ &+ \frac{2\Delta h}{3} (T^{3/2} - T_0^{3/2}) + 2\Delta i (\sqrt{T} - \sqrt{T_0}), \quad (10) \end{aligned}$$

$$\begin{aligned} \int_{T_0}^T \frac{\Delta_r C_{p,m}^{\circ}}{T} dT &= \Delta a \ln \left(\frac{T}{T_0} \right) + \Delta b (T - T_0) \\ &+ \frac{\Delta c}{2} (T^2 - T_0^2) + \frac{\Delta j}{3} (T^3 - T_0^3) \\ &- \Delta d \left(\frac{1}{T} - \frac{1}{T_0} \right) - \frac{\Delta e}{2} (T^{-2} - T_0^{-2}) \\ &- \frac{\Delta k}{3} (T^{-3} - T_0^{-3}) + \frac{\Delta f}{2} [(\ln T)^2 - (\ln T_0)^2] \end{aligned}$$

[†]This equation is used as a general form for the temperature dependency of the heat capacity in temperature intervals that do not involve any phase transition. For any specific system, only a few of these coefficients will be required (frequently a , b and e). Some of these terms should obviously not be used if the heat capacity equation is required to be valid as $T \rightarrow 0$, since they become infinite at that limit.

$$\begin{aligned}
& - \Delta g [T (1 - \ln T) - T_0 (1 - \ln T_0)] \\
& + 2\Delta h \left(\sqrt{T} - \sqrt{T_0} \right) - 2\Delta i \left(\frac{1}{\sqrt{T}} - \frac{1}{\sqrt{T_0}} \right), \quad (11)
\end{aligned}$$

where Δa , Δb , Δc ,... are the changes in the parameters a , b , c ,... of Eq. (9) with the reaction, *i.e.*,

$$\Delta a = \sum_i \nu_i a_i,$$

etc., and where ν_i are the stoichiometric coefficients of the species i of the reaction.

If equilibrium constants are known at several temperatures, the parameters of Eq. (8) (together with Eqs. (10) and (11)) can be evaluated from the experimental data by a least-squares procedure.

It is sometimes convenient to use “apparent” standard partial molar Gibbs energies and enthalpies, *cf.* Refs. [74HEL/KIR, 78HEL/DEL, 80TRE/LEB] defined as

$$\Delta_a G_m^\circ(i, T) = \Delta_f G_m^\circ(i, T_0) + (G_m^\circ(i, T) - G_m^\circ(i, T_0)) \quad (12)$$

and

$$\Delta_a H_m^\circ(i, T) = \Delta_f H_m^\circ(i, T_0) + \int_{T_0}^T C_{p,m}^\circ(i, T) dT. \quad (13)$$

Using the relationship

$$S_m^\circ(i, T) = S_m^\circ(i, T_0) + \int_{T_0}^T \frac{C_{p,m}^\circ(i, T)}{T} dT, \quad (14)$$

it is possible to rewrite Eq. (7),

$$\Delta_r G_m^\circ(T) = \sum_i \nu_i \Delta_a H_m^\circ(i, T) - T \sum_i \nu_i S_m^\circ(i, T) \quad (15)$$

$$= \sum_i \nu_i \Delta_a G_m^\circ(i, T) \quad (16)$$

$$\begin{aligned}
& = \sum_i \nu_i \left(\Delta_f G_m^\circ(i, T_0) - (T - T_0) S_m^\circ(i, T_0) \right. \\
& \quad \left. + \int_{T_0}^T C_{p,m}^\circ(i, T) dT - T \int_{T_0}^T \frac{C_{p,m}^\circ(i, T)}{T} dT \right). \quad (17)
\end{aligned}$$

If the heat capacity is expressed according to Eq. (9), the integrals in Eq. (17) have the same form as Eqs. (10) and (11) except that in Eqs. (10) and (11), $\Delta_r C_{p,m}^\circ$, Δa , Δb , Δc , etc., must be substituted for $C_{p,m}^\circ$, a , b , c , etc.

Eqs. (13) through (17) are especially useful when the assumption is made that for some of the reactants (or products) the heat capacity does not vary with temperature, whereas for the rest of the reactants (or products) Eq. (9) applies.

2.1 The hydrogen ion convention

The hydrogen ion convention states that the conventional standard partial molar Gibbs energy of formation, entropy and heat capacity of H^+ are all set equal to zero at all temperatures. This allows values to be assigned for the thermodynamic properties of each ionic species participating in a reaction. Therefore, it is possible to write

$$\Delta_r G_m^\circ(T) = \sum_i \nu_i G_m^\circ(i, T), \quad (18)$$

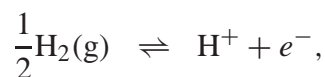
where $G_m^\circ(i, T)$ is the resulting standard state Gibbs energy of ion i based on the hydrogen ion convention.

As just stated, the hydrogen ion convention involves the arbitrary assignment of the standard ionic entropy of the aqueous hydrogen ion as being equal to zero at all temperatures, *i.e.*, $S_m^\circ(H^+, \text{aq}, T) = 0$. Another assumption of this convention is that the standard partial molar Gibbs energy of formation of the hydrogen ion is equal to zero at all temperatures, $\Delta_f G_m^\circ(H^+, \text{aq}, T) = 0$. However, the entropy of formation of an ion is equal to the temperature derivative of its Gibbs energy of formation:

$$\left(\frac{\partial \Delta_f G_m^\circ(i, T)}{\partial T} \right)_p = -\Delta_f S_m^\circ(i, T).$$

Thus the assumption that $\Delta_f G_m^\circ(H^+, \text{aq}, T) = 0$ also implies that $\Delta_f S_m^\circ(H^+, \text{aq}, T) = 0$, and according to Eq. (2) it also implies that $\Delta_f H_m^\circ(H^+, \text{aq}, T) = 0$.

The reaction for formation of the aqueous hydrogen ion is



for which the entropy of formation is given by

$$\begin{aligned} \Delta_r S_m^\circ(T) &= \Delta_f S_m^\circ(H^+, \text{aq}, T) \\ &= S_m^\circ(H^+, \text{aq}, T) + S_m^\circ(e^-, T) - \frac{1}{2}S_m^\circ(H_2, g, T) \end{aligned}$$

In this case the standard partial molar entropy of formation of the hydrogen ion is identical to the entropy of reaction. However, the standard partial molar entropy of formation of the hydrogen ion and its standard partial molar ionic entropy are both set equal to zero in the hydrogen ion convention, $\Delta_f S_m^\circ(\text{H}^+, \text{aq}, T) = S_m^\circ(\text{H}^+, \text{aq}, T) = 0$. Consequently, to remain consistent with the standard entropy of $\text{H}_2(\text{g})$, the “aqueous electron” must be assigned an effective molar entropy of

$$S_m^\circ(e^-, T) = \frac{1}{2} S_m^\circ(\text{H}_2, \text{g}, T)$$

At 298.15 K, the CODATA key values [89COX/WAG] at 1 bar pressure yield

$$S_m^\circ(e^-, T_0) = (65.340 \pm 0.001_5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

This value must be included when the entropy of an ionic species is being calculated from the entropies of the elements from which it is formed.

As an example, the ionic entropy of the divalent calcium ion will be calculated at 298.15 K from its entropy of formation. The formation reaction is



and the corresponding entropy of formation is given by

$$\begin{aligned} \Delta_f S_m^\circ(\text{Ca}^{2+}, \text{aq}, 298.15 \text{ K}) &= S_m^\circ(\text{Ca}^{2+}, \text{aq}, 298.15 \text{ K}) + 2S_m^\circ(e^-, 298.15 \text{ K}) \\ &\quad - S_m^\circ(\text{Ca}, \text{cr}, 298.15 \text{ K}) \end{aligned}$$

The entropy of formation of the calcium ion can be calculated from its standard Gibbs free energy of formation and the enthalpy of formation as given in the CODATA tables to yield $\Delta_f S_m^\circ(\text{Ca}^{2+}, \text{aq}, 298.15 \text{ K}) = (32.9 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Then,

$$\begin{aligned} S_m^\circ(\text{Ca}^{2+}, \text{aq}, 298.15 \text{ K}) &= S_m^\circ(\text{Ca}, \text{cr}, 298.15 \text{ K}) - 2S_m^\circ(e^-, 298.15 \text{ K}) \\ &\quad + \Delta_f S_m^\circ(\text{Ca}^{2+}, \text{aq}, 298.15 \text{ K}) \\ &= (41.6 \pm 0.4) - 2(65.340 \pm 0.001_5) + (32.9 \pm 5.0) \\ &= -(56.2 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \ddagger \end{aligned}$$

[‡]This calculated value of $S_m^\circ(\text{Ca}^{2+}, \text{aq}, 298.15 \text{ K})$ is identical to that given in the CODATA tables, whereas the uncertainties are quite different. This arises because the calculations involved different thermodynamic cycles.

2.2 Approximations

For many chemical reactions there is a lack of heat capacity functions for all or some of the species involved, and therefore approximations (as described in this section) or estimations (*cf.* Section 4) must be made in order to use Eqs. (7), (8) or (17). The method of choice will depend on the type of chemical reaction being considered.

2.2.1 Constant enthalpy of reaction

The simplest assumption to be made is that the heat capacity change of reaction is zero at all temperatures (*i.e.*, the standard molar enthalpy of reaction does not vary with temperature, *cf.* Eqs. (5) and (6)). In that case, Eq. (8) reduces to the integrated van't Hoff expression[§]

$$\log_{10} K^\circ(T) = \log_{10} K^\circ(T_0) + \frac{\Delta_r H_m^\circ(T_0)}{R \ln(10)} \left(\frac{1}{T_0} - \frac{1}{T} \right). \quad (19)$$

For a temperature range ($T - T_0$) equal or less than ± 10 K, the error introduced in $\log_{10} K^\circ(T)$ by this simplification will, in most cases, be well within its uncertainty limits.

Eq. (19) is applicable to chemical reactions in a single phase or a multiphase system at constant total pressure provided no further constraint is placed upon the system. For certain other cases, for example when the temperature dependence of a solubility product is being studied, the system is constrained to fall on the saturated solution curve, and Eq. (19) must be modified. See Section 2.3.

2.2.2 Constant heat capacity of reaction

Another approach, which is often used in conjunction with Eq. (8) when the extrapolation extends over a temperature range larger than about 20 K, is to assume that the heat capacity of the reaction does not vary with temperature. In that case Eq. (8) becomes

$$\log_{10} K^\circ(T) = \log_{10} K^\circ(T_0) + \frac{\Delta_r H_m^\circ(T_0)}{R \ln(10)} \left(\frac{1}{T_0} - \frac{1}{T} \right)$$

[§]By combining Eq. (3) and the relation $\Delta_r G_m^\circ(T) = -RT \ln K^\circ(T)$, it is possible to obtain, for a given constant pressure p :

$$\frac{d \ln K_p^\circ(T)}{dT} = \frac{\Delta_r H_m^\circ(T)}{RT^2}$$

which is called the *van't Hoff equation*.

$$+ \frac{\Delta_r C_{p,m}^\circ}{R \ln(10)} [(T_0/T) - 1 + \ln(T/T_0)], \quad (20)$$

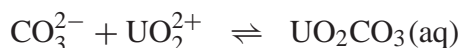
where, as mentioned earlier, the reference temperature is $T_0 = 298.15$ K.

Using Eq. (2) it is possible to rewrite this expression as follows (compare also with Eqs. (7) and (8)):

$$\begin{aligned} \Delta_r G_m^\circ(T) &= \Delta_r G_m^\circ(T_0) - (T - T_0) \Delta_r S_m^\circ(T_0) \\ &\quad + \Delta_r C_{p,m}^\circ [T - T_0 - T \ln(T/T_0)]. \end{aligned} \quad (21)$$

Use of Eqs. (20) or (21) to represent values of $\log_{10} K(T)$ will give enthalpies of reaction which are more reliable than those obtained assuming a “constant enthalpy of reaction”, Eq. (19), but the $\Delta_r C_{p,m}^\circ(T_0)$ values obtained will be imprecise [67HEL]. For most reactions the assumption made in Eqs. (20) and (21) will be appropriate for temperatures in the range 273 to 473 K.

As an example, Eq. (20) can be used to fit the high-temperature equilibrium constants reported by [72SER/NIK] for the reaction



which will be evaluated below as an isoelectric reaction. The resulting values are $\log_{10} K(T_0) = (9.90 \pm 0.07)$, $\Delta_r H_m^\circ(T_0) = -(1.8 \pm 3.4) \text{ kJ}\cdot\text{mol}^{-1}$, and $\Delta_r C_{p,m}^\circ(T_0) = (551 \pm 31) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. If the equilibrium constant at 298.15 K is not a fitting parameter, but instead is set equal to the recommended value of $\log_{10} K^\circ(T_0) = (9.68 \pm 0.04)$ [92GRE/FUG], the following results are obtained: $\Delta_r H_m^\circ(T_0) = (6 \pm 6) \text{ kJ}\cdot\text{mol}^{-1}$, and $\Delta_r C_{p,m}^\circ(T_0) = (499 \pm 74) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

A comparison between the results from Eq. (20) (using both sets of fitted parameters) and the experimental data is shown in Figure 1.

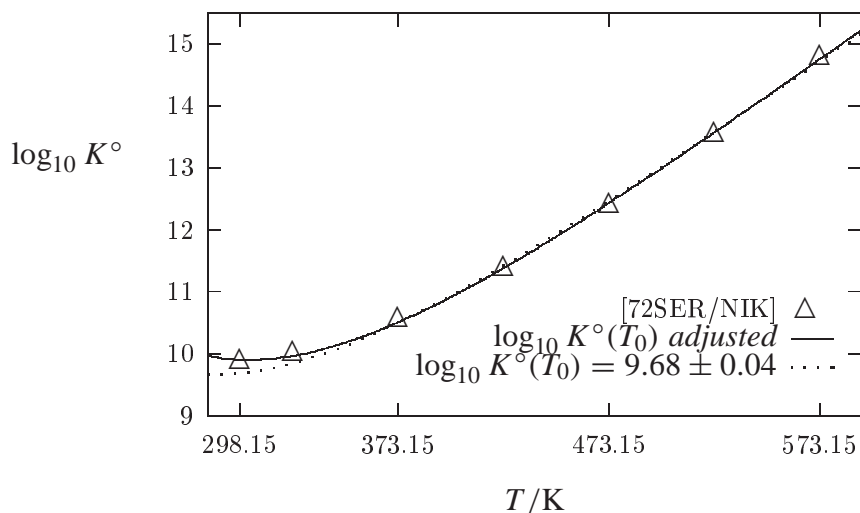
The reaction enthalpy is found in this case to be zero within the experimental error. The entropy of reaction is given (*cf.* Eq. (2)) by

$$\begin{aligned} \Delta_r S_m^\circ(T_0) &= \frac{\Delta_r H_m^\circ(T_0)}{T_0} + \ln(10) R \log_{10} K^\circ(T_0) \\ \sigma^2(\Delta_r S_m^\circ) &= 1.125 \times 10^{-5} \sigma^2(\Delta_r H_m^\circ) + 366.5 \sigma^2(\log_{10} K^\circ), \end{aligned}$$

which gives $\Delta_r S_m^\circ(T_0) = (183 \pm 12) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (when the equilibrium constant at 298.15 K is also fitted to Eq. (20)) or which gives $\Delta_r S_m^\circ(T_0) = (206 \pm 22) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (with $\log_{10} K^\circ(T_0)$ fixed at 9.68). Eqs. (20) and (21) are useful to calculate higher temperature equilibrium constants when average heat capacities for aqueous ions have been determined experimentally or estimated (*cf.* Section 4.1.2).

Alternatively, partial molar heat capacities at 298.15 K are sometimes considered to be constant with temperature. This assumption is based on the fact

Figure 1: Equilibrium constants from [72SER/NIK] for Reaction (28): $\text{CO}_3^{2-} + \text{UO}_2^{2+} \rightleftharpoons \text{UO}_2\text{CO}_3(\text{aq})$, compared with the two different least squares fits to the “constant $\Delta_r C_{p,m}^\circ$ ” equation, Eq. (20), described in the text.



that although values for ionic heat capacities generally increase with temperature, they usually also have a maximum around 325 to 375 K and then begin to decrease (see for example Figure 4 in Ref. [82PAT/SLO] and Figures 103 to 106 in Ref. [81HEL/KIR]). Therefore setting $C_{p,m}^\circ(T) \approx C_{p,m}^\circ(T_0)$ may be a valid simplification in the temperature range between 273 and 373 to 423 K depending on the nature of the reaction [67HEL]. However, using the heat capacity at the average temperature $C_{p,m}^\circ(\frac{T+T_0}{2})$ may be an even better approximation over some temperature intervals.

Partial molar heat capacities at 298.15 K for ions in aqueous solutions may be estimated from ionic entropies as discussed later, with some of the equations given in Refs. [64CRI/COB, 81HEL/KIR, 88SHO/HEL].

Once heat capacities have been estimated, they can then be used as follows [69HEL]:

- If the chemical reaction involves only aqueous ionic species, then the average heat capacities may be combined into a single average heat capacity of reaction, and Eqs. (20) or (21) can be used. This method is used for example in Ref. [80LEM/TRE].
- If the chemical reaction includes phases for which heat capacity functions

are available (*i.e.*, expressions compatible with Eq. (9)), it is convenient to use Eq. (15),

$$\Delta_r G_m^\circ(T) = \sum_i \nu_i \Delta_a H_m^\circ(i, T) - T \left(\sum_i \nu_i S_m^\circ(i, T) \right),$$

together with the following equations [69HEL] for the aqueous species (which are to be used instead of Eqs. (13) and (14)):

$$\Delta_a H_m^\circ(i, T) = \Delta_f H_m^\circ(i, T_0) + C_{p,m}^\circ|_{T_0}^T(i) (T - T_0) \quad (22)$$

$$S_m^\circ(i, T) = S_m^\circ(i, T_0) + C_{p,m}^\circ|_{T_0}^T(i) \ln(T/T_0), \quad (23)$$

while for the non-ionic species Eqs. (13) and (14) can be used, for which (as mentioned earlier) the integrals take the form of expressions like Eqs. (10) and (11) except that one must substitute $\Delta_r C_{p,m}^\circ$, Δa , Δb , ..., *etc.*, for $C_{p,m}^\circ$, a , b , c , ..., *etc.*

It may be interesting to note that, if $\Delta_r S_m^\circ$ and $\Delta_r C_{p,m}^\circ$ are comparable in magnitude, the term in Eq. (21) with $\Delta_r C_{p,m}^\circ$ becomes small compared to $\Delta_r S_m^\circ \Delta T$ over short temperature ranges, as shown in Table 1. In many cases, the $\Delta_r C_{p,m}^\circ$

Table 1: Temperature contributions in Eq. (21).

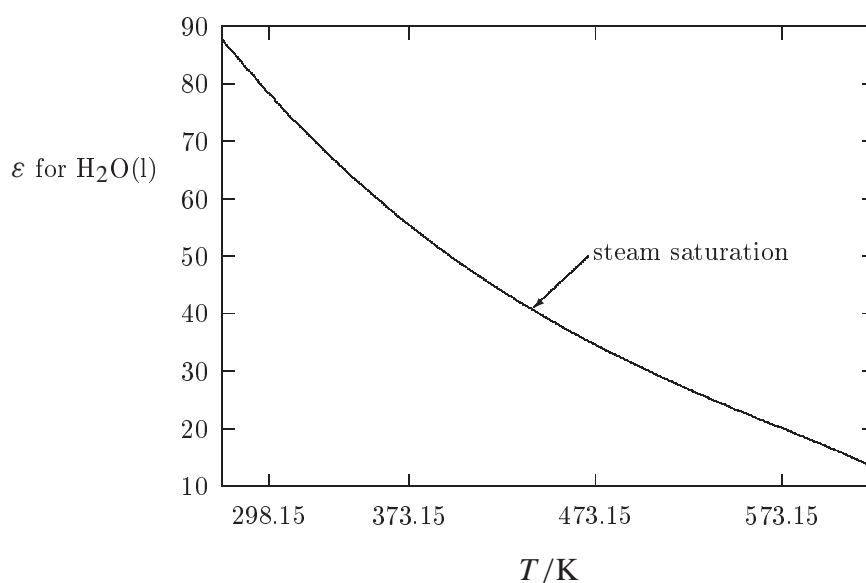
t (°C)	T (K)	$\Delta T = T - T_0$ (K)	$T \ln(T/T_0)$ (K)	$\Delta T - T \ln(T/T_0)$ (K)
0.00	273.15	-25.0	-23.92	1.08
15.00	288.15	-10.0	-9.83	0.17
20.00	293.15	-5.0	-4.96	0.04
25.00	298.15	0.0	0.0	0.0
30.00	303.15	5.0	5.04	-0.04
35.00	308.15	10.0	10.17	-0.17
50.00	323.15	25.0	26.02	-1.02
100.00	373.15	75.0	83.73	-8.73
200.00	473.15	175.0	218.5	-43.5

term can be neglected as it is probably smaller than the error in the estimates of $\Delta_r S_m^\circ$. This amounts to the assumption that $\Delta_r C_{p,m}^\circ = 0$ and, thus, $\Delta_r H_m^\circ$ and $\Delta_r S_m^\circ$ each have the same values for the reaction at any two different temperatures (Eq. (19)). This may be a good approximation for small temperature ranges.

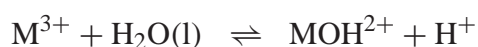
2.2.3 Isoelectric and isocoulombic reactions

For a reaction involving aqueous ionic species (but without oxidation/reduction), the enthalpy of reaction may be divided conceptually into two contributions: electrostatic and non-electrostatic. The main part of the enthalpy of reaction is due to the electrostatic interactions between the ionic species participating in the reaction, and between these ionic species and the solvent. Figure 2 shows that the dielectric constant of water decreases significantly with temperature, reaching values which at $T > 473$ K are similar to those of some organic solvents (acetone, ethanol, *etc.*) at room temperature. Because of this temperature dependence of the dielectric properties of water, electrostatic interactions will bring the largest contribution to the heat capacity of reaction [38GUR, 88SHO/HEL]. “Isoelectric”

Figure 2: Temperature dependence for the static dielectric constant of water calculated according to the equation of Bradley and Pitzer 79BRA/PIT at the standard pressure (1 bar) for $T < 373$ K and at the steam saturated pressure [69KEE/KEY, Eq. (17) in their Appendix], at $T \geq 373$ K.



reactions are defined as reactions in which **a)** the total amount of positive charges among the reactants equals the sum of positive charges among the products, and **b)** the same applies for negative charges among reactants and products. For example[¶]:



is an isoelectric reaction, while



is not.

In isoelectric reactions the electrostatic contributions to the temperature dependence will balance out to a large extent, and the heat capacities of reactions will be small and can be assumed constant with temperature. For these reactions, the “constant enthalpy of reaction”, Eq. (19), is generally a reliable approximation over a fairly large temperature interval (up to $T \leq 473$ K). Furthermore, the “constant heat capacity of reaction” approximation, Eq. (20), is generally reliable up to $T \leq 623$ K.

All ionic species participating in isoelectric reactions often (but not necessarily) have the same sign in the electrical charges [81BAE/MES], *i.e.*, either all charged species have positive or all have negative charges.

The term “isocoulombic” [80LIN, 85JAC/HEL] is used for isoelectric aqueous reactions in which the magnitude of the electrical charge of each individual ionic species also is balanced between reactants and products, for example



For this kind of reaction, $\Delta_r C_{p,m}^{\circ} \approx 0$ and thus Eq. (19) becomes an even better approximation of the experimental data. It should be noted that there is also an approximate cancellation of activity coefficients in the expression for the equilibrium constant of this reaction.

It is possible to estimate the solvation contribution to the absolute^{||} standard partial molar ionic heat capacity with a continuum electrostatic model. For example, using the Born equation [74HEL/KIR, their Eqs. (59), (61) and (66)], [88SHO/HEL, their Eq. (30)], [88TAN/HEL, their Appendix D],

$$\begin{aligned} C_{p,m,s}^{\circ,\text{abs}}(i, T) &= \frac{z_i^2}{r_{\text{eff},i}} \frac{N_A e^2}{8\pi \epsilon_0} T \frac{1}{\epsilon} \left[\left(\frac{\partial^2 \ln \epsilon}{\partial T^2} \right)_p - \left(\frac{\partial \ln \epsilon}{\partial T} \right)_p^2 \right] \\ &= \frac{z_i^2}{r_{\text{eff},i}} \frac{N_A e^2}{8\pi \epsilon_0} T X(T) \end{aligned} \quad (24)$$

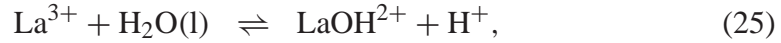
where the subscript “s” stands for solvation, and where $(N_A e^2 / (8\pi \epsilon_0)) = 6.947 \times 10^{-5} \text{ m} \cdot \text{J} \cdot \text{mol}^{-1}$; $X(T)$ is a temperature function of the solvent’s dielectric

[¶]“M”, “R” and “AN” are used as general abbreviations for metal, rare earth (lanthanide), and actinide respectively.

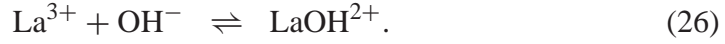
^{||}“Absolute” ionic standard partial molar thermodynamic values are defined in Section 4.1.2.1, p.62.

constant which at 298.15 K is equal to $-3.09 \times 10^{-7} \text{ K}^{-2}$ [88TAN/HEL, Table H-1], ; and r_{eff} (units m) is the effective electrostatic radius, which at $T < 423 \text{ K}$ is equal to the crystallographic radius to which is added an empirical valence-dependent constant (equal to $z_i \times 0.94 \times 10^{-10} \text{ m}$ for cations and zero for anions [88TAN/HEL, their Eq. (21)]).

The first hydrolysis step of the lanthanum(III) ion will be used as an example. The reaction may be written either as an isoelectric reaction,



or as a complexation reaction involving the hydroxide ion,



The solvation contribution, $\Delta_r C_{p,m,s}^\circ$ (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), to the heat capacity for the isoelectric Reaction (25) is, according to Eq. (24),

$$\begin{aligned} \Delta_r C_{p,m,s}^\circ(25, T_0) &= \frac{N_A e^2}{8\pi\epsilon_0} T_0 X(T_0) \left(\frac{4}{3.02 \times 10^{-10}} + \frac{1}{3.082 \times 10^{-10}} - \frac{9}{3.96 \times 10^{-10}} \right) \\ &= 39.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, \end{aligned}$$

where the crystallographic and effective radii for LaOH^{2+} were taken equal to that of La^{3+} ($r_i = 1.14 \times 10^{-10} \text{ m}$, given in [88SHO/HEL, Table 1]), and the effective radius for H^+ was taken from [88TAN/HEL, their Table 3]. The heat capacity change for Reaction (25) would then be estimated as

$$\begin{aligned} \Delta_r C_{p,m}^\circ(25, T_0) &\approx \Delta_r C_{p,m,s}^\circ(25, T_0) - C_{p,m}^\circ(\text{H}_2\text{O}, \text{l}, T_0) \\ &\approx -30.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}. \end{aligned}$$

For Reaction (26) the ionic radius for OH^- given in [88TAN/HEL, their Table 3], results in a solvent contribution of

$$\begin{aligned} \Delta_r C_{p,m,s}^\circ(26, T_0) &= \frac{N_A e^2}{8\pi\epsilon_0} T_0 X(T_0) \left(\frac{4}{3.02 \times 10^{-10}} - \frac{9}{3.96 \times 10^{-10}} - \frac{1}{1.40 \times 10^{-10}} \right) \\ &= 106.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, \end{aligned}$$

and the heat capacity change for Reaction (26) is therefore estimated to be $\approx 106.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. In this case the value of the estimated heat capacity change for Reaction (25) is about one third of that for Reaction (26). Similar results are obtained for the first hydrolysis step of a divalent cation like Fe^{2+} , or for a tetravalent cation like U^{4+} .

Although the examples given above only take into account solvation contributions to the heat capacity of reaction (furthermore estimated with an oversimplified

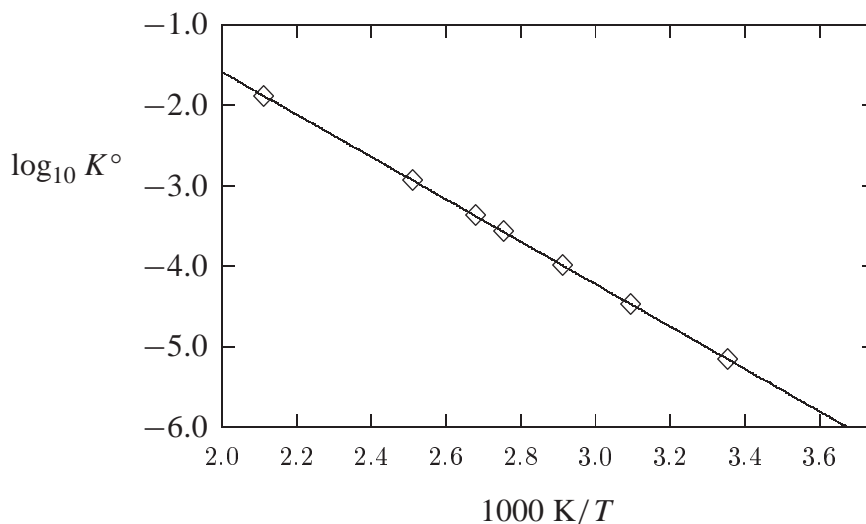
electrostatic model), they support the assertion that the approximation $\Delta_r C_{p,m}^\circ \approx \text{const.}$ is more appropriate for isoelectric reactions than for most other types of reactions. However, for isocoulombic reactions $\Delta_r C_{p,m}^\circ$ may be even closer to zero.

Many hydrolysis equilibria are isoelectric [88RUA]. As an example, the data reported by Nikolaeva [76NIK] (in the temperature range 298 to 473 K) for the reaction



are plotted in Figure 3. The values of $\log_{10} K^\circ$ are essentially a linear function of T^{-1} in this temperature interval, indicating that $\Delta_r C_{p,m}^\circ$ is small. Other examples with linear or nearly-linear regions for acid-base equilibria are given by Lindsay [80LIN], Cobble *et al.* [82COB/MUR, pp.4-11 to 4-15], and by Mesmer *et al.* [88MES/MAR, 91MES/PAL]. If a reaction of interest

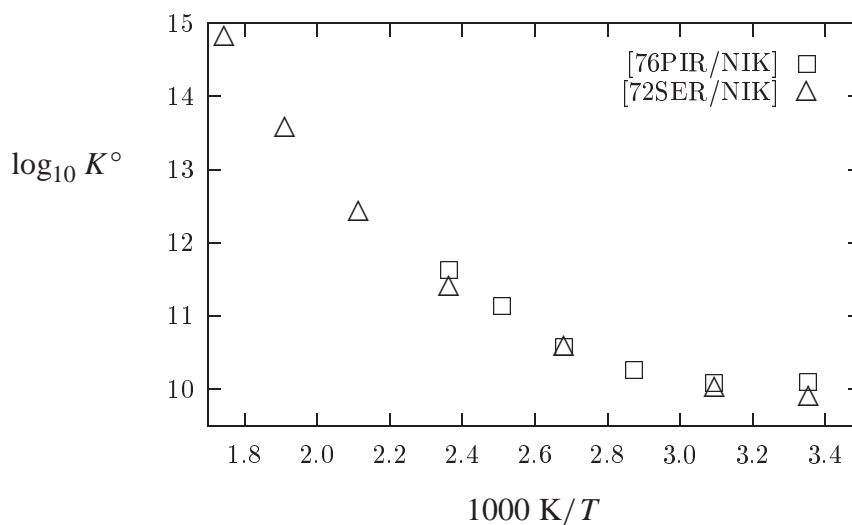
Figure 3: Equilibrium constants from [76NIK] for Reaction (27), $\text{H}_2\text{O}(\text{l}) + \text{UO}_2^{2+} \rightleftharpoons \text{H}^+ + \text{UO}_2\text{OH}^+$ (\diamond), compared with results from the “constant $\Delta_r H_m^\circ$ ” equation, Eq. (19), using $\log_{10} K^\circ(T_0) = -(5.157 \pm 0.005)$ and $\Delta_r H_m^\circ = (+50.4 \pm 0.1) \text{ kJ}\cdot\text{mol}^{-1}$ (solid line).



is neither isocoulombic nor isoelectric, it may be converted into an isocoulombic or isoelectric reaction by combination with an appropriate reaction for which accurate high-temperature equilibrium constants are known. This approach has been widely used, *e.g.*, [81BAE/MES, 83PHI/SIL, 85JAC/HEL,

88RUA, 89IZA/CHR, 89IZA/CHR2, 90OSC/GIL, 90OSC/IZA, 92IZA/OSC, 93CHE/GIL, 93CHE/GIL2, 93GIL/OSC]. The data by Piroshkov and Nikolaeva

Figure 4: Equilibrium constants from [72SER/NIK, 76PIR/NIK] for Reaction (28): $\text{CO}_3^{2-} + \text{UO}_2^{2+} \rightleftharpoons \text{UO}_2\text{CO}_3(\text{aq})$.

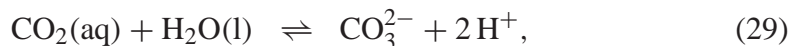


[76PIR/NIK] and by Sergeyeva *et al.* [72SER/NIK] in the temperature range 298 to 523 K for the equilibrium

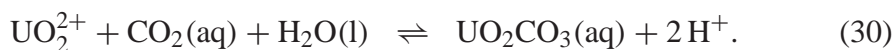


are used as an example.

It is readily seen in Figure 4 that Eq. (19) cannot be used directly to describe the experimental data since $\log_{10} K_{\text{eq}}$ is not linear in T^{-1} . However, it is possible to combine Eq. (28) with Eq. (29),



to obtain the isoelectric reaction



This example is used in two ways. Firstly, a discussion of the procedure to be taken to extrapolate high-temperature data to 298.15 K will be given, and secondly, a description will be presented of how Reactions (28) to (30) may be used together with Eq. (19) to calculate equilibrium constants at high temperatures.

Table 2: Experimental equilibrium constants^(a) for the ionisation of carbonic acid from Refs. [82PAT/SLO] and [84PAT/BUS].

$\log_{10} K^\circ$							
25°C (298.15 K)	50°C (323.15 K)	75°C (348.15 K)	100°C (373.15 K)	125°C (398.15 K)	150°C (423.15 K)	200°C (473.15 K)	250°C (523.15 K)
$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$:							
-10.337	-10.180	-10.117	-10.120	-10.171	-10.255	-10.491	-10.777
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3^- + \text{H}^+$:							
-6.349	-6.279	-6.305	-6.397	-6.539	-6.721	-7.189	-7.783
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CO}_3^{2-} + 2\text{H}^+$:							
-16.686	-16.459	-16.422	-16.517	-16.710	-16.976	-17.680	-18.560

^(a) Values at infinite dilution as extrapolated by the authors.

2.2.3.1 Correlation of high-temperature equilibrium constants

In order to make a temperature extrapolation of the $\log_{10} K^\circ(T)$ data like those available from Refs. [76PIR/NIK, 72SER/NIK] for Reaction (28), one adds the well-known $\log_{10} K^\circ(29, T)$ to $\log_{10} K^\circ(28, T)$. The values of $\log_{10} K^\circ(29, T)$ may be obtained from Table 5 in Ref. [82PAT/SLO] and Table IV of Ref. [84PAT/BUS], cf. Table 2. This converts the reaction to an isoelectric form.

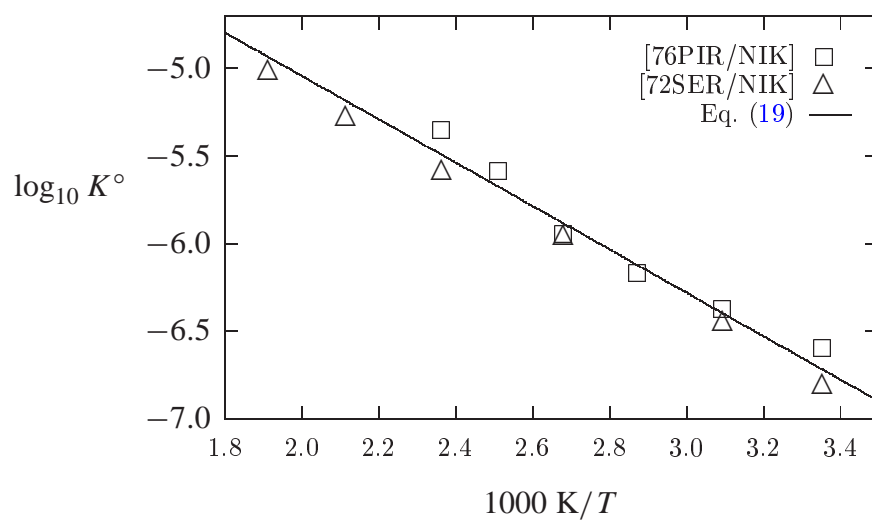
The values of the last row of Table 2 are added to the $\log_{10} K^\circ(T)$ for Reaction (28) reported in Refs. [72SER/NIK, 76PIR/NIK]. The resulting values are plotted in Figure 5. It can be seen that the isoelectric approach ($\Delta_r C_{p,m}^\circ \approx 0$) can be used successfully to describe the experimental data using Eq. (19), with $\log_{10} K^\circ(T_0) = -(6.72 \pm 0.11)$, and $\Delta_r H_m^\circ = (23.7 \pm 2.7) \text{ kJ}\cdot\text{mol}^{-1}$.

For data of higher quality, over larger temperature intervals, the ‘‘constant heat capacity of reaction’’ approximation, Eq. (20), should be used instead to obtain more reliable thermodynamic values at the reference temperature.

2.2.3.2 Extrapolation of 298.15 K data to higher temperatures

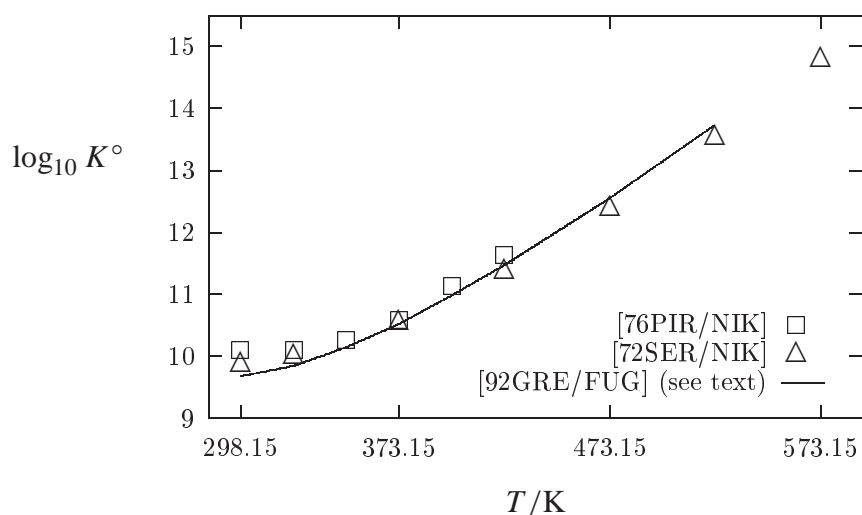
The following selected values for Reaction (28) are reported in Table III.2 of [92GRE/FUG]: $\log_{10} K^\circ(28, 298.15 \text{ K}) = (9.68 \pm 0.04)$, $\Delta_r H_m^\circ(28, 298.15 \text{ K}) = (5 \pm 2) \text{ kJ}\cdot\text{mol}^{-1}$. From the data for auxiliary compounds, the following res-

Figure 5: Equilibrium constants for Reaction (30): $\text{UO}_2^{2+} + \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{UO}_2\text{CO}_3(\text{aq}) + 2\text{H}^+$ (obtained by combining results from Refs. [76PIR/NIK, 72SER/NIK] for Reaction (28) with the values in the last row of Table 2). The line represents a least squares fit to the “constant $\Delta_r H_m^\circ$ ” equation, Eq. (19).



ults are obtained for Reaction (29) at 298.15 K: $\log_{10} K^\circ(29, 298.15 \text{ K}) = -(16.68 \pm 0.03)$ and $\Delta_r H_m^\circ(29, 298.15 \text{ K}) = (23.86 \pm 0.26) \text{ kJ}\cdot\text{mol}^{-1}$. Therefore, the following values are found: $\log_{10} K^\circ(30, 298.15 \text{ K}) = -(7.00 \pm 0.05)$ and $\Delta_r H_m^\circ(30, 298.15 \text{ K}) = (28.9 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$. Eq. (19) is now used to extrapolate the equilibrium constant of Reaction (30) to higher temperatures. Once this is done, it is possible to obtain the equilibrium constants of Reaction (28) at higher temperatures by subtracting the values for Reaction (29) at the same temperature (*cf.* Table 2). The results are shown in Figure 6, compared with the available literature data for Reaction (28). The practical importance of this

Figure 6: Equilibrium constants for the reaction $\text{CO}_3^{2-} + \text{UO}_2^{2+} \rightleftharpoons \text{UO}_2\text{CO}_3(\text{aq})$ from Refs. [72SER/NIK, 76PIR/NIK] compared with values obtained with the isoelectric procedure described in the text.



method is the fact that the approximation $\Delta_r C_{p,m}^\circ(30, 298.15 \text{ K}) = 0$ can be used. The values of the individual standard partial molar heat capacities of the reacting species are thus not required. For neutral complexes or molecular solutes this is very important because the available methods to estimate their standard partial molar heat capacities are less well developed than for electrolytes.

However, if a value of $\Delta_r C_{p,m}^\circ(298.15 \text{ K})$ is available, more accurate predictions of equilibrium constants at higher temperatures are obtained by using the “constant heat capacity of reaction” approximation, Eq. (20). The assumption $\Delta_r C_{p,m}^\circ(298.15 \text{ K}) = 0$ should only be used if heat capacities cannot be estimated.

The isoelectric method is, however, limited to reactions that are either isoelec-

tric in themselves, or which can be converted to such reactions. For reactions including species with electrical charges greater than ± 2 this is certainly a problem, because it is less probable that literature data can be found for an additional reaction which may be combined to obtain an isoelectric reaction (in the same way as Reaction (29) was used above).

2.3 Calculation of the enthalpy of solution from temperature dependence of solubility

Consider the dissolution of a hydrated salt to form a saturated solution,



for which the thermodynamic solubility product is given by:

$$K_s^\circ(T) = \nu_+^{\nu_+} \nu_-^{\nu_-} m_s^\nu \gamma_\pm^\nu a_w^x.$$

Here a_w is the activity of water in a saturated solution; γ_\pm the mean molal activity coefficient of the solute for a saturated solution; $\nu = \nu_+ + \nu_-$; z_+ and z_- the charges on the cation and anion, respectively; and m_s is the molality of the saturated solution.

The starting point for our calculations in the differential form of the van't Hoff equation (*cf.* Section 2.2.1, footnote on p.12):

$$\frac{d \ln K_s^\circ(T)}{dT} = \frac{\Delta_{\text{sol}}H_m^\circ}{RT^2},$$

where $\Delta_{\text{sol}}H_m^\circ$ is the enthalpy change that occurs when one mole of the hydrated solid is dissolved to form an infinitely dilute solution. Taking this derivative gives

$$\frac{d \ln K_s^\circ}{dT} = \nu \frac{d \ln m_s}{dT} + \nu \frac{d \ln \gamma_\pm}{dT} + x \frac{d \ln a_w}{dT},$$

where these derivatives are constrained to fall along the saturated solution molality curve at a constant pressure greater than or equal to the saturation vapour pressure of the saturated solution at the highest temperature considered. (At temperatures below about 500 K, the differences between values of these derivatives taken at constant pressure and those taken at the saturation vapour pressure of the solution will be insignificant compared to experimental error).

Since γ_\pm and a_w are being constrained to fall along the saturated solution molality curve, they are functions of both saturation molality and of temperature. Thus,

$$\frac{d \ln \gamma_\pm}{dT} = \left(\frac{\partial \ln \gamma_\pm}{\partial T} \right)_{m_s, p} + \left(\frac{\partial \ln \gamma_\pm}{\partial m_s} \right)_{T, p} \left(\frac{dm_s}{dT} \right)$$

and:

$$\frac{d \ln a_w}{dT} = \left(\frac{\partial \ln a_w}{\partial T} \right)_{m_s, p} + \left(\frac{\partial \ln a_w}{\partial m_s} \right)_{T, p} \left(\frac{dm_s}{dT} \right).$$

Combining the last four equations, and using the relationship

$$\frac{d \ln m_s}{dT} = \left(\frac{dm_s}{dT} \right) \left(\frac{1}{m_s} \right)$$

then gives:

$$\begin{aligned} \Delta_{\text{sol}}H_m^\circ &= RT^2 \frac{d \ln K_s^\circ(T)}{dT} \\ &= RT^2 \left\{ \left[\frac{v}{m_s} + v \left(\frac{\partial \ln \gamma_{\pm}}{\partial m_s} \right)_{T, p} + x \left(\frac{\partial \ln a_w}{\partial m_s} \right)_{T, p} \right] \left(\frac{dm_s}{dT} \right) \right. \\ &\quad \left. + \left[v \left(\frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{m_s, p} + x \left(\frac{\partial \ln a_w}{\partial T} \right)_{m_s, p} \right] \right\}. \end{aligned}$$

The last term can be recast using well known expressions for these temperature derivatives:

$$v \left(\frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{m_s, p} + x \left(\frac{\partial \ln a_w}{\partial T} \right)_{m_s, p} = -\frac{1}{RT^2} (vL_2 + xL_1)$$

where L_2 and L_1 are the relative partial molar enthalpies of solute and solvent in the saturated solution, respectively, relative to infinite dilution **. The enthalpy of

** L_1 and L_2 denote the excess (relative to the standard state of infinite dilution) or relative partial molar enthalpy of the solvent (water) and the solute, respectively. The total enthalpy of a solution is expressed as a function of its composition and the partial molar enthalpies of its constituents:

$$H(\text{solution}) = n_1H_1 + n_2H_2$$

where n_i and H_i are the amount and the partial molar enthalpy of a substance. The *excess* enthalpy is then

$$H(\text{solution}) - n_1H_1^\circ - n_2H_2^\circ = L = n_1L_1 + n_2L_2$$

and $L_i = H_i - H_i^\circ$. These relative partial molar enthalpies are related to the activities of the solute and solvent as follows:

$$L_1 = -RT^2 \left(\frac{\partial \ln a_w}{\partial T} \right)_{p, m}, \quad \text{and} \quad L_2 = -vRT^2 \left(\frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{p, m}.$$

Values of L_i are usually calculated from experimental measurements of enthalpies of either solution or dilution.

solution to form a saturated solution is related to the enthalpy of solution to form an infinitely dilute solution by:

$$\Delta_{\text{sol}}H_m(\text{sat}) = \Delta_{\text{sol}}H_m^\circ + (\nu L_2 + x L_1).$$

One additional simplification can be made. The Gibbs-Duhem equation for a binary solution can be cast into the form:

$$\left(\frac{\partial \ln a_w}{\partial m_s}\right)_{T,p} = -\left(\frac{m_s}{n_w}\right)\left(\frac{\partial \ln a_2}{\partial m_s}\right)_{T,p}$$

where a_2 is the activity of the solute in the saturated solution, and n_w is the number of moles of water in 1 kg of water. Taking this derivative yields:

$$\left(\frac{\partial \ln a_2}{\partial m_s}\right)_{T,p} = \nu \left(\frac{\partial \ln \gamma_{\pm}}{\partial m_s}\right)_{T,p} + \frac{\nu}{m_s}.$$

The final expression for the enthalpy of solution then becomes:

$$\Delta_{\text{sol}}H_m(\text{sat}) = \nu RT^2 \left(1 - \frac{x m_s}{n_w}\right) \left[\frac{1}{m_s} + \left(\frac{\partial \ln \gamma_{\pm}}{\partial m_s}\right)_{T,p} \right] \left(\frac{dm_s}{dT}\right).$$

By setting $\nu = 1$, this equation also becomes valid for a non-electrolyte, and by setting $x = 0$, for a solid anhydrous electrolyte or non-electrolyte.

We note that the temperature dependence of solubilities (*i.e.*, of m_s) gives $\Delta_{\text{sol}}H_m$ for the formation of a saturated solution and not for an infinitely dilute solution as is generally (and erroneously) assumed. These two types of solution enthalpies will differ very little for sparingly soluble solutes, but their differences can be substantial for more soluble electrolytes. Some numerical calculations of $\Delta_{\text{sol}}H_m(\text{sat})$ were given by Williamson [44WIL] and Brice [83BRI]. Williamson also gave the first systematic presentation of solubility equations for hydrated and non-hydrated electrolytes and non-electrolytes.

2.4 Alternative heat capacity expressions for aqueous species

As an alternative to the general heat capacity temperature function given in Eq. (9), Clarke and Glew [66CLA/GLE] proposed a Taylor series expansion for the temperature dependence of the heat capacity. This approach was used subsequently by Phillips and Silvester [84PHI/SIL]. Clarke and Glew's equations do not offer any special advantage over Eq. (9), and the Taylor series expansion requires more parameters than models described below, which are based either on the density of the solvent, or on the Born equation. However, as pointed out by Clarke and

Glew, it is not justifiable to set lower order temperature derivatives equal to zero in these expansions while retaining higher order ones (*e.g.*, do not set $c = 0$ in Eq. (9) if the jT^3 term is retained).

Electrostatic models can be used to predict electrolyte behaviour at high temperatures with a lesser number of parameters. The model that is perhaps most widely used among geochemists is that of Helgeson and co-workers (*e.g.*, [88SHO/HEL]). Some of their equations are presented below.

2.4.1 DQUANT Equation

The DQUANT equation was proposed by Helgeson [67HEL] and it is of historical interest because it has been used by several researchers, for example by Haas and Fisher [76HAA/FIS], Helgeson's group [85JAC/HEL], Smith, Popp and Norman [86SMI/POP], *etc.*, although the authors of Refs. [76HAA/FIS, 86SMI/POP] used additional terms for the non-electrostatic contributions to the heat capacity. Furthermore, the EQ3/6 geochemical computer program package [88JAC/WOL] uses the DQUANT equation to calculate high-temperature equilibrium constants of dissociation for neutral inorganic complexes.

The name of "DQUANT" appears to have its origin in the name of a computer program which was used earlier at the Laboratory of Theoretical Geochemistry, University of California, Berkeley.

Assuming that the temperature dependence of the heat capacity change of a dissociation reaction is proportional to the temperature dependence of the electrostatic contribution, Helgeson [67HEL, his Eqs. (21) and (22)] obtained the expression

$$\log_{10} K^\circ(T) = \frac{\Delta_r S_m^\circ(T_0)}{\ln(10)RT} \left\{ T_0 - \frac{\theta}{\omega} \left[1 - \exp \left(\exp(b + aT) - c + \frac{T - T_0}{\theta} \right) \right] \right\} - \frac{\Delta_r H_m^\circ(T_0)}{\ln(10)RT}, \quad (31)$$

which is consistent with the following expressions for the heat capacity change of the dissociation reaction and the dielectric constant (relative permittivity) for water:

$$\Delta_r C_{p,m}^\circ(T) = \frac{T \Delta_r S_m^\circ(T_0)}{\omega\theta} \exp \left(\exp(b + aT) - c + \frac{T - T_0}{\theta} \right) \times \left[[1 + \phi \exp(b + aT)]^2 + \phi^2 \exp(b + aT) \right] \quad (32)$$

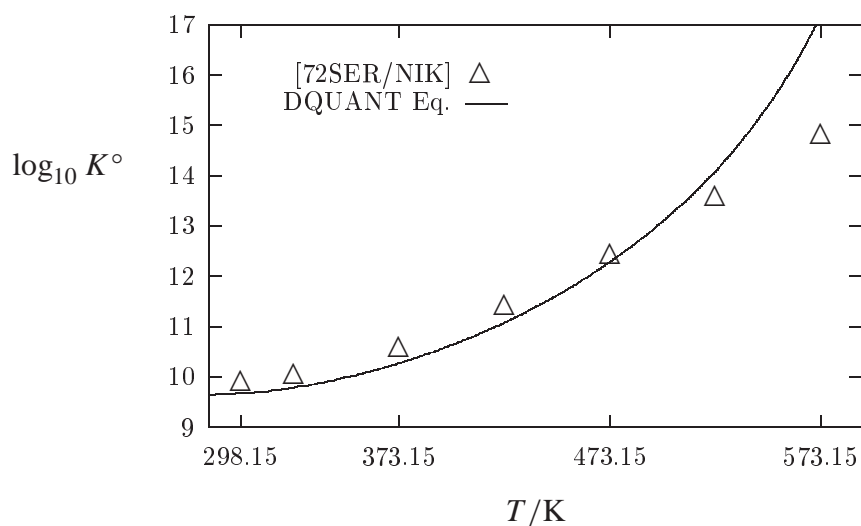
$$\varepsilon(T) = \varepsilon_0 \exp \left(- \exp(b + aT) - \frac{T}{\theta} \right),$$

where $\varepsilon_0 = 305.7$, $b = -12.741$, $a = 0.01875 \text{ K}^{-1}$, $\theta = 219 \text{ K}$, $c = \exp(b + aT_0) = 7.84 \times 10^{-4}$, $\omega = (1 + ac\theta) = 1.00322$ and $\phi = a\theta = 4.106$.

It should be noted that Eqs. (31) and (32) have been superseded by subsequent models of Helgeson and co-workers, described in next Section, which generally yield more reliable model fits.

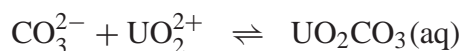
Helgeson [67HEL, 69HEL] claimed agreement of Eq. (31) with experimental values for most reactions in the temperature range 273 to 423 or to 523 K, with the upper temperature limit depending on the reaction. The errors at 473 K were of the order of 1 to 9 % of $\log_{10} K^\circ(T)$ [67HEL, p.3131] but increased with temperature. Note, however, that for some dissociation reactions whose $\Delta_r H_m^\circ(T_0)$ and $\Delta_r S_m^\circ(T_0)$, and/or the heat capacity of dissociation are positive, the use of Eqs. (31) and (32) is not recommended [67HEL, pp. 3131–3132]. Eq. (31) is of interest

Figure 7: Comparison of equilibrium constants from [72SER/NIK] for Reaction (28), $\text{CO}_3^{2-} + \text{UO}_2^{2+} \rightleftharpoons \text{UO}_2\text{CO}_3(\text{aq})$, with calculated values using the DQUANT equation, Eq. (31), and the following selected reaction values [92GRE/FUG]: $\log_{10} K(T_0) = (9.68 \pm 0.04)$, and $\Delta_r S_m^\circ(T_0) = (202.1 \pm 6.8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.



because it does not require any knowledge of the heat capacity change of a reaction. For neutral inorganic species in aqueous solution, except for a few simple dissolved gases, there are no known methods to estimate the standard molar heat capacities. Therefore, Eq. (31) is of special interest to estimate high-temperature equilibrium constants for dissociation of neutral species.

As an example, Figure 7 compares experimental results [72SER/NIK] for Reaction (28)



with calculated values of $\log_{10} K^\circ(T)$ using Eq. (31) and selected reaction parameters from [92GRE/FUG].

2.4.2 The revised Helgeson–Kirkham–Flowers model

The electrostatic heat capacity model used by Helgeson *et al.*, which was briefly described in Section 2.2.3, has evolved into a set of equations of state for the standard partial molar properties of aqueous species [88TAN/HEL, 88SHO/HEL, 89SHO/HEL, 89SHO/HEL2]. These equations of state, which constitute the “Revised Helgeson–Kirkham–Flowers” model (“Revised HKF” model), allow predictions to be made to 1273 K and to 5 kbar. Neither this equation nor the DQUANT equation are expected to be reliable near the critical “point” of water, 641.7 K and 220.7 bar [83LEV/KAM, 84HAA/GAL, 89SAU/WAG].

According to this model, the standard partial molar heat capacity for an aqueous ion i is given by

$$C_{p,m}^\circ(i) = c_1 + \frac{c_2}{(T - 228)^2} - \left(\frac{2T}{(T - 228)^3} \right) \left[a_3(p - p^\circ) + a_4 \ln \left(\frac{2600 + p}{2600 + p^\circ} \right) \right] \\ + \omega T X + 2TY \left(\frac{\partial \omega}{\partial T} \right)_p - T \left(\frac{1}{\varepsilon} - 1 \right) \left(\frac{\partial^2 \omega}{\partial T^2} \right)_p,$$

where $p^\circ = 1$ bar is the standard state pressure, the pressure p has units of bar, ε is the dielectric constant (relative permittivity) of $\text{H}_2\text{O}(\text{l})$ which is temperature and pressure dependent (see for example Figure 2, or [74HEL/KIR, Table 39]), c_1 , c_2 , a_3 and a_4 are temperature and pressure independent parameters and are specific to each ion i , and X , Y and ω are temperature and pressure dependent functions (*cf.* our Eq. (24) for X , Eq. (34) below for ω , and Ref. [88SHO/HEL, Eq. (28)], for Y), which were tabulated by Tanger and Helgeson [88TAN/HEL]. Equations for the partial derivatives of ω with regard to temperature and pressure are also given there [88TAN/HEL, Appendix B].

Pressure effects will be neglected here for the following reasons. The saturated pressure of steam at 573 K is 85.8 bar [74HEL/KIR, Table 38]. The effect that this pressure will have on equilibrium constants will depend on the reactants and products involved and on the partial molar volume change of reaction. For example, the effect that a pressure of 85.8 bar has on the chemical potential of $\text{H}_2\text{O}(\text{l})$ is about $0.15 \text{ kJ}\cdot\text{mol}^{-1}$ [81STU/MOR], which at 573 K would change an equilibrium constant involving one water molecule by $0.014 \log_{10}$ units. This

may be accounted for if the “apparent” Gibbs energy of H₂O(l) as calculated from Table III-5 of Ref. [89COX/WAG] (see also Eqs. (12) and (16)) is used in the calculations of the temperature effects on equilibrium constants. In general, the pressure effect on an equilibrium constant may be estimated assuming that the molar volume of reaction is independent of pressure [69HEL, p.742], [81STU/MOR, pp.73–78]:

$$\log_{10} K^\circ(p) = \log_{10} K^\circ(p_0) - \frac{\Delta_r V_m^\circ(p-1)}{RT 10^{-2} \ln(10)}.$$

For a partial molar volume change of reaction of 0.1 dm³ · mol⁻¹, this equation estimates the pressure effect, at 573 K and 85.8 bar, as -0.077 on $\log_{10} K^\circ$.

Since the major temperature range of interest for the modelling of aqueous systems is 273 to 573 K, and in order to simplify the equations of the “Revised HKF” model, pressure effects on temperature corrections will be neglected here. The reader interested in even higher temperatures (and therefore higher pressures) is referred to the original publications [88TAN/HEL, 88SHO/HEL, 89SHO/HEL, 89SHO/HEL2, 97SHO/SAS, 97SVE/SHO].

By neglecting the pressure effects, the following equation is obtained. The apparent standard partial molar Gibbs energy of an aqueous ion i , *cf.* Eqs. (12) and (17), is given by the expression

$$\begin{aligned} \Delta_a G_m^\circ(i, T) = & \Delta_f G_m^\circ(i, T_0) - S_m^\circ(i, T_0)(T - T_0) - c_1 \left[T_0 - T + T \ln \left(\frac{T}{T_0} \right) \right] \\ & - c_2 \left[\left(\frac{1}{T - 228} - \frac{1}{T_0 - 228} \right) \left(\frac{228 - T}{228} \right) \right. \\ & \quad \left. - \frac{T}{(228)^2} \ln \left\{ \frac{T_0(T - 228)}{T(T_0 - 228)} \right\} \right] \\ & + \omega(T) \left(\frac{1}{\varepsilon} - 1 \right) - \omega(T_0) \left(\frac{1}{\varepsilon_0} - 1 \right) \\ & + (T - T_0)\omega(T_0)Y(T_0), \end{aligned} \quad (33)$$

where c_1 and c_2 are the non-solvation parameters specific to each aqueous ion; the dielectric constant (relative permittivity) of H₂O(l), ε , is temperature and pressure dependent [74HEL/KIR, Table 39] (at 298.15 K and 1 bar $\varepsilon_0 = 78.4$, *cf.* Table 4); and $Y(T_0)$ has the value $-5.81 \times 10^{-5} \text{ K}^{-1}$ [88TAN/HEL, Table H-4].

The temperature (and pressure) dependent function $\omega(T)$ is defined for ionic aqueous species as [88TAN/HEL, Eq. (B-9)]:

$$\omega(i, T) = \frac{N_A e^2}{8\pi \varepsilon_0} \left(\frac{z_i^2}{r_i + |z_i|(k_z + g(T))} - \frac{z_i}{3.082 \times 10^{-10} + g(T)} \right), \quad (34)$$

where $(N_A e^2 / (8\pi \epsilon_0))$ is equal to $6.9466 \times 10^{-5} \text{ m} \cdot \text{J} \cdot \text{mol}^{-1}$, r_i is the crystallographic ionic radius, k_z is a charge dependent constant (equal to zero for anions and $0.94 \times 10^{-10} \text{ m}$ for cations), and $g(T)$ is a non salt-specific function which accounts for the dependence of the effective electrostatic ionic radius on temperature and pressure (at the steam saturated pressure, g is zero for $T < 448 \text{ K}$ [88TAN/HEL, Table H-8], [92SHO/OEL, Table 5]). As Eq. (34) shows, the Revised HKF model uses an effective radius for the electrostatic interactions between the dissolved species and the solvent:

$$r_{\text{eff},i}(T) = r_i + |z_i|(k_z + g(T)). \quad (35)$$

For neutral species, the model function ω , *cf.* Eq. (34), is assumed to be independent of temperature and pressure, and thus becomes a model parameter. Correlations at 298.15 K with standard partial molar entropies [89SHO/HEL2, their Eqs. (44) and (45)] give for volatile neutral non-polar aqueous species (noble and diatomic elemental gases)

$$\omega(i) = -1514.4 S_m^\circ(i, T_0),$$

and for neutral polar aqueous species ($\text{H}_2\text{S}(\text{aq})$, $\text{CO}_2(\text{aq})$, $\text{SiO}_2(\text{aq})$, *etc.*)

$$\omega(i) = 1.422 \times 10^5 - 1514.4 S_m^\circ(i, T_0), \quad (36)$$

where ω is in units of $\text{J} \cdot \text{mol}^{-1}$.

The c_1 and c_2 parameters for Eq. (33) of this model are temperature and pressure independent, and are correlated at 298.15 K with the standard partial molar ionic heat capacity as follows [88SHO/HEL, Eqs. (29), (31), (35) and (89)], [88TAN/HEL, p.36, Eqs. (19), (24), (28c), and (48)]:

$$\begin{aligned} c_2 &= -1.26968 \times 10^5 + 2037 C_{p,m}^\circ(i, T_0) \\ c_1 &= C_{p,m}^\circ(i, T_0) - c_2 \left(\frac{1}{T_0 - 228} \right)^2 + 9.213 \times 10^{-5} \omega(i, T_0), \end{aligned}$$

where c_1 and c_2 are in units of $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and $\text{J} \cdot \text{K} \cdot \text{mol}^{-1}$ respectively.

The crystallographic ionic radius, r_i , in Eq. (34) is correlated to the standard partial molar ionic entropy [88SHO/HEL, Eq. (58)],

$$r_i = \frac{-458.8 \times 10^{-10} z_i^2}{S_m^\circ(i, T_0) - a_z} - |z_i| k_z, \quad (37)$$

where a_z is a charge dependent regression constant (equal to 301, 590 and $883 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for mono-, di- and trivalent ions, respectively, and $a_z = 299.2|z_i|$ for cations or anions with $z_i > 3$ [88SHO/HEL, Eq. (56)]).

If the chemical reaction only involves aqueous species, the calculations can be done with Eqs. (16) and (33). If the chemical reaction includes phases for which heat capacity functions (of type Eq. (9)) are available (*e.g.*, solid phases or H₂O(l)), it is convenient to use Eq. (33) for aqueous species, and Eqs. (13) and (14) for the solid phases. As mentioned earlier, the integrals in Eqs. (13) and (14) may have expressions like Eqs. (10) and (11), except that one must disregard the delta signs on the right hand side of Eqs. (10) and (11). For water, the apparent Gibbs energy should be calculated from values given in the CODATA tables [89COX/WAG].

In order to avoid computational errors, it is advantageous to use a computer program to do the calculations described here. The computer program SUPCRT is available from Helgeson's laboratory at Berkeley [92JOH/OEL] and on the GEOPIG home page (<http://zonvark.wustl.edu/geopig>). That program also includes a mineral and aqueous species data base.

As it stands, Eq. (33) contains five parameters for each aqueous species (standard partial molar ionic entropy and standard Gibbs energy of formation, as well as c_1 , c_2 , and r_i). When Eqs. (36) and (37) are included in the model, only three parameters remain in Eq. (33): the standard partial molar entropy, the standard partial molar Gibbs energy of formation, and the standard partial molar heat capacity.^{††}

Tremaine, Sway and Barbero [86TRE/SWA] and Apps and Neil [90APP/NEI] have reanalysed some experimental data using the Helgeson-Kirkham-Flowers equations.

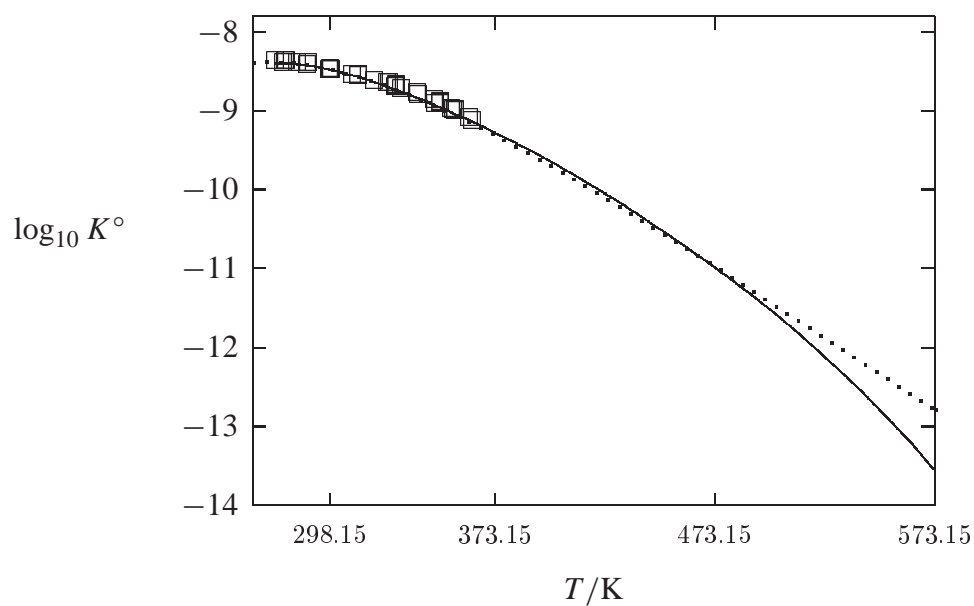
As an example of the application of Eq. (33) to predict high-temperature equilibrium constants, the calcite dissolution reaction is used:



The data for the aqueous ions are taken from CODATA [89COX/WAG] except for the standard partial molar ionic heat capacities which are not given in the CODATA publication, and are taken instead from Ref. [76DES/VIS]. For calcite, the value for the entropy and the heat capacity function of CODATA [87GAR/PAR] are used, whereas the standard Gibbs energy of formation is adjusted to $-1129.1 \text{ kJ}\cdot\text{mol}^{-1}$ in order to force the logarithm of the equilibrium constant at 298.15 K to be $\log_{10} K^\circ(38) = -8.480$ as recommended by Plummer and Busenberg [82PLU/BUS]. The predicted temperature dependence of the equilibrium constant for calcite dissolution is shown in Figure 8, together with experimental values from Ref. [82PLU/BUS]. Large differences in calculated values are in general obtained at $T \geq 423 \text{ K}$ between the "constant $\Delta_r C_{p,m}^\circ$ "

^{††}Note added in press: Sverjensky, Shock and Helgeson [97SVE/SHO] have recently published several examples of this technique. Furthermore they present several correlation strategies to estimate thermodynamic properties of aqueous complexes (mostly inorganic).

Figure 8: Comparison of experimental equilibrium constants for calcite dissolution [82PLU/BUS], Reaction (38), with those predicted with the simplified “Revised Helgeson-Kirkham-Flowers model” described in the text (continuous line). The predictions with the “constant $\Delta_r C_{p,m}^\circ$ ” equation, Eq. (20), using $\Delta_r S_m^\circ = -198 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $\Delta_r C_{p,m}^\circ = -377 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ are shown as a dotted line.



equation, Eq. (20), and the simplified revised HKF model, Eq. (33) and Eqs. (36) to (37).

The fitting capabilities of the revised Helgeson, Kirkham and Flowers model are very high, because of the large number of parameters for each dissolved species. With the simplification introduced by Eqs. (36) and (37), the number of parameters is reduced, but still one must avoid overfitting experimental data. Only good quality data in a broad temperature range should be used to determine the model parameters. This is due to the fact that ionic heat capacities generally show gentle maxima at about 325 to 375 K, and have a steep decrease as the temperature approaches the critical temperature of water (~ 647.1 K) [83LEV/KAM, 84HAA/GAL, 89SAU/WAG]. The heat capacities for ions are usually not determined reliably by a least-squares representation of equilibrium constants in the range 273 to 423 K.

As an example of the uncertainties that might be found in fitting S_m° or $C_{p,m}^\circ$ to experimental values of equilibrium constants, the data on the solubility of zincite are used. The equilibrium constants for the reaction



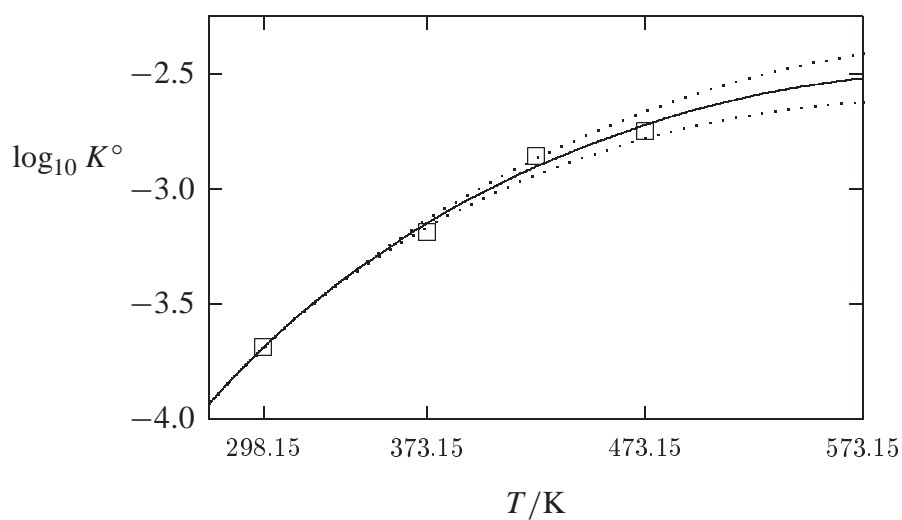
are taken from Khodakovskiy and Yelkin [75KHO/YEL, their Table 3]. For zincite, the standard entropy and the heat capacity function are taken from Kubaschewski *et al.* [93KUB/ALC] and the standard Gibbs energy of formation from the US NBS tables [82WAG/EVA]. For ZnOH^+ , the standard ionic partial molar Gibbs energy is set to the value required for achieving an equilibrium constant at 298.15 K of $\log_{10} K^\circ = -3.69$, which is the value recommended in Ref. [75KHO/YEL]. A least-squares fit to the simplified ‘‘Revised HKF model’’ on the four experimental values of $\log_{10} K^\circ$ (39) yields $S_m^\circ(\text{ZnOH}^+, \text{aq}, T_0) = (24 \pm 17) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $C_{p,m}^\circ(\text{ZnOH}^+, \text{aq}, T_0) = (44 \pm 102) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and is shown in Figure 9. The large uncertainties are due to the correlation between $S_m^\circ(T_0)$ and $C_{p,m}^\circ(T_0)$. A more precise value of $C_{p,m}^\circ(T_0)$ is obtained by a least-squares fit if the value of $S_m^\circ(\text{ZnOH}^+, \text{aq}, T_0)$ is fixed to $24 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (the value obtained above), namely $C_{p,m}^\circ(\text{ZnOH}^+, \text{aq}, T_0) = (41 \pm 16) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Figure 9 shows that data at higher temperatures are needed in order to constrain the least-squares fits sufficiently to obtain unambiguous thermodynamic parameters for ZnOH^+ .

An example where experimental data up to 573 K are available [82PAT/SLO] is the reaction



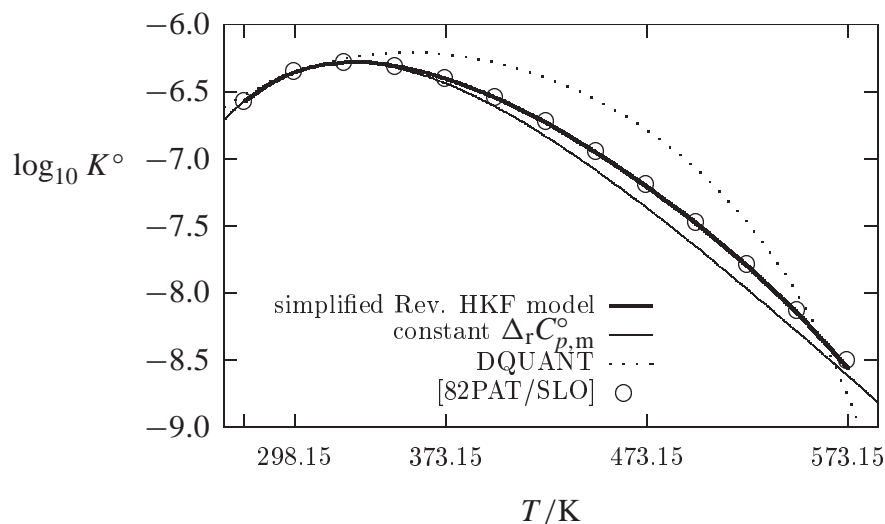
The thermodynamic data are taken from CODATA [89COX/WAG], except for the standard partial molar heat capacities of the bicarbonate ion, which is taken

Figure 9: Comparison of experimental equilibrium constants [75KHO/YEL] for Reaction (39), $\text{ZnO}(\text{cr}) + \text{H}^+ \rightleftharpoons \text{ZnOH}^+$, with a least-squares fit to the simplified “Revised HKF model”. The dotted lines reflect the effect of an uncertainty of $\pm 16 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ in $C_{p,m}^\circ(\text{ZnOH}^+, \text{aq}, T_0)$.



from Ref. [76DES/VIS], and of $\text{CO}_2(\text{aq})$, which is fitted by least-squares to the experimental equilibrium constants of [82PAT/SLO]. The calculation yields $C_{p,m}^\circ(\text{CO}_2, \text{aq}, T_0) = (208.5 \pm 2.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and the model results are shown in Figure 10. For comparison, results obtained with the DQUANT expression,

Figure 10: Comparison of experimental equilibrium constants for the hydrolysis of $\text{CO}_2(\text{aq})$ [82PAT/SLO], Reaction (40), with those obtained from fitting $C_{p,m}^\circ(\text{CO}_2, \text{aq}, T_0)$ with the simplified “Revised HKF model”. Results obtained using the DQUANT equation, Eq. (31), and the “constant $\Delta_r C_{p,m}^\circ$ ” equation, Eq. (20) (with $\Delta_r H_m^\circ(T_0) = 9.16 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_r S_m^\circ(T_0) = -90.91 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and $\Delta_r C_{p,m}^\circ = -334 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), are also displayed for comparison.



Eq. (31), and the “constant $\Delta_r C_{p,m}^\circ$ ” Eq. (20), with a heat capacity of reaction of $-334 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, are also displayed. The approximation expressed by the DQUANT equation, Eq. (31), resulted in errors of up to ± 0.3 in $\log_{10} K^\circ(T)$.

A better fit of the data could be achieved by using the isocoulombic reaction:



and the “constant $\Delta_r C_{p,m}^\circ$ ” approximation, Eq. (20). Reaction (40) has been used for illustrative purposes only.

2.4.3 The Ryzhenko–Bryzgalin model

Ryzhenko and Bryzgalin [81RYZ, 82BRY/RAF, 91RYZ/BRY] and Bryzgalin [86BRY, 89BRY] describe the temperature dependence of mononuclear complex

formation reactions using a simple electrostatic model where the Gibbs energy of reaction $\Delta_r G_m^\circ(T, p)$ is described as a sum of two contributions (an idea first proposed in detail by Gurney [53GUR, Chapter 7]):

$$\Delta_r G_m^\circ(T, p) = \Delta_r G_{m,\text{nonel}}^\circ + \Delta_r G_{m,\text{electr}}^\circ(T, p) \quad (41)$$

where $\Delta_r G_{m,\text{nonel}}^\circ$ is a temperature and pressure independent non-electrostatic contribution to the Gibbs energy, and $\Delta_r G_{m,\text{electr}}^\circ(T, p)$ is a temperature and pressure dependent electrostatic contribution given by the following Coulomb-type equation:

$$\Delta_r G_{m,\text{electr}}^\circ(T, p) = -\frac{|Z_c Z_a|_{\text{eff}} N_A e^2}{r_{\text{eff}} 4\pi\epsilon_0} \frac{1}{\epsilon(T, p)} \quad (42)$$

where e is the elementary charge and N_A is the Avogadro constant ($N_A e^2 / (4\pi\epsilon_0) = 1.38935 \times 10^{-4} \text{ m} \cdot \text{J} \cdot \text{mol}^{-1}$); $\epsilon(T, p)$ is the relative permittivity of the solvent (in this case the dielectric constant of water); r_{eff} is an effective bond distance, which in most cases is approximately equal to the sum of radii of the central ion and ligand, and it is independent of the total number of ligands in the complex; $|Z_c Z_a|_{\text{eff}}$ is an ‘‘effective charge’’, which is a function of the formal charges of the anion and the cation (Z_a and Z_c , respectively), and of the number of ligands and geometry of the complex. The model can only be applied to monodentate ligands, but protonation equilibria for polybasic acids can be described by considering complexes where the central ion is the anion, and the ligands are protons [87RYZ/BRY].

Bryzgalin and Rafal’skiy [82BRY/RAF] give the following equation to calculate $|Z_c Z_a|_{\text{eff}}$ for a number of different coordination geometries:

$$|Z_c Z_a|_{\text{eff}} = |Z_c Z_a|L - QZ_a^2 + \frac{\alpha_a Z_c^2 L}{2r_{\text{eff}}^3} - \frac{(\alpha_a Z_c)^2 Q}{2r_{\text{eff}}^6} \quad (43)$$

where L is the total number of ligands in the mononuclear complex; Q is a stereochemical factor, $Q = (3L^2 - 5L + 2)/8$; and α_a is the polarisability of the ligand (*cf.* Table 3). The first term on the right hand side of Eq. (43) takes into account the attraction between the central ion and each of the ligands; the second term includes mutual repulsions between ligands; the third term deals with the attractive interactions between the central ion and the induced dipoles in the ligands; and the last term considers the mutual repulsion among the dipoles induced in the ligands [82BRY/RAF]. For 1:1 complexes $L = 1$, $Q = 0$, and the last term of Eq. (43) is modified so that the effective charge is instead given by [83BRY]:

$$|Z_c Z_a|_{\text{eff}} = |Z_c Z_a| + \frac{\alpha_a Z_c^2}{2r_{\text{eff}}^3} + \frac{\alpha_c Z_a^2}{2r_{\text{eff}}^3} \quad (44)$$

Table 3: Polarisabilities of ions in aqueous solutions from Ref. [66NIK, p.385], (also reported in [85RYZ/SHA, 87RYZ/BRY]). We note however that there are inconsistencies between the values listed in this table and the data found in Refs. [40RIC, 50SYR/DYA], apparently because the latter two references contain electronic ionic polarisabilities of ions either in vacuo or in crystal lattices.

Anion	$\alpha \times 10^{30}$ (m ³)	Cation	$\alpha \times 10^{30}$ (m ³)	Cation	$\alpha \times 10^{30}$ (m ³)
OH ⁻	2.04	H ⁺	-0.21	Zn ²⁺	0.24
F ⁻	1.03	Li ⁺	-0.13	Cd ²⁺	0.92
Cl ⁻	3.59	Na ⁺	0.08	Hg ²⁺	2.22
Br ⁻	5.02	K ⁺	0.90	Mn ²⁺	0.55
I ⁻	3.62	Rb ⁺	1.50	Mn ³⁺	0.0
CN ⁻	3.30	Cs ⁺	2.59	Mn ⁴⁺	0.0
NO ₃ ⁻	4.37	Mg ²⁺	-0.71	Fe ²⁺	0.48
HCOO ⁻	3.92	Ca ²⁺	0.28	Fe ³⁺	1.13
SiO ₄ ⁴⁻	5.30	Sr ²⁺	0.75	Co ²⁺	0.51
SO ₄ ²⁻	5.83	Ba ²⁺	1.73	Ni ²⁺	0.30
CO ₃ ²⁻	4.81	Pb ²⁺	3.48	Al ³⁺	-1.00
CrO ₄ ²⁻	10.62	Cu ²⁺	0.15	Y ³⁺	0.0
				La ³⁺	0.0

where α_c is the polarisability of the central ion (*cf.* Table 3).

Electrostatic models are based on incompressible spherical ions. The thermodynamic values obtained by such models require the conversion from the molar volume of the ideal gas to that of a solution at $1 \text{ mol} \cdot (\text{kg H}_2\text{O})^{-1}$. This correction is adsorbed by adjustable parameters in the Helgeson-Kirkham-Flowers model which is described in Section 2.4.2.

The Ryzhenko-Bryzgalin model yields thermodynamic data in volumetric concentration units [69PRU], *i.e.*, on the molar concentration scale. The conversion of equilibrium constants from molar to molal units is straightforward (see the TDB-5 guideline). The factor for the conversion of molality to molarity, ϱ , at infinite dilution becomes equal to the density of $\text{H}_2\text{O}(l)$, $\rho(T, p)$ in $\text{kg} \cdot \text{dm}^{-3}$, and (at infinite dilution) this conversion factor is ≈ 1 at $T < 323 \text{ K}$. Taking this units conversion into account, it is possible to obtain, from Eqs. (41) to (44), an expression for the formation equilibrium constants of mononuclear complexes:

$$\begin{aligned} \log_{10} K^\circ(T, p) = & \frac{T_0}{T} \log_{10} K^\circ(T_0, p^\circ) \\ & + \frac{|Z_a Z_c|_{\text{eff}}}{r_{\text{eff}}} \frac{N_A e^2}{4\pi \epsilon_0 R T \ln(10)} \left(\frac{1}{\epsilon(T, p)} - \frac{1}{\epsilon(T_0, p^\circ)} \right) \\ & - \sum_i v_i \log_{10} \rho(T, p) \end{aligned} \quad (45)$$

provided that r_{eff} is assumed to be independent of temperature and pressure. In this equation it is seen that the model requires only two parameters: the equilibrium constant at one temperature and an effective bond distance r_{eff} .

For the standard partial molar entropy of a reaction involving the formation of mononuclear complexes the following expression is obtained:

$$\begin{aligned} \Delta_r S_m^\circ(T, p) = & - \left(\frac{\partial \Delta_r G_m^\circ}{\partial T} \right)_p \\ = & - \frac{|Z_c Z_a|_{\text{eff}}}{r_{\text{eff}}} \frac{N_A e^2}{4\pi \epsilon_0 \epsilon(T, p)^2} \left(\frac{\partial \epsilon(T, p)}{\partial T} \right)_p - \sum_i v_i R \ln \rho(T, p) \\ & + \sum_i v_i R T \alpha_T(T, p) \end{aligned} \quad (46)$$

where $\alpha_T(T, p) = (1/V_m^\circ) (\partial V_m^\circ / \partial T)_p = -(1/\rho) (\partial \rho / \partial T)_p = -(\partial \ln \rho / \partial T)_p$ is the coefficient of thermal expansion of water, *cf.* Table 4 (here V_m° represents the molar volume of pure liquid water in $\text{cm}^3 \cdot \text{mol}^{-1}$, $V_m^\circ(T, p) = 18.0153/\rho(T, p)$). At 298.15 K, and 1 bar the contribution of the second term is negligible, and one

can then write:

$$\Delta_r S_m^\circ(T_0, p^\circ) \approx \left(81.4 \times 10^{-10} \frac{|Z_c Z_a|_{\text{eff}}}{r_{\text{eff}}} + 0.64 \sum_i \nu_i \right) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \quad (47)$$

where r_{eff} is in units of m. Similarly, for the standard partial molar heat capacity of a reaction involving the formation of mononuclear complexes the following equation is obtained:

$$\begin{aligned} \Delta_r C_{p,m}^\circ(T, p) &= T \left(\frac{\partial \Delta_r S_m^\circ}{\partial T} \right)_p \\ &= -T \frac{|Z_c Z_a|_{\text{eff}}}{r_{\text{eff}}} \frac{N_A e^2}{4\pi \epsilon_0 \epsilon(T, p)^2} \left(\left(\frac{\partial^2 \epsilon(T, p)}{\partial T^2} \right)_p - \frac{2}{\epsilon(T, p)} \left(\frac{\partial \epsilon(T, p)}{\partial T} \right)_p^2 \right) \\ &\quad + 2 \sum_i \nu_i RT \alpha_T(T, p) + \sum_i \nu_i RT^2 \left(\frac{\partial \alpha_T(T, p)}{\partial T} \right)_p \end{aligned} \quad (48)$$

At 298.15 K and 1 bar the contribution of the second term is negligible and the following equation can be used:

$$\Delta_r C_{p,m}^\circ(T_0, p^\circ) \approx \left(115 \times 10^{-10} \frac{|Z_c Z_a|_{\text{eff}}}{r_{\text{eff}}} + 7.1 \sum_i \nu_i \right) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \quad (49)$$

The uncertainty in this expression is $\sim 20\%$ (as estimated from the uncertainty in the derivatives $(\partial \epsilon / \partial T)_p$ and $(\partial^2 \epsilon / \partial T^2)_p$). The expression for the standard partial molar volume of a reaction involving the formation of mononuclear complexes is:

$$\begin{aligned} \Delta_r V_m^\circ(T, p) &= \left(\frac{\partial \Delta_r G_m^\circ}{\partial p} \right)_T \\ &= \frac{|Z_c Z_a|_{\text{eff}}}{r_{\text{eff}}} \frac{N_A e^2}{4\pi \epsilon_0 \epsilon(T, p)^2} \left(\frac{\partial \epsilon(T, p)}{\partial p} \right)_T + \sum_i \nu_i RT k_T \end{aligned} \quad (50)$$

where $k_T(T, p) = -(1/V_m^\circ) (\partial V_m^\circ / \partial p)_T = (\partial \ln \rho / \partial p)_T$ is the coefficient of isothermal compressibility of pure water. At 298.15 K and 1 bar the following equation may be used:

$$\Delta_r V_m^\circ(T_0, p^\circ) \approx \left(8.23 \times 10^{-10} \frac{|Z_c Z_a|_{\text{eff}}}{r_{\text{eff}}} + 1.1 \sum_i \nu_i \right) \text{cm}^3 \cdot \text{mol}^{-1}$$

The uncertainty in $\Delta_r V_m^\circ(T_0, p^\circ)$ should be $\sim 10\%$ (from the estimated uncertainty in $(\partial\varepsilon/\partial p)_T$).

The values of the temperature and pressure derivatives of the dielectric constant of water, which are needed in Eqs. (46) to (50), can be calculated from the equations of Refs. [91JOH/NOR, 92SHO/OEL], or from the equations of Archer and Wang [90ARC/WAN] together with an equation of state for water to calculate the density of liquid water, $\rho(T, p)$ (such equations of state may be found for example in Refs. [84HAA/GAL, 84KES/SEN, 89SAU/WAG, 93WAG/PRU]). All the data needed to use the Ryzhenko-Bryzgalin model for aqueous solutions from 273.15 K to 573.15 K are given in Table 4.

The Ryzhenko-Bryzgalin model considers thermodynamic quantities at zero ionic strength, hence it is in general necessary to recalculate the experimental data to $I = 0$. This can be done, for example, by using the specific ion interaction theory as described in the TDB-2 Guideline.

As mentioned above, the Ryzhenko-Bryzgalin model is a two parameter model, requiring only $K(T_0, p^\circ)$ and r_{eff} . If the value of $\Delta_r S_m^\circ$ for the reaction is known at 298.15 K (or may be estimated, *cf.* Section 4.2.2, *p.*72), the required value of the distance parameter r_{eff} may be calculated with Eq. (47). However, in general it is possible to estimate the “distance” parameter r_{eff} from the sum of crystallographic radii of the central ion and the ligand. This allows the calculation of preliminary values of $\log_{10} K^\circ(T, p)$, even when all thermodynamic properties of reaction are lacking except for $\log_{10} K^\circ(T_0, p^\circ)$.

2.4.3.1 Example: the mononuclear $\text{Al}^{3+}\text{-OH}^-$ system

This section describes the procedure used and indicates the accuracy of the method. Further details on this example are given in Ref. [94PLY/GRE].

In the system $\text{Al}^{3+}\text{-OH}^-$ the following mononuclear complexes have been established [76BAE/MES]: Al^{3+} , AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3(\text{aq})$, and $\text{Al}(\text{OH})_4^-$. Standard values of the equilibrium constants of formation of these complexes, $\log_{10} \beta_i^\circ$, at 298.15 K have been selected by Plyasunov and Grenthe [94PLY/GRE] from recent literature studies: (9.04 ± 0.03) , (17.44 ± 0.19) , (25.50 ± 0.50) and (33.10 ± 0.06) for $i = 1$ to 4, respectively. The second step is to find r_{eff} for this system. Several estimations of this parameter are given in [94PLY/GRE]. Preliminary calculations readily show that a reasonable agreement with the available experimental data can be achieved with $r_{\text{eff}} = (2.10 \pm 0.05) \times 10^{-10}$ m. The results obtained with Eq. (45) are compared with the literature equilibrium constants for the first and last hydrolysis steps (for which more accurate data have been obtained experimentally) in Figures 11 and 12. In addition, calculated and experimental equilibrium constants for the step-wise reaction:



Table 4: Temperature and pressure variation of the density and dielectric constant (relative permittivity) of liquid water at the standard pressure ($p^\circ = 1$ bar) for $T \leq 373.15$ K and at the vapour saturation pressure at $T > 373.15$ K, as well as some other properties of liquid water at the reference temperature, T_0 , and at the standard pressure, p° , namely: the coefficient of thermal expansion and its temperature derivative, the coefficient of isothermal compressibility, the first and second temperature derivatives and the pressure derivative of the dielectric constant. These values have been calculated with the equation of state of Kestin *et al.* [84KES/SEN] and the equation of Archer and Wang [90ARC/WAN] for the dielectric constant of water.

t (°C)	T (K)	p (bar)	ρ	ε (g · cm ⁻³)
0.00	273.15	1.000	0.9998	87.90
25.00	298.15	1.000	0.9970	78.38
50.00	323.15	1.000	0.9880	69.88
75.00	348.15	1.000	0.9749	62.29
100.00	373.15	1.013	0.9584	55.52
125.00	398.15	2.32	0.9391	49.47
150.00	423.15	4.76	0.9171	44.06
175.00	448.15	8.92	0.8923	39.19
200.00	473.15	15.5	0.8647	34.77
225.00	498.15	25.5	0.8339	30.73
250.00	523.15	39.8	0.7991	26.99
275.00	548.15	59.4	0.7592	23.47
300.00	573.15	85.8	0.7124	20.09

Values at $T_0 = 298.15$ K and $p^\circ = 1$ bar:

$$\begin{aligned}
 \alpha_T &= 2.594 \times 10^{-4} \text{ K}^{-1} \\
 (\partial \alpha_T / \partial T)_{p^\circ} &= 9.56 \times 10^{-6} \text{ K}^{-2} \\
 k_T &= 4.522 \times 10^{-5} \text{ bar}^{-1} \\
 (\partial \varepsilon / \partial T)_{p^\circ} &= -3.60 \times 10^{-1} \text{ K}^{-1} \\
 (\partial^2 \varepsilon / \partial T^2)_{p^\circ} &= 1.60 \times 10^{-3} \text{ K}^{-2} \\
 (\partial \varepsilon / \partial p)_{T_0} &= 3.64 \times 10^{-3} \text{ bar}^{-1}
 \end{aligned}$$

Figure 11: Comparison of experimental equilibrium constants for the reaction of formation of AlOH^{2+} with those obtained on the basis of the Ryzhenko-Bryzgalin model. Adapted from Ref. [94PLY/GRE].

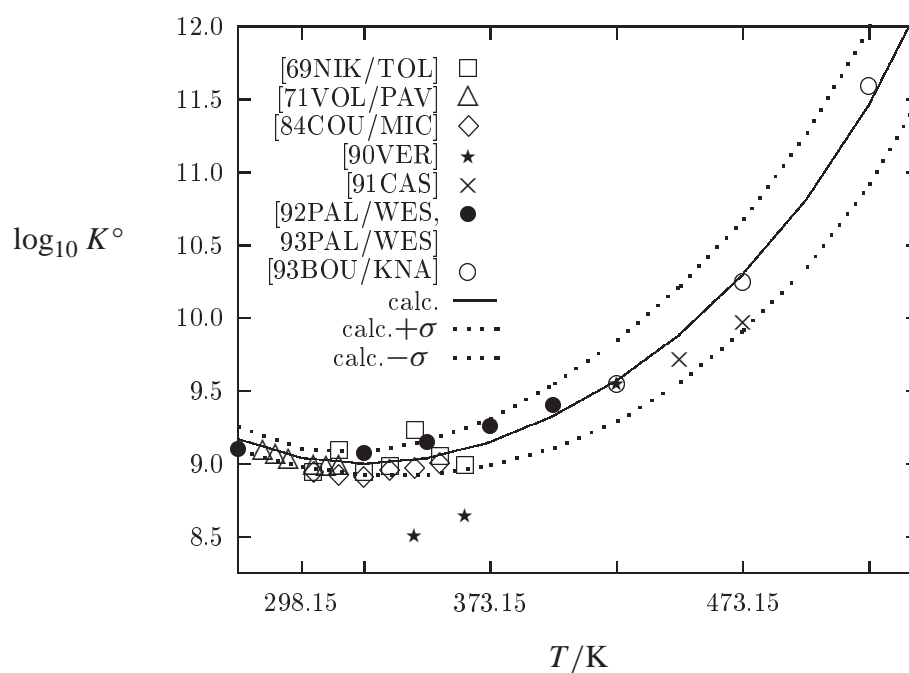
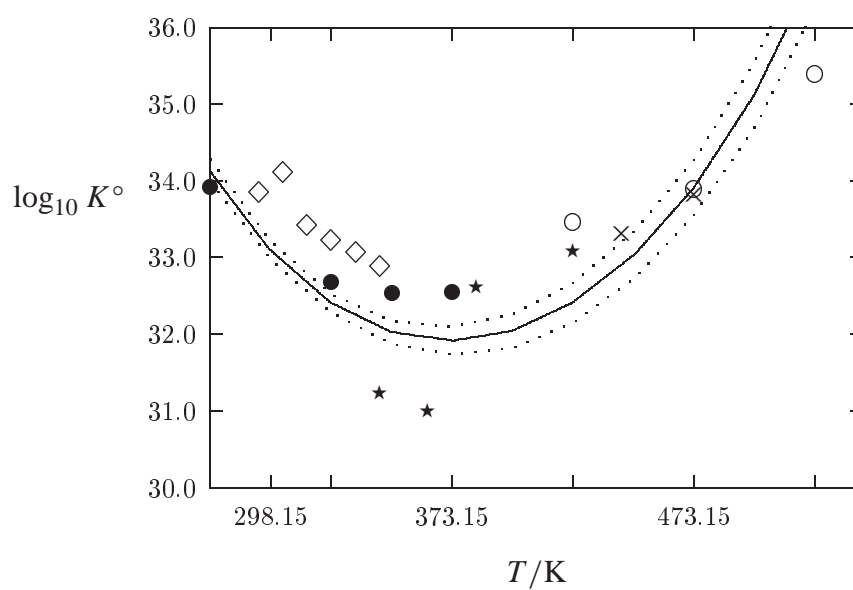
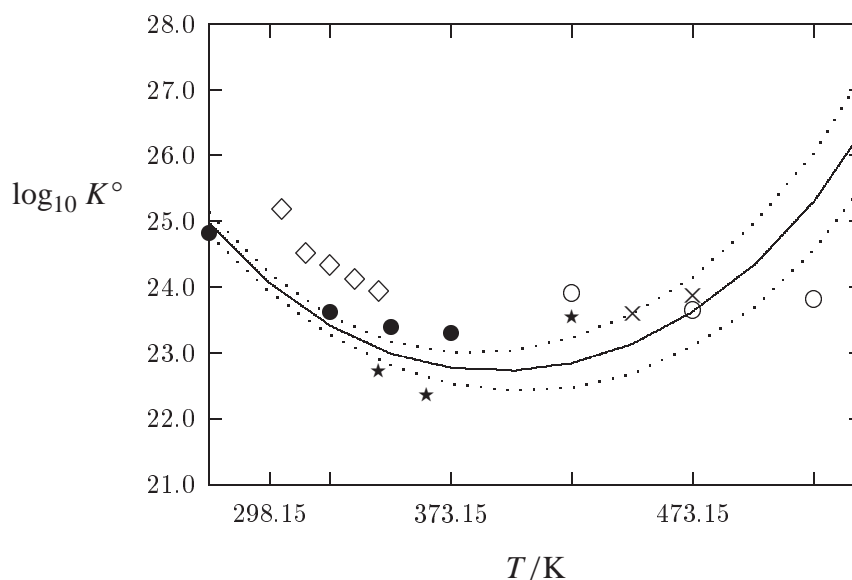


Figure 12: Comparison of experimental equilibrium constants for the reaction of formation of $\text{Al}(\text{OH})_4^-$ from Al^{3+} and OH^- with those obtained on the basis of the Ryzhenko-Bryzgalin model. See Figure 11 for symbols. Adapted from Ref. [94PLY/GRE].



are compared in Figure 13.

Figure 13: Comparison of experimental equilibrium constants for the reaction $\text{AlOH}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Al}(\text{OH})_4^-$ with those obtained on the basis of the Ryzhenko-Bryzgalin model. See Figure 11 for symbols. Adapted from Ref. [94PLY/GRE].



The calculations indicate that the simple electrostatic model of Ryzhenko and Bryzgalin is able to describe at least semiquantitatively the temperature dependence of the formation constants for the mononuclear hydroxy complexes of aluminium up to 473 or 523 K using the values of stability constants at 298.15 K with only one fitting parameter, r_{eff} , which has *the same value for all mononuclear complexes formed in the system*. At higher temperatures the calculated values of K° differ systematically from the equilibrium constants determined experimentally.

The model is put to a more rigorous test by trying to predict $\Delta_r S_m^\circ$, $\Delta_r C_{p,m}^\circ$ and $\Delta_r V_m^\circ$, for the formation reactions, with Eqs. (46) to (50), and the same size parameter as above ($r_{\text{eff}} = (2.10 \pm 0.05) \times 10^{-10}$ m). Precise experimental values for $\Delta_r S_m^\circ$, $\Delta_r C_{p,m}^\circ$ and $\Delta_r V_m^\circ$ at 298.15 K and 1 bar are only available for one of the aluminium hydrolysis reactions:

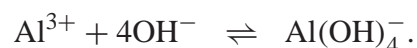


Table 5 shows that the calculated values of $\Delta_r S_m^\circ$, $\Delta_r C_{p,m}^\circ$ and $\Delta_r V_m^\circ$ are only in qualitative agreement with the experimental determinations. This reflects

Table 5: The calculated and experimental values of $\Delta_r S_m^\circ$, $\Delta_r C_{p,m}^\circ$ and $\Delta_r V_m^\circ$ for reaction $\text{Al}^{3+} + 4\text{OH}^- \rightleftharpoons \text{Al}(\text{OH})_4^-$ at 298.15 K and 1 bar. Adapted with revisions from Ref. [94PLY/GRE]. The experimental values were derived in Ref. [94PLY/GRE] from experimental results presented in the literature sources.

Property	Calculated value	Experimental value	Literature source
$\Delta_r S_m^\circ$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	$435 \pm 17^{(a)}$	501 ± 9.1 470.1 ± 14	[92PAL/WES] [91CHE/XU, 89COX/WAG]
$\Delta_r C_{p,m}^\circ$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	$660 \pm 30^{(a)}$	790 784 829 ± 37	[88HOV/HEP] [92PAL/WES] [92PAL/WES]
$\Delta_r V_m^\circ$ ($\text{cm}^3 \cdot \text{mol}^{-1}$)	$45 \pm 3^{(b)}$	108	[88HOV/HEP]

(a) The \pm term is based on the uncertainty in r_{eff} .

(b) The \pm term has been estimated from the uncertainty in $(\partial\varepsilon/\partial p)_T$, cf. Eq. (50).

the limitations of this simple electrostatic model, for example the assumption that $\Delta_r G_{m,\text{nonel}}^\circ$ is independent of T and p . More sophisticated models, *e.g.*, the revised Helgeson-Kirkham-Flowers model, consider the non-electrostatic term to be a function of temperature and pressure.

It should be noted that in order to improve the predictive capabilities of this simple electrostatic model, Ryzhenko [81RYZ] suggested the following empirical temperature and pressure dependence of r_{eff} :

$$r_{\text{eff}}(T, p) = r_{\text{eff}}(T_0, p^\circ) \left(\frac{V_m^\circ(\text{H}_2\text{O}, 1, T, p)}{V_m^\circ(\text{H}_2\text{O}, 1, T_0, p^\circ)} \right)^{1/3} \quad (51)$$

where values for the molar volume of pure water are needed both at the T and p of interest, and at the reference temperature $T_0 = 298.15 \text{ K}$ and the standard pressure $p^\circ = 1 \text{ bar}$. In later publications Ryzhenko and Bryzgalin [85RYZ/BRY, 86BRY, 87RYZ/BRY, 89BRY] used a somewhat different function:

$$r_{\text{eff}}(T, p) = r_{\text{eff}}(T_0, p^\circ) \left(\frac{\rho(T_0, p^\circ)}{\rho(T, p)} \right)^{\rho(T, p)/5} \quad (52)$$

Eqs. (51) and (52) are perhaps indirect attempts to take into account both differences in concentration units (molar to molal, as discussed above) as well as physical phenomena occurring when the molar volume of water increases. Eqs. (51) and (52) predict a gradual *increase* of r_{eff} with temperature, typically in the range

$(0.2 \text{ to } 0.6) \times 10^{-10}$ m at 573 K. It should be noted that in the revised Helgeson-Kirkham-Flowers model, *cf.* Eq. (35), the effective radius *decreases* with temperature because the function $g(T)$ has negative values [88TAN/HEL, 92SHO/OEL, Table H-8, Table 5]. From Eqs. (43) and (44) it follows that if r_{eff} is temperature and pressure dependent, then $|Z_c Z_a|_{\text{eff}}$ will also be a function of T and p , and Eqs. (45) and (46), *etc.*, must be rewritten accordingly. See, for example, Ref. [94PLY/GRE] for r_{eff} given by Eq. (51). Nevertheless, in both the Ryzhenko-Bryzgalin and in the revised Helgeson-Kirkham-Flowers models the effects of the variation in r_{eff} with increasing temperature are essentially negligible at $T \leq 473$ K. For simplicity, the examples in this guideline have been worked out with Eqs. (45) to (50), that is, assuming that r_{eff} is independent of temperature and pressure. Plyasunov and Grenthe [94PLY/GRE] presented the results of the Ryzhenko-Bryzgalin model on the Al(III)-OH⁻ system using Eq. (51) to describe the T and p dependence of r_{eff} .

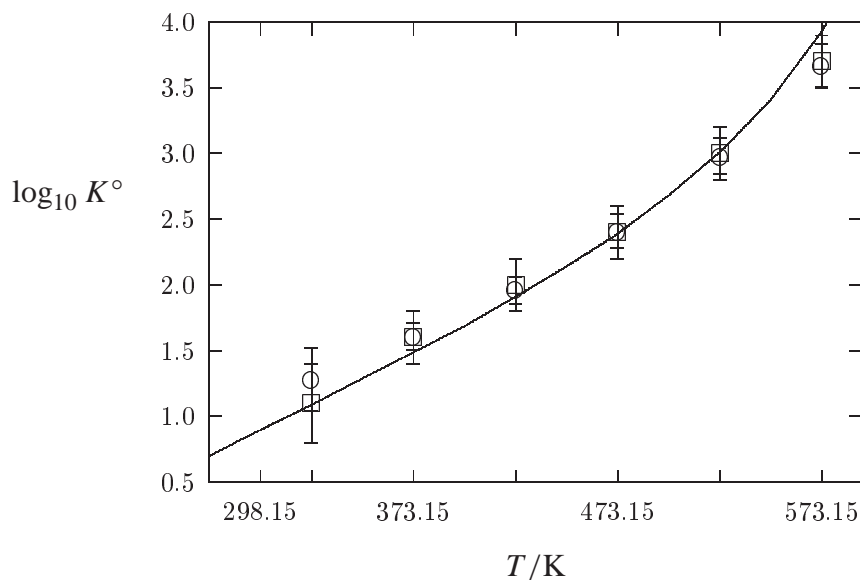
2.4.3.2 Example: the stability of acetate complexes of Fe²⁺

Palmer *et al.* [88PAL/DRU, 93PAL/HYD] have used a potentiometric method to study the stability of acetate complexes of Fe(II) in aqueous solutions at temperatures between 323 and 568 K (at steam saturated pressures above 373 K). Palmer and co-workers obtained equilibrium constants for the formation of FeCH₃COO⁺ and Fe(CH₃COO)₂(aq), and observed indications of the presence of Fe(CH₃COO)₃⁻ at high concentrations of acetate. The experimental equilibrium constants [88PAL/DRU, 93PAL/HYD] are compared in Figures 14 and 15 with those obtained with the Ryzhenko-Bryzgalin model using $r_{\text{eff}} = 2.6 \times 10^{-10}$ m and a polarisability of zero for the acetate ion.

2.4.4 The density or “complete equilibrium constant” model

The density model is based on the experimental observation that in aqueous systems the logarithm of the equilibrium constants of many reactions at isothermal conditions are linear functions of the logarithm of the density of the solvent over large p and T ranges [56FRA, 61FRA]. The theoretical basis for this has been discussed by many authors, and a comprehensive review of the literature is given by Anderson *et al.* [91AND/CAS]. The conclusion from these discussions is that the origin of the linear relationship is unknown, *cf.* [91AND/CAS, pp.1772–1773]. The model postulates a direct proportionality between $\log_{10} K^\circ(T, p)$, for reactions involving aqueous species, and $\log_{10} \rho(T, p)$, where $\rho(T, p)$ is the density of pure water. This proportionality was discovered by Franck [56FRA, 61FRA] during his conductimetric investigations of the electrolytic properties of KCl and other electrolytes at temperatures between 573 to 1073 K at a wide range of pres-

Figure 14: Comparison of experimental equilibrium constants (squares: [88PAL/DRU], circles: [93PAL/HYD]) for reaction: $\text{Fe}^{2+} + \text{CH}_3\text{COO}^- \rightleftharpoons \text{FeCH}_3\text{COO}^+$ with those obtained on the basis of the Ryzhenko-Bryzgalin model.

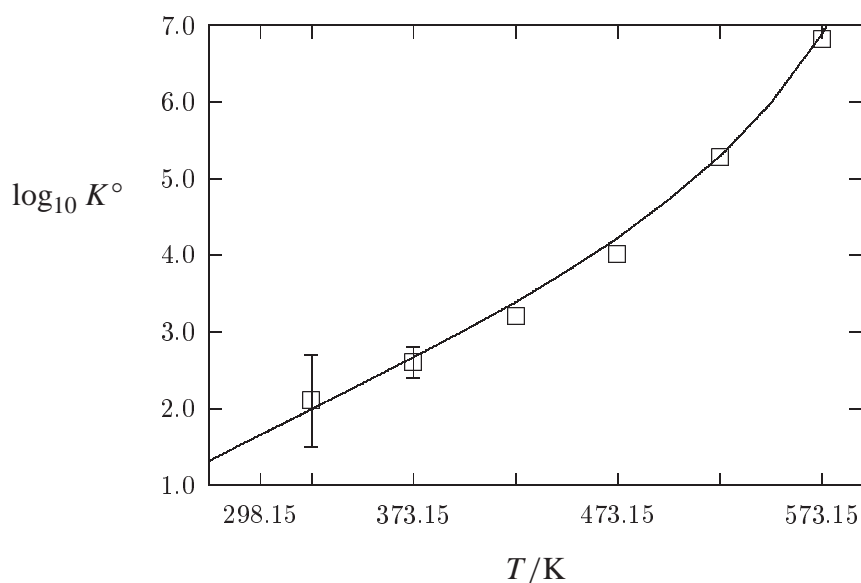


tures. Later, Marshal [70MAR, 72MAR] confirmed this observation and formulated the concept of “complete equilibrium constant” on the basis of determinations of dissociation constants of many salts and acids at temperatures above 673 K. This concept is outlined by the following relation:

$$\log_{10} K^\circ(T, p) = \log_{10} K'(T) + k(T) \log_{10} \rho(T, p) \quad (53)$$

where $K^\circ(T, p)$ stands for the conventional equilibrium constant in molar concentration units, which depends both on temperature and pressure; $K'(T)$ is the “complete equilibrium constant”, which is assumed to depend on temperature only; $k(T)$ is a function which Marshal [70MAR, 72MAR] considered to represent the change in hydration numbers between the products and the reactants; and $\rho(T, p)$ is the density of pure water. It must be pointed out that Eq. (53) has *no* rigorous thermodynamic basis. However, it provides a remarkably good correlation, valid over a very wide range of state parameters. It describes the dissociation constants for HCl [84FRA/MAR], HBr [68QUI/MAR], NaCl [68QUI/MAR3], NaBr [68QUI/MAR2], NaI [69DUN/MAR] and NH_4OH [68QUI/MAR4] in the temperature range 673 to 973-1073 K and a water density of 0.3 or 0.4 to 0.8 $\text{g} \cdot \text{cm}^{-3}$, as well as the pressure dependence of $\log_{10} K^\circ(T, p)$ for the dissociation of a number of electrolytes up to 4 kbar at room temperature [72MAR],

Figure 15: Comparison of experimental equilibrium constants [88PAL/DRU] for reaction: $\text{Fe}^{2+} + 2 \text{CH}_3\text{COO}^- \rightleftharpoons \text{Fe}(\text{CH}_3\text{COO})_2(\text{aq})$ with those obtained on the basis of the Ryzhenko-Bryzgalin model.



etc. Eq. (53) also describes the thermodynamic solubility product for salts, for instance, that of $\text{CaSO}_4(\text{s})$ at temperatures between 373 and 573 K, and pressures up to 1000 bar [72MAR].

The following type of equation was used by Marshall and Franck [81MAR/FRA] to describe the molal ion product of water as a function of p and T , and the same expression can also be used for other chemical equilibria:

$$\log_{10} K^\circ(T, p) = \left(A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} \right) + \left(E + \frac{F}{T} + \frac{G}{T^2} \right) \log_{10} \rho(T, p) \quad (54)$$

Eq. (54) is a formulation issued by the International Association for the Properties of Steam [81MAR/FRA] which describes the dissociation constant of pure water up to 1273 K and 10 kbar, practically within the experimental uncertainties in the whole T - p range (at least at densities above $\sim 0.3 \text{ g} \cdot \text{cm}^{-3}$).

The density model is a useful empirical generalization of a large number of experimental data on the thermodynamic behaviour of solutes at high temperatures and pressures.

The full set of coefficients of Eq. (54) can be determined only if experimental data on $\log_{10} K^\circ(T, p)$ are available in a wide range of temperature and pressure (or solvent density). Anderson *et al.* [91AND/CAS] cited Mesmer for the use of a simplified form of Eq. (54):

$$\ln K^\circ(T, p) = a_1 + \frac{a_2}{T} + \frac{a_3}{T} \ln \rho(T, p) \quad (55)$$

where a_1 , a_2 , and a_3 are independent of T and p . This equation is very useful for correlations up to 400 or 553 K depending on the system. Standard thermodynamic relationships allow the derivation of the parameters a_1 , a_2 , and a_3 as follows [91AND/CAS]:

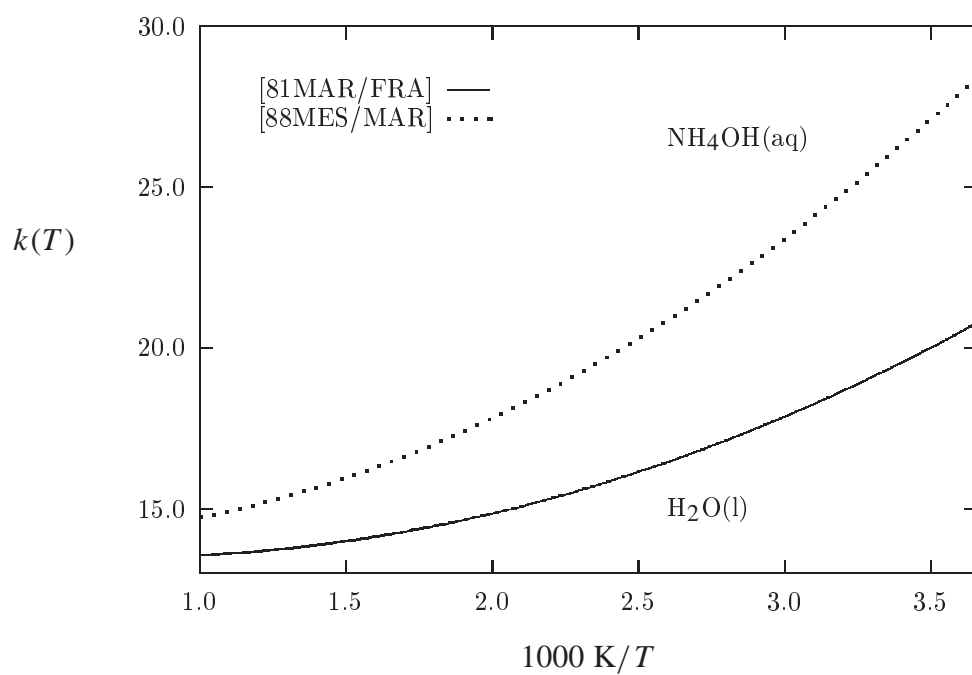
$$\begin{aligned} a_1 &= \ln K^\circ(T_0, p^\circ) + \frac{\Delta_r H_m^\circ(T_0, p^\circ)}{RT_0} - \frac{\Delta_r C_{p,m}^\circ(T_0, p^\circ) \alpha_T(T_0, p^\circ)}{RT_0 (\partial \alpha_T / \partial T)_{p^\circ}} \\ a_2 &= -\frac{\Delta_r H_m^\circ(T_0, p^\circ)}{R} + \frac{(T_0 \alpha_T(T_0, p^\circ) + \ln \rho(T_0, p^\circ)) \Delta_r C_{p,m}^\circ(T_0, p^\circ)}{RT_0 (\partial \alpha_T / \partial T)_{p^\circ}} \\ a_3 &= -\frac{\Delta_r C_{p,m}^\circ(T_0, p^\circ)}{RT_0 (\partial \alpha_T / \partial T)_{p^\circ}} = -\frac{\Delta_r V_m^\circ(T_0, p^\circ)}{Rk_T(T_0, p^\circ)} \end{aligned}$$

where α_T and k_T are the coefficient of thermal expansion of water and the coefficient of isothermal compressibility of water, respectively, and the subscript “ p° ” in the derivative $(\partial \alpha_T / \partial T)_{p^\circ}$ indicates that the derivative is taken at T_0 and p° . The values for α_T , k_T , and $(\partial \alpha_T / \partial T)_{p^\circ}$ needed to calculate a_1 , a_2 , and a_3 are given in Table 4. Values for the density of water, ρ , which are needed in Eq. (55), may be calculated at the steam saturated pressure and for any temperature below the critical point with the equation given by Wagner and Pruss [93WAG/PRU].

A comparison of Eqs. (53) and Eq. (55) shows that the latter equation assumes the simplest possible temperature dependence for $\log_{10} K'(T)$ and a simple T^{-1} dependence of $k(T)$. This simplification reduces the temperature range of applicability of Eq. (55), because the true temperature dependence of $k(T)$ might be more complicated, for example as in Eq. (54). Among the most reliable expressions available for $k(T)$ are those for the dissociation of H_2O and NH_4OH . These expressions are shown in Figure 16, which shows that $k(T)$ can be considered to be approximately linear functions of T^{-1} only up to about 550 K. Anderson *et al.* [91AND/CAS] estimated the upper temperature limit of applicability of Eq. (55) to be ~ 573 K.

An important feature of the “density” model in the Anderson-Castet-Schott-Mesmer modification [91AND/CAS] is the possibility of using experimentally determined thermodynamic quantities like $\Delta_r H_m^\circ(T_0, p^\circ)$, $\Delta_r C_{p,m}^\circ(T_0, p^\circ)$ (or alternatively $\Delta_r S_m^\circ(T_0, p^\circ)$, $\Delta_r V_m^\circ(T_0, p^\circ)$, *etc.*) together with the value of

Figure 16: The temperature dependence of parameter $k(T)$ of Eq. (53) between 273.15 and 1000 K, from experimental studies on the dissociation equilibria of $\text{H}_2\text{O}(\text{l})$ [81MAR/FRA] and $\text{NH}_4\text{OH}(\text{aq})$ [88MES/MAR].



$\log_{10} K^\circ(T_0, p^\circ)$ to predict values of $\log_{10} K^\circ(T, p)$. This calculation also requires the numerical values of $\rho(T, p)$, $\alpha_T(T_0, p^\circ)$, $k_T(T_0, p^\circ)$ and $(\partial\alpha_T/\partial T)_{p^\circ}$ for pure water at saturation water vapour pressure, which are well known. All the data needed to use the “density” model of Anderson *et al.* [91AND/CAS] are given in Table 4, p. 42.

Unlike the electrostatic model of Ryzhenko and Bryzgalin, which is valid only for formation (or dissociation) reactions involving exclusively aqueous species, the “density” model can be used for any reaction involving aqueous species, including reactions where solid phases participate (see [91AND/CAS] for further details), and the “density” model appears to be as general as the revised Helgeson-Kirkham-Flowers model described in Section 2.4.2. However, relatively fewer aqueous systems have been analysed with the “density” model.

We will demonstrate the accuracy of the method by using experimental data for the first deprotonation constant of $\text{CO}_2(\text{aq})$ from [82PAT/SLO], *cf.* Figure 10.

From the experimental values at 298.15 K and 1 bar ($\log_{10} K^\circ(T_0, p^\circ) = -6.349 \pm 0.005$, $\Delta_r H_m^\circ(T_0, p^\circ) = (9.16 \pm 0.12) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_r C_{p,m}^\circ(T_0, p^\circ) = -(338 \pm 27) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) we obtain the following values of the parameters a_1 to a_3 in Eq. (55): $a_1 = -7.274$, $a_2 = -2149.2 \text{ K}$, $a_3 = 14078 \text{ K}$. The calculated values of $\log_{10} K^\circ$ (the solid curve) and the experimental values are shown in Figure 17. The maximal deviations are ~ 0.2 logarithmic units at 473 - 548 K.

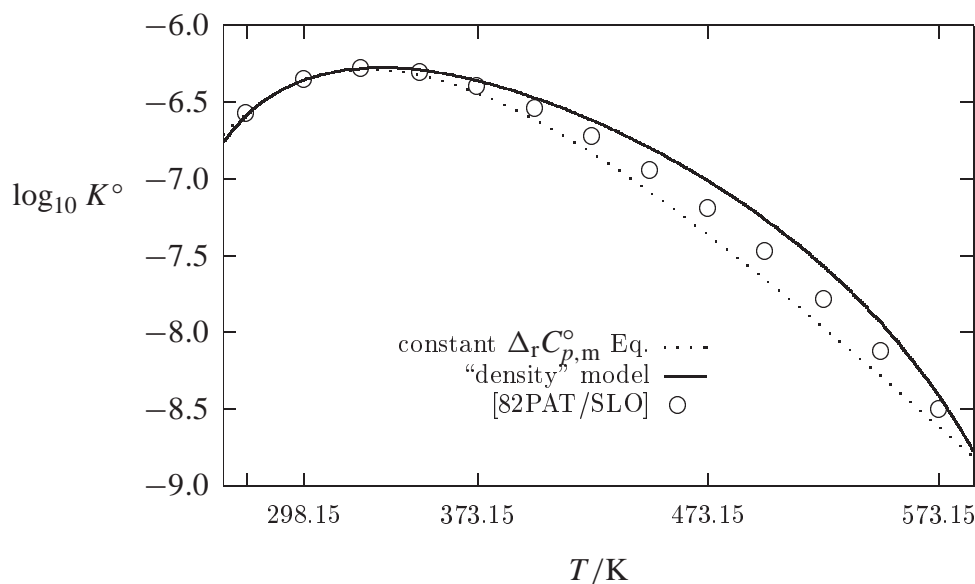
3 Third-law method

The second-law method of extrapolation described in previous sections is frequently used, and it is well suited for extrapolation of Gibbs energy data when only a small temperature interval is involved. However, if a temperature extrapolation over a large temperature range is required, and the original Gibbs energy data are for a restricted temperature interval, then the second-law extrapolation method can be very sensitive to extrapolation errors. This arises because the integral on the right hand side of Eq. (4) depends on $\Delta_r H_m^\circ(T)$. For experimental Gibbs energy data over a short temperature range, the derived values $\Delta_r H_m^\circ(T)$ and $\Delta_r S_m^\circ(T)$ can be very inaccurate (even if $\Delta_r G_m^\circ(T)$ is fairly accurately known) since they depend on the intercept and slope of

$$\Delta_r G_m^\circ(T) = \Delta_r H_m^\circ(T) - T \Delta_r S_m^\circ(T).$$

This issue has been discussed in many textbooks. For example, according to the revised version of Lewis and Randall’s *Thermodynamics* [61LEW/RAN, p.178]: “Often temperature-dependent errors are difficult to eliminate from the equilibrium measurements, and while the resulting equilibrium constants or free energies

Figure 17: Comparison of experimental equilibrium constant for the reaction $\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3^- + \text{H}^+$ [82PAT/SLO] with those calculated on the basis of the “density” model and the constant $\Delta_r C_{p,m}^\circ$ method. See Eq. (20) (Section 2.2.2) and Figure 10.



of reaction are approximately correct, the temperature coefficient and the corresponding heat of reaction from the second law ... may be greatly in error. The third-law method will also yield the heat of reaction when ΔF° values have been determined over too small a temperature interval to determine the temperature coefficient accurately”.

The preferred method to obtain $\Delta_f H_m^\circ(T_0)$ of a compound or ion is by direct use of calorimetric measurements[†]. For example, both Ca(cr) and CaO(cr) readily dissolve in aqueous solutions of strong mineral acids, and these $\Delta_{\text{sol}} H_m^\circ$ values can be combined to yield $\Delta_f H_m^\circ(\text{CaO}, \text{cr}, T_0)$. However, for some systems this type of measurement is not possible. That approach cannot be used for Tc(cr) and TcO₂(cr), Ru(cr) and RuO₂(cr), Pd(cr) and PdO(cr), *etc.*, and other oxides which are only very slightly soluble in aqueous solutions of mineral acids, and where the metals are even less reactive. Direct combustion of the metal with O₂(g) under pressure can sometimes be used instead to yield direct calorimetric values of $\Delta_f H_m^\circ(T_0)$, but the desired oxide is not always obtained or the reaction may be incomplete or yield more than one product. Combustion of Tc(cr) yields mainly Tc₂O₇(cr), for example, so it will not yield data for TcO₂(cr).

[†] T_0 stands for the reference temperature (= 298.15 K).

An alternative way of obtaining thermodynamic data is by use of Gibbs energy measurements at very high temperatures. For example, a reaction such as



can be studied by means of oxygen decomposition pressure measurements or solid state emf measurements. (This reaction does not occur for some metal-oxide systems, *e.g.*, in the case of $\text{TcO}_2(\text{cr})$, since it sublimes rather than decomposes at high temperatures.) In many cases it may be necessary to use temperatures of 1000 K or higher to obtain a significant vapour pressure of oxygen from decomposition of a MO_2 , and 700 to 800 K or higher to obtain sufficient solid state diffusion required for a solid state emf measurement. A third-law extrapolation of such $\Delta_r G_m^\circ(T)$ data to 298.15 K will, in general, be much more reliable than direct use of the second-law method.

The third-law method makes use of the free energy functions for reactants and products

$$\frac{G_m^\circ(T) - H_m^\circ(T_0)}{T},$$

which have much smaller variations with temperature than $G_m^\circ(T)$. Thus, this method can generally be used for numerical or graphical interpolations or extrapolations with a higher degree of precision than direct calculations with either $G_m^\circ(T)$ or $H_m^\circ(T)$.

The third-law method equation can be written in the general form

$$\begin{aligned} \Delta_r \left(\frac{G_m^\circ(T) - H_m^\circ(T_0)}{T} \right) &= \sum_{\text{products}} \left(\frac{G_m^\circ(T) - H_m^\circ(T_0)}{T} \right) \\ &\quad - \sum_{\text{reactants}} \left(\frac{G_m^\circ(T) - H_m^\circ(T_0)}{T} \right) \\ &= \frac{\Delta_r G_m^\circ(T)}{T} - \frac{\Delta_r H_m^\circ(T_0)}{T}. \end{aligned} \quad (56)$$

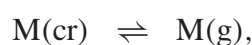
For this equation to be used the value of $\Delta_r G_m^\circ(T)$ must be known from low-temperature calorimetric data or from high-temperature Gibbs energy measurements, and the value of $\Delta_r H_m^\circ(T_0)$ needs to be obtained. Once $\Delta_r H_m^\circ(T_0)$ has been determined, it can be used to derive $\Delta_r H_m^\circ(T_0)$ of one of the reactants or products. Two different cases will now be considered.

3.1 Evaluation from high and low-temperature calorimetric data

If both low-temperature (heat capacity) and high-temperature (relative enthalpies as from drop calorimetry) thermal data are available, then the calculation of $\Delta_r H_m^\circ$

(T_0) is straightforward. The middle terms of Eq. (56), $\frac{G_m^\circ(T) - H_m^\circ(T_0)}{T}$, are then known, and they can be combined with each experimental $\Delta_r G_m^\circ(T)$ point at each temperature to yield a value of $\Delta_r H_m^\circ(T_0)$. If there is no drift in the calculated values of $\Delta_r H_m^\circ(T_0)$ within the temperature range over which $\Delta_r G_m^\circ(T)$ was measured, then the thermodynamic data are internally consistent and the average of these $\Delta_r H_m^\circ(T_0)$ should be reliable. We now give a specific example of this type of calculation.

Consider the simple case of the calculation of $\Delta_{\text{sub}} H_m^\circ(T_0)$ from high-temperature sublimation data of a pure metal to form its monoatomic vapour. The reaction is thus



and $\Delta_r G_m^\circ(T)$ becomes $\Delta_{\text{sub}} G_m^\circ(T)$. For the solid phase

$$G_m(\text{cr}, T) = G_m^\circ(\text{cr}, T),$$

and for the vapour phase

$$G_m(\text{g}, T) = G_m^\circ(\text{g}, T) + RT \ln f,$$

where f is the fugacity of M(g). Vapour pressures of metals are generally quite low at temperatures used for sublimation measurements, so the fugacity can be equated to the vapour pressure

$$G_m(\text{g}, T) = G_m^\circ(\text{g}, T) + RT \ln p.$$

For the sublimation process,

$$\begin{aligned} \Delta_{\text{sub}} G_m(T) &= G_m(\text{g}, T) - G_m(\text{cr}, T) \\ &= G_m^\circ(\text{g}, T) + RT \ln p - G_m^\circ(\text{cr}, T) \\ &= [G_m^\circ(\text{g}, T) - G_m^\circ(\text{cr}, T)] + RT \ln p \\ &= \Delta_{\text{sub}} G_m^\circ(T) + RT \ln p. \end{aligned}$$

Vapour pressure measurements are measurements of an equilibrium property, so $\Delta_{\text{sub}} G_m(T) = 0$ at each T . Thus for a closed system,

$$\begin{aligned} \Delta_{\text{sub}} G_m^\circ(T) &= G_m^\circ(\text{g}, T) - G_m^\circ(\text{cr}, T) \\ &= -RT \ln p. \end{aligned}$$

For this case, the third-law extrapolation Eq. (56) becomes

$$\begin{aligned} \Delta_{\text{sub}} H_m^\circ(T_0) &= T \left(\frac{G_m^\circ(\text{cr}, T) - H_m^\circ(\text{cr}, T_0)}{T} - \frac{G_m^\circ(\text{g}, T) - H_m^\circ(\text{g}, T_0)}{T} \right) \\ &\quad - RT \ln p. \end{aligned}$$

The T values were not cancelled in the first term of the right hand side of this equation, since free energy functions will be used to interpolate thermal data.

As a numerical example, we will reanalyse ruthenium vapour pressure measurements reported by Carrera *et al.* [64CAR/WAL]. They were measured from 1932 to 2377 K by use of weight loss recorded with a microbalance (Langmuir method). Values of $[G_m^\circ(T) - H_m^\circ(T_0)]$ both for Ru(cr) and Ru(g) are taken from Hultgren *et al.* [73HUL/DES]; thermodynamic properties for the vapour phase in that report were obtained from statistical thermodynamic calculations. Values of $[G_m^\circ(\text{cr}, T) - H_m^\circ(\text{cr}, T_0)]$, $[G_m^\circ(\text{g}, T) - H_m^\circ(\text{g}, T_0)]$ and \sum/T are summarised in Table 6. Here \sum denotes

$$\sum = [G_m^\circ(\text{cr}, T) - H_m^\circ(\text{cr}, T_0)] - [G_m^\circ(\text{g}, T) - H_m^\circ(\text{g}, T_0)].$$

Table 6: Free energy functions needed for the evaluation of sublimation data of ruthenium. From Ref. [73HUL/DES].

T (K)	$G_m^\circ(\text{cr}, T) - H_m^\circ(\text{cr}, T_0)$ (kJ·mol ⁻¹)	$G_m^\circ(\text{g}, T) - H_m^\circ(\text{g}, T_0)$ (kJ·mol ⁻¹)	\sum/T (kJ · K ⁻¹ ·mol ⁻¹)
1800	-96.32	-377.61	0.15627
2000	-112.20	-424.13	0.15597
2200	-128.81	-471.19	0.15563
2400	-146.14	-518.77	0.15526

Carrera *et al.* [64CAR/WAL] reported a large number of vapour pressures, but we will reanalyse only a few representative values. The results of these calculations are given in Table 7; pressures in atm are converted to bar, and values of \sum/T at each temperature T are obtained graphically from a plot of \sum/T against T . There is no trend in the calculated values of $\Delta_{\text{sub}}H_m^\circ(T_0)$ with the temperature of measurement. They yield an average value of $\Delta_{\text{sub}}H_m^\circ(T_0) = (650.4 \pm 6.3)$ kJ·mol⁻¹. Carrera *et al.* [64CAR/WAL] reported a third-law standard enthalpy of sublimation of $\Delta_{\text{sub}}H_m^\circ(T_0) = (653.1 \pm 4.6)$ kJ·mol⁻¹ based on an analysis of all 94 of their most reliable vapour pressures. Our value of $\Delta_{\text{sub}}H_m^\circ(T_0) = (650.4 \pm 6.3)$ kJ·mol⁻¹ from analysis of a five point subset of their vapour pressures is in good agreement.

Since $\Delta_{\text{sub}}H_m^\circ(T_0) = [\Delta_fH_m^\circ(\text{g}, T_0) - \Delta_fH_m^\circ(\text{cr}, T_0)]$ and $\Delta_fH_m^\circ(\text{cr}, T_0) = 0$, we then have a value of $\Delta_fH_m^\circ(\text{Ru}, \text{g}, T_0)$. This can be combined with the calculated statistical thermodynamic entropy of Ru(g) to yield a calculated value of $\Delta_fG_m^\circ(\text{Ru}, \text{g}, T_0)$.

Table 7: Ruthenium vapour pressure data [64CAR/WAL] and standard sublimation enthalpies calculated with the third-law extrapolation method.

T (K)	p (bar)	$-R \ln p$ (kJ · K ⁻¹ · mol ⁻¹)	\sum/T (kJ · K ⁻¹ · mol ⁻¹)	$\Delta_{\text{sub}}H_{\text{m}}^{\circ}(T_0)$ (kJ · mol ⁻¹)
1940	3.59×10^{-10}	0.18082	0.15607	653.6
2023	2.72×10^{-9}	0.16398	0.15593	647.2
2107	9.82×10^{-9}	0.15331	0.15580	651.3
2199	5.83×10^{-8}	0.13850	0.15563	646.8
2324	2.75×10^{-7}	0.12560	0.15540	653.0

3.2 Evaluation from high-temperature data

There are some systems for which low-temperature heat capacities (and thus entropies) have not been measured, but for which high-temperature thermal and Gibbs energy results are available. These can be analysed by a variant of the third-law method to yield approximate values of $\Delta_{\text{r}}H_{\text{m}}^{\circ}(T_0)$ and $\Delta_{\text{r}}S_{\text{m}}^{\circ}(T_0)$.

Our fundamental equation for the third-law analysis, Eq. (56), can be rearranged into the form

$$\frac{\Delta_{\text{r}}G_{\text{m}}^{\circ}(T)}{T} - \frac{\Delta_{\text{r}}H_{\text{m}}^{\circ}(T_0)}{T} = -\Delta_{\text{r}}S_{\text{m}}^{\circ}(T_0) - [\Delta_{\text{r}}S_{\text{m}}^{\circ}(T) - \Delta_{\text{r}}S_{\text{m}}^{\circ}(T_0)] + \frac{\Delta_{\text{r}}H_{\text{m}}^{\circ}(T) - \Delta_{\text{r}}H_{\text{m}}^{\circ}(T_0)}{T},$$

where $\Delta_{\text{r}}G_{\text{m}}^{\circ}(T)$ is known, and both $[\Delta_{\text{r}}S_{\text{m}}^{\circ}(T) - \Delta_{\text{r}}S_{\text{m}}^{\circ}(T_0)]$ and $[\Delta_{\text{r}}H_{\text{m}}^{\circ}(T) - \Delta_{\text{r}}H_{\text{m}}^{\circ}(T_0)]$ can be calculated from high-temperature thermal (relative enthalpy) results. This equation has two unknowns, $\Delta_{\text{r}}S_{\text{m}}^{\circ}(T_0)$ and $\Delta_{\text{r}}H_{\text{m}}^{\circ}(T_0)$. One approach is to use a least-squares fit to obtain values of $\Delta_{\text{r}}S_{\text{m}}^{\circ}(T_0)$ and of $\Delta_{\text{r}}H_{\text{m}}^{\circ}(T_0)$ from all of the experimental temperatures. This would yield greater uncertainties than in the case discussed in Section 3.1.

As an example we will reanalyse the same vapour pressure data for ruthenium that were used in the preceding section. Rearrangement of the last equation for the case of sublimation yields:

$$\begin{aligned} \frac{\Delta_{\text{sub}}H_{\text{m}}^{\circ}(T_0)}{T} - \Delta_{\text{sub}}S_{\text{m}}^{\circ}(T_0) &= \frac{\Delta_{\text{sub}}G_{\text{m}}^{\circ}(T)}{T} - \left[\frac{\Delta_{\text{sub}}H_{\text{m}}^{\circ}(T) - \Delta_{\text{sub}}H_{\text{m}}^{\circ}(T_0)}{T} \right] \\ &\quad + [\Delta_{\text{sub}}S_{\text{m}}^{\circ}(T) - \Delta_{\text{sub}}S_{\text{m}}^{\circ}(T_0)] \\ &= -R \ln p + \sum^*, \end{aligned}$$

where:

$$\sum^* = - \left[\frac{\Delta_{\text{sub}} H_{\text{m}}^{\circ}(T) - \Delta_{\text{sub}} H_{\text{m}}^{\circ}(T_0)}{T} \right] + [\Delta_{\text{sub}} S_{\text{m}}^{\circ}(T) - \Delta_{\text{sub}} S_{\text{m}}^{\circ}(T_0)]$$

Table 8: Thermodynamic values for the reanalysis of sublimation data for ruthenium.

T (K)	$[\Delta_{\text{sub}} H_{\text{m}}^{\circ}(T) - \Delta_{\text{sub}} H_{\text{m}}^{\circ}(T_0)]/T$ (J·K ⁻¹ ·mol ⁻¹)	$[\Delta_{\text{sub}} S_{\text{m}}^{\circ}(T) - \Delta_{\text{sub}} S_{\text{m}}^{\circ}(T_0)]$ (J·K ⁻¹ ·mol ⁻¹)	\sum^* (J·K ⁻¹ ·mol ⁻¹)
1800	-2.5639	-4.1547	-1.5908
2000	-3.2175	-5.1087	-1.8912
2200	-3.8930	-6.1212	-2.2282
2400	-4.5815	-7.1797	-2.5982

Table 9: Recalculation of ruthenium vapour pressures [64CAR/WAL] by the third-law extrapolation method without fixing the entropies of Ru(cr) and Ru(g) at $T_0 = 298.15$ K.

T (K)	$-R \ln p$ (J·K ⁻¹ ·mol ⁻¹)	\sum^* (J·K ⁻¹ ·mol ⁻¹)	$-R \ln p + \sum^*$ (J·K ⁻¹ ·mol ⁻¹)
1940	180.82	-1.79 ₄	179.03
2023	163.98	-1.92 ₇	162.05
2107	153.31	-2.07 ₀	151.24
2199	138.50	-2.22 ₈	136.27
2324	125.60	-2.44 ₆	123.15

Table 8 contains values of \sum^* at round values of the temperature, which were calculated from the tabulated critically assessed thermodynamic values of Hultgren *et al.* [73HUL/DES].

Table 9 contains the results obtained by reanalysis of the five selected vapour pressures. Values of \sum^* at each experimental temperature were obtained by graphical interpolation from a plot of \sum^* against T .

By using a linear least-squares analysis of the values in Table 9, we obtain:

$$\frac{\Delta_{\text{sub}} H_{\text{m}}^{\circ}(T_0)}{T} - \Delta_{\text{sub}} S_{\text{m}}^{\circ}(T_0) = \frac{(654.250 \pm 51.995) \times 10^3}{T} - (159.69 \pm 24.70)$$

with a correlation coefficient of 0.9975. Thus this calculation yields $\Delta_{\text{sub}} S_{\text{m}}^{\circ}(T_0) = (159.69 \pm 24.70) \text{ J·K}^{-1}\cdot\text{mol}^{-1}$ and $\Delta_{\text{sub}} H_{\text{m}}^{\circ}(T_0) =$

3.3. A brief comparison of enthalpies derived from the second and third-law method 59

$(654.250 \pm 51.995) \text{ kJ}\cdot\text{mol}^{-1}$. This value of $\Delta_{\text{sub}}H_{\text{m}}^{\circ}(T_0)$ is in very good agreement with the value obtained by a standard third-law extrapolation (*cf.* Section 3.1), $(650.4 \pm 6.3) \text{ kJ}\cdot\text{mol}^{-1}$ but is considerably more uncertain. The larger uncertainty arises because two parameters are now being determined by the same five data points whereas in the standard third-law extrapolation only $\Delta_{\text{sub}}H_{\text{m}}^{\circ}(T_0)$ was determined. It is possible to reduce these large uncertainties somewhat by using more of the published vapour pressures in the calculation. However, the same basic conclusion will still be reached, *i.e.*, that the third law calculation of a standard enthalpy of reaction will always yield significantly larger uncertainties when no reliable values of the standard entropies are available than when the calculation is constrained using the standard entropies.

For the examples just given involving the sublimation of ruthenium metal, both types of third-law extrapolations give values of $\Delta_{\text{sub}}H_{\text{m}}^{\circ}(T_0)$ in good agreement. However, consider a case where either the vapour pressures or high-temperature calorimetric data have a temperature-dependent systematic error (or, if the calorimetric “data” were estimated and these estimated values were systematically in error). An analysis of such data by the standard third-law method as described in Section 3.1 would yield values of $\Delta_{\text{r}}H_{\text{m}}^{\circ}(T_0)$ that vary with the temperature of the measurements. It would thus be obvious that there was an error in one or more of the input values for the calculations.

In contrast, if the calculations were done as described in the present section, then the errors due to certain types of systematic errors could be adsorbed into the coefficients of the linear fit. Consequently, both $\Delta_{\text{sub}}H_{\text{m}}^{\circ}(T_0)$ and $\Delta_{\text{sub}}S_{\text{m}}^{\circ}(T_0)$ would be in error, but it would not be obvious to the person doing the calculations. The standard third-law method should be considered more trustworthy in most cases, and it should be used when sufficient calorimetric data are available.

3.3 A brief comparison of enthalpies derived from the second and third-law methods

The starting point for a second-law calculation of the standard enthalpy of reaction from Gibbs energy of reaction data is

$$\Delta_{\text{r}}G_{\text{m}}^{\circ}(T) = \Delta_{\text{r}}H_{\text{m}}^{\circ}(T) - T \Delta_{\text{r}}S_{\text{m}}^{\circ}(T).$$

where $\Delta_{\text{r}}H_{\text{m}}^{\circ}(T)$ is extracted from a linear or higher-order fit of the Gibbs energy of reaction data as a function of temperature. If a linear fit is appropriate, then the assessed value of $\Delta_{\text{r}}H_{\text{m}}^{\circ}(T)$ refers to the mean temperature of the measurements T_{av} . The standard enthalpy of reaction is then calculated from the integration of Eq. (5) from T_0 to the mean temperature of the high-temperature Gibbs energy of

reaction measurements:

$$\Delta_{\text{r}}H_{\text{m}}^{\circ}(T_0) = \Delta_{\text{r}}H_{\text{m}}^{\circ}(T_{\text{av}}) - \int_{T_0}^{T_{\text{av}}} \Delta_{\text{r}}C_{p,\text{m}}^{\circ}(T) dT$$

Carrera *et al.* [64CAR/WAL] have compared values of $\Delta_{\text{sub}}H_{\text{m}}^{\circ}(T_0)$ derived from second and third-law analyses of their vapour pressures. There is no point in repeating those calculations and we merely cite their results. They performed five series of measurements and a separate analysis of each data set gave third-law values of $\Delta_{\text{sub}}H_{\text{m}}^{\circ}(T_0)$ ranging from (648.1 ± 2.5) to (656.5 ± 3.3) $\text{kJ}\cdot\text{mol}^{-1}$. In contrast, their analysis by the second-law method of these same five data sets gave values of $\Delta_{\text{sub}}H_{\text{m}}^{\circ}(T_0)$ ranging from (600.0 ± 22.2) to (659.4 ± 10.9) $\text{kJ}\cdot\text{mol}^{-1}$. Quite clearly, the third-law based values are more precise and more consistent than the second-law based values.

Although third-law based values of $\Delta_{\text{r}}H_{\text{m}}^{\circ}(T_0)$ are usually more precise and consistent than second-law based values, this better consistency is not in itself a proof that the original Gibbs energy measurements were completely accurate since there are certain types of systematic errors that do not affect these consistency checks. Agreement of second-law and third-law based values of $\Delta_{\text{r}}H_{\text{m}}^{\circ}(T_0)$ within their “experimental” precision is usually a better indication that the high-temperature Gibbs energy data and the corresponding calorimetric data are of high quality.

4 Estimation methods

Experimental or estimated values of $C_{p,\text{m}}^{\circ}$ and S_{m}° are needed in order to calculate high-temperature equilibrium constants either with Eqs. (7) or (17), or with Eq. (20) (which assumes a temperature independent heat capacity of reaction). The same situation applies to the electrostatic models described in Section 2.4.

Therefore, estimation methods for $C_{p,\text{m}}^{\circ}(T)$ and $S_{\text{m}}^{\circ}(T)$ will be described here. For a broader presentation of thermodynamic estimation techniques, the reader is referred to the discussions in references [86NOR/MUN, Section 11-8], [93KUB/ALC, Chapter 3], [61LEW/RAN, pp.515–525], and [52LAT, Appendix III].

Recently, heat capacities have been measured for several aqueous electrolytes and non-electrolytes to about 720 K. See the article by Wood *et al.* [94WOO/CAR] for references to many of the original studies. Since these measurements do not yet include the majority of aqueous electrolytes and non-electrolytes, estimated values are still required for most applications.

4.1 Estimation methods for heat capacities

4.1.1 Heat capacity estimations for solid phases

Kopp's rule of additivity [86NOR/MUN, Eq. (11-52)] may be used to estimate the heat capacity of a solid phase as the sum of the molar heat capacities of the elements present:

$$C_{p,m}^{\circ} = \sum_i v_i C_{p,m}^{\circ}(i).$$

This rule is only valid for elements which are also solid in their standard state. However, effective contributions can be used for elements that are not solid in the standard state and adjustments can be made to the entropies of the solid light elements to improve the accuracy of the estimated values. Sturtevant [59STU, pp.557–558] reported the following effective atomic contributions (in units of $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) for the light elements: C, 7.53; H, 9.62; B, 11.3; Si, 15.9; O, 16.7; F, 20.9; P, 22.6; S, 22.6; and 25.9 for the heavier atoms.

Kubaschewski, Alcock and Spencer [93KUB/ALC] reported a technique similar to that of Latimer's method for standard entropies (*cf.* Section 4.2.1, p.68) to estimate heat capacities of solids at 298.15 K by adding the contributions from the cationic and anionic groups present in a solid phase. Cationic and anionic contributions are listed in [93KUB/ALC, their Tables IX and X]. Coefficients for temperature functions of the type

$$C_{p,m}^{\circ}(T) = a + bT - cT^{-2}$$

may be estimated by their approach if the melting temperature of the solid phase is known [93KUB/ALC, their Eqs. (117) and (118)].

Parameter estimates for the same type of heat capacity function for oxide minerals were made by Helgeson *et al.* [78HEL/DEL, Eqs. (78), (80) and (85)] using the sum of the heat capacities for the constituent oxides.

For estimations on chalcogenides, the discussion given by Mills should be consulted [74MIL, Section 2.3.3]. For a discussion of the chalcogenides of rare earths and actinides, see Ref. [74MIL, Section 3.3.2.a].

4.1.2 Heat capacity estimations for aqueous species

For standard partial molar heat capacities of aqueous ions the estimation methods are mainly of two types:

- Correlations between $C_{p,m}^{\circ}(T_0)$ and standard partial molar ionic entropies at 298.15 K. The method of Criss and Cobble [64CRI/COB2, 64CRI/COB]

will be described because of its historical interest. The equations of Helgeson and co-workers [81HEL/KIR, 88SHO/HEL, 97SHO/SAS, 97SVE/SHO] are modern correlations of this kind.

- Electrostatic models of ion hydration. These types of $C_{p,m}^{\circ}(T)$ estimations are described as alternative temperature functions for the heat capacity (Section 2.4).

The first type of estimation methods (correlations between $C_{p,m}^{\circ}(T_0)$ and ionic entropies at 298.15 K) are limited to a few ion types, which do not yet include metal ligand complexes, and which sometimes exclude neutral aqueous species. Therefore these methods are not always useful unless further assumptions are made. For example, Baes and Mesmer [81BAE/MES] assigned partial molar heat capacities for a mononuclear hydrolysis product equal to that of another metal cation having the same ionic radius as that of the unhydrolysed cation of interest, and having the same charge as the hydrolysis product of interest. Another approximation for metal-ligand complexes, which was used by Lemire and Tremaine [80LEM/TRE], is to use the correlation parameters for simple cations and anions.

4.1.2.1 Criss and Cobble's method

The method developed by Criss and Cobble [64CRI/COB2, 64CRI/COB] is of interest because it was widely used during the 1970s and there are many publications which have used it. It has however several associated problems which are discussed below, and nowadays it has been largely superseded by the correlation equations of Helgeson and co-workers described in Section 4.1.2.3.

Criss and Cobble [64CRI/COB2, 64CRI/COB] observed that by assigning a specific value to the standard partial molar ionic entropy of H^+ at each temperature, for simple ions a linear correspondence could be obtained between the standard partial molar ionic entropies at 298.15 K and at other temperatures,

$$S_m^{\circ,abs}(i, T) = a(T) + b(T)S_m^{\circ,abs}(i, T_0), \quad (57)$$

where $a(T)$ and $b(T)$ are temperature dependent parameters which differ for different ion types (*i.e.*, for simple cations, simple anions, oxyanions, and acid oxyanions), and $S_m^{\circ,abs}(i, T)$ are "absolute" partial molar entropies (referred to a specific value for $S_m^{\circ,abs}(H^+, aq, T)$). At 298.15 K the optimum value of $S_m^{\circ,abs}(H^+, aq, T_0)$ was found to be equal to $-20.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [64CRI/COB2, 64CRI/COB], and therefore the relationship between "absolute" and conventional entropies at 298.15 K is

$$\begin{aligned} S_m^{\circ}(i, T_0) &= S_m^{\circ,abs}(i, T_0) - z_i S_m^{\circ,abs}(H^+, aq, T_0), \\ &= S_m^{\circ,abs}(i, T_0) + 20.9 z_i, \end{aligned} \quad (58)$$

where z_i is the charge of the ion i .

A related type of correlation was given by Couture and Laidler several years earlier [57COU/LAI], in which $S_m^\circ(T_0)$ was related to the mass of the ion and a term in the inverse of the ionic radius (of the same basic form as the Born solvation term). In that study $S_m^{\circ,\text{abs}}(\text{H}^+, \text{aq}, T_0) = -23.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, which is similar to Criss and Cobble's value [64CRI/COB2, 64CRI/COB].

Criss and Cobble [64CRI/COB2] found that one set of $a(T)$ and $b(T)$ was appropriate for simple cations, another for simple anions, a third set for oxyanions and a fourth for their oxyacids. They tabulated values of $a(T)$, $b(T)$ and $S_m^{\circ,\text{abs}}(\text{H}^+, \text{aq}, T)$ at 298.15, 333.15, 373.15 and 423.15 K.

The practical importance of Eq. (57) is that ionic partial molar heat capacities can be estimated from the ionic partial molar entropies of these ions averaged between two temperatures. Criss and Cobble [64CRI/COB] calculated (*cf.* our Eq. (6))

$$C_{p,m}^{\circ,\text{abs}}|_{T_0}^T(i) = \frac{S_m^{\circ,\text{abs}}(i, T) - S_m^{\circ,\text{abs}}(i, T_0)}{\ln(T/T_0)}, \quad (59)$$

in which case the “constant $\Delta_r C_{p,m}^\circ$ ” equations, Eqs. (20) and (21), may be used to calculate equilibrium constants at higher temperatures. By substituting Eq. (57) into Eq. (59), Criss and Cobble obtained average “absolute” heat capacities:

$$\begin{aligned} C_{p,m}^{\circ,\text{abs}}|_{T_0}^T(i) &= \frac{a(T) - (1 - b(T))S_{p,m}^{\circ,\text{abs}}(i, T_0)}{\ln(T/T_0)} \\ &= \alpha(T) + \beta(T)S_{p,m}^{\circ,\text{abs}}(i, T_0), \end{aligned} \quad (60)$$

where

$$C_{p,m}^{\circ,\text{abs}}(i, T) = C_{p,m}^\circ(i, T) + z_i C_{p,m}^{\circ,\text{abs}}(\text{H}^+, \text{aq}, T) \quad (61)$$

with

$$C_{p,m}^{\circ,\text{abs}}(\text{H}^+, \text{aq}, T_0) = 117.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Two extra digits were retained from the conversion of $28 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ to this value.

An alternative procedure is to estimate values for conventional standard partial molar ionic entropies at higher temperatures (Eqs. (57) and (58)), and to do a least-squares fit on these values to the constant heat capacity equation:

$$S_m^\circ(i, T) = S_m^\circ(i, T_0) + C_{p,m}^\circ|_{T_0}^T(i) \ln(T/T_0).$$

This method was used for example by Lemire and Tremaine [80LEM/TRE].

Similarly to Eq. (57), Criss and Cobble found a linear correlation between “absolute” standard partial molar ionic heat capacities and “absolute” standard partial molar ionic entropies at 298.15 K,

$$\begin{aligned} C_{p,m}^{\circ,\text{abs}}(i, T_0) &= A + BS_m^{\circ,\text{abs}}(i, T_0) \\ &= A + B(S_m^{\circ}(i, T_0) - 20.9z_i), \end{aligned}$$

and, using Eq. (61),

$$C_{p,m}^{\circ}(i, T_0) = A + BS_m^{\circ}(i, T_0) - z_i(20.9B + 117.1). \quad (62)$$

The last equation relates conventional standard partial molar ionic heat capacities to conventional standard partial molar ionic entropies and to the electrical charge of aqueous ionic species. Criss and Cobble [64CRI/COB] give the A and B parameters listed in our Table 10.

Table 10: Heat capacity parameters for Eq. (62). Units of A are $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, whereas B is unitless.

Species	A	B
Cations	174.1	-0.523
Anions including OH^-	-236.4	0.179
Oxyanions	-607	2.20
Acid oxyanions	-569	3.07

For temperatures above 373 K, Criss and Cobble [64CRI/COB] noted that $a(T)$ and $b(T)$ in Eqs. (57) and (60) could each be assumed to be linear functions of the temperature †:

$$\begin{aligned} a(T) &= a_1 + b_1T \\ b(T) &= a_2 + b_2T. \end{aligned}$$

However, these equations imply that the standard partial molar ionic heat capacities are also approximately linear functions of the temperature at $T \leq 500$ K [64CRI/COB, 70LEW, 78TAY] which is in direct disagreement with experimental evidence which shows that they go through a maximum as a function of temperature and decrease asymptotically towards $-\infty$ at the critical point of water (see

†Tremaine *et al.* [77TRE/MAS] note that the value of $a(T)$ at 573 K for simple anions including OH^- should be $-47.2 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ instead of the value of $-49.2 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ given in [64CRI/COB] which is presumably a misprint.

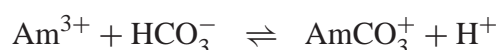
for example Figure 4 in Ref. [82PAT/SLO]). For this reason the $a(T)$ and $b(T)$ parameters of Criss and Cobble are not recommended for use above 423 K.

Note that Criss and Cobble [64CRI/COB] recommended these linear equations for $373 \text{ K} < T < 473 \text{ K}$ and Taylor [78TAY] for $T < 523 \text{ K}$.

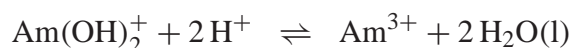
Criss and Cobble's equation, our Eq. (62), has been criticised by Shock and Helgeson [88SHO/HEL] since it does not agree very well with some more recent experimental data for M^{3+} and some M^{2+} , especially for aqueous ions whose $S_m^\circ(T_0)$ are less than about $-125 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

4.1.2.2 Isocoulombic method

For neutral aqueous species and metal complexes, the isocoulombic approach (Section 2.2.3) might be used to estimate a value for their $C_{p,m}^\circ(i)$. For example, for the estimation of the heat capacity for AmCO_3^+ , the isoelectric reaction



can be combined with the reactions



and



to yield the isocoulombic reaction,



If the assumption is made that $\Delta_r C_{p,m}^\circ = 0$ for this last reaction, then,

$$0 = C_{p,m}^\circ(\text{AmCO}_3^+, \text{aq}, T_0) + C_{p,m}^\circ(\text{OH}^-, \text{aq}, T_0) + C_{p,m}^\circ(\text{H}_2\text{O}, \text{l}, T_0) \\ - C_{p,m}^\circ(\text{HCO}_3^-, \text{aq}, T_0) - C_{p,m}^\circ(\text{Am}(\text{OH})_2^+, \text{aq}, T_0).$$

As the heat capacities of $\text{H}_2\text{O}(\text{l})$, OH^- and HCO_3^- have been determined experimentally, and as the heat capacity for the hydrolysis product, $\text{Am}(\text{OH})_2^+$, can be estimated with Criss and Cobble's method, our Eq. (62) (using the parameters for cations and an estimated entropy for $\text{Am}(\text{OH})_2^+$), the heat capacity for AmCO_3^+ can then be estimated directly without a need to estimate its ionic entropy or to make further assumptions.

4.1.2.3 Other correlation methods

There are not many alternatives to Eq. (62), which was derived from equations proposed by Criss and Cobble [64CRI/COB]. Helgeson and co-workers presented correlations for similar ions with equal charge, *cf.* [81HEL/KIR, Eq. (282)] and [88SHO/HEL, Eq. (91)],

$$C_{p,m}^{\circ}(i, T_0) = a + bS_m^{\circ}(i, T_0), \quad (63)$$

where the parameters a and b are tabulated by Shock and Helgeson [88SHO/HEL]. These values should only be used with the same $S_m^{\circ}(i, T_0)$ used by Shock and Helgeson to derive them.

It seems rather strange to us that the parameters of Shock and Helgeson [88SHO/HEL] for the light and heavy tripositive rare earth ions should differ so greatly. These large differences may be a computational artifact because $C_{p,m}^{\circ}(T_0)$ was poorly determined at that time for those M^{3+} ions. We note that Shock and Helgeson [88SHO/HEL] derived values for the standard partial molar ionic heat capacities for the aqueous tripositive rare earth ions in the range -132.6 to $-199.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, with values for the light rare earths generally being more negative than those for the heavy. However, a reanalysis by Rard [92RAR] of all the available heat capacities for aqueous rare earth chlorides and perchlorates gave values for the ionic heat capacities $C_{p,m}^{\circ}(T_0)$ that ranged from -50 to $-110 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the lighter rare earth ions and from -40 to $-72 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the heavier rare earths. In addition, Xiao and Tremaine [96XIA/TRE] reported experimental values of $C_{p,m}^{\circ}(T_0) = -(101 \pm 2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for La^{3+} and $-74 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for Gd^{3+} , which differ significantly from Shock and Helgeson's values of -156 and $-150 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. Differences at some other temperatures are even larger. Thus the values of $C_{p,m}^{\circ}(T_0)$ reported by Shock and Helgeson are probably too negative by about 50 to $100 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ or more. Consequently, Eq. (63) should not be used for M^{3+} ions.*

Modified equations of this type were proposed by Khodakovskiy [69KHO],

$$C_{p,m}^{\circ}(i, T_0) = a - d|z_i| - \frac{2}{3}S_m^{\circ}(i, T_0)$$

and

$$S_m^{\circ}(i, T) = \frac{a(T - T_0)}{T_0} - \frac{d(T - T_0)}{T_0}|z_i| + [1 + 0.00224(T - T_0)]S_m^{\circ}(i, T_0),$$

*Note added in press: Recently Shock *et al.* [97SHO/SAS] have re-evaluated the parameters for Eq. (63) excluding rare earth cations.

for conventional standard state properties. He found that one set of coefficients worked well for cations, a different set worked well for non-oxygenated anions (mainly halides) and unionised dissolved gases (Ar, Kr, N₂, O₂, H₂, H₂S), and a third set worked well for oxyacids and their oxyanions. These equations have the advantage of working for some dissolved gases also. Khodakovskiy's recommended values of a and d for each of these three cases are given in Table 11.

Table 11: Parameters for Khodakovskiy's equations [69KHO]. Units of a and d are J·K⁻¹·mol⁻¹.

Cases	a	d
Cations	212.5	124.7
Non-oxygenated anions and dissolved gases	212.5	311.3
Oxyacids and oxyanions	334.7	311.3

Unfortunately, these various correlations do not yet include inorganic complexes and, therefore, extra assumptions are needed to use them for reactions that involve metal complexes. Some preliminary work in this area was done by Cobble [53COB2] for halide, cyanide, and a few other complexes by using "hydration corrected" entropies.

Another method proposed is a heat capacity correlation among redox couples [85JAC/HEL]:

$$\frac{C_{p,m,oxd1}^{\circ}(T) - C_{p,m,red1}^{\circ}(T)}{z_{oxd1} - z_{red1}} = \frac{C_{p,m,oxd2}^{\circ}(T) - C_{p,m,red2}^{\circ}(T)}{z_{oxd2} - z_{red2}}.$$

If the heat capacity temperature functions for a redox couple are known (say Fe²⁺/Fe³⁺) and $C_{p,m}^{\circ}(T)$ for a member of another couple is known, then this method allows the estimation of the unknown temperature variation for the heat capacity of the other member of the second redox couple. However, the reliability of this estimation method has been tested for only a few aqueous systems.

4.1.3 Heat capacity estimation methods for reactions in aqueous solutions

The Ryzhenko-Bryzgalin model, which is described in Section 2.4.3, may be used to estimate $\Delta_r C_{p,m}^{\circ}$, cf. Eq. (49), and for "isocoulombic" reactions, $\Delta_r C_{p,m}^{\circ}$ may be estimated to be equal to zero, as discussed in Sections 2.2.3 and 4.1.2.2.

Smith *et al.* [86SMI/POP] have proposed a set of average values of $\Delta_r C_{p,m}^{\circ}$ that may be used for the estimation of this quantity for proton dissociation reactions of acid oxyanions.

Sverjensky [87SVE] has proposed correlations between the $\Delta_r C_{p,m}^\circ$ for metal complexation reactions with halide and hydroxide ions and the value of $C_{p,m}^\circ$ for the metal cation.*

4.2 Entropy estimation methods

4.2.1 Entropy estimation methods for solid phases

For ionic compounds Latimer's method [52LAT] involves estimating entropies by adding empirically estimated ionic contributions. Based on later experimental data, Naumov *et al.* [71NAU/RYZ, Tables I-2 and I-3] prepared a revised table of parameters to be used with Latimer's method.

Langmuir [78LAN] described improved parameters for estimating entropy values for solid compounds containing the UO_2^{2+} moiety. In his procedure, the contributions of UO_2^{2+} to the entropy of $\gamma\text{-UO}_3$, $\beta\text{-UO}_2(\text{OH})_2$ and schoepite were used to estimate the contribution of UO_2^{2+} to the entropies of other uranium compounds.

Although Latimer [52LAT] and Naumov *et al.* [71NAU/RYZ] suggested a value of $39.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the entropy of each water of hydration in a crystalline solid hydrate, Langmuir [78LAN] considered the value of $44.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, the value for the entropy of ice I from the compilation of Robie and Waldbaum [68ROB/WAL], to be more appropriate.

Ionic contributions to the entropy also have slightly different values for the different sources of parameters for Latimer's method. Thus, the entropies in the literature, calculated by Latimer's method, may vary significantly, depending on the exact set of parameters used in the estimation. Table 12 presents the parameter values selected for the NEA's uranium review [92GRE/FUG].

Also, for some compounds, especially binary solids, better entropy values may be estimated by comparison with values for closely related solids than by Latimer's method. For chalcogenides the reader is referred to the discussion given by Mills [74MIL, Section 2.4.2].

Helgeson and co-workers [78HEL/DEL] gave entropy estimation techniques for oxide minerals using the sum of the entropies for the constituent oxides [78HEL/DEL, their Eqs. (62) and (75)].

For some elements and ions, including most of the rare earths and actinides, the metals and ions have magnetic contributions to their entropies that depend mainly on their ground state electronic configurations. The S_{mag}° values range

*Note added in press: Recently Sverjensky, Shock and Helgeson [97SVE/SHO] have proposed correlations for $\Delta_r C_{p,m}^\circ$ for complex formation reactions between divalent cations and monovalent ligands.

Table 12: Contributions to entropies of solids ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), mainly from Refs. [71NAU/RYZ] and [92GRE/FUG]. The values in parentheses were not directly based on experimental values, but were estimated by Naumov, Ryzhenko and Khodakovsky [71NAU/RYZ].

Anion	Average cation charge			
	+1	+2	+3	+4
OH^-	30.5	19.2	17.5	(19.2)
O^{2-}	8.4	2.5	2.1	1.3
F^-	23.0	17.6	16.1	20.1
Cl^-	43.9	32.6	29.3	33.1
Br^-	56.1	45.2	41.8	49.8
I^-	63.2	54.4	55.2	51.0
IO_3^-	104.6	(92)		
CO_3^{2-}	64.9	49.4		
NO_3^-	90.8	73.2		
SO_3^{2-}	83.3	62.3	50.2	(46) ^(a)
SO_4^{2-}	92.9	67.8	57.3	(50)
PO_4^{3-}	79.5	62.8	57.3	(50) ^(a)
PO_3^-	66.9	54.0	(50.0)	(48) ^(a)
HPO_4^-	87.9	72.4	66.9	(63)
<hr/>				
H_2O	44.7			
UO_2^{2+} ^(b)	94.7			
U ^(c)	66.9			

^(a) Estimated by [92GRE/FUG].

^(b) Treated as a dipositive ion for the purpose of selecting anion contributions.

^(c) For uranium compounds not containing $\text{U}^{\text{VI}}\text{O}_2^{2+}$.

from 0.0 to $23.56 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for various rare earth and actinide ions[†] M^{2+} , M^{3+} , and M^{4+} at 298.15 K. Values for the total entropy $S_{\text{m}}^{\circ}(T_0)$ vary by $39 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $\text{RCl}_3(\text{cr})$ across the series, for R_2O_3 by $49 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ($24.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ per rare earth ion), and for R^{3+} by $57 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [77SPE/RAR, 92RAR]. It is clear that S_{mag}° is a significant fraction of the total variation of $S_{\text{m}}^{\circ}(T_0)$ across the rare earth series, and it must be taken into consideration for any accurate scheme for estimating $S_{\text{m}}^{\circ}(T_0)$. At 298.15 K there are three different structural types of $\text{RCl}_3(\text{cr})$ and three of $\text{R}_2\text{O}_3(\text{cr})$ for the rare earth series, so there are also structural factors that affect series trends.

For lanthanides and actinides and their cations, the $4f$ or $5f$ electrons are shielded by their outer electrons from the electric fields of their neighbouring ions, so their orbital angular momentum is not quenched and Russell-Saunders coupling applies; thus the J quantum number remains a valid measure of total angular momentum. If this is true, the degeneracies of the lanthanide and actinide cations are not altered significantly by their ionic environments and thus the J retain approximately their free-ion values. Consequently, the magnetic (electronic) entropies are then fully developed by room temperature and take the values $S_{\text{mag}}^{\circ} = R \ln(2J + 1)$. For a few cases (*e.g.*, Sm^{3+} and Eu^{3+}) S_{mag}° also contains small contributions from low-lying excited electronic levels that can become thermally occupied at room temperature. Hinchey and Cobble [70HIN/COB] noted that excited level term contributions add an extra $0.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ to $S_{\text{mag}}^{\circ}(T_0)$ for Sm^{3+} and $9.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for Eu^{3+} . Table 13 contains a listing of S_{mag}° for various M^{2+} , M^{3+} , and M^{4+} .

The electronic levels contribute to the total heat capacities through the Schottky heat capacity term, $C_{\text{Sch}}(T)$, see Ref. [83WES]. It is mathematically related to the Einstein heat capacity function.

For most lanthanide and actinide ions, the maximum in $C_{\text{Sch}}(T)$ appears at a temperature around 50 to 150 K, and this contribution to $C_{p,\text{m}}^{\circ}(T)$ becomes fairly small at temperatures near 298.15 K. For systems with low-lying excited electronic levels that can become thermally occupied, this is no longer true. For example, $C_{\text{Sch}}(T)$ for $\text{EuCl}_3(\text{cr})$ is essentially zero up to about 60 K, it increases to slightly greater than R up to 200 K, and then it very slowly decreases at higher temperatures [83WES]. Hinchey and Cobble [70HIN/COB] noted that $C_{\text{Sch}}(T_0) = 1.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for Sm^{3+} and $8.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for Eu^{3+} . Schottky contributions to the heat capacities are still significant at T_0 for some rare earth sesquioxides [83WES].

Westrum [83WES] has shown that for a particular type of solid containing a

[†]“M”, “R” and “AN” are used as general abbreviations for metal, rare earth (lanthanum and the lanthanides), and actinide respectively.

Table 13: Magnetic (electronic) contributions to entropies at 298.15 K.

4f or 5f configu- ration	Ground state ^(a)	S_{mag}° ^(b) (J·K ⁻¹ ·mol ⁻¹)	Ions
f ⁰	¹ S ₀	0.0	La ³⁺ , Ce ⁴⁺ , Th ⁴⁺ , Pa ⁵⁺ , U ⁶⁺ (UO ₂ ²⁺), Ac ³⁺
f ¹	² F _{5/2}	14.90	Ce ³⁺ , Th ³⁺ , Pa ⁴⁺ , U ⁵⁺ , Np ⁶⁺ , Pu ⁷⁺
f ²	³ H ₄	18.27	Pr ³⁺ , U ⁴⁺ , Np ⁵⁺ , Pu ⁶⁺ , Pa ³⁺
f ³	⁴ I _{9/2}	19.14	Nd ³⁺ , U ³⁺ , Np ⁴⁺ , Pu ⁵⁺
f ⁴	⁵ I ₄	18.27	Pm ³⁺ , Np ³⁺ , Pu ⁴⁺
f ⁵	⁶ H _{5/2}	14.90	Pu ³⁺ , Am ⁴⁺
f ⁵	⁶ H _{5/2}	15.2	Sm ³⁺
f ⁶	⁷ F ₀	0.00	Sm ²⁺ , Am ³⁺ , Cm ⁴⁺
f ⁶	⁷ F ₀	9.3	Eu ³⁺
f ⁷	⁸ S _{7/2}	17.29	Eu ²⁺ , Gd ³⁺ , Tb ⁴⁺ , Am ²⁺ , Cm ³⁺ , Bk ⁴⁺
f ⁸	⁷ F ₆	21.33	Tb ³⁺ , Bk ³⁺ , Cf ⁴⁺
f ⁹	⁶ H _{15/2}	23.05	Dy ³⁺ , Cf ³⁺
f ¹⁰	⁵ I ₈	23.56	Dy ²⁺ , Ho ³⁺ , Es ³⁺
f ¹¹	⁴ I _{15/2}	23.05	Er ³⁺ , Es ²⁺ , Fm ³⁺
f ¹²	³ H ₆	21.33	Tm ³⁺ , Fm ²⁺
f ¹³	² F _{7/2}	17.29	Tm ²⁺ , Yb ³⁺ , Md ²⁺
f ¹⁴	¹ S ₀	0.00	Yb ²⁺ , Lu ³⁺ , No ²⁺
–	¹ S ₀	0.00	Y ³⁺

^(a) Term symbols were taken from Refs. [70HIN/COB2, 70HIN/COB, 86EDE/GOF].

^(b) The S_{mag}° were calculated from $S_{\text{mag}}^{\circ} = R \ln(2J + 1)$. Values for S_{mag}° for Sm³⁺ and Eu³⁺ contain contributions from thermally-populated higher electronic states. Similar contributions may be present for some of the actinide ions.

trivalent lanthanide ion (RCl_3 , R_2O_3 , $\text{R}(\text{OH})_3$, R_2S_3), values of the “lattice entropy”, $S_{\text{lat}}^\circ(T_0) = S_{\text{m}}^\circ(T_0) - S_{\text{mag}}^\circ$, show a very smooth variation with the molar volume for an isostructural series of compounds with the same anion. These molar volumes can be calculated from crystallographic unit cell parameters. Note that each series of RX_3 or R_2X_3 (where “X” represents either a halogen, a chalcogen or an OH-group) undergoes one or more structural changes in going from light to heavy rare earths except for a few cases like $\text{R}(\text{OH})_3$; the smooth variation of $S_{\text{lat}}^\circ(T_0)$ with the molar volume applies only for compounds of the same stoichiometry with a common structure.

When S_{mag}° is added to interpolated values of S_{lat}° , the resulting $S_{\text{m}}^\circ(T_0)$ are generally highly accurate, frequently to within $0.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ of experimental values for the rare earth compounds. The uncertainties in estimated values may be much greater for many actinide compounds, where available thermodynamic data are much less complete.

4.2.2 Entropy estimation methods for aqueous species

Several methods are available to estimate entropies of aqueous species and entropies of reaction at 298.15 K. These methods use correlations between ionic entropies and a combination of crystallographic radii, molar volumes and mass, electrical charge, *etc.*

For some aqueous ions, including most of the rare earths and actinides, there are magnetic contributions to their entropies that depend mainly on the electronic configuration of their ground state (*cf.* Section 4.2.1, *p.* 68).

Hinchey and Cobble [70HIN/COB] calculated the ionic entropies of the aqueous trivalent rare earth ions (lanthanides and yttrium) from available thermodynamic data for hydrated rare earth chlorides. These data include low-temperature heat capacities for the crystals, and enthalpies and Gibbs free energies of solution. They found that $[S_{\text{m}}^\circ - S_{\text{mag}}^\circ]$ was a linear function of r^{-2} within the scatter of the then available values. Here r is the crystal radius for rare earth ions for a CN^\dagger of 6, and S_{mag}° is the magnetic contribution described in Section 4.2.1 and listed in Table 13. However, they had to estimate Gibbs free energies of solution for seven of the hydrated salts and entropies for six of them. In addition, some of the experimental enthalpies of solution later proved to be inaccurate. Spedding, Rard and Habenschuss [77SPE/RAR] recalculated these ionic entropies and included more complete and accurate data that were published after Hinchey and Cobble’s report. Spedding, Rard and Habenschuss [77SPE/RAR] found that $[S_{\text{m}}^\circ(T_0) - S_{\text{mag}}^\circ]$ actually had a tilted S shape as a

[†]CN is used as an abbreviation for “coordination number”.

function of r^{-2} , and this S shape correlated fairly well with the overall hydration of the rare earth ions.

Powell and Latimer [51POW/LAT] found that $(S_m^\circ - \frac{3}{2}R \ln M)$ was a linear function of r^{-2} for aqueous ions of various stoichiometries, whereas Couture and Laidler [57COU/LAI] found that $(S_m^{\circ, \text{abs}}(T_0) - \frac{3}{2}R \ln M)$ was a linear function of $z^2/(Nr_{\text{adj}})$ for oxyanions, where M is the mass of the oxyanion under consideration, N the number of coordinated oxygen atoms present in this anion, and r_{adj} the covalent radius of the central atom plus the van der Waals radius of an oxygen. Here $S_m^{\circ, \text{abs}}(T_0) = (S_m^\circ(T_0) + 23.0|z|)$ changed the conventional scale to an “absolute” scale by using $23.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the “absolute entropy” of H^+ . Related equations are those of Cobble [53COB, 53COB3] and (without the mass term) Cobble [53COB2], Powell [54POW], Helgeson *et al.* [69HEL, Eq. (26)], [88SHO/HEL, Eq. (55)], [81HEL/KIR, Eq. (283)], [85JAC/HEL, Eqs. (22) and (25)], and also Ruaya [88RUA, Eq. (6)], Sassani and Shock [92SAS/SHO], and Shock *et al.* [97SHO/SAS].

The importance of Powell and Latimer’s [51POW/LAT] and Couture and Laidler’s [57COU/LAI] work is that they showed that entropies of very different types of ions could be correlated using ionic mass, charge type, and simple structural features. The $\frac{3}{2}R \ln M$ term is derived from the statistical thermodynamic calculation of the absolute entropy of a gas phase ion. An entropy of an aqueous ion can be considered as the sum of its gas phase entropy and the entropy of hydration of that ion by liquid water. The entropy of hydration should mainly depend on the sign and charge of the ion and the ionic radius. The presence of the $\frac{3}{2}R \ln M$ is then justified by assuming this is a gas phase feature that is not lost when the ion becomes hydrated in aqueous solutions.

The same type of mass dependence was included by David [86DAV2, 86DAV] in his comprehensive analysis of ionic entropies of the aqueous tripositive lanthanide and actinide ions. David [86DAV2, his Fig. (10)] found that the adjusted entropy,

$$S_{\text{adj}}^\circ(T_0) = S_m^\circ(T_0) - S_{\text{mag}}^\circ - \frac{3}{2}R \ln M$$

was a simple and symmetrical function of the $\text{CN} = 8$ tripositive rare earth crystal radii. This curve was S -shaped, in agreement with the findings of Spedding, Rard and Habenschuss [77SPE/RAR], and that shape was understandable in terms of changes of total hydration of the rare earth ions as a function of the ionic radius. David also noted that the hydrated radii of actinide ions AN^{3+} were essentially proportional to those for rare earths R^{3+} , and thus the curve for rare earths can be used to estimate $S_{\text{adj}}^\circ(T_0)$ for AN^{3+} with a fairly high degree of confidence. An experimental value of $S_{\text{adj}}^\circ(T_0)$ is available only for Pu^{3+} among the actinides; although it falls slightly off the curve based upon values for the for R^{3+} , it does

agree with its interpolated position on the $S_{\text{adj}}^{\circ}(T_0)$ curve for AN^{3+} within its uncertainty limits. These estimated values of $S_{\text{adj}}^{\circ}(T_0)$ for AN^{3+} were then used by David for calculation of his $S_{\text{m}}^{\circ}(T_0)$ values.

David [86DAV2, 86DAV] also estimated $S_{\text{m}}^{\circ}(T_0)$ values for all possible R^{2+} , AN^{2+} , R^{4+} , and AN^{4+} . The dipositive ion values were based on $S_{\text{adj}}^{\circ}(T_0)$ for Ca^{2+} and Sr^{2+} with $\text{CN} = 6$, and those for the tetrapositive ions were based on Ce^{4+} and Th^{4+} with $\text{CN} = 8$. Since there are insufficient data to establish series trends as a function of ionic radii in these cases, David's estimated entropies have much greater uncertainties than for the tripositive R^{3+} and AN^{3+} ions.

Powell and Latimer [51POW/LAT] found that the entropies of a variety of non-electrolytes in aqueous solution could be represented by the equation

$$S_{\text{m}}^{\circ}(T_0) = \frac{3}{2}R \ln M + S_{\text{int}}^{\circ} + 41.8 - 0.92 V_{\text{m}},$$

where V_{m} is the molar volume of the non-electrolyte in $\text{cm}^3 \cdot \text{mol}^{-1}$ for its pure liquid state, and S_{int}° is the "internal" contribution to the entropy as calculated for an ideal gas using statistical thermodynamic methods for rotational, vibrational, and electronic contributions. In general, non-polar inorganic gases (inert gases, halogens, O_2), a few polar gases (H_2O , HF , NO , N_2O , COS), and some saturated alkanes (CH_4 , C_2H_6) were well represented by this equation, with deviations of only 1 to 5 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. However, a number of other polar gases and liquids (H_2S , CO , SO_2 , CO_2 , NH_3 , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$) and also N_2 showed deviations of 10 to 25 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Cobble [53COB3] gave an extended version of this equation which is valid for small and medium sized organic molecules, but it fails for larger molecules. A more general and accurate correlation for non-electrolytes is certainly needed.

An alternative to the Powell and Latimer equation has been proposed by Laidler [56LAI], Eqs. (64) and (65) below. The relative merits of this and Powell and Latimer type of equations have been discussed by Scott and Huhus [57SCO/HUG] and Laidler [57LAI]. The following two empirical equations have been proposed for the estimation of the partial molar entropy of ions in aqueous solution

$$S_{\text{m}}^{\circ, \text{abs}}(i, T_0) = \frac{3}{2}R \ln M_i + 42.68 - 4.853 \times 10^{-9} \frac{z_i^2}{r_{u,i}} \quad (64)$$

and

$$S_{\text{m}}^{\circ, \text{abs}}(i, T_0) = \frac{3}{2}R \ln M_i + 152.7 - 1.347 \times 10^{-17} \frac{z_i}{r_{\text{eff},i}^2} \quad (65)$$

where r_u is Pauling's univalent radius [60PAU, Table 13-3] converted from units of Å to metre, and r_{eff} is an effective ion radius. The "ordinary" and absolute entropy

scales differ by the *assigned* values of the entropy of H^+ , which are -23.0 and $0.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. Hence these two entropies for an ion i of charge z_i are related by the equation

$$S_{\text{m}}^{\circ, \text{abs}}(i, T_0) = S_{\text{m}}^{\circ}(i, T_0) - 23.0 z_i \quad (66)$$

The equations above are able to describe the absolute ion entropies within 10 to 15 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. From the discussion given in [57SCO/HUG] and [57LAI] it is clear that the theoretical foundations of both the Powell and Latimer and the Laidler type of equations are rather weak. However they provide some guidelines for entropy estimations.

For aqueous complex ions of uranium, Langmuir [78LAN, Figure 1] gave a simple correlation between $S_{\text{m}}^{\circ}(i, T_0)$ and the ionic charge, z_i . The parameters for this correlation were obtained by fitting data to a 4th degree polynomial of z_i (see also [80LAN/HER, Fig. 1] for Th(IV) complexes).

For halide and hydroxide complexes, Helgeson gave two equations that relate the entropy of a complex with either crystallographic radii only ([81HEL/KIR, Eq. (283)] for neutral complexes, or effective electrostatic radii [88SHO/HEL, Eq. (58)] for ionic species), or in combination with the stoichiometry of the complex, see Ref. [85JAC/HEL, Eqs. (22) and (25)], and also [88RUA, Eq. (6)].

The following methods are available to estimate standard reaction entropies:

- For hydrolysis reactions, Baes and Mesmer gave correlations for the reaction entropy for the first mononuclear hydrolysis product [81BAE/MES, their Eq. (11)], for the polynuclear products (their Eq. (20)), and for step-wise mononuclear hydrolysis (their Eq. (23)).
- Entropies of dissociation for a group of aqueous metal complexes (halide, *etc.*) may be estimated with equations similar to that given by Helgeson for charged and neutral metal chloride complexes, see Ref. [69HEL, Eq. (27)] and Ref. [81HEL/KIR, Eq. (283)] for neutral complexes.*
- Electrostatic models of complex formation were compared by Langmuir [79LAN]. The simplest model [79LAN, Eq. (4)] was used for making crude estimations of the entropy of formation of sulphate and fluoride complexes, *cf.* [79LAN, Figures 12 and 14].
- The Ryzhenko-Bryzgalin model as described in Section 2.4.3 (*cf.* Eq. (47)).

*Note added in press: Sverjensky, Shock and Helgeson [97SVE/SHO] have recently proposed correlations for $\Delta_{\text{r}}S_{\text{m}}^{\circ}$ for complex formation reactions involving monovalent ligands as well as SO_4^{2-} and CO_3^{2-} .

- Sverjensky [87SVE] has proposed correlations between the $\Delta_r S_m^\circ$ for metal complexation reactions with halide ions and the values of S_m° for the metal cation and the ligand.

4.3 Examples

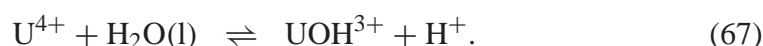
Criss and Cobble's publications [64CRI/COB2, 64CRI/COB] appeared before the heat capacity for Co^{2+} and Th^{4+} had been determined experimentally, and therefore these ions are suitable to do test calculations with Eqs. (62) and (63). For Co^{2+} , the standard partial molar entropy given by NBS, $-113 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [82WAG/EVA], is used here:

Reference	$C_{p,m}^\circ$ (Co^{2+} , aq, 298.15 K)/ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)
[78SPI/SIN] (experimental)	$-25 \pm (2 \text{ to } 3)$
Eq. (62)	+21
Eq. (63)	-38

For Th^{4+} , the NBS tables [82WAG/EVA] give an entropy of $-422.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. For this example Eq. (63) is not applicable since there are insufficient data for M^{4+} ions to determine values of a and b . The estimation with Eq. (62) gives an ionic heat capacity for Th^{4+} of $-30 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, as compared with the experimental value of $-(1 \pm 11) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [76MOR/MCC].

These results give some indication on the accuracy expected from these kinds of estimations.

A more practical example is to predict high-temperature equilibrium constants for a reaction such as



The entropy and heat capacity for water at 298.15 K are taken from CODATA [89COX/WAG], and the corresponding values for U^{4+} from the NEA-TDB review [92GRE/FUG], while the values for H^+ are zero by the hydrogen ion convention. Therefore, only the standard partial molar entropy and heat capacity at 298.15 K for UOH^{3+} will be estimated here.

Langmuir's equation [78LAN, p.554] gives an estimate of $-218 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the standard partial molar ionic entropy of uranium species with an electrical charge of +3. In contrast, Shock and Helgeson's equation which ignores magnetic contributions to the entropy [88SHO/HEL, Eq. (58)], using a ionic radius of $0.97 \times 10^{-10} \text{ m}$ for UOH^{3+} (equal to that of U^{4+}), gives an estimate of $-207 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

In order to use Eq. (10) in Ref. [81BAE/MES], the U–O distance of 2.42×10^{-10} m given in [81BAE/MES, Table 2] may be used. The logarithm of the equilibrium constant is also needed, and the recommended value in the NEA–TDB uranium report will be used, $\log_{10} K_1^\circ(67, 298.15 \text{ K}) = -(0.54 \pm 0.06)$ [92GRE/FUG]. This results in an entropy of reaction of $+128 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Finally, adding the entropy values for $\text{H}_2\text{O}(\text{l})$ and U^{4+} , the value of $-219 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is obtained for the estimate of $S_m^\circ(\text{UOH}^{3+}, \text{aq}, 298.15 \text{ K})$.

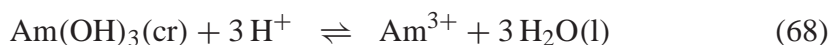
Thus, the estimated values for the standard partial molar entropy of UOH^{3+} are:

Reference/Method	$S_m^\circ(\text{UOH}^{3+}, \text{aq}, T_0) / (\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$
[78LAN, p.554]	–218
[81BAE/MES, their Eq. (10)]	–219
[88SHO/HEL, their Eq. (58)]	–207

To estimate the standard partial molar heat capacity for UOH^{3+} with Criss and Cobble’s equation, our Eq. (62), the standard partial molar ionic entropy is needed. The value of $-219 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ will be used as a “selected estimation”. The derived heat capacity is then $-30 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The change in heat capacity of Reaction (67) is therefore estimated at $-57 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This small calculated heat capacity of reaction agrees with our discussion on isoelectric reactions (*cf.* Sections 2.2.3, p.16).

A comparison between experimental values for the equilibrium constant of Reaction (67) [78NIK] and the calculated high-temperature values with Eq. (20) (*i.e.*, constant $\Delta_r C_{p,m}^\circ$) is given in Figure 18.

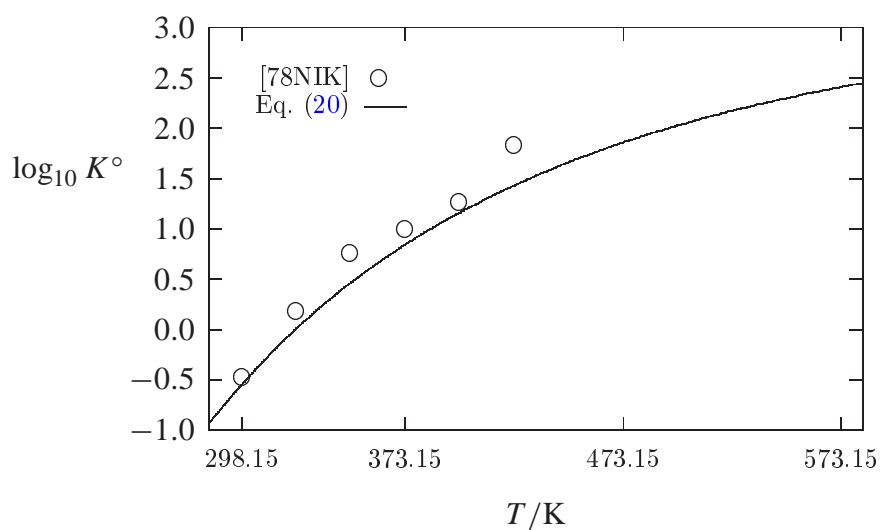
The solubility reaction



is used as an example for an equilibrium involving a solid phase. As before, the properties of water are taken from CODATA [89COX/WAG]. For the entropy of $\text{Am}(\text{OH})_3(\text{cr})$ the method of Latimer [52LAT] will be used with the following entropy contributions: Am^{3+} : $71 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (estimated from [52LAT, Appendix III, Figure 7]); OH^- with +3 cation: $17.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [71NAU/RYZ, TableI-3]. The magnetic contribution to S_m° is zero in this case. Therefore, $S_m^\circ(\text{Am}(\text{OH})_3, \text{cr}, T_0) = 71 + 3 \times 17.6 = 124 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

For the estimation of the heat capacity of $\text{Am}(\text{OH})_3(\text{cr})$, the method described in Chapter 3 of Ref. [93KUB/ALC] will be used. The contribution to the heat capacity for Am^{3+} is estimated as $29 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (from the trend between Th and U of Table IX in Ref. [93KUB/ALC]), and that of OH^- in a solid compound is given as $30.96 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [93KUB/ALC, Table X]. The estimated value is therefore $C_{p,m}^\circ(\text{Am}(\text{OH})_3, \text{cr}, T_0) = 122 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Figure 18: Equilibrium constants from Nikolaeva [78NIK] for Reaction (67), $U^{4+} + H_2O(l) \rightleftharpoons UOH^{3+} + H^+$, compared with the calculated values using the “constant $\Delta_r C_{p,m}^\circ$ ” equation, Eq. (20), with $\log_{10} K^\circ(T_0) = -0.54$ and the estimated values (see text) of $\Delta_r C_{p,m}^\circ = -57 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $\Delta_r S_m^\circ(T_0) = +128 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.



The standard partial molar entropy of Am^{3+} was estimated as $-(201 \pm 13) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ by Fuger and Oetting [76FUG/OET]. Using this value, the standard partial molar heat capacity estimated by Criss and Cobble's equation, our Eq. (62), is then $C_{p,m}^{\circ}(\text{Am}^{3+}, \text{aq}, T_0) = -39 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Shock and Helgeson's equation, our Eq. (63) [88SHO/HEL], with the correlation parameters for the heavy rare earths would result in $C_{p,m}^{\circ}(\text{Am}^{3+}, \text{aq}, T_0) = -162 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ instead. However, this value has no experimental or theoretical basis and the values of $C_{p,m}^{\circ}(\text{R}^{3+}, \text{aq}, T_0)$ for rare earth ions derived by Shock and Helgeson [88SHO/HEL] seem to be much too negative (*cf.* the comments on $C_{p,m}^{\circ}$ estimation methods for aqueous species in p.66, Section 4.1.2.3); consequently the heat capacity obtained with the method of Criss and Cobble will be used here.

Therefore, for Reaction (68) the following values are estimated:

$$\begin{aligned}\Delta_r S_m^{\circ}(T_0) &= 3 \times 69.95 + (-201) - 124 = -115 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ \Delta_r C_{p,m}^{\circ}(T_0) &= 3 \times 75.35 + (-39) - 122 = 65 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.\end{aligned}$$

5 Concluding remarks

Second-law extrapolation procedures must be used with caution in the absence of experimental heat capacities. When fitting high-temperature equilibrium constants, more than one equation should be tested (for example both the “constant $\Delta_r C_{p,m}^{\circ}$ ” equation, Eq. (20), and the Revised Helgeson-Kirkham-Flowers model, Eq. (33)), and the resulting reaction properties obtained at 298.15 K with different methods (*e.g.*, entropy and heat capacity) should be compared, as should their uncertainties and the difference between the calculated and experimental equilibrium constants at all temperatures.

When extrapolating equilibrium constants to higher temperatures from lower temperature data, several methods should also be tested and the results compared with each other (*cf.* Figures 8 to 10). Comparison of the results from these alternative methods will give a good estimate of the magnitude of the extrapolation error. This uncertainty, which differs for different methods of extrapolation, gives increased uncertainty to the thermodynamic reaction properties at higher temperatures compared to 298.15 K.

A similar attitude should be adopted with estimated thermodynamic properties which are used to make temperature extrapolations. If possible, several estimation methods should be compared. It is unfortunate that there are only a few estimation methods of $C_{p,m,i}^{\circ}$ for aqueous species, all of which have a limited field of application. This necessitates the use of less reliable methods like the DQUANT equation, Eq. (32), and the isocoulombic approach (*cf.* Section 4.1.2.2). The measurement of aqueous solution heat capacities should be given a high priority.

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