3.3 Ionic activity coefficients

Electromotive force (e.m.f.) measurements on cells without liquid-liquid junctions (or other less direct experimental techniques) lead to experimental values of mean activity coefficients of an electrolyte but not to individual ionic activity coefficients. In particular, the electromotive force of the cell

$$\text{H}_2, \text{Pt} \quad | \quad \text{solution containing} \quad | \quad \text{AgCl} \quad | \quad \text{Ag} \qquad \qquad \text{(I)}$$
$$| \quad \quad \text{H}^+ \text{ and Cl}^- \quad \quad | \quad \quad |$$

leads directly to the value of $m_H m_{Cl} \gamma^2_{H,Cl}$ and, if the value of m_{Cl} is known, indirectly to that of $m_H \gamma^2_{H,Cl}$.

It is permissible, and often convenient, to write

$$\gamma^2_{H,Cl} = \gamma_H \gamma_{Cl} \qquad \qquad 3.01$$
$$\gamma^2_{Na,Cl} = \gamma_{Na} \gamma_{Cl} \qquad \qquad 3.02$$
$$\gamma^2_{K,Cl} = \gamma_K \gamma_{Cl} \qquad \qquad 3.03$$

and so on, but the values of the *ionic activity coefficients* γ_H, γ_{Na}, γ_K and γ_{Cl} are not uniquely defined. In each solution, an arbitrary value may be conventionally assigned to γ for any one chosen ionic species. This does not mean that one convention may not be more convenient than another. In particular, all 1-1 electrolytes present in a solution of total molality less than 0.01 may be considered to have equal *mean activity coefficients*. Under these conditions, it is natural to equate the ionic activity coefficients to the common mean activity coefficient. In fact, any other convention would be unjustified.

At higher molalities, different electrolytes in the same solution have different mean activity coefficients and, consequently, the convention must be less simple. If M is used to denote a cation and X an anion, then

$$\frac{\gamma_H}{\gamma_M} \equiv \frac{\gamma_H \gamma_X}{\gamma_M \gamma_X} \equiv \frac{\gamma^2_{H,X}}{\gamma^2_{M,X}} \qquad \qquad 3.04$$

is thermodynamically well defined because $\gamma_M \gamma_X \equiv \gamma^2_{M,X}$. The convention for defining γ_H is

$$\ln \gamma_H = \frac{\sum_M m_M \ln(\gamma_H / \gamma_M) + \sum_X m_X \ln(\gamma_H \gamma_X)}{\sum_M m_M + \sum_X m_X} \qquad \qquad 3.05$$

with the analogous definition for a typical anion, say Br⁻:

$$\ln \gamma_{Br} = \frac{\sum_M m_M \ln(\gamma_M \gamma_{Br}) + \sum_X m_X \ln(\gamma_{Br} / \gamma_X)}{\sum_M m_M + \sum_X m_X} \qquad \qquad 3.06$$

The conventional relationships automatically satisfy the thermodynamic requirement

$$\ln \gamma_H + \ln \gamma_{Br} = 2 \ln \gamma_{H,Br} \qquad\qquad 3.07$$

When there is only a single electrolyte present, say HBr, and the solutions are dilute, these conventions reduce to:

$$\ln \gamma_H = \ln \gamma_{Br} = \ln \gamma_{H,Br} \qquad\qquad 3.08$$

This convention which treats all ionic species similarly is the simplest possible. It is aesthetically satisfying, but it has little practical utility because the values of all the mean activity coefficients of the several electrolytes present are usually not known. (In the more general case of ions with various charges, the formulae are more complicated.)

It is, therefore, necessary to use a much simpler, though less symmetrical, convention. One that has proven especially useful is to define the activity coefficient of the chloride ion, at an ionic strength I not exceeding 0.1, by

$$\log \gamma_{Cl} = - \frac{A I^{\frac{1}{2}}}{1 + (Ba)I^{\frac{1}{2}}} \qquad\qquad 3.09$$

where A has at each temperature the value given by the theory of Debye and Hückel, and Ba has a specified value; when the recommended value is $Ba = 1.5\ mol^{-\frac{1}{2}}kg^{-\frac{1}{2}}$, then equation 3.09 is called the Bates-Guggenheim convention.

An empirical extension of the Debye-Hückel equation, proposed by Davies and given by equation 3.10 for an ion of valency z,

$$\log \gamma = -A z^2 \left(I^{\frac{1}{2}} / [1 + I^{\frac{1}{2}}] - 0.3 I \right) \qquad\qquad 3.10$$

has been used successfully for the estimation of activity coefficients in solutions with concentrations as high as $0.15\ mol\ kg^{-1}$.

At higher ionic strengths these simple formulae are inadequate, as specific interactions between the ion and different counter ions become important. The methods most frequently used for estimation of activity coefficients in concentrated electrolyte solutions with short range interactions are the specific ion interaction models. These models, such as that based upon the Pitzer formalism and equations, which is a particularly important example, can be used to account for the influence of both ionic strength and medium composition on stability constants.

Once the value of the activity coefficient of the single ion, such as the chloride ion in HCl, has been conventionally defined, this value may be combined with the value of $m_H \gamma^2_{H,Cl}$ to obtain the value of $m_H \gamma_H$ or of $p(m_H \gamma_H) = -\log_{10} m_H \gamma_H$.