The McMillan–Mayer framework and the theory of electrolyte solutions

Martin P. Breil*, Jørgen M. Mollerup

IVC-SEP, Department of Chemical Engineering, Building 229, Technical University of Denmark, DK-2800 Lyngby, Denmark

Abstract

In electrolyte thermodynamics one often speaks of two thermodynamic frameworks; the Lewis–Randall framework (characterised by temperature, pressure, and mole numbers) and the McMillan–Mayer framework (characterised by temperature, total volume, solute mole numbers, and solvent chemical potential). However, there is only *one* framework in thermodynamics; the apparent difference between the two 'frameworks' is, in electrolyte thermodynamics, due to the change in the pressure caused by the charging process at constant volume and solvent chemical potential.

The so-called McMillan–Mayer framework is set in the context of the classical thermodynamics and the use of it is examplified by the Debye–Hückel theory. The so-called McMillan–Mayer framework is superfluous when the thermodynamics of the electrolyte solutions is described by the Helmholtz energy functions.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Electrolyte thermodynamics; McMillan–Mayer framework; Charging process; Semi-canonical ensemble

1. Introduction

The aim is to show how the McMillan–Mayer (MM) framework is related to the Lewis–Randall (LR) framework and furthermore that the difference is due to the choice of independent variables. The LR framework is at constant pressure and mole numbers, whereas the MM framework is at constant volume, solute mole numbers and solvent chemical potential. If a proper state function is applied, the description does not depend on the choice of independent variables since the partial derivatives of the state function complete the description of the system, i.e., provide the dependent variables.

Section 2 is devoted to the definition of the framework in terms of statistical mechanics and derivation of the fundamental equation relating LR to MM. Section 3 illustrates how electrolyte thermodynamics can be interpreted entirely within the framework of the classical thermodynamics. Section 4 is a short outline of the Debye–Hückel model based on the original paper from 1923, and serves to illustrate the results derived in Section 3.

2. McMillan–Mayer

The paper of McMillan and Mayer [1] presents a thermodynamic framework that is characterised by temperature, volume, the solute mole numbers, and the solvent chemical potential. The solvent of the system is regarded as a dielectric continuum, and the permittivity of the system is that of the pure solvent. The description of a single phase (containing C components) requires the specification of $C + 2$ independent variables according to Gibbs' phase rule.

The McMillan–Mayer framework is not very convenient since it involves the chemical potential of the solvent which is not a favourable independent variable to use. Nevertheless, this framework is often encountered in electrolyte thermodynamics since the solvent chemical potential during the charging process is considered to be constant.

It is important to stress that the McMillan–Mayer framework is not a thermodynamic framework detached from the rest of the classical thermodynamics. It is just an alternative

* Corresponding author. Tel.: +45 4525 2891; fax: +45 4588 2258.
   E-mail address: mpb@kt.dtu.dk (M.P. Breil).

level of description. The framework of classical thermodynamics is developed within the concepts of the classical physics. Therefore it is imperative to have a both well-defined and concise definition of the McMillan–Mayer framework and to be able to accommodate it within the classical thermodynamics.

The solution theory of McMillan and Mayer is also presented by Hill [2, p. 262] who offers a thorough presentation. A key paper in the understanding and hence the application of the McMillan–Mayer framework has been the one by Friedman [3] who describes the conversion of thermodynamic properties from the Lewis–Randall framework to the McMillan–Mayer framework. To cite [3, p. 388]: "the independent variables for the application of the McMillan–Mayer theory are c, T and P_0". c is the molar concentrations of the solute particles and P_0 is the pressure of the pure solvent. Thus the number of independent variables in Friedman's treatment is $C + 1$, all of which are intensive variables.

Lately, Haynes and Newman [4] also present the conversion between the frameworks but from a statistical mechanical view point. Cabezas and O'Connell [5] discuss some uses and misuses of thermodynamic models for dilute liquid solutions, including the McMillan–Mayer framework.

The thermodynamic framework of electrolyte solutions—of both single-component and multi-component solvent—have been investigated [6,7]. The thermodynamic consistency and reference scale conversion in multi-solvent electrolyte solutions have also been addressed by Lee [8]. The electrostatic forces of these electrolyte solutions are often modelled by the Debye–Hückel model [9] and this is also the model used in this paper. However, Simonin [10,11] has presented both the conversion of the McMillan–Mayer framework when the electrostatic MSA model is applied.

Recently, Curtis et al. [12] have used the McMillan–Mayer framework for converting thermodynamic properties of systems with multiple solvents in order to interpret light-scattering data. A closely related topic is that of molecular light scattering which can be used for the determination of osmotic virial coefficients [13]. The thermodynamics involved is often described in terms of the McMillan–Mayer framework [14]. Furthermore, the framework has also been applied to the physics of surfactants and micelles [14,15].

2.1. Equilibrium state description

Consider a phase containing C components. In accord with Gibbs' phase rule, this phase will have $C + 2$ degrees of freedom. Usually, the independent variables are the temperature T, the mole numbers $\boldsymbol{n}$ and either the volume V or the pressure P. By introducing the continuum concept, the solvent of the system is no longer regarded as a molecular part of the system but as a medium with a dielectric constant $\varepsilon_r \varepsilon_0$ in which the solutes are distributed. In the McMillan–Mayer framework, the solvent is characterised by its chemical potential rather than the dielectric constant. Hence the system is characterised by the state $(T, V, \boldsymbol{n} \backslash n_0, \mu_0)$ where μ_0 is the solvent chemical potential and $\boldsymbol{n} \backslash n_0$ means the vec-

tor $[n_1, n_2, n_3, \ldots]$, that is all mole numbers except the solvent mole number n_0. Thus μ_0 replaces n_0 as an independent variable.

2.2. A statistical mechanical explanation

In the paper [1], McMillan and Mayer state that the framework is equal to that of an imperfect gas where the vacuum has been replaced by a solvent. This is identical to the continuum concept. This is in agreement with Simonin's statement [10]: "an important feature of the McMillan–Mayer description level is that the thermodynamic functions are calculated at constant solvent chemical potential."

Thermodynamic state functions can be developed from statistical mechanics [1,4]. In that aspect, it is easy to visualise the relation between the Lewis–Randall framework and the McMillan–Mayer framework.

A semi-grand canonical ensemble is derived from the canonical ensemble [16]. The number of solvent molecules N_0 (in the canonical ensemble) is replaced by the molecular chemical potential of the solvent, μ_0^m. Next, we define a semi-grand canonical partition function $\Psi(T, V, \boldsymbol{N} \backslash N_0, \mu_0^m)$ [4] and [17, p. 66]. Given a system of C components, the relationships between the semi-grand canonical partition function and those of the canonical and grand canonical ensembles are

$$\Xi(T, V, \boldsymbol{\mu}^m) = \sum_{N_1} \cdots \sum_{N_C} \exp\left(\beta \sum_{i=1}^{C} N_i \mu_i^m\right)$$
$$\times \Psi(T, V, \boldsymbol{N} \backslash N_0, \mu_0^m)$$

and

$$\Psi(T, V, \boldsymbol{N} \backslash N_0, \mu_0^m) = \sum_{N_0} \exp\left(\beta N_0 \mu_0^m\right) Q(T, V, \boldsymbol{N}) \quad (1)$$

where $\beta = 1/kT$, Q and Ξ are the partition functions of the canonical and grand canonical ensembles, respectively. The partition function Q is a function of all mole numbers including N_0.

The theory of fluctuation [17, p. 63] states that if the total number of molecules N_0 is large, the summation in Eq. (1) can be replaced by a single term where N_0 is replaced by the average number of molecules $\bar{N}_0$. That is

$$\Psi(T, V, \boldsymbol{N} \backslash \bar{N}_0, \mu_0^m) = \exp\left(\beta \bar{N}_0 \mu_0^m\right) Q(T, V, \boldsymbol{N}). \quad (2)$$

The partition function Q is now a function of the average number of solvent molecules. The characteristic thermodynamic function of the partition function Ψ will therefore consist of two terms

$$-kT \ln \Psi(T, V, \boldsymbol{N} \backslash \bar{N}_0, \mu_0^m) = -\bar{N}_0 \mu_0^m - kT \ln Q(T, V, \boldsymbol{N})$$
$$(3)$$

of which the last term by definition is the Helmholtz energy $A(T, V, \boldsymbol{n})$ [16,17]. The left-hand side of Eq. (3) is defined as the

McMillan–Mayer state function, B,

$$B(T, V, \boldsymbol{n} \backslash n_0, \mu_0) = -n_0 \mu_0 + A(T, V, \boldsymbol{n}), \tag{4}$$

where μ_0 is the molar chemical potential of the solvent and n_0 is the mole number of solvent. It is worth noting that B only depends indirectly on the number of solvent molecules. Based on Eq. (4), the McMillan–Mayer state function can be converted to the Helmholtz energy—and vice versa—through differential equations, Eqs. (5) and (6):

$$A(T, V, \boldsymbol{n}) = B(T, V, \boldsymbol{n} \backslash n_0, \mu_0) - \mu_0 \left(\frac{\partial B}{\partial \mu_0} \right)_{T, V, \boldsymbol{n} \backslash n_0} \tag{5}$$

$$B(T, V, \boldsymbol{n} \backslash n_0, \mu_0) = A(T, V, \boldsymbol{n}) - n_0 \left(\frac{\partial A}{\partial n_0} \right)_{T, V, \boldsymbol{n} \backslash n_0} \tag{6}$$

These two differential equations, Eqs. (5) and (6), are both Legendre transformations [18]; Eq. (5) is the first Legendre transform of B with respect to μ_0, and Eq. (6) is the first Legendre transform of A with respect to n_0. A Legendre transformation does not result in any loss in the information content.

2.3. Derivation of the excess of the McMillan–Mayer state function

The McMillan–Mayer state function obtained from statistical mechanics, Eq. (4), is

$$B(T, V, \boldsymbol{n} \backslash n_0, \mu_0) = A(T, V, \boldsymbol{n}) - n_0 \mu_0$$
$$= G(T, P, \boldsymbol{n}) - PV - n_0 \mu_0, \tag{7}$$

and as shown in Appendix A, the McMillan–Mayer state function of an ideal solution is

$$B^{\mathrm{id}}(T, V, \boldsymbol{n} \backslash n_0, \mu_0) = G^{\mathrm{id}}(T, P, \boldsymbol{n}) - PV - n_0 \mu_0. \tag{8}$$

The resulting *excess* energy is given by subtracting Eq. (8) from Eq. (7)

$$B^{\mathrm{E}}(T, V, \boldsymbol{n} \backslash n_0, \mu_0) = G^{\mathrm{E}}(T, P, \boldsymbol{n}).$$

Thus there is no difference between $B^{\mathrm{E}}(T, V, \boldsymbol{n} \backslash n_0, \mu_0)$ and $G^{\mathrm{E}}(T, P, \boldsymbol{n})$. However, this does not mean that the partial derivatives of these two functions are identical as well. Differentiation of $G^{\mathrm{E}}(T, P, \boldsymbol{n})$ with respect to n_i at constant temperature, pressure, and mole numbers of the remaining species, gives

$$\left(\frac{\partial G^{\mathrm{E}}}{\partial n_i} \right)_{T, P, \boldsymbol{n} \backslash n_i} = \left(\frac{\partial B^{\mathrm{E}}}{\partial n_i} \right)_{T, P, \boldsymbol{n} \backslash n_i} = \left(\frac{\partial B^{\mathrm{E}}}{\partial n_i} \right)_{T, V, \boldsymbol{n} \backslash (n_i, n_0), \mu_0}$$
$$+ \left(\frac{\partial B^{\mathrm{E}}}{\partial V} \right)_{T, \boldsymbol{n} \backslash n_0, \mu_0} \left(\frac{\partial V}{\partial n_i} \right)_{T, P, \boldsymbol{n} \backslash n_i}$$
$$+ \left(\frac{\partial B^{\mathrm{E}}}{\partial \mu_0} \right)_{T, V, \boldsymbol{n} \backslash n_0} \left(\frac{\partial \mu_0}{\partial n_i} \right)_{T, P, \boldsymbol{n} \backslash n_i}. \tag{9}$$

The derivatives of B^{E} are by definition

$$\left(\frac{\partial B^{\mathrm{E}}}{\partial n_i} \right)_{T, V, \boldsymbol{n} \backslash (n_i, n_0), \mu_0} \equiv RT \ln \gamma_i^{\mathrm{MM}}(T, V, \boldsymbol{n} \backslash n_0, \mu_0)$$

$$\left(\frac{\partial B^{\mathrm{E}}}{\partial V} \right)_{T, \boldsymbol{n} \backslash n_0, \mu_0} \equiv -P^{\mathrm{E}}(T, V, \boldsymbol{n} \backslash n_0, \mu_0)$$

$$\left(\frac{\partial B^{\mathrm{E}}}{\partial \mu_0} \right)_{T, V, \boldsymbol{n} \backslash n_0} \equiv -n_0^{\mathrm{E}}(T, V, \boldsymbol{n} \backslash n_0, \mu_0).$$

where $n_0^{\mathrm{E}} = n_0 - n_0^{\mathrm{id}}$. Eq. (9) strictly leads to an expression

$$RT \ln \gamma_i(T, P, \boldsymbol{n}) = RT \ln \gamma_i^{\mathrm{MM}} - P^{\mathrm{E}} \bar{V}_i - n_0^{\mathrm{E}} \left(\frac{\partial \mu_0}{\partial n_i} \right)_{T, P, \boldsymbol{n} \backslash n_0} \tag{10}$$

The last term of Eq. (10) is zero because μ_0 is an independent variable and does as such not depend on n_i. Therefore the relationship for a solute i is

$$RT \ln \gamma_i(T, P, \boldsymbol{n}) = RT \ln \gamma_i^{\mathrm{MM}}(T, V, \boldsymbol{n} \backslash n_0, \mu_0)$$
$$- \bar{V}_i P^{\mathrm{E}}(T, V, \boldsymbol{n} \backslash n_0, \mu_0) \tag{11}$$

The Lewis–Randall activity coefficient is at constant system pressure; whereas the McMillan–Mayer activity coefficient is at constant system volume and solvent chemical potential. The difference is due to the choice of independent variables.

3. Electrolyte solutions

Most often the McMillan–Mayer framework is associated with the theory of electrolyte solutions. The reason for this is probably that the solvent is often considered as a dielectric continuum and hence the chemical potential of the solvent is considered constant during the charging process. This implies that the dielectric constant is also constant during the charging process. The charging process of a solute at constant volume is sketched in Fig. 1. Compartments A and B are divided by an imaginary rigid membrane that only allows the solvent to penetrate, hence the solvent chemical potential is the same in the two compartments. Compartment A is the situation prior to the charging process and compartment B is the situation afterwards. It is important to realise that the temperatures, the volumes, the compositions, and the solvent chemical potentials are identical in both compartments. The number of solute molecules in compartments A and B are identical. However, in compartment B they are charged; half of them carry a positive charge and the other half carry a negative charge as indicated in Fig. 1.

In consequence of the charging process, the pressure will change from P in compartment A to $P + P^{\mathrm{elec}}$ in compartment B. The pressure P^{elec} is minus the volumetric derivative of the electrostatic Helmholtz function. An example hereof is the model derived by Debye and Hückel [9] which we will address in Section 4.

Since the solvent chemical potential prior to the charging, μ_0^A, is identical to the solvent chemical potential afterwards, μ_0^B, we
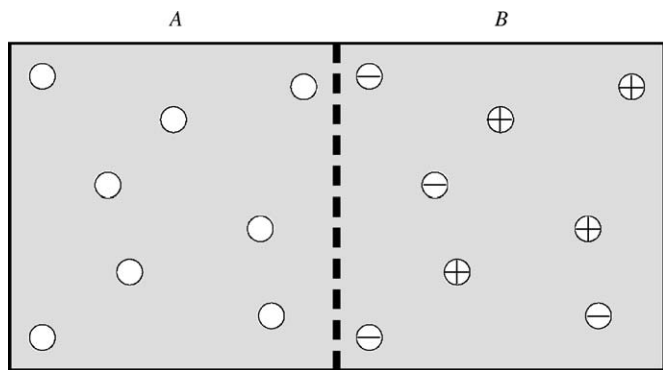
Fig. 1. A schematic representation of charging process at constant volume. Compartments A and B are divided by an imaginary rigid membrane that only allows the solvent to penetrate. Compartment A is the situation prior to the charging process and compartment B is the situation afterwards.

have

$$\mu_0^A(T, P, \boldsymbol{n}) = \mu_0^B(T, P + P^{\text{elec}}, \boldsymbol{n}). \tag{12}$$

The solvent chemical potential in compartment B is adjusted to the same pressure as in compartment A

$$\mu_0^B(T, P + P^{\text{elec}}, \boldsymbol{n})$$

$$= \mu_0^B(T, P, \boldsymbol{n}) + \int_P^{P+P^{\text{elec}}} \left(\frac{\partial \mu_0(T, P, \boldsymbol{n})}{\partial P} \right)_{T, \boldsymbol{n}} dP$$

$$= \mu_0^B(T, P, \boldsymbol{n}) + \int_P^{P+P^{\text{elec}}} \bar{V}_0 dP$$

$$= \mu_0^B(T, P, \boldsymbol{n}) + \bar{V}_0 P^{\text{elec}}, \tag{13}$$

where $\bar{V}_0$ is the partial molar volume of the solvent. By combining Eqs. (12) and (13) and furthermore by writing the chemical potentials in terms of the reference chemical potentials of the pure solvent and the solvent activities, we get

$$\mu_0^A(T, P) + RT \ln a_0^A(T, P, \boldsymbol{n})$$

$$= \mu_0^B(T, P) + RT \ln a_0^B(T, P, \boldsymbol{n}) + \bar{V}_0 P^{\text{elec}}. \tag{14}$$

where of course $\mu_0^A(T, P) = \mu_0^B(T, P)$. Furthermore, the activity is the product of the mole fraction and the activity coefficient; and since $x_0^A = x_0^B$, it follows that

$$\ln \gamma_0^B(T, P, \boldsymbol{n}) - \ln \gamma_0^A(T, P, \boldsymbol{n}) = -\frac{\bar{V}_0 P^{\text{elec}}}{RT} \tag{15}$$

This means that the solvent activity coefficient changes when the system is charged at constant temperature, volume, solute composition and solvent chemical potential.

For the charged system, compartment B in Fig. 1, the Helmholtz energy comprises of a classical and an additional electrostatic part, $A^B(T, V, \boldsymbol{n}) = A^{\text{classical}} + A^{\text{elec}}$ [9]. Therefore the Helmholtz energy prior to the charging process is identical to the classical Helmholtz energy. The change in the solvent activity coefficient is given by Eq. (15) where the electrostatic

pressure P^{elec} is given by

$$P^{\text{elec}}(T, V, \boldsymbol{n}\backslash n_0) \equiv - \left(\frac{\partial A^{\text{elec}}}{\partial V} \right)_{T, \boldsymbol{n}}, \tag{16}$$

and the partial molar volume $\bar{V}_0$ by

$$\bar{V}_0 \equiv \left(\frac{\partial V}{\partial n_0} \right)_{T, P, \boldsymbol{n}\backslash n_0} = -\frac{\left(\frac{\partial P}{\partial n_0} \right)_{T, V, \boldsymbol{n}\backslash n_0}}{\left(\frac{\partial P}{\partial V} \right)_{T, \boldsymbol{n}}} = -\frac{\left(\frac{\partial^2 A^B}{\partial V \partial n_0} \right)_T}{\left(\frac{\partial^2 A^B}{\partial V^2} \right)_{T, \boldsymbol{n}}}.$$

Given an electrostatic model A^{elec}, the electrostatic contribution to the chemical potential of a solute is

$$\mu_i^{\text{elec}}(T, V, \boldsymbol{n}\backslash n_0) = \left(\frac{\partial A^{\text{elec}}(T, V, \boldsymbol{n}\backslash n_0)}{\partial n_i} \right)_{T, V, \boldsymbol{n}\backslash n_i} \tag{17}$$

but note that

$$\left(\frac{\partial A^{\text{elec}}(T, V, \boldsymbol{n}\backslash n_0)}{\partial n_0} \right)_{T, V, \boldsymbol{n}\backslash n_0} = 0.$$

It is essential to realise that A^{elec} is *not* a residual Helmholtz function nor an excess function, but an electrostatic contribution to a classical Helmholtz function. Therefore, the chemical potentials of the solutes include the additional term, μ_i^{elec},

$$\mu_i^B(T, V, \boldsymbol{n}) = \mu_i^{\text{classical}} + \mu_i^{\text{elec}} = \mu_i^B(T, P + P^{\text{elec}}, \boldsymbol{n})$$

Thus the chemical potential at constant system pressure is

$$\mu_i^B(T, P, \boldsymbol{n}) = \mu_i^B(T, V, \boldsymbol{n}) - P^{\text{elec}} \bar{V}_i$$

$$= \mu_i^B(T, P + P^{\text{elec}}, \boldsymbol{n}) - P^{\text{elec}} \bar{V}_I, \tag{18}$$

and thus in form we get

$$RT \ln \gamma_i^B(T, P, \boldsymbol{n}) = RT \ln \gamma_i^B(T, V, \boldsymbol{n}\backslash n_0, \mu_0) - P^{\text{elec}} \bar{V}_i \tag{19}$$

since the activity coefficients $\ln \gamma_i^B(T, P + P^{\text{elec}}, \boldsymbol{n}) = \ln \gamma_i^B(T, V, \boldsymbol{n}\backslash n_0, \mu_0)$.

We note that the expression derived by classical thermodynamics, Eq. (19), is similar to the expression obtained by statistical mechanics, Eq. (11).

4. The Debye–Hückel theory

The origin of the electrolyte thermodynamics is to a large extend the work of Debye and Hückel [9]. They presented an expression for the change in the Helmholtz energy due to the charging process. They denoted this additional energy as *Zusatzenergie*, Eq. (20), which is identical to Eq. (28) in the original paper [9]. Note that G in the original paper [9] is identical to $-A/T$, see Eq. (1) in the original paper.

$$\frac{A^{\text{elec}}(T, V, \boldsymbol{n}\backslash n_0)}{RT} = -\frac{F^2}{4\pi\varepsilon_r\varepsilon_0 RT} \frac{1}{N_A} \sum_i \frac{n_i z_i^2}{3} \kappa \chi_i \tag{20}$$

where F is Faraday's constant, N_A the Avogadro's number, z_i the dimensionless charge, and κ is the Debye length

$$\kappa^2 = \frac{F^2}{\varepsilon_r \varepsilon_0 RTV} \sum_i z_i^2 n_i,$$

and the function χ_i is

$$\chi_i = \frac{3}{(\kappa a_i)^3} \left[\tfrac{3}{2} + \ln(1 + \kappa a_i) - 2(1 + \kappa a_i) + \tfrac{1}{2}(1 + \kappa a_i)^2 \right].$$

where a_i is the distance of closest approach (*Annäherungsabstand*, [9, p. 192, Section b]) of the ions. The function χ_i is always positive. The theory is limited to dilute systems where the ionic strength is less than approximately 0.01 M. However, it is at these low concentrations that the electrostatics is the most important physical interaction in the solution.

From Eq. (20), one can derive the contribution (or *Zusatzpotential*) to the chemical potentials (due to the charging process) of any solutes

$$\mu_j^{\text{elec}}(T, V, \boldsymbol{n} \backslash n_0) = \left(\frac{\partial A^{\text{elec}}}{\partial n_j} \right)_{T,V}$$

$$= -\frac{F^2}{4\pi \varepsilon_r \varepsilon_0} \frac{\kappa z_j^2}{6 N_A} \left[2\chi_j + \frac{\sum_i n_i z_i^2 \sigma_i}{\sum_i n_i z_i^2} \right], \quad (21)$$

where $\sigma_i = (\mathrm{d}(\kappa \chi_i)/\mathrm{d}\kappa) > 0$. Since Eq. (20) is the contribution to the Helmholtz energy due to the charging process and not an excess energy function, it is a misconception to define $RT \ln \gamma_j^{\text{elec}} \equiv \mu_j^{\text{elec}}$ since μ_j^{elec} is not an excess chemical potential.

The contribution to the pressure (or *Zusatzdruck*)

$$P^{\text{elec}}(T, V, \boldsymbol{n} \backslash n_0) = -\left(\frac{\partial A^{\text{elec}}}{\partial V} \right)_{T,\boldsymbol{n}}$$

$$= -\frac{F^2}{4\pi \varepsilon_r \varepsilon_0} \frac{\kappa}{6 N_A V} \sum_i n_i z_i^2 \sigma_i. \quad (22)$$

It is noted that the electrostatic contribution to the pressure, P^{elec}, is always negative. Since the system is restricted to constant T and V, the pressure decreases upon charging.

4.1. Simplified model, all a_i are identical

The usual, but also gross, simplification of the Debye–Hückel theory is to assume that the distance of closest approach is the same for all ions. In that case the chemical potential and pressure reduce to

$$\tilde{\mu}_j^{\text{elec}} = -\frac{F^2}{8\pi \varepsilon_r \varepsilon_0} \frac{z_j^2}{N_A} \frac{\kappa}{1 + \kappa a} = -RT A_{\text{DH}} \frac{z_j^2 \sqrt{I}}{1 + b\sqrt{I}} \quad (23)$$

and

$$\tilde{P}^{\text{elec}} = -\frac{RT}{24\pi} \frac{\kappa^3 \sigma}{N_A} = -\frac{2 RT A_{\text{DH}}}{b^3}$$

$$\times \left[1 + b\sqrt{I} - \frac{1}{1 + b\sqrt{I}} - 2\ln\left(1 + b\sqrt{I}\right) \right]. \quad (24)$$

where $\kappa a \equiv b\sqrt{I}$, and hence the Debye–Hückel constant, A_{DH}, is

$$A_{\text{DH}} = \frac{F^2}{8\pi \varepsilon_r \varepsilon_0 RTN_A} \sqrt{\frac{2F^2}{\varepsilon_r \varepsilon_0 RT}} = \frac{1}{16\pi N_A} \left(\frac{b}{a} \right)^3,$$

the b-parameter is

$$b = a \sqrt{\frac{2F^2}{\varepsilon_r \varepsilon_0 RT}},$$

and the ionic strength is

$$I = \frac{1}{2V} \sum_i z_i^2 n_i.$$

Note that the ionic strength according to [9] depends on the volume of the solution and not on the mass of the solvent. It is obvious from Eq. (23) that the electrostatic contribution to the chemical potential converges asymptotically to a constant of $-RT A_{\text{DH}} z_j^2 / b$, whereas the electrostatic contribution to the pressure Eq. (24) converges asymptotically to a slope of $-2 RT A_{\text{DH}} / b^3$. So even though the model Eq. (20) reaches a constant contribution to the chemical potential of the solutes, the contribution to the pressure of the system decreases when the ionic strength is increasing. The change in the logarithm of the solvent activity coefficient due to the charging process is $-\tilde{P}^{\text{elec}} \bar{V}_0 / RT$, see Eq. (15).

The Helmholtz energy $\tilde{A}^{\text{elec}}$ is calculable from the fundamental relationship

$$A = -PV + \sum_j n_j \mu_j$$

and therefore from Eqs. (23) and (24) we find that the change in the Helmholtz energy due to the charging is

$$\frac{\tilde{A}^{\text{elec}}}{RT} = -\frac{4V A_{\text{DH}}}{b^3} \left[\tfrac{3}{2} + \ln(1 + b\sqrt{I}) \right.$$

$$\left. - 2(1 + b\sqrt{I}) + \tfrac{1}{2}(1 + b\sqrt{I})^2 \right]$$

By an inspection of Eq. (25) we see that it is similar to Eq. (20) for $a_i = a$; we have a (thermodynamically) consistent formulation of the charging process. Sometimes [19, p. 396], the right-hand side of Eq. (25) (as stated here) is interpreted as a Gibbs energy which is only true if the chemical work, PV, is zero; an assumption that cannot be justified [6].

5. Discussion

Thermodynamic models describing the charging processes, whether it be the Debye–Hückel theory [9], the mean spherical approximation theory [20], or other models, are expressed in terms of an add-on (or *Zusatz*) Helmholtz energy. However, the model variables are the temperature, the volume and the solute composition. Neither the solvent mole number nor the solvent chemical potential are specified. It could be argued (based on the Gibbs' phase rule) that one degree of

freedom is unspecified and the system is not uniquely described. But as Fowler and Guggenheim [19, p. 384] state, the solvent is also described by the dielectric constant. The dielectric constant is itself a function of temperature, volume, dipole moment and polarizability, see [21, pp. 415]. In that sense the charging process is fully described by the Helmholtz function given by the Debye–Hückel theory or the MSA theory.

The electrostatic function of Debye and Hückel [9] and the MSA of Simonin et al. [20] are electrostatic Helmholtz functions describing the charging process. Since the solvent is not charged, there cannot be an electrostatic contribution to the chemical potential of the solvent, thus $\mu_0^{\text{elec}} = (\partial A^{\text{elec}}/\partial n_0)_{T,V} = 0$. Accordingly, the electrostatic Helmholtz function, like Eq. (20), does not give a contribution to the solvent chemical potential. However, this does not mean that the solvent *activity coefficient* is unaffected by the charging process. The electrostatic contribution to the solvent activity coefficient is given by Eq. (15).

The McMillan–Mayer framework has embedded in its theory that the solvent chemical potential is constant. This fact could lead to the conclusion that the electrostatic models are derived as *McMillan–Mayer state functions* and that these models as a consequence only are to be used in the odd framework of McMillan–Mayer. But that is not the case. As demonstrated by Debye and Hückel [9], the charging process results in an additional term (like Eq. (20)) to the classical Helmholtz energy function derived from the classical theory of electrostatics. Any solution theory, like the Debye–Hückel theory, that are derived from classical physics can of course always be interpreted entirely within the framework of classical thermodynamics. Classical thermodynamics is a subdivision of classical physics. In our opinion, the McMillan–Mayer framework adds more to the confusion than it clarifies.

List of symbols

a	distance of closest approach (m)
A	Helmholtz energy (J)
A_{DH}	Debye–Hückel constant $((\text{m}^3/\text{mole})^{1/2})$
b	Debye–Hückel constant $((\text{m}^3/\text{mol})^{1/2})$
B	McMillan–Mayer state function (J)
C	number of components
F	Faraday's constant (C/mol)
G	Gibbs energy (J)
I	ionic strength (mol/m^3)
k	Boltzmann's constant (J/K)
n	mole number (mol)
N	molecular number
N_{A}	Avodagro's number (1/mol)
P	pressure (Pa)
Q	canonical partition function
R	gas constant (J/(mol K))
S	entropy (J/K)
T	temperature (K)
V	volume (m^3)
$\bar{V}$	partial molar volume (m^3/mol)
z	dimensionless charge

Greek letters

β	$1/kT$ (1/J)
γ	activity coefficient
$\varepsilon_r \varepsilon_0$	dielectric constant $(\text{C}^2/(\text{J m}))$
κ	Debye length (1/m)
μ	molar chemical potential (J/mol)
μ^m	molecular chemical potential (J)
Ξ	grand canonical partition function
σ	auxiliary function, $= \text{d}(\kappa\chi)/\text{d}\kappa$
χ	auxiliary function
Ψ	semi-grand canonical partition function

Superscript

id	ideal solution
E	excess property, $M^{\text{E}} = M - M^{\text{id}}$
elec	electrostatic
MM	McMillan–Mayer framework property

Appendix A. Derivation of B^{id}

The derivation of B in the ideal solution does not depend on how one defines the ideal solution in terms of activities as the following derivation clearly demonstrates.

Logically, the McMillan–Mayer state function of an ideal solution is defined as

$$B^{\text{id}}(T, V, \boldsymbol{n}\backslash n_0, \mu_0) \equiv [G(T, P, \boldsymbol{n}) - PV - n_0\mu_0]^{\text{id}}$$
$$= [G(T, P, \boldsymbol{n})]^{\text{id}} - P^{\text{id}}V - n_0^{\text{id}}\mu_0. \quad \text{(A.1)}$$

$V^{\text{id}} = V$ and $\mu_0^{\text{id}} = \mu_0$ since the independent variables in the real and the ideal systems are identical. However, the solvent mole number is a dependent variable and hence different in the two cases; real and ideal

$$n_0 = \frac{V - \sum_{i\neq 0} n_i \bar{V}_i}{\bar{V}_0} \quad \text{and} \quad n_0^{\text{id}} = \frac{V - \sum_{i\neq 0} n_i v_i}{v_0}$$

where $\bar{V}_i$ is the partial molar volume and v_i is the molar volume of component i. The Gibbs energy of the ideal solution at P^{id} and n_0^{id} in relation to the Gibbs energy of an ideal solution at P and n_0 is

$$[G(T, P, \boldsymbol{n})]^{\text{id}} \equiv G^{\text{id}}(T, P^{\text{id}}, \boldsymbol{n}\backslash n_0, n_0^{\text{id}})$$

$$= G^{\text{id}}(T, P, \boldsymbol{n}\backslash n_0, n_0) + \int_P^{P^{\text{id}}} \left(\frac{\partial G^{\text{id}}}{\partial P}\right)_{T,\boldsymbol{n}} \text{d}P$$

$$+ \int_{n_0}^{n_0^{\text{id}}} \left(\frac{\partial G^{\text{id}}}{\partial n_0}\right)_{T,\boldsymbol{n}\backslash n_0} \text{d}n_0 = G^{\text{id}}(T, P, \boldsymbol{n})$$

$$+ \int_P^{P^{\text{id}}} V^{\text{id}}\text{d}P + \int_{n_0}^{n_0^{\text{id}}} \mu_0^{\text{id}}\text{d}n_0 = G^{\text{id}}(T, P, \boldsymbol{n})$$

$$+ V(P^{\text{id}} - P) + \mu_0(n_0^{\text{id}} - n_0) \quad \text{(A.2)}$$

since the independent variables in the real and the ideal systems are similar and constant. Inserting Eq. (A.2) into Eq. (A.1) gives

the relation for the ideal solution

$$B^{id}(T, V, \boldsymbol{n} \backslash n_0, \mu_0) = G^{id}(T, P, \boldsymbol{n}) + V(P^{id} - P)$$
$$+ \mu_0(n_0^{id} - n_0) - P^{id}V - n_0^{id}\mu_0$$
$$= G^{id}(T, P, \boldsymbol{n}) - PV - n_0\mu_0.$$

The authors of [4] have presented the same result but they have used four different definitions of ideal mixtures. The relations between the fundamental thermodynamic properties do not depend on which definition of ideality we use.

References

[1] W.G. McMillan Jr., J.E. Mayer, J. Chem. Phys. 13 (1945) 276–305.

[2] T.L. Hill, Statistical Mechanics–Principles and Selected Applications, McGraw-Hill Book Company Inc., Toronto, Canada, 1956.

[3] H.L. Friedman, J. Solution Chem. 1 (1972) 387–412.

[4] C.A. Haynes, J. Newman, Fluid Phase Equilib. 145 (1998) 255–268.

[5] H. Cabezas Jr., J.P. O'Connell, Ind. Eng. Chem. Res. 32 (1993) 2892–2904.

[6] M.J.E. de M. Cardoso, J.P. O'Connell, Fluid Phase Equilib. 33 (1987) 315–326.

[7] B.A. Pailthorpe, D.J. Mitchell, B.W. Ninham, J. Chem. Soc. Faraday Trans. II 80 (1984) 115–139.

[8] L.L. Lee, J. Mol. Liq. 87 (2000) 129–147.

[9] P. Debye, E. Hückel, Physik. Zeits. 24 (1923) 179–207.

[10] J.P. Simonin, J. Chem. Soc. Faraday Trans. 92 (1996) 3519–3523.

[11] J.P. Simonin, Fluid Phase Equilib. 165 (1999) 41–58.

[12] R.A. Curtis, J. Newman, H.W. Blanch, J.M. Prausnitz, Fluid Phase Equilib. 192 (2001) 131–153.

[13] P. Debye, J. Phys. Colloid Chem. 51 (1947) 18–32.

[14] W. Kunz, L. Belloni, O. Bernard, B.W. Ninham, J. Phys. Chem. B 108 (2004) 2398–2404.

[15] N. Zoeller, L. Lue, D. Blankenschtein, Langmuir 13 (1997) 5258–5275.

[16] T.L. Hill, An Introduction to Statistical Thermodynamics, Addison-Wesley Publishing Company Inc., London, England, 1962.

[17] D.A. McQuarrie, Statistical Mechanics, Haper & Row, Publishers Inc., New York, 1976.

[18] B.L. Beegle, M. Modell, R.C. Reid, AIChE J. 20 (1974) 1194–1200.

[19] R. Fowler, E.A. Guggenheim, Statistical Thermodynamics, Cambridge at the University Press, Cambridge, England, 1965.

[20] J.P. Simonin, L. Blum, P. Turq, J. Phys. Chem. 100 (1996) 7704–7709.

[21] N. Davidson, Statistical Mechanics, McGraw-Hill Book Company, New York, USA, 1962.