SYSTEM OF THERMODYNAMIC QUANTITIES
IN THE McMILLAN–MAYER SOLUTION THEORY

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The McMillan-Mayer (MM) free energy per unit volume of solution A_{MM}, is employed as a generating function of the MM system of thermodynamic quantities for solutions in the state of osmotic equilibrium with pure solvent. This system can be defined by replacing the quantities G, T, P, and m in the definition of the Lewis–Randall (LR) system by A_{MM}, T, P_0, and c (P_0 being the pure solvent pressure). Following this way the LR to MM conversion relations for the first derivatives of the free energy are obtained in a simple form. New relations are derived for its second derivatives.

Computed thermodynamic properties of electrolyte solutions in the McMillan–Mayer theory[1] are obtained in terms of the MM system of excess quantities[1] and pertain to solutions in the state of osmotic equilibrium with pure solvent. On the other hand experimental data are usually reported in terms of the Lewis–Randall system[2-4] for solutions under atmospheric pressure. In order to compare computed and experimental data, relations are needed between excess quantities defined in the two different systems and referring to solutions under different pressures, the so called LR to MM conversions (or corrections)[5,6]. As the MM theory yields only the values of excess quantities, one can understand why the corresponding absolute quantities have not been found so far. As a consequence, however, for one thing the derivation of the LR to MM corrections is somewhat cumbersome and the corrections alone are rather complicated[6,7], for another an uncertainty is reported as to their use in some cases[7]. It is the purpose of this paper to present a generalized definition of the MM system, based on the MM free energy[8], to elucidate the nature of the quantities encountered in it, and to derive exact conversion relations up to the second derivatives of the free energy.

Lewis–Randall System

In the thermodynamics of electrolyte solutions systems of quantities with asymmetric solvent–solute relation are used. The one most commonly employed is the Lewis–Randall system, associated with the molality as a composition variable. Its elementary version[2,3], hitherto in use, had been developed, largely in connection with single

electrolyte solutions, in the early part of this century, however, a consistent definition of the system was given only in 1960 by Friedman[4]. For our purposes we define this rationalized LR system by

a) The generating function, $G = G(T, P, \boldsymbol{m})$, where G is the Gibbs energy of solution per unit mass of solvent and $\boldsymbol{m}$ is the vector of solute molalities. All other thermodynamic functions in this system are introduced upon partial differentiating G with respect to the LR independent variables[4], *e.g.*, $\mu_i = \partial G / \partial m_i$ is the chemical potential of ith solute component $(i = 1, ..., s$ and s is the number of solute components).

b) The standard state of solution for given (T, P),

$$\mu_{i,\mathrm{LR}}^{\circ} = \lim_{m \to 0} \left[\mu_i - RT \ln \left(m_i / m^{\circ} \right) \right], \quad i = 1, ..., s, \tag{1}$$

where $m = m_1 + ... + m_s$ is the total solute molality and $m^{\circ} = 1 \; \mathrm{mol \; kg^{-1}}$ is the standard molality.

c) The reference state of solution for given $(T, P, \boldsymbol{m})$,

$$\mu_{i,\mathrm{LR}}^{\mathrm{id}} = \mu_{i,\mathrm{LR}}^{\circ} + RT \ln \left(m_i / m^{\circ} \right), \quad i = 1, ..., s. \tag{2}$$

Excess quantities are defined as $X^{\mathrm{E}} = X - X^{\mathrm{id}}$, where X and X^{id} are the corresponding absolute and reference quantities, respectively.

We note that the total differential of the Gibbs energy in the LR system does not include solvent quantities explicitly:

$$dG = \boldsymbol{\mu} \, d\boldsymbol{m} - S \, dT + V \, dP. \tag{3}$$

Here $\boldsymbol{\mu}$ is the vector of the chemical potentials of solute components, S is the entropy and V is the volume of solution in the LR system (*i.e.*, both S and V refer to solution containing a unit mass of solvent).

McMillan–Mayer System

An arbitrary state of a solution can be described using the variables $(T, \mu_0, \boldsymbol{c})$, where μ_0 is the chemical potential of solvent in the solution and $\boldsymbol{c}$ is the vector of the amount-of-substance concentrations of solute components. Once the solution is in the MM state, *i.e.* in the state of the osmotic equilibrium with the pure solvent, there is a corresponding state of the pure solvent, (T, μ_0), with a pressure P_0. It is then possible to describe the solution state with the variables[5] $(T, P_0, \boldsymbol{c})$. A solution in the MM state is best characterized with the McMillan–Mayer free energy[8], which will refer

to a unit volume of solution throughout this paper,

$$A_{MM} = c\mu - \Pi . \tag{4}$$

Here Π is the osmotic pressure which is a measure of the solvent "escaping tendency"[2] and which indeed has the role of the solvent partial specific free energy in the MM system. As A_{MM} is a function of T, P_0, and c and $(\partial A_{MM}/\partial c)_{T,P_0} = \mu$, its total differential will read:

$$dA_{MM} = \mu\, dc - S_{MM}\, dT + V_{MM}\, dP_0 , \tag{5}$$

where the symbols $-S_{MM}$ and V_{MM} are chosen to denote the partial derivatives of A_{MM} with respect to T and P_0, respectively.

It is instructive to compare Eqs (3) and (5). We can define the MM system simply by replacing the quantities G, T, P_0, and m in the definition of the LR system given above by the quantities A_{MM}, T, P_0, and c. Thus the generating function in the MM system is the MM free energy, $A_{MM} = A_{MM}(T, P_0, c)$, and the standard and reference states are given by

$$\mu_{i,MM}^{\circ} = \lim_{c \to 0} \left[\mu_i - RT \ln\left(c_i/c^{\circ}\right)\right], \quad i = 1, ..., s \tag{6}$$

$$\mu_{i,MM}^{id} = \mu_{i,MM}^{\circ} + RT \ln\left(c_i/c^{\circ}\right), \quad i = 1, ..., s \tag{7}$$

for given (T, P_0) and (T, P_0, c), respectively, where c is the total solute concentration and $c^{\circ} = 1 \text{ mol dm}^{-3}$ is the standard concentration. It can easily be proved that this definition of the MM system is, as far as the excess quantities are concerned, equivalent to the earlier definition[1], according to which the excess Helmholtz energy A^E, is given by

$$\left[\partial\left(A^E/c\right)/\partial(1/c)\right]_{T,P_0,x} = -\Pi^E , \quad A^E \to 0 \quad \text{as} \quad c \to 0 , \tag{8}$$

where $x = c/c$ and $\Pi^E = \Pi - RTc$ is the excess osmotic pressure. It is evident that the excess Helmholtz energy defined by Eq. (8) is identical with the excess MM free energy from the present definition of the MM system.

The formal definition of the MM system given above is quite sufficient for further purposes. Yet it seems appropriate to show how the functions V_{MM} and S_{MM} can simply be interpreted in terms of the usual osmotic experiment. Consider a vessel divided into two parts with a semipermeable partition, illustrated in Fig. 1. At first the vessel contains only pure solvent (Fig. 1a) and the pressure on both sides of the partition is P_0. Now suppose that another substances are added into part I and the volume of the vessel is varied in such a manner that the pressure on the pure solvent in part II is still equal to P_0. Provided the solution in part I has a unit volume, the

volume change is just V_{MM}. This volume change is given by the difference between the volume of the solution $\left(\text{at pressure } P = P_0 + \Pi\right)$ and that of the pure solvent $\left(\text{at pressure } P_0\right)$ in the amount in which it is in the solution. In terms of LR quantities it can be written as $V_{MM} = \left(V - V_0^\circ\right)/V$, where V is the solution LR volume at P and V_0° is the pure solvent specific volume at P_0. A similar equation holds also for the function $S_{MM} : S_{MM} = \left(S - S_0^\circ\right)/V$. Both equations can easily be proved when starting with the relation of the difference of the Helmholtz energies of the two systems illustrated in Fig. 1 to the MM free energy. These equations can also be obtained by the more formal way presented in the next part.

Lewis–Randall to McMillan–Mayer Conversion

In order to compare theoretically computed and experimental data one needs conversion relations between the excess quantities in the MM system at pressure $P = P_0 + \Pi$ and those in the LR system for solution with the same molality, but at pressure P_0. For simplicity the following notation will be used: Absolute LR quantities referring to the pressure P are denoted by the common symbols (X). Absolute LR quantities for the pressure P_0 are denoted with the primed symbols (X'). Standard, reference, and excess LR quantities will refer to the pressure P_0 only, but will not be primed. Under integrals ower pressure the common symbol (X) designates an LR
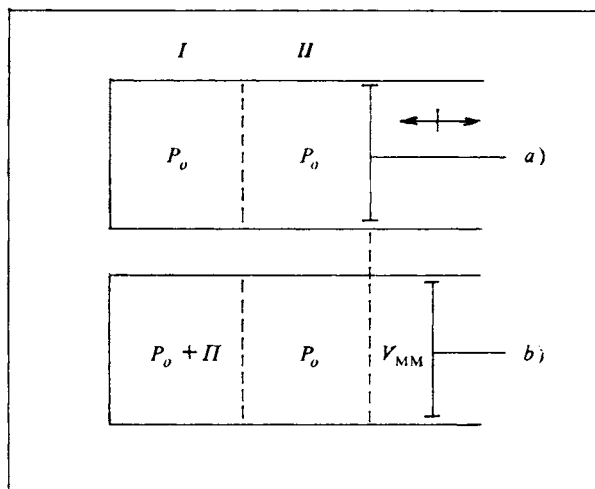

FIG. 1

Illustration of the quantity V_{MM}. a) The system contain pure solvent only. b) Another substances are added into part I

quantity as a function of the pressure. Now we can write for total quantities:

$$X_{MM}^E/c - X_{LR}^E/m = (X_{MM} - X_{MM}^{id})/c - [(X' - X_0^\circ) - (X_{LR}^{id} - X_0^\circ)]/m$$

and after a simple rearrangement,

$$X_{MM}^E/c - X_{LR}^{\underline{\circ}}/m = [(X_{LR}^{id} - X_0^\circ)/m - X_{MM}^{id}/c] +$$

$$+ (1/m) \int_{P_0}^{P} (\partial X/\partial p)_{LR} \, dp + [X_{MM}/c - (X - X_0^\circ)/m] \,, \qquad (9)$$

where X_0° is a specific quantity of pure solvent at P_0. An equation formally identical with (9) holds also for solvent quantities (osmotic pressure). In this case however the first term on the right is zero. A similar relation is found for partial molar solute quantities:

$$X_{i,MM}^E - X_{i,LR}^E = (X_{i,LR}^{id} - X_{i,MM}^{id}) + \int_{P_0}^{P} (\partial X_i/\partial p)_{LR} \, dp + (X_{i,MM} - X_i) \,. \quad (10)$$

In Eqs (9) and (10) the subscript LR indicates the constancy of the other LR variables.

The first terms on the right-hand sides of Eqs (9) and (10) arise from the differences between the definitions of the standard and reference states in the LR and MM systems. They are determined by pure solvent properties at P_0 only, except for the free energy and entropy where, because of the ideal mixing terms, the volume of the solution at P must also be known. They can easily be derived using Eqs (1), (2), (6), and (7). We note that

$$X_{i,LR}^{id} - X_{i,MM}^{id} = (X_{LR}^{id} - X_0^\circ)/m - X_{MM}^{id}/c \,.$$

The second terms on the right-hand sides of Eqs (9) and (10) represent the differences between the corresponding LR quantities at P and P_0 and they deserve no comments. Finally, the third terms are given by the differences between the corresponding MM and LR absolute quantities at P (i.e., for the same solution). Equations needed for their derivation are developed in Appendix.

In Eqs (9) and (10) the differences between excess quantities in the MM and LR systems are expressed in terms of LR quantities and the osmotic pressure. The osmotic pressure, considered as an MM quantity, cannot be written explicitly as a function of LR quantities. It is calculated from the LR osmotic coefficient, ϕ_{LR}, solving the equation

$$RTm\phi_{LR} = \int_{P_0}^{P_0 + \Pi} V_0 \, dp \,, \qquad (11)$$

where V_0 is the partial specific volume of solvent.

Conversion relation for the excess free energy derived from Eq. (9) is identical with that derived earlier[5]. The conversion relations for the first derivatives of the free energy are equivalent to those given in[5], they are however much simpler. As examples we give here exact relations for activity coefficients, excess volumes, and excess entropies.

$$\ln \left(\gamma_{i,MM} / \gamma_{i,LR} \right) = \ln \left(V / V_0^\circ \right) + \left(1/RT \right) \int_{P_0}^{P} V_i \, dp \tag{12}$$

$$V_{MM}^{E}/c - V_{LR}^{E}/m = RT \varkappa_0 - \int_{P_0}^{P} K \, dp \tag{13}$$

$$S_{MM}^{E}/c - S_{LR}^{E}/m = RT \alpha_0 - \int_{P_0}^{P} E \, dp - R \ln \left(V / V_0^\circ \right) \tag{14}$$

Here $\varkappa_0$ is the isothermal compressibility coefficient of pure solvent at P_0, $K = \left(\partial V / \partial P \right)_{LR}$ is the isothermal compressibility of solution, α_0 is the cubic expansion coefficient of pure solvent at P_0, and $E = \left(\partial V / \partial T \right)_{LR}$ is the cubic expansion of solution. Third terms of Eqs (9) and (10) are given in Appendix for several second derivatives.

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APPENDIX

Relations for the third terms on the right-hand sides of Eqs (9) and (10), *i.e.*, the differences between the corresponding MM and LR quantities of solution at $P = P_0 + \Pi$, can be obtained on partial differentiating the equation for the free energy,

$$A_{MM} = \left(G - G_0^\circ \right) / V - \Pi \,, \tag{A1}$$

where G_O^0 is the specific Gibbs energy of pure solvent at P_0 and all the other quantities refer to the pressure P. To be able to do that we need to know the partial derivatives of LR quantities with respect to the MM independent variables. For an LR quantity $X = X(P)$ we can write in a condensed form:

$$\begin{pmatrix} \partial X / \partial T \\ \partial X / \partial P_0 \\ \partial X / \partial c \end{pmatrix}_{MM} = \begin{pmatrix} 1 & \partial P / \partial T & \partial m / \partial T \\ 0 & \partial P / \partial P_0 & \partial m / \partial P_0 \\ 0 & \partial P / \partial c & \partial m / \partial c \end{pmatrix}_{MM} \begin{pmatrix} \partial X / \partial T \\ \partial X / \partial P \\ \partial X / \partial m \end{pmatrix}_{LR} \tag{A2}$$

where the subscripts MM and LR indicate that the matrix elements are partial derivatives with respect to the MM or LR independent variables. To derive expressions for the elements of the transformation matrix in (A2) we employ the equality

$$m_i = c_i V \tag{A3}$$

and the Gibbs–Duhem equation in the MM system,

$$0 = \mathbf{c}\, d\boldsymbol{\mu} + S_{\mathrm{MM}}\, dT - V_{\mathrm{MM}}\, dP_0 - d\Pi \qquad (A4a)$$

which can be rewritten in terms of LR quantities as

$$0 = \mathbf{m}\, d\boldsymbol{\mu} + \left(S - S_0^{\circ}\right) dT + V_0^{\circ}\, dP_0 - V\, dP. \qquad (A4b)$$

When $(T, \mathbf{c})$ is constant, the only LR variables that do not remain constant are P and m (the others are T and $\mathbf{x}$ in this case). The changes of these two variables are not independent. It follows from $(4b)$:

$$V_0^{\circ} = V_0 \left(\partial P/\partial P_0\right)_{\mathrm{MM}} + \left(\partial G_0/\partial m\right)_{\mathrm{LR}} \left(\partial m/\partial P_0\right)_{\mathrm{MM}}.$$

We denote

$$\pi_{\mathrm{p}} = \left(\partial P/\partial P_0\right)_{\mathrm{MM}} = 1 - V_{0,\mathrm{MM}}.$$

Then using $(A3)$ we get

$$\left(\partial m_i/\partial P_0\right)_{\mathrm{MM}} = -\left(K/V_0\right) m_i \pi_{\mathrm{p}} \qquad (A5)$$

$$\pi_{\mathrm{p}} = \frac{V_0^{\circ}/V_0}{1 - \left(K/V_0^2\right) m \left(\partial G_0/\partial m\right)_{\mathrm{LR}}} \qquad (A6)$$

and

$$V_{i,\mathrm{MM}} \equiv \left(\partial \mu_i/\partial P_0\right)_{\mathrm{MM}} = \left[V_i - \left(K/V_0\right) m\left(\partial \mu_i \partial(\partial m_i/m)_{\mathrm{LR}}\right)\right] \pi_{\mathrm{p}}. \qquad (A7)$$

In these equations X_0 $(X = G, V, \dots)$ is a partial specific quantity of solvent at pressure P. The MM derivatives with respect to temperature are obtained in a similar way:

$$\left(\partial m_i/\partial T\right)_{\mathrm{MM}} = \left(m_i/V_0\right)\left[E - K(\partial P/\partial T)_{\mathrm{MM}}\right] \qquad (A8)$$

$$-S_{i,\mathrm{MM}} \equiv \left(\partial \mu_i/\partial T\right)_{\mathrm{MM}} = -S_i + V_i(\partial P/\partial T)_{\mathrm{MM}} +$$
$$+ \left(m/V_0\right)\left(\partial \mu_i/\partial m\right)_{\mathrm{LR}}\left[E - K(\partial P/\partial T)_{\mathrm{MM}}\right] \qquad (A9)$$

$$S_{0,\mathrm{MM}} \equiv \left(\partial P/\partial T\right)_{\mathrm{MM}} =$$
$$= \pi_{\mathrm{p}}\left[(S_0 - S_0^{\circ})/V_0^{\circ} - (E/V_0 V_0^{\circ}) m(\partial G_0/\partial m)_{\mathrm{LR}}\right], \qquad (A10)$$

where $S_0 - S_0^{\circ}$ can be replaced by $(H_0 - H_0^{\circ})/T$. Finally, for the derivatives with respect to the concentration, c_j, of jth solute component we get:

$$\left(\partial m_i/\partial c_j\right)_{\mathrm{MM}} = \delta_{ij}V + \left(V/V_0\right) V_j m_i - \left(K/V_0\right) m_i(\partial P/\partial_1 c_j)_{\mathrm{MM}} \qquad (A11)$$

$$\left(\partial \mu_k/\partial c_j\right)_{\mathrm{MM}} = V\left(\partial \mu_k/\partial m_j\right)_{\mathrm{LR}} - \left(V/V_0\right) V_j(\partial G_0/\partial m_k)_{\mathrm{LR}} +$$
$$+ \left[V_k + \left(K/V_0\right)\left(\partial G_0/\partial m_k\right)_{\mathrm{LR}}\right]\left(\partial P/\partial c_j\right)_{\mathrm{MM}} \qquad (A12)$$

$$\left(\partial P/\partial c_j\right)_{\mathrm{MM}} = -\pi_{\mathrm{p}}\left(V/V_0^{\circ}\right)\left[\left(\partial G_0/\partial m_j\right)_{\mathrm{LR}} + \left(V_j/V_0\right) m(\partial G_0/\partial m)_{\mathrm{LR}}\right]. \qquad (A13)$$

Now equations for other second derivatives of the free energy can be derived:

$$K_{MM}/c - (K - K_0^\circ)/m = (K/m)(\pi_p V_0^\circ/V_0 - 1) \qquad (A14)$$

$$C_{MM}/c - (C_p - C_{P0}^\circ)/m = -(TE/m)(S_0 - S_0^\circ)/V_0 +$$
$$+ (TK/m)[(S_0 - S_0^\circ)/V_0 - (E/K)](\partial P/\partial T)_{MM} . \qquad (A15)$$

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