
Harold L. Friedman

Received May 2, 1972

Derivations are given for the equations expressing the McMillan–Mayer functions in terms of Lewis–Randall functions.

KEY WORDS: Thermodynamic; excess functions; free energy; enthalpy; volume.

1. INTRODUCTION

The significance of the problem attacked here, the method, and the notation are all described in Sec. 1 of the preceding paper in this series,\(^{(1)}\) to which reference should be made for the definitions of the partial-differentiation notation used as well as for the definitions of the various thermodynamic variables. In Part I the variables \(T\) and \(P_1\) are fixed, while here we seek the relation of the excess energy per unit volume in the MM system

\[
E^{ex} = \left[\frac{\partial(A^{ex}/T)}{\partial(1/T)}\right]_{MM}
\]

(1)

to the excess enthalpy per kilogram of solvent in the LR system

\[
H^{ex} = \left[\frac{\partial(G^{ex}/T)}{\partial(1/T)}\right]_{LR}
\]

(2)

and the relation of the excess volume in the MM system

\[
V^{ex}_{MM} = \left(\frac{\partial A^{ex}}{\partial P_0}\right)_{MM}
\]

(3)

to the excess volume per kg of solvent in the LR system

\[
V^{ex} = \left(\frac{\partial G^{ex}}{\partial P_1}\right)_{LR}
\]

(4)

\(^{1}\) Department of Chemistry, State University of New York, Stony Brook, New York 11790.

Unlike the other functions in these equations, $V_{\text{MM}}^\text{ex}$ has no precedent in solution thermodynamics, but at least, as dimensional analysis of Eq. (3) shows, $V_{\text{MM}}^\text{ex}$ has the units of volume per volume of solution, in analogy to $E^\text{ex}$. Also, it may be noted that $G^\text{ex}$ is related to the partial molal excess functions $\phi$ (osmotic coefficient) and $\gamma_\pm$ (mean ionic activity coefficient) in the LR system by the equation\textsuperscript{(2,3)}

$$G^\text{ex} = RTm(1 - \phi + \ln \gamma_\pm)$$

The results for the $H^\text{ex}$ to $E^\text{ex}$ and $V^\text{ex}$ to $V_{\text{MM}}^\text{ex}$ conversions which are derived here differ from those reported before,\textsuperscript{(4)} which seem to be wrong.

2. $H^\text{ex}$ TO $E^\text{ex}$

We begin with the equation [ref. 1, Eq. (9)]

$$A^\text{ex}/cRT = G^\text{ex}/mRT + Q$$

and differentiate with respect to $1/T$, holding the other LR variables fixed, to get

$$[\partial(A^\text{ex}/cRT)/\partial(1/T)]_{\text{LR}} = H^\text{ex}/mR + \partial Q/\partial(1/T)$$

To evaluate the left side of this equation, we note that for any MM function $f(c, T, P_0)$, we have

$$df = f_c d(1/c) + f_T d(1/T) + f_P dP_0$$

for any variation in which the relative amount $c/c$ of each solute does not change. The subscripts indicate the appropriate MM partial derivatives, i.e.,

$$f_c = \partial f/\partial(1/c), \quad f_T = \partial f/\partial(1/T), \quad \text{and} \quad f_P = \partial f/\partial P_0$$

Thus Eq. (8) is an adaptation of Eq. (A.3) of ref. 1. If we identify $f$ with $A^\text{ex}/cRT$, we have

$$f_c = a_w$$

$$f_T = E^\text{ex}/cR$$

$$f_P = V_{\text{MM}}^\text{ex}/cRT$$

The first of these equations may be found in ref. 2; the others are definitions given above. We also have

$$[\partial(1/c)/\partial(1/T)]_{\text{LR}} = m^{-1} \partial \gamma^*/\partial(1/T)$$

$$[\partial P_0/\partial(1/T)]_{\text{LR}} = [\partial P_1/\partial(1/T)]_{\text{LR}} = 0$$

and Eq. (7) becomes

$$E^\text{ex}/cR + (a_w/m) \partial \gamma^*/\partial(1/T) = H^\text{ex}/mR + \partial Q/\partial(1/T)$$