

Thermodynamic Pair Interaction Parameters on Various Concentration Scales

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Derivations are given for the relationships of the conversions of thermodynamic pair interaction parameters on various concentration scales. A comparison is made between the free energy pair interaction parameters obtained from different measurement methods or conversions, indicating that the values on the same concentration scale are in good agreement with each other.

Introduction

In the McMillan–Mayer theory¹ of ternary systems, the excess thermodynamic functions (F), such as free energy (G), entropy (S), enthalpy (H), volume (V), isotonic heat capacity (C_p), etc., can be expressed in terms of pair, triplet, and higher-order interactions between the two solutes. For an electrolyte (E)–nonelectrolyte (N)–water (W) system, as an example, a function of transfer of nonelectrolyte ($\Delta_t F_N$) from W to W + E can be written as²

$$\Delta_t F_N(W \rightarrow W + E) = 2\nu f_{EN} m_E + 3\nu^2 f_{EEN} m_E^2 + 3\nu f_{ENN} m_E m_N + \dots \quad (1)$$

where f_{EN} , f_{EEN} , and f_{ENN} are the pair and triplet interaction parameters, m_E and m_N are the molalities of E and N relative per kilogram of pure water, and ν is the number of moles of ions into which the electrolyte dissociates. For the transfer of electrolyte, a similar equation can be written as

$$\Delta_t F_E(W \rightarrow W + N) = 2\nu f_{EN} m_N + 3\nu^2 f_{ENN} m_N^2 + 3\nu f_{EEN} m_E m_N + \dots \quad (2)$$

For standard functions of transfer, the terms in m_N or m_E on the right-hand side of eq 1 or eq 2 will vanish. For instance, eq 2 will be reduced for the free energy to

$$\Delta_t G_E^0(W \rightarrow W + N) = 2\nu g_{EN} m_N + 3\nu g_{ENN} m_N^2 + \dots \quad (3)$$

Pair interaction parameters f_{EN} are an average of interactions of anions and cations with the nonelectrolyte³

$$f_{EN} = (\nu^+ f_{M^{v^+-}N} + \nu^- f_{X^{v^--}N})/\nu \quad (4)$$

Pair interaction parameters represent the contribution to the thermodynamic functions when the two solutes (N and E) approach each other from infinity to some critical distance. Therefore, they are significant for exploring interactions of solutes in dilution solutions and have been applied widely to ternary systems by many authors.^{2–9}

Values of free energy and entropy pair interaction parameters depend on the concentration scales chosen. This paper is devoted

to derivations and interpreting the relations of the conversion of pair interaction parameters based on various concentration scales.

Conversions of Pair Interaction Parameters

The interaction parameters can be obtained by fitting experimental data to eq 1 or eq 2. However, the values of the free energy and entropy parameters depend on the concentration scales of the solute. We take the transfer of E from W to W + N as an example. Concentration correlations can be expressed by

$$x_E = \frac{0.001 c_E \bar{M}_S}{\rho + 0.001 c_E (\nu \bar{M}_S - M_E)} = \frac{m_E^M}{1000/\bar{M}_S + \nu m_E^M} \quad (5)$$

$$m_E^W = (1 + 0.001 m_N M_N) m_E^M \quad (6)$$

$$m_N = \frac{1000 wt}{M_N(1 - wt)} \quad (7)$$

where x_E and c_E are the mole fraction and molarity of E, m_E^M and m_E^W are molalities of E per kilogram of mixed solvent (N + W) and per kilogram of pure water (m_E^W is simply written as m_E in eqs 1 and 2 and the following), wt is the mass fraction of N to mixed solvent (N + W), M_E and M_N are the mole masses of E and N, \bar{M}_S is the average mole mass of the mixed solvent (N + W), and ρ is the density of the ternary solution.

The chemical potential of electrolyte in the ternary solution can be expressed, in any concentration scale, as

$$\mu_E = \mu_E^0 + RT \ln a_E \quad (8)$$

where a_E is the activity of E, μ_E^0 is the standard chemical potential of E (i.e., standard free energy, G_E^0), depending on the concentration scale of E. For the free energy, we get

$$G_E^{0x} = G_E^{0c} + \nu RT \ln \frac{1000 \rho_S}{\bar{M}_S} = G_E^{0m(M)} + \nu RT \ln \frac{1000}{\bar{M}_S} \quad (9)$$

$$G_E^{0m(W)} = G_E^{0m(M)} - \nu RT \ln(1 + 0.001 m_N M_N) \quad (10)$$

where superscripts x , c , $m(M)$, and $m(W)$ indicate the concentration scales for G_E^0 and ρ_S is the density of the mixed solvent (W + N).

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TABLE 1: Comparison between Free Energy Pair Interaction Parameters on Different Concentration Scales at 298.15 K

electrolyte—nonelectrolyte	$2\nu g_{\text{EN}}^x / \text{J kg mol}^{-2}$	$2\nu g_{\text{EN}}^{m(\text{M})} / \text{J kg mol}^{-2}$	$2\nu g_{\text{EN}}^{m(\text{W})} / \text{J kg mol}^{-2}$				
			c	d	e	f	g
KCl—glucose ^h	109 ± 9	902 ± 11	17 ± 8	19	9	9	
NaCl—glucose ^h	296 ± 7	1089 ± 6	205 ± 7	207	196	207	217 ^l
HCl—glucose ^h	484 ± 33	1251 ± 39	363 ± 40	395	358	395	467 ± 16 ^m
MgCl ₂ —glucose ^h	13 ± 28	1197 ± 16	−130 ± 14	−121	−143	~0	
CaCl ₂ —glucose ^h	925 ± 11	2159 ± 9	832 ± 12	818	819	877	
NaCl—fructose ⁱ	94 ± 7	879 ± 14	7 ± 7	2	−14	12 ⁿ	
CaCl ₂ —ribose		−1160 ^j			−2277		
					−2200 ^k		
CaCl ₂ —arabinose		950 ^j			−169		
					−100 ^k		

^a Obtained from the plot of $\Delta_t G_{\text{E}}^{0x}/m_{\text{E}}$ versus m_{E} , where the values of $\Delta_t G_{\text{E}}^{0x}$ were converted from $\Delta_t G_{\text{E}}^{0m(\text{M})}$ using eq 11. ^b Obtained from the plot of $\Delta_t G_{\text{E}}^{0m(\text{M})}/m_{\text{E}}$ versus m_{E} . ^c Obtained from the plot of $\Delta_t G_{\text{E}}^{0m(\text{W})}/m_{\text{E}}$ versus m_{E} , where the values of $\Delta_t G_{\text{E}}^{0m(\text{W})}$ were converted from $\Delta_t G_{\text{E}}^{0m(\text{M})}$ using eq 12. ^d Converted from $2\nu g_{\text{EN}}^x$ using eq 15. ^e Converted from $2\nu g_{\text{EN}}^{m(\text{M})}$ using eq 15. ^f Taken from ref 16. ^g Obtained from the plot of $\Delta_t G_{\text{E}}^{0m(\text{W})}/m_{\text{E}}$ versus m_{E} , where $\Delta_t G_{\text{E}}^{0m(\text{W})}$ was calculated from the emf values for m_{E}^{W} . ^h Values of $\Delta_t G_{\text{E}}^{0m(\text{M})}$ were taken from ref 16. ⁱ Values of $\Delta_t G_{\text{E}}^{0m(\text{M})}$ were taken from ref 9. ^j Taken from ref 7. ^k Taken from ref 11. ^l Taken from ref 19. ^m Taken from ref 17. ⁿ Taken from ref 9.

From these relations, we can derive the conversion equations between the standard free energies of transfer ($\Delta_t G_{\text{E}}^0$) on different concentration scales

$$\Delta_t G_{\text{E}}^{0x} = \Delta_t G_{\text{E}}^{0c} + \nu RT \ln \left[\frac{\rho_{\text{S}}}{\rho_{\text{W}}} \frac{M_{\text{W}}}{M_{\text{S}}} \right] = \Delta_t G_{\text{E}}^{0m(\text{M})} + \nu RT \ln \frac{M_{\text{W}}}{M_{\text{S}}} \quad (11)$$

$$\Delta_t G_{\text{E}}^{0m(\text{W})} = \Delta_t G_{\text{E}}^{0m(\text{M})} - \nu RT \ln(1 + 0.001 m_{\text{N}} M_{\text{N}}) \quad (12)$$

where M_{W} is the mole mass of water.

To obtain the pair interaction parameters, values of the free energies of transfer are first converted into ones on the m_{E}^{W} scale from eqs 11 and 12, then used to fit eq 2 or eq 3. If the free energies of transfer don't be converted into ones on the m_{E}^{W} scale, the obtained pair interaction parameters from eq 2 or eq 3 are necessary to be converted into ones on the m_{E}^{W} scale. We will derive these conversion equations for the free energy pair interaction parameters as follows.

From eqs 1 and 2, we have

$$\left(\frac{\partial \Delta_t F_{\text{E}}}{\partial m_{\text{N}}} \right)_{m_{\text{E}}=0} = \left(\frac{\partial \Delta_t F_{\text{N}}}{\partial m_{\text{E}}} \right)_{m_{\text{N}}=0} = 2\nu f_{\text{EN}} \quad (13)$$

Particularly, for the free energy function in the standard state, this equation reduces to

$$\left(\frac{\partial \Delta_t G_{\text{E}}^0}{\partial m_{\text{N}}} \right)_{m_{\text{N}}=0} = \left(\frac{\partial \Delta_t G_{\text{N}}^0}{\partial m_{\text{E}}} \right)_{m_{\text{E}}=0} = 2\nu g_{\text{EN}} \quad (14)$$

From eqs 11–14, we have

$$\begin{aligned} 2\nu g_{\text{EN}}^{m(\text{W})} &= 2\nu g_{\text{EN}}^{m(\text{M})} - 2\nu \frac{RT}{2} \frac{M_{\text{N}}}{1000} = 2\nu g_{\text{EN}}^x - 2\nu \frac{RT}{2} \frac{M_{\text{w}}}{1000} \\ &= 2\nu g_{\text{EN}}^c - 2\nu \frac{RT}{2} \frac{M_{\text{N}}}{1000} + \frac{2RT M_{\text{N}}}{1000 \rho_{\text{W}}} \left(\frac{d\rho_{\text{S}}}{dwt} \right)_{wt=0} \end{aligned} \quad (15)$$

where $g_{\text{EN}}^{m(\text{W})}$, $g_{\text{EN}}^{m(\text{M})}$, g_{EN}^x , and g_{EN}^c are the free energy pair interaction parameters on m_{E}^{W} , m_{E}^{M} , x , and c scales, respectively.

Similarly, the entropy interaction parameters depend also on the concentration scales. From eqs 11 and 12 and the differential

correlation $S = (\partial G / \partial T)_p$, the following relations between the entropies of transfer on various scales have been derived

$$\Delta_t S_{\text{E}}^{0x} = \Delta_t S_{\text{E}}^{0c} + \nu R \ln \frac{\rho_{\text{S}}}{\rho_{\text{W}}} = \Delta_t S_{\text{E}}^{0m(\text{M})} + \nu R \ln \frac{M_{\text{W}}}{M_{\text{S}}} \quad (16)$$

$$\Delta_t S_{\text{E}}^{0m(\text{W})} = \Delta_t S_{\text{E}}^{0m(\text{M})} - \nu R \ln(1 + 0.001 m_{\text{N}} M_{\text{N}}) \quad (17)$$

Through the use of these equations, one can convert values of standard entropies of transfer of E from one concentration scale to another. However, the relations between entropy pair interaction parameters on different concentration scales can also be derived from eq 15 and the basic thermodynamic relation $s_{\text{EN}} = (\partial g_{\text{EN}} / \partial T)_p$

$$\begin{aligned} 2\nu s_{\text{EN}}^{m(\text{W})} &= 2\nu s_{\text{EN}}^{m(\text{M})} - 2\nu \frac{R}{2} \frac{M_{\text{N}}}{1000} = 2\nu s_{\text{EN}}^x - 2\nu \frac{R}{2} \frac{M_{\text{w}}}{1000} \\ &= 2\nu s_{\text{EN}}^c - 2\nu \frac{R}{2} \frac{M_{\text{N}}}{1000} + \frac{2R M_{\text{N}}}{1000 \rho_{\text{W}}} \left(\frac{d\rho_{\text{S}}}{dwt} \right)_{wt=0} \end{aligned} \quad (18)$$

It is easy to verify that some interaction parameters, such as enthalpy (h_{EN}), volume (v_{EN}), and isotonic heat capacity ($c_{p,\text{EN}}$), are independent of the concentration scales.

Discussion

Enthalpic interaction parameters can be obtained from the enthalpies of dilution and mixing.^{7,4,10} Isotonic heat capacity interaction parameters can be determined by microcalorimetry or derived from $c_{p,\text{EN}} = (\partial h_{\text{EN}} / \partial T)_p$.¹¹ Volumetric interaction parameters can be evaluated from density measurements. These parameters are independent of concentration scales. Free energy interaction parameters can be evaluated from freezing point depression,^{12,13} chromatography,¹⁴ solubility,¹⁵ and electromotive force (emf) measurements.^{3,4,11,16,17} The emf method has been used widely for evaluating the g_{EN} values. It can be divided into two types: one based on the m_{E}^{M} scale^{3,11,16,18} and the other on m_{E}^{W} scale.^{4,17,19} In the first method, standard emf's are determined on the m_{E}^{M} scale, and then standard free energies on this scale are calculated from

$$\Delta_t G_{\text{E}}^{0m(\text{M})} = -nF(E_{\text{M}}^0 - E_{\text{W}}^0) \quad (19)$$

where E_{M}^0 and E_{W}^0 are standard emf's in mixed solvent and in

water, respectively. In the second method, standard free energies and interaction parameters are obtained from^{4,17, 19}

$$\begin{aligned}\Delta_{\text{t}}G_{\text{E}}^{m(\text{W})}(\text{W} \rightarrow \text{W} + \text{N}) &= -nF\Delta E \\ &= 2\nu g_{\text{EN}}m_{\text{N}} + 3\nu g_{\text{ENN}}m_{\text{N}}^2 + \\ &\quad 6\nu^2 g_{\text{EEN}}m_{\text{N}}m_{\text{E}} + \dots \quad (20)\end{aligned}$$

or, at $m_{\text{E}} \rightarrow 0$,

$$\begin{aligned}\Delta_{\text{t}}G_{\text{E}}^{0m(\text{W})}(\text{W} \rightarrow \text{W} + \text{N}) &= -nF\Delta E^0 \\ &= 2\nu g_{\text{EN}}m_{\text{N}} + 3\nu g_{\text{ENN}}m_{\text{N}}^2 + \dots \quad (21)\end{aligned}$$

where ΔE is the difference in emf's, $\Delta E_{\text{M}} = E_{\text{M}} - E_{\text{W}}$ and $\Delta E_{\text{M}}^0 = E_{\text{M}}^0 - E_{\text{W}}^0$.

On the basis of different methods and conversions, some free energy pair interaction parameters were obtained and listed in Table 1. It can be seen from Table 1 that the $g_{\text{EN}}^{m(\text{W})}$ values evaluated from the emf measurements based on the m_{E}^{M} scale are in good agreement with ones on the m_{E}^{W} scale. In my opinion, the g_{EN} values obtained from experimental measurements on the m_{E}^{W} scale are more accurate than ones on the m_{E}^{M} scale, because in the former, the g_{EN} values can be obtained directly using the emf values from experimental measurements. However, through the use of a set of measured data (i.e., on the m_{E}^{M} scale), there are different processes for evaluating the g_{EN} values. Thus, obtained values are consistent with each other.

It is necessary to point out that a lot of data on the thermodynamic functions of transfer has been published in the literature.²⁰ Therefore, they can be applied to calculate the corresponding interaction parameters. At the same time, the pair interaction parameters can be conversed from one concentration scale to another by using the equations derived in this paper. This will make it possible to explore further the interactions between the solute molecules (electrolytes and/or nonelectrolytes) in water or in other solvents using the literature data and

to compare them with ones obtained from new experimental measurements.

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