

Derivation of General Equations of Chemical Potentials for Non-ideal Solutions Consisting of Multicomponent Polymer Homologue and Single Solvent

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General equations of the chemical potentials of the solvent $\Delta\mu_0$ and of the polymer with the molar volume ratio to the solvent X_i (i.e., the X_i -mer) $\Delta\mu_{X_i}$ are derived for multicomponent polymer homologue in single solvent system through use of their pseudo-excess functions $\Delta\mu_0^{PE}$ and $\Delta\mu_{X_i}^{PE}$, which are calculated using the polymer-solvent thermodynamic interaction parameter χ , semi-empirically determined as functions of temperature, polymer concentration and polymer molecular weight.

Key word : Chemical Potential, Polymer Solution, Non-ideal Solution, Quasi-ideal Solution, Real Solution

Enthalpy, entropy, and the Gibbs free energy of mixing for ideal multicomponent polymer homologue solution which is formed by 'random' mixing of long liner chain polymer solute molecule with single solvent without any enthalpy change (i.g., the 'random' mixing-athermal solution ; here after referred simply to as quasi-ideal solution) ΔH^{qid} , ΔS^{qid} , and ΔG^{qid} , can be given by¹⁾ :

$$\Delta H^{qid} = 0 \quad (1)$$

$$\Delta S^{qid} = -R(N_0 \ln v_0 + \sum_{i=1}^m N_{X_i} \ln v_{X_i}) \quad (2)$$

$$\Delta G^{qid} = \Delta H^{qid} - T\Delta S^{qid} = RT(N_0 \ln v_0 + \sum_{i=1}^m N_{X_i} \ln v_{X_i}) \quad (3)$$

where R is the gas constant, T , The Kelvin temperature, N_0 and N_{X_i} , the mole numbers of the solvent and X_i -mer, respectively, v_0 and v_{X_i} , the volume fractions of the solvent and X_i -mer, n_0 and n_{X_i} , (i.e., the molar volume ratio of i -th component of the polymer to the solvent), m , total number of components existing in the polymer. If v_0 and v_{X_i} in Eq 2 and Eq 3 are replaced by the mole fractions of the solvent and X_i -mer, n_0 and n_{X_i} , or when $X_i = 1$ for all i ($i = 1 \sim m$), Eq 2 and 3 reduce straightforward to those for truly ideal solution

Chemical potentials of solvent and polymer (X_i -mer), $\Delta\mu_0^{qid}$ and $\Delta\mu_{X_i}^{qid}$, for the above quasi-ideal solution are derived by differentiations of ΔG^{qid} (Eq 3) by N_0 and by N_{X_i} , respectively in the form :²⁾

$$\Delta\mu_0^{qid} \equiv \left(\frac{\partial \Delta G^{qid}}{\partial N_0} \right)_{T,P,n_{X_j}(j=1 \sim m)} = RT \left\{ \ln(1 - v_p) + \left(1 - \frac{1}{X_n} \right) v_p \right\} \quad (4)$$

$$\Delta\mu_{X_i}^{qid} \equiv \left(\frac{\partial \Delta G^{qid}}{\partial N_{X_i}} \right)_{T,P,n_{X_j}(j \neq i)} = RT \left\{ \ln v_{X_i} - (X_i - 1) + X_i \left(1 - \frac{1}{X_n} \right) v_p \right\} \quad (5)$$

Here v_p is the overall polymer volume fraction $\left(\equiv \sum_{i=1}^m v_{X_i} \right)$.

For real solution, the Gibbs free energy of mixing ΔG is

$$\Delta G = \Delta G^{qid} + \Delta G^{PE} \quad (6)$$

where ΔG^{PE} is the pseudo-excess function, which is defined, for the sake of convenience, by the

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difference of the thermodynamic quantities (in this case ΔG) between real polymer solution and quasi-ideal solution.

Chemical potentials $\Delta\mu_0$ and $\Delta\mu_{X_i}$ for the real polymer solution are :

$$\Delta\mu_0 \equiv \left(\frac{\partial \Delta G}{\partial N_0} \right)_{T,P,n_{X_j}(j=1\sim m)} = RT \left\{ \ln(1-v_p) + \left(1 - \frac{1}{X_n} \right) v_p \right\} + \Delta\mu_0^{PE} \quad (7)$$

$$\Delta\mu_{X_i} \equiv \left(\frac{\partial \Delta G}{\partial N_{X_i}} \right)_{T,P,n_{X_j}(j \neq i)} = RT \left\{ \ln v_{X_i} - (X_i - 1) + X_i \left(1 - \frac{1}{X_n} \right) v_p \right\} + \Delta\mu_{X_i}^{PE} \quad (8)$$

Here $\Delta\mu_0^{PE}$ and $\Delta\mu_{X_i}^{PE}$ are the pseudo-excess chemical potentials for the solvent and X_i -mer, respectively. Flory regarded Eq 7 as $\Delta\mu_0^E$ (in this notation)(see Eq 41 of reference 1)). This is apparently overestimation of the excess chemical potential and should be subtracted with $RT \ln N_0$. Kamide's treatment, given in his book(chapter 1)²⁾, is rather obscure because he did not keep strict distinction between ideal and quasi-ideal solutions throughout the chapter,

Comparison of Eq 6 with Eq 7 or Eq 8 leads to the following relations :²⁾

$$\Delta G^{PE} = \int_0^{N_0} \Delta\mu_0^{PE} dN_0 \quad (9a)$$

$$= \int_0^{N_{X_i}} \Delta\mu_{X_i}^{PE} dN_{X_i} \quad (9b)$$

or

$$\Delta\mu_0^{PE} \equiv \left(\frac{\partial \Delta G^{PE}}{\partial N_0} \right)_{T,P,n_{X_j}(j=1\sim m)} = RT x v_p^2 \quad (10)$$

$$\Delta\mu_{X_i}^{PE} \equiv \left(\frac{\partial \Delta G^{PE}}{\partial N_{X_i}} \right)_{T,P,n_{X_j}(j \neq i)} \quad (11a)$$

$$= \frac{\partial}{\partial N_{X_i}} \int_0^{N_0} \left(\frac{\partial \Delta G^{PE}}{\partial N_0} \right)_{T,P,n_{X_j}(j=1\sim m)} dN_0 \quad (11b)$$

$$= RT \left\{ \frac{\partial}{\partial N_{X_i}} \int_0^{N_0} x v_p^2 dN_0 \right\} \quad (11c)$$

$$= RT \left\{ -x v_p (1 - v_p) + \int_{v_p}^1 x d v_p \right\} \quad (11d)$$

Here, x is the polymer-solvent interaction parameter. Note that in derivation of Eq 10 van Laar-Scatchard type heat of dilution is assumed and in other words ΔG^{PE} is regarded to be exclusively caused by the heat of dilution ΔH ($\equiv \Delta H^{PE} = \Delta H^E$, ΔH^E is the excess function).

All possible disparities of real non-quasi-ideal polymer solutions from the hypothesis employed in the theory, such as the 'random' mixing of polymer chains with solvents on lattice sites and van Laar-Scatchard type expression of the heat of mixing, will reflect on χ parameter in Eq 10. Then, χ experimentally determined should be considered as the summation of the entropy term x_s and the enthalpy term x_h :

$$x = x_s + x_h \quad (12)$$

$$x_h \equiv \chi = \Delta H_0 / (RT v_p^2) = \Delta H_0^E / (RT v_p^2)$$

χ is the Flory's enthalpy parameter, depending phenomenologically on both T and v_p (Eq 13) and ΔH_0 is the partial molar heat of dilution.

$$\chi = \chi_0 + \chi_1 v_p + \chi_2 v_p^2 + \dots \quad (13)$$

$$\chi_0 = \lim_{v_p \rightarrow 0} \left\{ \Delta H_0 / (RT v_p^2) \right\} \quad (14)$$

χ can be experimentally determined by (1) temperature dependence of vapour pressure and

membrane osmometry, (2) critical solution temperature T_c and critical solution concentration v_p^c for a series of solutions of polymers, (3) temperature dependence of the second virial coefficient in the vicinity of the Flory theta temperature θ and (4) calorimetry. Kamide et al. indicated for atactic polystyrene (PS)-cyclohexane (CH) and PS-trane-decalin (D) systems that excellent agreement (± 0.02) was confirmed between k_0 values at θ deduced by the above methods at the same molecular weight and k_0 depends significantly on the average molecular weight.³⁾

x can be semi-empirically expressed as⁴⁻⁹⁾

$$x = x_0 \left(1 + \sum_{j=1}^n p_j v_p^j \right) \quad (15)$$

$$x_0 = x_{00} \left(1 + \frac{k'}{X_n} \right) \quad (16)$$

$$x_{00} = (1/2 - \varphi_0) + \frac{\theta \varphi_{00}}{T} \quad (17)$$

$$k' = k_0 (1 - \theta/T) \quad (18)$$

p_j is concentration-dependence parameter, x_{00} is a parameter independent of v_p and X_i , k' , a molecular weight-dependence parameter, X_n , the number-average X , φ_{00} , Flory entropy parameter, θ , Flory theta temperature, k_0 , the parameter independent of T and X .

If we can assume that all virial coefficients vanish at $T = \theta$ for upper critical solution point, we obtain⁸⁾

$$x_0 = 1/2 \quad (19)$$

$$p_1 = \frac{2}{3}, p_2 = \frac{2}{4}, p_3 = \frac{2}{5}, \dots, p_n = \frac{2}{n+2} \quad (20)$$

These are the theoretically predicated values for x_0 and p_j ($j=1, \dots, n$), provided that all the hypothesis in the theory are accepted. p_1 and p_2 can be experimentally determined by the following methods²⁾: (1) osmotic pressure, (2) isothermal distillation, (3) vapour pressure, (4) ultracentrifuge, (5) coexisting curve (i.e., binodal curve), (6) cloud point curve and (7) critical solution point. Note that applicability of methods (1)~(4) are severely limited to rather rough estimation of p_1 only and method (7), proposed by Koningsveld et al.¹⁰⁾ and by Kamide and his coworkers^{6,9)}, gives the (most accurate and reliable values of p_1 and p_2 and this method was successfully applied by) Kamide et al. to the literature data on upper and/or lower critical solution points of ten polystyrene-solvent pairs and sixteen polyethylene-solvent pairs in very systematic manner⁸⁾.

Combination of Eq 10 with Eq 15 and 16 yields

$$\Delta \mu_0^{PE} = RT x_{00} \left(1 + \frac{k'}{X_n} \right) \left(1 + \sum_{j=1}^n p_j v_p^j \right) v_p^2 \quad (21)$$

Substitution of Eq 21 into Eq 9a yields

$$\begin{aligned} \Delta G^{PE} &= \int_0^{N_0} \left\{ RT x_{00} \left(1 + \frac{k'}{X_n} \right) \left(1 + \sum_{j=1}^n p_j v_p^j \right) v_p^2 \right\} dN_0 \\ \Delta G^{PE} &= \int_0^{N_0} \left\{ RT x_{00} \left(1 + \frac{k'}{X_n} \right) \left(1 + \sum_{j=1}^n p_j v_p^j \right) v_p^2 \right\} dN_0 \\ &= RT \left(N_0 + \sum_{i=1}^m N_{X_i} X_i \right) \left\{ x_{00} \left(1 + \frac{k'}{X_n} \right) \left(1 + \sum_{j=1}^n \frac{p_j}{j+1} \cdot \frac{1 + v_p^{j+1}}{v_0} \right) \right\} v_0 v_p \end{aligned} \quad (22)$$

From Eq 22 and 11a, we obtain

$$\begin{aligned} \Delta \mu_{X_i}^{PE} &= RT \left[x_{00} \left(1 + \frac{k'}{X_n} \right) X_i \left\{ (1 - v_p)^2 + \sum_{j=1}^n P_j \left(\frac{1}{j+1} - \frac{j+2}{j+1} v_p^{j+1} + v_p^{j+2} \right) \right\} \right] \\ &\quad + x_{00} k' X_j \left(\frac{1}{X_i} - \frac{1}{X_n} \right) \left\{ (1 - v_p) + \sum_{j=1}^n \frac{P_j}{j+1} (1 - v_p^{j+1}) \right\} \end{aligned}$$

$$\begin{aligned}
&= RTX_i(1-v_p)^2x_{00}\left[\left(1+\frac{k'}{X_n}\right)\left\{1+\sum_{j=1}^n P_j\left\{\sum_{q=0}^n (q+1)v_p^q\right\}\right\}\right. \\
&\quad \left.+k'\left(\frac{1}{X_i}-\frac{1}{X_n}\right)\left(\frac{1}{1-v_p}+\sum_{j=1}^n \frac{P_j}{j+1}\left(\sum_{q=0}^j \frac{v_p^q}{1-v_p}\right)\right)\right] \quad (23)
\end{aligned}$$

This is Kamide et al.'s approach, proposed in 1970¹¹⁾. We can also derive Eq 23 from Eq 11d and Eq 12. This is an alternative route to derive Eq 23 [Approach of Kurata¹²⁾, who first derived Eq 11d in 1975].

Therefore, $\Delta\mu_0$ (Eq 7) and $\Delta\mu_{X_i}$ (Eq 8) can be generally expressed as

$$\begin{aligned}
\Delta\mu_0 &= \Delta\mu_0^{id} + \Delta\mu_0^{PE} \\
&= RT\left\{\ln(1-v_p) + \left(1-\frac{1}{X_n}\right)v_p + x_{00}\left(1+\frac{k'}{X_n}\right)\left(1+\sum_{j=1}^n P_j v_p^j\right)v_p^2\right\} \quad (24)
\end{aligned}$$

$$\begin{aligned}
\Delta\mu_{X_i} &= \Delta\mu_{X_i}^{qi} + \Delta\mu_{X_i}^{PE} \\
&= RT\left[\ln v_{X_i} - (X_i-1) + X_i\left(1-\frac{1}{X_n}\right)v_p\right. \\
&\quad \left.+ X_i(1-v_p)^2x_{00}\left[\left(1+\frac{k'}{X_n}\right)\left\{1+\sum_{j=1}^n P_j\left\{\sum_{q=0}^j (q+1)v_p^q\right\}\right\}\right.\right. \\
&\quad \left.\left.+k'\left(\frac{1}{X_i}-\frac{1}{X_n}\right)\left(\frac{1}{1-v_p}+\sum_{j=1}^n \frac{P_j}{j+1}\left(\sum_{q=0}^j \frac{v_p^q}{1-v_p}\right)\right)\right)\right] \quad (25)
\end{aligned}$$

Of course it can be shown that Eq 24 and 25 satisfy the Gibbs-Duhem relations (Eq26) unconditionally.

$$N_0 d(\Delta\mu_0) + \sum_{i=1}^m N_{X_i} d(\Delta\mu_{X_i}) = 0 \quad (26)$$

Eq 24 and 25 correspond to Eq 4 and Eq 5 of reference 6).

Table 1 summarises some characteristics of three typical solutions and their relations.

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Table 1 Some characteristics of three typical solutions

Solutions	Characteristics
ideal	random mixing (solute=solvent in size) zero heat of mixing
quasi-ideal	'random' mixing (solute>solvent in size) zero heat of mixing
real	non-'random' mixing (solute >> solvent in size) non-zero heat of mixing

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