33. A New Model of the Excess Gibbs Energy of Mixing for a Regular Solution

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Abstract: The excess Gibbs energy of mixing for a regular solution can be derived systematically by defining the interaction energy for particle groups composed of closest neighbors at equivalent site. The internal energy of a system is regarded as the sum of the interaction energy for particle groups and the excess function is derived from the sum of the interaction energy change caused by the formations of particle groups.

In the present paper, we have derived the excess Gibbs energy of mixing for ternary and quaternary regular solutions with a closest packing. For a ternary regular solution, the molar excess Gibbs energy of mixing is given as follows,

$$\begin{aligned}\bar{G}^{ex} = & X_A X_B (X_A W_{AAB} + X_B W_{ABB}) + X_B X_C (X_B W_{BBC} + X_C W_{BCC}) \\ & + X_C X_A (X_C W_{CCA} + X_A W_{CAA}) + 2X_A X_B X_C W_{ABC},\end{aligned}$$

where X_i is a mole fraction of the component i and W_{ijk} is an interaction parameter of $[ijk]$ triplet. The following expressions for n -component systems are derived by the similar method by supposing interaction energy among r particles. Some previously proposed models can be derived from our model.

$$n=2, r=2: \bar{G}^{ex} = X_A X_B W_{AB} \quad (\text{symmetric binary regular solution model})$$

$$n=2, r=3: \bar{G}^{ex} = X_A X_B (X_A W_{AAB} + X_B W_{ABB}) \quad (\text{asymmetric binary regular solution model})$$

$$n=3, r=2: \bar{G}^{ex} = X_A X_B W_{AB} + X_B X_C W_{BC} + X_C X_A W_{CA} \quad (\text{symmetric ternary regular solution model})$$

$$\begin{aligned}n=3, r=3: \bar{G}^{ex} = & X_A X_B (X_A W_{AAB} + X_B W_{ABB}) + X_B X_C (X_B W_{BBC} + X_C W_{BCC}) \\ & + X_C X_A (X_C W_{CCA} + X_A W_{CAA}) + 2X_A X_B X_C W_{ABC} \\ & (\text{new ternary model: stated above})\end{aligned}$$

$$\begin{aligned}n=4, r=4: \bar{G}^{ex} = & X_A^3 X_B W_{AAAB} + X_B^3 X_A W_{BBBA} + X_A^3 X_C W_{AAAC} + X_C^3 X_A W_{CCCA} \\ & + X_A^3 X_D W_{AAAD} + X_D^3 X_A W_{DDDA} + X_B^3 X_C W_{BBBC} + X_C^3 X_B W_{CCCB} \\ & + X_B^3 X_D W_{BBBD} + X_D^3 X_B W_{DDDB} + X_C^3 X_D W_{CCCD} + X_D^3 X_C W_{DDDC} \\ & + \frac{3}{2} X_A^2 X_B^2 W_{AABB} + \frac{3}{2} X_A^2 X_C^2 W_{AACC} + \frac{3}{2} X_A^2 X_D^2 W_{AADD} \\ & + \frac{3}{2} X_B^2 X_C^2 W_{BBCC} + \frac{3}{2} X_B^2 X_D^2 W_{BBDD} + \frac{3}{2} X_C^2 X_D^2 W_{CCDD} \\ & + 3X_A^2 X_B X_C W_{AABC} + 3X_A^2 X_B X_D W_{AABD} + 3X_A^2 X_C X_D W_{AACD} \\ & + 3X_B^2 X_A X_C W_{BBAC} + 3X_B^2 X_A X_D W_{BBAD} + 3X_B^2 X_C X_D W_{BBCD} \\ & + 3X_C^2 X_A X_B W_{CCAB} + 3X_C^2 X_A X_D W_{CCAD} + 3X_C^2 X_B X_D W_{CCBD} \\ & + 3X_D^2 X_A X_B W_{DDAB} + 3X_D^2 X_A X_C W_{DDAC} + 3X_D^2 X_B X_C W_{DDBC} \\ & + 6X_A X_B X_C X_D W_{ABCD}. \\ & (\text{new quaternary model})\end{aligned}$$

Key words: Regular solution; ternary system; quaternary system; thermodynamics; excess Gibbs energy.

Introduction. *Regular solution*, originally introduced by Hildebrand,¹⁾ is one of the simplest solution models that have ever been derived. For a binary regular solution,

symmetric regular solution model is established by introducing the interaction energy of particle pairs (Guggenheim²), and then *subregular solution model* is derived as a higher expansion in the empirical method (Hardy³). For ternary and quaternary regular solutions, algebraical solutions and empirical approaches are proposed by Anderson and Lindsley,⁴ Barron,⁵ Kohler⁶ and Wohl^{7,8}) but physical model have not been given yet.

The purpose of the present paper is to derive the excess Gibbs energy of mixing for ternary and quaternary regular solutions by introducing *triplet* and *quadruplet*, respectively, originally appeared in Guggenheim⁹ for a binary system.

Symbols.

G^{ex}	Excess Gibbs energy of mixing,
$\bar{G}^{ex}$	Molar excess Gibbs energy of mixing,
$[ijk]$	Triplet composed of the particles i , j and k ,
N	Avogadro's number,
N_i	Number of the particle i ,
N_{ijk}	Number of $[ijk]$ triplets,
$\langle N_{ijk} \rangle$	Average number of $[ijk]$ triplets,
n	Number of components in a system,
n_i	Number of moles of the component i ,
r	Number of particles constituting a particle group,
U	Internal energy,
U^{ex}	Excess internal energy,
W_{ijk}	Interaction parameter of $[ijk]$ triplet,
X_i	Mole fraction of the component i ; $\sum X_i = 1$,
z	Coordination number; $z=12$ for a closest packing,
ϵ_{ijk}	Interaction energy of $[ijk]$ triplet,
ω_{ijk}	Interaction energy change of formation of $[ijk]$ triplet,
μ_i^{ex}	Excess chemical potential of the component i ,
φ^{ijk}	Probability of occurrence for $[ijk]$ triplet.

Ternary regular solution. The authors derive the excess Gibbs energy of mixing for a ternary regular solution on the following assumptions:

- The total internal energy of the system is expressed as the sum of the interaction energy of all particle groups.
- Particles are of the same size and are distributed randomly without volume change at equivalent site.
- Only closest neighbors are subjected to interactions. Long range interactions such as electrostatic force can be ignored.
- Each particle is directly surrounded by other z particles. The value of z is 12 for a closest packing, but no assignment of z value is needed.

From the assumption (a), the internal energy of the system can be expressed as the sum of the internal energy of each triplet:

$$U = \epsilon_{AAA}N_{AAA} + \epsilon_{BBB}N_{BBB} + \epsilon_{CCC}N_{CCC} + \epsilon_{AAB}N_{AAB} + \epsilon_{ABB}N_{ABB} + \epsilon_{BBC}N_{BBC} + \epsilon_{BCC}N_{BCC} + \epsilon_{CCA}N_{CCA} + \epsilon_{CAA}N_{CAA} + \epsilon_{ABC}N_{ABC}. \quad (1)$$

As each particle is shared by $2z$ triplets, shown in Fig. 1, we have the following relations between the number of triplets (N_{ijk}) and the number of particles (N_i):

$$3N_{AAA} + 2N_{AAB} + 2N_{CAA} + N_{ABB} + N_{CCA} + N_{ABC} = 2zN_A. \quad (2)$$

$$3N_{BBB} + 2N_{ABB} + 2N_{BBC} + N_{AAB} + N_{BCC} + N_{ABC} = 2zN_B, \quad (3)$$

$$3N_{CCC} + 2N_{CCA} + 2N_{BCC} + N_{CAA} + N_{BBC} + N_{ABC} = 2zN_C. \quad (4)$$

The total number of triplets is given by the sum of the equations (2), (3) and (4):

Fig. 1. A closest cubic packing composed of 24 triplets. [012], [016], [019], [01A], [023], [027], [02A], [034], [037], [03B], [045], [048], [04C], [056], [058], [05A], [069], [06C], [078], [079], [089], [0AC], [0BC] and [0BC], or composed of 8 quadruplets: [012A], [0237], [034B], [0458], [056C], [0169], [0ABC] and [0789]. A centered particle is surrounded by 12 closest neighbors.

$$N_{AAA} + N_{BBB} + N_{CCC} + N_{AAB} + N_{BBC} + N_{CCA} + N_{ABB} + N_{BCC} + N_{CAA} + N_{ABC} = \frac{2}{3} z(N_A + N_B + N_C), \quad (5)$$

Equations (1) to (4) give the following expression for the internal energy of the system:

$$U = \frac{2}{3} z N_A \epsilon_{AAA} + \frac{2}{3} z N_B \epsilon_{BBB} + \frac{2}{3} z N_C \epsilon_{CCC} + N_{AAB} \{ \epsilon_{AAB}^{-1/3} (\epsilon_{AAA} + \epsilon_{AAA} + \epsilon_{BBB}) \} + N_{ABB} \{ \epsilon_{ABB}^{-1/3} (\epsilon_{AAA} + \epsilon_{BBB} + \epsilon_{BBB}) \} + N_{BBC} \{ \epsilon_{BBC}^{-1/3} (\epsilon_{BBB} + \epsilon_{BBB} + \epsilon_{CCC}) \} + N_{BCC} \{ \epsilon_{BCC}^{-1/3} (\epsilon_{BBB} + \epsilon_{CCC} + \epsilon_{CCC}) \} + N_{CCA} \{ \epsilon_{CCA}^{-1/3} (\epsilon_{CCC} + \epsilon_{CCC} + \epsilon_{AAA}) \} + N_{CAA} \{ \epsilon_{CAA}^{-1/3} (\epsilon_{CCC} + \epsilon_{AAA} + \epsilon_{AAA}) \} + N_{ABC} \{ \epsilon_{ABC}^{-1/3} (\epsilon_{AAA} + \epsilon_{BBB} + \epsilon_{CCC}) \}. \quad (6)$$

Considering the mixing process as the formation of the triplets expressed by the following seven reactions,

$$\begin{aligned} \frac{1}{3}[AAA] + \frac{1}{3}[AAA] + \frac{1}{3}[BBB] &= [AAB], \quad \frac{1}{3}[AAA] + \frac{1}{3}[BBB] + \frac{1}{3}[BBB] = [ABB], \\ \frac{1}{3}[BBB] + \frac{1}{3}[BBB] + \frac{1}{3}[CCC] &= [BBC], \quad \frac{1}{3}[BBB] + \frac{1}{3}[CCC] + \frac{1}{3}[CCC] = [BCC], \\ \frac{1}{3}[CCC] + \frac{1}{3}[CCC] + \frac{1}{3}[AAA] &= [CCA], \quad \frac{1}{3}[CCC] + \frac{1}{3}[AAA] + \frac{1}{3}[AAA] = [CAA], \\ \text{and } \frac{1}{3}[AAA] + \frac{1}{3}[BBB] + \frac{1}{3}[CCC] &= [ABC], \end{aligned} \quad (7)$$

the interaction energy changes of formation of [ijk] triplets in equation (7) are defined as,

$$\begin{aligned} \omega_{AAB} &= \epsilon_{AAA}^{-1/3} (\epsilon_{AAA} + \epsilon_{AAA} + \epsilon_{BBB}), \quad \omega_{ABB} = \epsilon_{AAA}^{-1/3} (\epsilon_{AAA} + \epsilon_{BBB} + \epsilon_{BBB}), \\ \omega_{BBC} &= \epsilon_{BBB}^{-1/3} (\epsilon_{BBB} + \epsilon_{BBB} + \epsilon_{CCC}), \quad \omega_{BCC} = \epsilon_{BBB}^{-1/3} (\epsilon_{BBB} + \epsilon_{CCC} + \epsilon_{CCC}), \\ \omega_{CCA} &= \epsilon_{CCC}^{-1/3} (\epsilon_{CCC} + \epsilon_{CCC} + \epsilon_{AAA}), \quad \omega_{CAA} = \epsilon_{CCC}^{-1/3} (\epsilon_{CCC} + \epsilon_{AAA} + \epsilon_{AAA}), \\ \text{and } \omega_{ABC} &= \epsilon_{AAA}^{-1/3} (\epsilon_{AAA} + \epsilon_{BBB} + \epsilon_{CCC}), \text{ respectively.} \end{aligned} \quad (8)$$

Therefore, the internal energy can be rewritten using equation (8) as

$$U = \frac{1}{3} z N_A \epsilon_{AAA} + \frac{2}{3} z N_B \epsilon_{BBB} + \frac{2}{3} z N_C \epsilon_{CCC} + N_{AAB} \omega_{AAB} + N_{ABB} \omega_{ABB} + N_{BBC} \omega_{BBC} + N_{BCC} \omega_{BCC} + N_{CCA} \omega_{CCA} + N_{CAA} \omega_{CAA} + N_{ABC} \omega_{ABC}, \quad (9)$$

and then the excess internal energy is given by

$$U^{ex} = N_{AAB} \omega_{AAB} + N_{ABB} \omega_{ABB} + N_{BBC} \omega_{BBC} + N_{BCC} \omega_{BCC} + N_{CCA} \omega_{CCA} + N_{CAA} \omega_{CAA} + N_{ABC} \omega_{ABC}. \quad (10)$$

Based on the assumption (b), the Gibbs energy can be considered to be the same as the internal energy. Therefore, equation (10) will be rewritten as

$$G^{ex} = N_{AAB} \omega_{AAB} + N_{ABB} \omega_{ABB} + N_{BBC} \omega_{BBC} + N_{BCC} \omega_{BCC} + N_{CCA} \omega_{CCA} + N_{CAA} \omega_{CAA} + N_{ABC} \omega_{ABC}. \quad (11)$$

From the random distribution of particles in the assumption (b), the probability of occurrence for [ijk] triplet is defined as follows;

$$\begin{aligned}
\varphi_{AAB} &= \frac{3N_A^2 N_B}{(N_A + N_B + N_C)^3}, \quad \varphi_{ABB} = \frac{3N_A N_B^2}{(N_A + N_B + N_C)^3}, \quad \varphi_{BBC} = \frac{3N_B^2 N_C}{(N_A + N_B + N_C)^3}, \\
\varphi_{BCC} &= \frac{3N_B N_C^2}{(N_A + N_B + N_C)^3}, \quad \varphi_{CCA} = \frac{3N_C^2 N_A}{(N_A + N_B + N_C)^3}, \quad \varphi_{CAA} = \frac{3N_C N_A^2}{(N_A + N_B + N_C)^3}, \\
\text{and } \varphi_{ABC} &= \frac{6N_A N_B N_C}{(N_A + N_B + N_C)^3}.
\end{aligned} \tag{12}$$

Equations (5) and (12) give the average number of triplets in the system as

$$\begin{aligned}
\langle N_{AAB} \rangle &= \frac{2zN_A^2 N_B}{(N_A + N_B + N_C)^2} = \frac{2zn_A^2 n_B}{(n_A + n_B + n_C)^2} N, \quad \langle N_{ABB} \rangle = \frac{2zN_A N_B^2}{(N_A + N_B + N_C)^2} = \frac{2zn_A n_B^2}{(n_A + n_B + n_C)^2} N, \\
\langle N_{BBC} \rangle &= \frac{2zN_B^2 N_C}{(N_A + N_B + N_C)^2} = \frac{2zn_B^2 n_C}{(n_A + n_B + n_C)^2} N, \quad \langle N_{BCC} \rangle = \frac{2zN_B N_C^2}{(N_A + N_B + N_C)^2} = \frac{2zn_B n_C^2}{(n_A + n_B + n_C)^2} N, \\
\langle N_{CCA} \rangle &= \frac{2zN_C^2 N_A}{(N_A + N_B + N_C)^2} = \frac{2zn_C^2 n_A}{(n_A + n_B + n_C)^2} N, \quad \langle N_{CAA} \rangle = \frac{2zN_B N_A^2}{(N_A + N_B + N_C)^2} = \frac{2zn_C n_A^2}{(n_A + n_B + n_C)^2} N, \\
\text{and } \langle N_{ABC} \rangle &= \frac{4zN_A N_B N_C}{(N_A + N_B + N_C)^2} = \frac{4zn_A n_B n_C}{(n_A + n_B + n_C)^2} N.
\end{aligned} \tag{13}$$

Substituting N_{ijk} in equation (11) with $\langle N_{ijk} \rangle$ in equation (13), the excess Gibbs energy of mixing is rewritten as

$$\begin{aligned}
G^{ex} &= 2z \frac{n_A^2 n_B}{(n_A + n_B + n_C)^2} \omega_{AAB} N + 2z \frac{n_A n_B^2}{(n_A + n_B + n_C)^2} \omega_{ABB} N + 2z \frac{n_B^2 n_C}{(n_A + n_B + n_C)^2} \omega_{BBC} N \\
&\quad + 2z \frac{n_B n_C^2}{(n_A + n_B + n_C)^2} \omega_{BCC} N + 2z \frac{n_C^2 n_A}{(n_A + n_B + n_C)^2} \omega_{CCA} N + 2z \frac{n_C n_A^2}{(n_A + n_B + n_C)^2} \omega_{CAA} N \\
&\quad + 4z \frac{n_A n_B n_C}{(n_A + n_B + n_C)} \omega_{ABC} N.
\end{aligned} \tag{14}$$

Rewriting on the molar basis gives:

$$\begin{aligned}
\bar{G}^{ex} &= 2zX_A X_B (X_A \omega_{AAB} + X_B \omega_{ABB}) N + 2zX_B X_C (X_B \omega_{BBC} + X_C \omega_{BCC}) N + 2zX_C X_A (X_C \omega_{CCA} \\
&\quad + X_A \omega_{CAA}) N + 4zX_A X_B X_C \omega_{ABC} N.
\end{aligned} \tag{15}$$

As each particle is shared by 2z triplets, *interaction parameter* is defined as

$$W_{ijk} = 2z\omega_{ijk} N. \tag{16}$$

Using equation (16), the molar excess Gibbs energy of mixing can be rewritten in the following form:

$$\begin{aligned}
\bar{G}^{ex} &= X_A X_B (X_A W_{AAB} + X_B W_{ABB}) + X_B X_C (X_B W_{BBC} + X_C W_{BCC}) \\
&\quad + X_C X_A (X_C W_{CCA} + X_A W_{CAA}) + 2X_A X_B X_C W_{ABC}.
\end{aligned} \tag{17}$$

The excess chemical potential of the component i , derived by partial differentiation of G^{ex} with respect to n_i , is given by

$$\begin{aligned}
\mu_A^{ex} &= 2X_A X_B (1 - X_A) W_{AAB} + X_B^2 (1 - 2X_A) W_{ABB} + X_C^2 (1 - 2X_A) W_{CCA} + 2X_C X_A (1 - X_A) W_{CAA} \\
&\quad - 2X_B^2 X_C W_{BBC} - 2X_B X_C^2 W_{BCC} + 2X_B X_C (1 - 2X_A) W_{ABC},
\end{aligned} \tag{18}$$

$$\begin{aligned}
\mu_B^{ex} &= 2X_B X_C (1 - X_B) W_{BBC} + X_C^2 (1 - 2X_B) W_{BCC} + X_A^2 (1 - 2X_B) W_{AAB} + 2X_A X_B (1 - X_B) W_{ABB} \\
&\quad - 2X_C^2 X_A W_{CCA} - 2X_C X_A^2 W_{CAA} + 2X_C X_A (1 - 2X_B) W_{ABC},
\end{aligned} \tag{19}$$

$$\begin{aligned}
\text{and } \mu_C^{ex} &= 2X_C X_A (1 - X_C) W_{CCA} + X_A^2 (1 - 2X_C) W_{CAA} + X_B^2 (1 - 2X_C) W_{BBC} + 2X_B X_C (1 - X_C) W_{BCC} \\
&\quad - 2X_A^2 X_B W_{AAB} - 2X_A X_B^2 W_{ABB} + 2X_A X_B (1 - 2X_C) W_{ABC}.
\end{aligned} \tag{20}$$

Binary regular solution. For a binary solution, by substituting zero for X_C in equation (17), the following expression is obtained:

$$\bar{G}^{ex} = X_A X_B (X_A W_{AAB} + X_B W_{ABB}). \quad (21)$$

Quaternary regular solution. In order to describe $\bar{G}^{ex}$ for a quaternary regular solution, we need to introduce *quadruplet*, instead of *triplet*, that forms a tetrahedron. As each particle is shared by $2/3z$ quadruplets as shown in Fig. 1, interaction parameter is defined as

$$W_{ijkl} = \frac{2}{3} z \omega_{ijkl} N. \quad (22)$$

Then the following expression is obtained for a quaternary system by the same procedure as for a ternary solution:

$$\begin{aligned} \bar{G}^{ex} = & X_A^3 X_B W_{AAAB} + X_B^3 X_A W_{BBBA} + X_A^3 X_C W_{AAAC} + X_C^3 X_A W_{CCCA} + X_A^3 X_D W_{AAAD} \\ & + X_D^3 X_A W_{DDDA} + X_B^3 X_C W_{BBBC} + X_C^3 X_B W_{CCCB} + X_B^3 X_D W_{BBBD} + X_D^3 X_B W_{DDDB} \\ & + X_C^3 X_D W_{CCCD} + X_D^3 X_C W_{DDDC} \\ & + \frac{3}{2} X_A^2 X_B^2 W_{AABB} + \frac{3}{2} X_A^2 X_C^2 W_{AACC} + \frac{3}{2} X_A^2 X_D^2 W_{AADD} + \frac{3}{2} X_B^2 X_C^2 W_{BBCC} \\ & + \frac{3}{2} X_B^2 X_D^2 W_{BBDD} + \frac{3}{2} X_C^2 X_D^2 W_{CCDD} \\ & + 3X_A^2 X_B X_C W_{AABC} + 3X_A^2 X_B X_D W_{AABD} + 3X_A^2 X_C X_D W_{AACD} + 3X_B^2 X_A X_C W_{BBAC} \\ & + 3X_B^2 X_A X_D W_{BBAD} + 3X_B^2 X_C X_D W_{BBCD} + 3X_C^2 X_A X_B W_{CCAB} + 3X_C^2 X_A X_D W_{CCAD} \\ & + 3X_C^2 X_B X_D W_{CCBD} + 3X_D^2 X_A X_B W_{DDAB} + 3X_D^2 X_A X_C W_{DDAC} + 3X_D^2 X_B X_C W_{DDBC} \\ & + 6X_A X_B X_C X_D W_{ABCD}. \end{aligned} \quad (23)$$

Margules model. The Margules expansion,¹⁰⁾ essentially the same as the Guggenheim expansion,¹¹⁾ is often applied to the expression of the excess Gibbs energy of mixing.

$$\bar{G}^{ex} = A + BX_2 + CX_2^2 + DX_2^3 + \dots \quad : \text{Binary system} \quad (25)$$

$$\bar{G}^{ex} = A + BX_2 + CX_3 + DX_2^2 + EX_2X_3 + FX_3^2 + GX_2^3 + HX_2X_3^2 + IX_2^2X_3 + JX_3^3 + \dots \quad : \text{Ternary system} \quad (26)$$

The degree of Margules expansion corresponds to the number of interactive closest neighbors (r) of our model. The Margules expansion to the second-degree terms gives the same expression as equation (21) for a binary regular solution.

$$\bar{G}^{ex} = X_1 X_2 (X_1 W_{12} + X_2 W_{21}). \quad (27)$$

For a ternary regular solution, the similar expression to our model can be derived from equation (26) to the third-degree terms:

$$\begin{aligned} \bar{G}^{ex} = & X_1 X_2 (X_1 W_{12} + X_2 W_{21}) + X_2 X_3 (X_2 W_{23} + X_3 W_{32}) \\ & + X_3 X_1 (X_3 W_{31} + X_1 W_{13}) + X_1 X_2 X_3 W_{123}. \end{aligned} \quad (28)$$

The difference between equations (17) and (28),

$$W_{123} = 2W_{ABC}, \quad (29)$$

is caused by the fact that each coefficient in Margules model is just a fitting parameter, whereas each *interaction parameter* in our model signifies the molar excess interaction energy change of formation of [ijk] triplet.

Thompson's model. *Symmetric ternary regular solution model*, known as Thompson's model,¹²⁾ can be algebraically derived from the Margules expansion or empirically deduced from *symmetric binary regular solution model*.

By decomposing *triplets* into *pairs*, our model results in *symmetric ternary regular solution model*. As each pair is shared by four triplets, interaction energy of triplet can be rewritten using that of pair (ϵ_{ij}):

$$\begin{aligned}
\varepsilon_{AAB} &= 1/4(\varepsilon_{AA} + \varepsilon_{AB} + \varepsilon_{AB}), & \varepsilon_{ABB} &= 1/4(\varepsilon_{BB} + \varepsilon_{AB} + \varepsilon_{AB}), \\
\varepsilon_{BBC} &= 1/4(\varepsilon_{BB} + \varepsilon_{BC} + \varepsilon_{BC}), & \varepsilon_{BCC} &= 1/4(\varepsilon_{CC} + \varepsilon_{BC} + \varepsilon_{BC}), \\
\varepsilon_{CCA} &= 1/4(\varepsilon_{CC} + \varepsilon_{CA} + \varepsilon_{CA}), & \varepsilon_{CAA} &= 1/4(\varepsilon_{AA} + \varepsilon_{CA} + \varepsilon_{CA}), \\
\varepsilon_{ABC} &= 1/4(\varepsilon_{AA} + \varepsilon_{BC} + \varepsilon_{CA}). & &
\end{aligned} \tag{30}$$

By defining the excess interaction energy of pair (ω_{ij}) in the same way as that of triplet;

$$\omega_{AB} = \varepsilon_{AB} - 1/2(\varepsilon_{AA} + \varepsilon_{BB}), \quad \omega_{BC} = \varepsilon_{BC} - 1/2(\varepsilon_{BB} + \varepsilon_{CC}), \quad \text{and} \quad \omega_{CA} = \varepsilon_{CA} - 1/2(\varepsilon_{CC} + \varepsilon_{AA}), \tag{31}$$

the excess interaction energy of triplet can be expressed with that of pair as follows;

$$\begin{aligned}
\omega_{AAB} &= \omega_{ABB} = 1/2\omega_{AB}, & \omega_{BBC} &= \omega_{BCC} = 1/2\omega_{BC}, & \omega_{CCA} &= \omega_{CAA} = 1/2\omega_{CA}, \\
\text{and } \omega_{ABC} &= 1/4(\omega_{AB} + \omega_{BC} + \omega_{CA}). & & & &
\end{aligned} \tag{32}$$

Substituting equation (32) into (16), interaction parameter of triplet (W_{ijk}) can be rewritten using that of pair (W_{ij}):

$$\begin{aligned}
W_{AAB} &= W_{ABB} = z\omega_{AB}N(\equiv W_{AB}), & W_{BBC} &= W_{BCC} = z\omega_{BC}N(\equiv W_{BC}), \\
W_{CCA} &= W_{CAA} = z\omega_{CA}N(\equiv W_{CA}), & W_{ABC} &= 1/2(W_{AB} + W_{BC} + W_{CA}). &
\end{aligned} \tag{33}$$

This is a consequence that each particle is shared by z pairs and then each pair by two triplets. By substituting equation (33) into (17), Thompson's model is obtained:

$$\bar{G}^{ex} = X_A X_B W_{AB} + X_B X_C W_{BC} + X_C X_A W_{CA}. \tag{34}$$

Substituting zero for X_C , equation (34) results in *symmetric binary solution model*:

$$\bar{G}^{ex} = X_A X_B W_{AB}. \tag{35}$$

The following model proposed by Thompson¹²⁾ as *asymmetric ternary regular solution model* is not consistent with our model given by equation (17).

$$\bar{G}^{ex} = X_A X_B (X_A W_{AB} + X_B W_{BA}) + X_B X_C (X_B W_{BC} + X_C W_{CB}) + X_C X_A (X_C W_{CA} + X_A W_{AC}). \tag{36}$$

Remarks. The present regular solution model still contains the contradiction in the assumption such that random mixing takes place in spite of non-zero excess energy of mixing. However, the present model has advantage that the coefficients in our model have physical meanings (*interaction parameter*) and our model can derive several previous models.

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