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Development of the Scatchard-Hildebrand and Wohl Equations in Terms of Pair and Triplet Weighting Functions

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A previous paper introduced the pair-type-probability (PTP) function for use in molecular corresponding states theory. The present paper develops the predictive equations of Scatchard and Hildebrand and the correlation equations of Wohl from particular pair and triplet weighting functions for clusters of two and three molecules in a liquid mixture. The cluster-weighting idea therefore unifies the major prediction and correlation schemes now in engineering use.

In a previous paper (*15*) the idea of a pair-type-probability (PTP) function was introduced and preliminary numerical results were given to show that use of this idea, together with other flexibilities in molecular corresponding states theory, enabled the theoretical equations to serve as correlating expressions for the thermodynamic properties of highly nonideal mixtures. The purpose of this paper is to show that the predictive excess free energy equations of Scatchard and Hildebrand (*4*) and the correlation equations of Wohl (*17, 18*) may be developed from the idea of a probability weighting function for clusters of 2, 3, . . . molecules in a liquid mixture, and therefore that the cluster-weighting idea underlies the majority of prediction and correlation schemes now in engineering use.

The cluster-weighting (or cluster-probability function) idea enters the various molecular formulations of the corresponding states idea (*1, 10, 11, 13, 15, 19*), the Scatchard–Hildebrand equations, and the Wohl equations at the same point. This point is the expression for the potential energy of a mixture. All the equation schemes referred to above employ for the mixture a pure-component form of the potential energy function. Except for Wohl equations of third and higher order (see the discussion below), the expression used for the mixture potential energy is the pairwise-additive form,

$$U_x = \sum_{i<j}\sum u_{xx}(r_{ij}) \tag{1}$$

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where $u_{xx}(r_{ij})$ stands for the interaction between the i^{th} and j^{th} molecules in a mixture, whatever the species of these molecules may be. The pair potential $u_{xx}(r_{ij})$ is given in applied work by some expression containing empirical parameters, for example, the Lennard-Jones form

$$u_{xx}(r_{ij}) = \frac{-\mu_{xx}}{(r_{ij})^m} + \frac{\nu_{xx}}{(r_{ij})^n} \tag{2}$$

Equation (1) is referred to here as a pure-component form because, as for a pure component, every term in the summation has the same parameter values.

In all the equation schemes referred to above, the pair potential $u_{xx}(r_{ij})$ is obtained by taking an average of the types of pair interactions that are possible in a given mixture. The weighting function used in this average is the cluster type of probability function. Where only pairwise interactions are considered, the clusters are pairs and Equation (1) may be expressed as

$$U_x = \sum_{i<j}\sum \sum_a\sum_b \text{PTP}(a, b)\, u_{ab}\,(r_{ij}) \tag{3}$$

where a and b are used to identify molecular species and PTP(a, b) is the probability weighting function for the (a, b) type of pair interaction, that is, the PTP function (*15*).

In the discussion to follow, the Scatchard-Hildebrand and Wohl equations for excess free energy will be developed by focusing attention on the expression for the potential energy of a mixture and by making the assumptions usually made in developments of the equations. Wheeler (*14*) gives details of the algebra that are omitted here. Attention will be limited to binary mixtures solely to reduce equation bulk.

SCATCHARD-HILDEBRAND EQUATIONS

The Scatchard-Hildebrand formulation may be considered to employ the following weighting function

$$\text{PTP}(a, b) = \frac{x_a x_b V_a V_b}{\sum_a\sum_b x_a x_b V_a V_b} \tag{4}$$

where V_a and V_b are the molar volumes of components a and b. The formal lack of resemblance between the Scatchard-Hildebrand and corresponding states formulations seems to result from the manner in which the expression for the total potential energy of a mixture is set up and the procedure used to obtain numerical results.

In any binary mixture, there are $N_1(N_1 - 1)/2$ molecular pairs of type (1, 1); there are $N_1\ N_2$ pairs of type (1, 2) and $N_2(N_2 - 1)/2$ pairs of type (2, 2), where N_1 and N_2 are the numbers of molecules of species 1 and 2, respectively, in the mixture being considered. The physical content of the mixture potential energy expression, Equation (3), is not altered if the terms in the (i, j) summation are grouped according to which pair type they are associated with. Therefore, Equation (3) may be re-expressed, in combination with Equation (4), as

$$U_x(\bar{r}) = \frac{1}{\sum\sum x_a x_b V_a V_b}\Bigg[\sum_{k<p}\sum x_1 x_1 V_1 V_1 \mu_{11}(r_{kp}) + 2\sum_{c}\sum_{\substack{d\\ d>N_1}} x_1 x_2 V_1 V_2 u_{12}(r_{cd}) + \sum_{s<t}\sum x_2 x_2 V_2 V_2 u_{22}(r_{st})\Bigg] \tag{5}$$

where the (k, p) indices are those associated with molecular pairs of type (1, 1), the (c, d) indices apply to (1, 2) pairs, and the (s, t) indices apply to (2, 2) pairs.

The usual development (*4*) of the Scatchard-Hildebrand equations does not employ Equation (5) but is instead expressed in the form of an expected value, $-E_c$, for the configurational internal (that is, cohesive) energy. This is given by

$$-E_c = \frac{1}{\prod_a N_a!\ CI_x}\int_V \ldots \int_V U_x(\bar{r}) \exp\left(-\frac{U_x}{kT}\right) d\bar{r}_1 \ldots d\bar{r}_N \tag{6}$$

where CI_x is the configurational integral for the mixture and the integration is over the entire volume occupied by the mixture.

Insertion of Equation (5) into Equation (6) gives

$$-E_c = \frac{1}{D^2}\sum_a\sum_b x_a x_b V_a V_b I_{ab} \tag{7}$$

where

$$D^2 = \sum_a\sum_b x_a x_b V_a V_b = \left(\sum_a x_a V_a\right)^2 \tag{8}$$

and the I_{ab}'s refer to integrals. For example

$$I_{11} = \int \ldots_V\int \sum_{k<p}\sum \frac{u_{11}(r_{kp}) \exp\left(-\frac{U_x}{kT}\right) d\bar{r}_1 \ldots d\bar{r}_N}{\prod_a N_a!\ CI_x} \tag{9}$$

The $\sum_{k<p}\sum$ summation in Equation (9) has $N_1(N_1 - 1)/2$ terms in it and Equation (9) will consist of $N_1(N_1 - 1)/2$ integrals of the form

$$\int \ldots_V\int u_{11}(r_{12}) \exp\left(-\frac{U_x}{kT}\right) d\bar{r}_1 \ldots d\bar{r}_N$$

where the term in $\sum_{k<p}\sum$ that represents the pair formed from the first and second molecules has been used in the example. Note, however, that the form of the dependence of U_x on $|\bar{r}_k - \bar{r}_p| = r_{kp}$ is the same for all $k < p$. Therefore, the integrands of all $N_1(N_1 - 1)/2$ integrals are of the same functional form. The integration limits are the same for all the integrals. Therefore, all of the $N_1(N_1 - 1)/2$ integrals of the form shown above have the same numerical value. Then Equation (9) may be expressed as

$$I_{11} = \frac{N_1(N_1 - 1)}{2}\int \ldots_V\int \frac{u_{11}(r_{12}) \exp\left(-\frac{U_x}{kT}\right) d\bar{r}_1 \ldots d\bar{r}_N}{\prod_a N_a!\ CI_x} \tag{10}$$

By identical argument the analogous expressions for I_{12} and I_{22} may be obtained. These may be written as

$$I_{12} = N_1 N_2 \int \ldots_V\int \frac{u_{12}(r_{12}) \exp\left(-\frac{U_x}{kT}\right) d\bar{r}_1 \ldots d\bar{r}_N}{\prod_a N_a!\ CI_x} \tag{11}$$

and

$$I_{22} = \frac{N_2(N_2-1)}{2} \int \cdots {}_V\!\int \frac{u_{22}(r_{12}) \exp\left(-\frac{U_x}{kT}\right) d\bar{r}_1 \ldots d\bar{r}_N}{\prod_a N_a!\; CI_x} \qquad (12)$$

It is possible to make the final cohesive energy expression more compact by using the generic distribution functions for mixtures (*5, 7, 10*). For example

$$n_{12}^{(2)} = n_{21}^{(2)} = N_1 N_2 \int \cdots {}_V\!\int \frac{\exp\left(-\frac{U_x}{kT}\right)}{\prod_a N_a!\; CI_x} d\bar{r}_3 \ldots d\bar{r}_N \qquad (13)$$

Then I_{12} may be written as

$$I_{12} = \frac{1}{2}\left[\int_V \int_V u_{12}(r_{12}) n_{12}^{(2)} d\bar{r}_1 d\bar{r}_2 + \int_V \int_V u_{21}(r_{12}) n_{21}^{(2)} d\bar{r}_1 d\bar{r}_2\right] \qquad (14)$$

where the single integral of Equation (11) has been rewritten as half the sum of two equal-valued integrals. The index switching on the pair potentials makes no change in the integral values and involves no assumption that potential energy is unaffected by interchange of molecules between locations because each integral considers all possible locations of all molecules.

By a definition entirely analogous to Equation (13), I_{11} may be written as

$$I_{11} = \int_V \int_V u_{11}(r_{12}) n_{11}^{(2)} d\bar{r}_1 d\bar{r}_2$$

This integral has the form of an expected value of the configurational internal energy of all the (1, 1) molecular pairs in the liquid mixture, that is, an expected value of the energy of evaporation of $N_1(N_1 - 1)/2$ such molecular pairs from the liquid mixture to the ideal gas state (*13*). To reflect this interpretation, the following notation will be defined.

$$(\Delta E^{V*})_{ab} = I_{ab} \quad a, b = 1, 2 \qquad (15)$$

Using Equations (13) through (15) plus the analogous relations for the different pair types in Equation (*6*), we can write the mixture cohesive energy as

$$-E_c = \frac{\sum_a \sum_b x_a x_b V_a V_b (\Delta E^{V*})_{ab}}{\sum_a \sum_b x_a x_b V_a V_b} \qquad (16)$$

or by Equation (8), plus the usual (*4*) assumption of no volume change upon mixing, that is, $V = x_1 V_1 + x_2 V_2$,

$$-E_c = \frac{x_1^2 V_1^2 \frac{(\Delta E^{V*})_{11}}{V} + 2x_1 x_2 V_1 V_2 \frac{(\Delta E^{V*})_{12}}{V} + x_2^2 V_2^2 \frac{(\Delta E^{V*})_{22}}{V}}{x_1 V_1 + x_2 V_2} \qquad (17)$$

Exact determination of E_c from Equation (17) requires evaluation of the integrals in the various I_{ab} expressions. The service of the Scatchard–Hildebrand approach has been to provide a prescription, antedating present molecular corresponding states theory by some 20 years (*8, 12*) for obtaining numerical results from the theoretical expressions. The prescription is as follows.

First, define the solubility parameter (*4*) of component 1 by

$$(\delta_{11})^2 V_1 = [(\Delta E^{V*})_{11}]_{\text{pure}} \qquad (18)$$

where the right-hand side of Equation (18) is given by Equation (17) with $x_1 = 1.0$.

Second, define δ_{12} by

$$(\delta_{12})^2 V = (\Delta E^{V*})_{12} \qquad (19)$$

Third, make three assumptions:

$$\frac{[(\Delta E^{V*})_{11}]_{\text{pure}}}{V_1} = \frac{(\Delta E^{V*})_{11}}{V} \qquad (20)$$

$$\frac{[(\Delta E^{V*})_{22}]_{\text{pure}}}{V_2} = \frac{(\Delta E^{V*})_{22}}{V} \qquad (21)$$

and

$$(\delta_{12})^2 = \delta_{11}\ \delta_{22} \qquad (22)$$

Equations (17) through (22) give

$$-E_c = \frac{\sum_a \sum_b x_a x_b V_a V_b\ \delta_{aa}\ \delta_{bb}}{\sum_a x_a V_a} \qquad (23)$$

This is the Scatchard–Hildebrand expression, from which is derived (*3, 4*) the free energy relation.

$$F^E = \frac{x_1 V_1 x_2 V_2 (\delta_1 - \delta_2)^2}{x_1 V_1 + x_2 V_2} \qquad (24)$$

The viewpoint of the present work is that, aside from the assumptions made in Equations (20), (21), and (22) to permit numerical evaluation, the essential feature of the Scatchard–Hildebrand approach is to use molar volumes to introduce some effect of molecular size into the theoretical forms.

THIRD-ORDER WOHL EQUATIONS

First of all, it is noted that Wohl's second-order (two-suffix) equations may be developed exactly as was Equation (24) if v_a is everywhere replaced by q_a, the effective molar volume, and the fitting constants of the Wohl expressions are properly defined.

Development of the third-order (three-suffix) Wohl equations involves addition of third-order terms to the second-order development. The only thing needed is some analytical representation of the fact that if molecules of certain species have a relatively strong tendency to cluster together amidst the turmoil of thermal motion, triplet as well as pair clusters should be considered. Representation of triplet effects are included in the Wohl formulation by use of a triplet-type-probability (TTP) function analogous to Equation (4).

$$\text{TTP}(a, b, c) = \frac{x_a x_b x_c q_a q_b q_c}{\sum_a \sum_b \sum_c x_a x_b x_c q_a q_b q_c} \qquad (25)$$

where the q's are Wohl's effective molar volumes and a, b, and c index the components of the mixture ($a, b, c = 1, 2 \ldots C$).

The third-order Wohl equations consider the interaction of triplets of molecules in a mixture. Development of these equations may be effected by expressing the total potential energy of a mixture as

$$U_x(\bar{r}) = \sum_{i<j}\sum u_{\text{pair}}(r_{ij}) + \sum_{i\neq j\neq k}\sum\sum u_{\text{trip}}(r_{ij}, r_{ik}, r_{jk}) \qquad (26)$$

where $u_{\text{trip}}(r_{ij}, r_{ik}, r_{jk})$ stands for the incremental potential energy of the molecule triplet whose mass centers are located at positions $\bar{r}_i$, $\bar{r}_j$, and $\bar{r}_k$. *Incremental* here means that $u_{\text{trip}}(r_{ij}, r_{ik}, r_{jk})$ represents that part of the potential energy of the i, j, k triplet that is not given by summing the pair potentials of the (i, j), (i, k), and (j, k) pairs. The $u_{\text{pair}}\ (r_{ij})$ function in Equation (26) has here the same functional form as the $u_{xx}(r_{ij})$ in Equation (1), but the parameter values in the two functions will differ because Equations (1) and (26) are different expressions for the same quantity U_x. The u_{trip} function is defined to have zero value when any two of the molecules in the triplet are infinitely separated. This definition seems reasonable, because triplets having one member at effectively infinite separation will contribute to the assembly potential energy the potential energy of a single pair. But this contribution has already been included in the $\sum\limits_{i<j}\sum$ summation. This zero definition for μ_{trip} comports formally with theoretical developments of Kihara (6). These developments were made for a single triplet of molecules, and they suggest the form of Equation (26).

To reduce the bulk of the equations to be given below, parts of them that are formally identical to equations already developed will be referred to by the appropriate equation number. In the referenced equations, V should be replaced everywhere by q. As with Equation (5), the terms in Equation (26) may be grouped according to pair and triplet types, and Equation (25) used, to give

$$U_x(\bar{r}) = \text{Eq. } (5) + \frac{1}{\sum\limits_a\sum\limits_b\sum\limits_c x_a x_b x_c q_a q_b q_c}$$

$$\sum_h\sum_m\sum_n x_1^3 q_1^3 u_{111} + 3\sum_o\sum_p\sum_f x_1^2 x_2 q_1^2 q_2 u_{112}$$

$$+ 3\sum_r\sum_g\sum_v x_1 x_2^2 q_1 q_2^2 u_{122} + \sum_w\sum_y\sum_z x_2^3 q_2^3 u_{222}\Big] \qquad (27)$$

Define

$$B^3 \equiv \sum_a\sum_b\sum_c x_a x_b x_c q_a q_b q_c = \left(\sum_a x_a q_a\right)^3 \qquad (28)$$

The expression for cohesive energy is Equation (6), which here may be expressed as

$$-E_c = \text{Eq. } (7) + \frac{1}{B^3}\,[(x_1q_1)^3 I_{111}$$

$$+ 3\,x_1^2q_1^2x_2q_2\,I_{112} + 3\,x_1q_1x_2^2q_2^2\,I_{122} + (x_2q_2)^3\,I_{222}] \qquad (29)$$

where the triply suffixed I's refer to integrals such as

$$I_{112} = \frac{1}{3}\Big[\int\ldots\int_V u_{112}\, n^{(3)}_{112}\, d\bar{r}_1 d\bar{r}_2 d\bar{r}_3$$

$$+ \int\ldots\int_V u_{121}\, n^{(3)}_{121}\, d\bar{r}_1 d\bar{r}_2 d\bar{r}_3$$

$$+ \int\ldots\int_V u_{211} n^{(3)}_{211}\, d\bar{r}_1 d\bar{r}_2 d\bar{r}_3\Big] \qquad (30)$$

and $n^{(3)}_{112}$ is a generic distribution function given by

$$n^{(3)}_{112}\,(\bar{r}_1, \bar{r}_2, \bar{r}_3) = n^{(3)}_{121} = n^{(3)}_{211}$$

$$= \frac{N_1(N_1-1)N_2}{2}\int\ldots\int_V \frac{\exp\left(\dfrac{-U_x}{kT}\right)}{\prod\limits_a Na!\ CI_x}\, d\bar{r}_4 \ldots d\bar{r}_N \qquad (31)$$

Entirely analogous expressions exist for all the subscript combinations on the I's in Equation (29). Compare Equations (9) to (14).

Define now, by analogy to Equation (15)

$$(\Delta E^{V*})_{abc} = I_{abc}; \quad a, b, c = 1, 2, \ldots C \qquad (32)$$

Equations (29) to (32), plus all the analogous relations, give

$$-E_c = \text{Eq. } (16) + \frac{\sum\limits_a\sum\limits_b\sum\limits_c x_a x_b x_c q_a q_b q_c\ (\Delta E^{V*})_{abc}}{B^3} \qquad (33)$$

Define now

$$t_{aa} = \frac{[(\Delta E^{V*})_{aa}]_{\text{pure}}}{q_a}; \quad t_{ab} = \frac{(\Delta E^{V*})_{ab}}{\sum\limits_a x_a q_a}$$

$$t_{aab} = \frac{(\Delta E^{V*})_{aab}}{\sum\limits_a x_a q_a}; \quad t_{aaa} = \frac{[(\Delta E^{V*})_{aaa}]_{\text{pure}}}{q_a}$$

and assume for all compositions and every $a = 1, 2, \ldots C$

$$\frac{[(\Delta E^{V*})_{aa}]_{\text{pure}}}{q_a} = \frac{(\Delta E^{V*})_{aa}}{\sum\limits_a x_a q_a} = t_{aa}$$

$$\frac{[(\Delta E^{V*})_{aaa}]_{\text{pure}}}{q_a} = \frac{(\Delta E^{V*})_{aaa}}{\sum\limits_a x_a q_a} = t_{aaa}$$

Then the cohesive energy may be written

$$-E_c = {}^2(E_c) + {}^3(E_c)$$

where

$${}^2(E_c) = \frac{\sum\limits_a\sum\limits_b x_a x_b q_a q_b t_{ab}}{B}$$

and

$${}^3(E_c) = \frac{\sum\limits_a\sum\limits_b\sum\limits_c x_a x_b x_c q_a q_b q_c t_{abc}}{B^2}$$

For a binary

$${}^3(E_c) = (x_1q_1 + x_2q_2)\ [t_{111}z_1 + t_{222}z_2$$

$$- 2z_1z_2(t_{111} + t_{222}) + 3z_1^2z_2(t_{112} + t_{222}/3)$$

$$+ 3z_1z_2^2(t_{122} + t_{111}/3)]$$

where

$$z_a = \frac{x_a q_a}{\sum\limits_a x_a q_a}; \quad a = 1, \ldots C$$

is the effective volume fraction of Wohl. For $x_a = 1.0$, note that

$$x_a({}^3(E_c)_a) = x_a q_a t_{aaa} = (\Sigma x_a q_a)\ z_a\ t_{aaa}. \qquad (34)$$

The change of cohesive energy upon mixing at constant volume is given by

$$\Delta E_c{}^M = {}^2(\Delta E_c{}^M) + {}^3(\Delta E_c{}^M)$$

where

$$^2(\Delta E_c{}^M) = {}^2(E_c) - \Sigma x_a \, ({}^2(E_c)_a)$$
$$= (x_1q_1 + x_2q_2) \, z_1z_2 \, (t_{11} + t_{22} - 2t_{12}) \quad (35)$$

and, using Equation (34)

$$^3(\Delta E^M) = {}^3(E_c) - \underset{a}{\Sigma} x_a \, ({}^3(E_c)_a)$$
$$= (x_1q_1 + x_2q_2) \, [-2z_1z_2(t_{111} + t_{222})]$$
$$+ (x_1q_1 + x_2q_2) \, [3z_1{}^2z_2(t_{112} + t_{222}/3)$$
$$+ 3z_1z_2{}^2(t_{122} + t_{222}/3)] \quad (36)$$

Then, to the approximation used in the Scatchard–Hildebrand equations (*3, 4, 14*)

$$F^E = \Delta E_c{}^M$$
$$= \text{Eq. (35)} + \text{Eq. (36)}$$

which is Wohl's third-order expression

$$\frac{F^E}{2.3RT} = (x_1q_1 + x_2q_2)$$
$$[2a_{12} \, z_1z_2 + 3a_{112} \, z_1{}^2z_2 + 3a_{122} \, z_1z_2{}^2] \quad (37)$$

where the following definitions have been made to give Wohl's form.

$$a_{12} = \left[\frac{t_{11} + t_{22}}{2} - t_{12} - t_{111} - t_{222} \right] \Big/ \, 2.3RT$$

$$a_{112} = [t_{112} + t_{222/3}]/2.3RT$$

$$a_{122} = [t_{122} + t_{111/3}]/2.3RT$$

Several comments may be made on the development just given. First of all, the sum of the t_{aa} and t_{aaa} constants may reasonably be approximated, as in the Scatchard–Hildebrand approach, by the ratio of pure-component energy of vaporization values to q_a; that is

$$t_{11} + t_{111} \doteq \frac{[(\Delta E^{V*})_{11} + (\Delta E^{V*})_{111}]_{\text{pure}}}{q_1}$$

The pure-component constants might be estimated on this basis. The t_{112} and t_{122} constants remain obscure but might be fitted separately to data or obtained from some combination rule as is done [Equation (22)] in the Scatchard–Hildebrand approach. The vaporization-energy interpretation of the constants might be useful, along with the q's (or their counterparts from a different cluster-weighting function) to give calculated values for the logarithms of the infinite-dilution activity coefficients. Then the development made here might be used to give some additional theoretical expression of the work of Pierotti et al. (9), Deal et al. (2), and Wilson and Deal (*16*).

Second, the pair-cluster constant of Wohl may be considered to contain some pure-component triplet effects and the triplet constants a_{112} and a_{122} contain some pure-component contributions.

Finally, the particular grouping of constants that led to Equation (36) is not unique, because Equation (36) could be arranged in several equivalent ways.

NOTATION

a_{ij}, a_{ijk} = constants in the Wohl equation
B = quantity as defined in Equation (28)
CI_x = configurational integral for a mixture
D = quantity as defined in Equation (8)
E_c = cohesive energy of Scatchard–Hildebrand
$^2(E_c)$ = pairwise-additive cohesive energy
$^3(E_c)$ = triplet-additive cohesive energy
$^3(\Delta E^M)$ = third-order or three-suffix energy change upon mixing
$(\Delta E^{V*})_{abc}$ = incremental cohesive energy of a molecular triplet
$(\Delta E^{V*})_{ab}$ = cohesive energy of an (a, b) pair
I = quantity as defined in Equations (9) and (30)
m = pair potential attraction exponent
n = pair potential repulsion exponent
$n^{(2)}_{ab}$ = generic distribution function, Equation (13)
$n^{(3)}_{abc}$ = generic distribution function, Equation (31)
N_a = number of molecules of species a in an assembly
PTP = pair-type-probability function
q_i = Wohl's effective molar volumes
$\overline{r}$ = set of mass-center position vectors for all molecules of an assembly
r_{ij} = distance between molecules i and j
$\overline{r_i}$ = center of mass position vector of system i
R = gas constant
t_{ab}, t_{abc} = functions in Wohl development
T = temperature
$u(r_{ij})$ = potential energy of molecules i and j
$u_{ab}(r_{ij})$ = potential energy of molecules i and j when molecule i is of species a and molecule j is of species b
U = total potential energy of a molecular assembly
V = volume of a mole of a substance
z_i = Wohl's effective volume fraction
δ_i = Scatchard–Hildebrand solubility parameter for species i
μ = pair-potential attraction parameter
ν = pair-potential repulsion parameter

Subscripts

a, b = mixture components
x = mixture function

Superscripts

$*$ = ideal gas state
Δ = change from state 1 to state 2

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