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Effect of Attractive Solvent-Solvent and Solvent-Solute Interactions on Partial Molal Quantities

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The effect of the perturbation due to attractive solute-solvent and solvent-solvent interactions on the partial molal volume (PMV), entropy (PME), and enthalpy in infinitely dilute solution has been formulated on the basis of the first-order perturbation theory which comes from the van der Waals picture of liquid. PMV is found to be composed of the two compensating factors which arise from the solute-solvent and solvent-solvent attractive interactions treated as the perturbation; when the former is larger than the latter PMV becomes smaller. PME is influenced only indirectly by the attractive perturbation through the volume change due to the perturbation interactions. The limitations of the basic expressions derived are discussed in the case of large solute.

Although the perturbation theory of liquid has been developed to a large extent for the past two decades,[1-3] some fundamental problems still remain to be solved for its extensive application to the interpretation of the partial molal volume, entropy, and enthalpy in solution. In this paper we attempt to show how theoretical expressions for the partial molal quantities simply due to repulsive interactions are modified by the attractive interactions between solvent and solvent molecules and between solvent and solute molecules. This kind of study on the partial molal quantities is required for an advance in solution chemistry because it provides a theoretical framework for the molecular interpretation of the accurate experimental data accumulated for a variety of solution systems.

To understand the partial molal quantities, an interesting model was put forward by Sisskind and Kasarnowsky (SK) half a century ago.[4] This may be called "two-step dissolution theory" because a gaseous solute molecule is introduced into solvent in the following two steps: (i) the creation of a cavity in the solvent to accommodate the solute molecule and (ii) the introduction of the solute molecule into the cavity where the attractive interaction between the solute and solvent molecules is switched on. Pierotti used the SK model when he first transferred the fruit of the modern liquid theory to solution chemists.[5,6] He considered the first step in the reference system where no attractive interactions exist, and calculated changes in thermodynamic quantities accompanying the first step by applying the scaled particle theory. This SK picture is instructive but likely to make it ambiguous the role of the solvent-solvent interaction, as pointed out by Neff and McQuarrie (NM) on the basis of the mean field theory (a first-order perturbation theory).[7] Though a perturbation due to attractive interactions between solvent molecules is explicitly taken into account in the NM theory, the role of the solute-solvent and solvent-solvent interactions is not clearly explained. We shall present here simple and meaningful expressions for the partial molal quantities.

The standard form of the perturbation theory comes from the van der Waals (VDW) picture of liquid.[1-3] The VDW picture implies that the liquid structure is determined mainly by repulsive forces between molecules, and that attractive interactions can be regarded as the background mean field; the former forces are treated in the reference system and the latter as a perturbation. Although the VDW picture appears simple and intuitively perceptible, its implication is not so simple when it is applied to the partial molal quantities and their related properties. For example, the isothermal compressibility depends on the presence of attractive interactions as disclosed in this paper. On the other hand, however, the compressibility is directly related through the compressibility equation to the structure factor of liquid which is said to be dominated by repulsive interactions according to the VDW picture. Here we examine in detail how the two different views are related, and present a formulation of the partial molal volume, entropy, and enthalpy at infinite dilution on the basis of the first order perturbation theory. The present work is hoped to provide a perspective for understanding the molecular aspects of each partial molal quantity in solution.

Model of Solution

Our model system is composed of two species S and X; S is the solvent and X is the solute dissolved in S at infinite dilution. For simplicity, all the molecules are assumed to have the spherical symmetry. The molecules are characterized by the pair potentials

$$u_{YZ}(r) = u_{YZ}^{(0)}(r) + u_{YZ}^{(1)}(r), \qquad (1)$$

where Y and Z denote S or X, and the superscripts (0) and (1) indicate the reference and the perturbed systems, respectively, and r is the separation. According to the VDW theory, the repulsive part of the intermolecular interaction is taken as the reference interaction and the attractive part as the perturbation. We take the number density of the reference system to be equal to that of the perturbed system.

In general, the repulsive interaction is very large and short-ranged. We assume that the reference potential is due to the hard-sphere interaction:

$$\begin{array}{lll} u^{(0)}_{YZ}(r)=+\infty & 0<r<\sigma_{YZ} & \\ \quad 0 & \sigma_{YZ}\leqq r, & (2) \end{array}$$

where the hard-core collision diameter σ_{YZ} is assumed to be independent of temperature and density. Since the reference system consists of the hard-sphere molecules, the radial distribution functions in the reference system are independent of temperature, and some restrictions are imposed on the thermodynamic behavior of the perturbed system as well as the reference system; see Appendix.

The attractive perturbation interactions $u^{(0)}_{YZ}(r)$ in Eq. 1 are assumed to vary slowly compared with σ_{SS} which characterizes the short range liquid structure determined by the hard-sphere molecules. This postulate is of great importance for making the mean field theory valid.

The van der Waals Picture for Solution Properties

Mean Field Theory of Solution. According to the present model of solution, the Hamiltonian of the system is described as

$$\mathscr{H}=\mathscr{H}^{(0)}+\mathscr{H}^{(1)}, \qquad (3)$$

where $\mathscr{H}^{(0)}$ is composed of the kinetic energy and the hard-core repulsive interactions between molecules and $\mathscr{H}^{(1)}$ is the perturbation due to the attractive interactions between molecules. According to the Bogoliubov variational theorem,[8] the following equation holds for the Helmholtz free energy A:

$$A\leqq A^{(0)}+\langle\mathscr{H}^{(1)}\rangle_0, \qquad (4)$$

where $A^{(0)}$ is the free energy of the reference system and $\langle\mathscr{H}^{(1)}\rangle_0$ is the ensemoble average of the perturbation in the reference system. In the mean field approximation (a primitive perturbation theory),[8] both sides of Eq. 4 are equal:

$$A=A^{(0)}+\langle\mathscr{H}^{(1)}\rangle_0. \qquad (5)$$

The pertubation term in Eq. 5 can be rewritten in terms of the radial distribution functions as follows:

$$\langle\mathscr{H}^{(1)}\rangle_0 = \frac{N_S^2}{2V}\int u^{(1)}_{SS}(r)\,g^{(0)}_{SS}(r)\,d\mathbf{r} + \frac{N_S N_X}{V}\int u^{(1)}_{SX}(r)\,g^{(0)}_{SX}(r)\,d\mathbf{r}, \qquad (6)$$

where $g^{(0)}_{YZ}(r)$ denotes the radial distribution function between Y and Z, which are X or S, in the reference system, N_S and N_X are the numbers of the solvent and solute molecules, respectively, and V is the volume of the solution. Though the second term in Eq. 6 disappears in the limit of infinite dilution of solute X, we need to retain it to derive expressions for the partial molal quantities of the solute as shown below.

In the reference system, the molecules occupy only one potential energy state, say 0, because they are hard. Since no changes in the population among the energy states and the probability density in the configurational space take place in the reference system, the entropy of the system is unaffected by the perturbation at the level of the mean field theory; this is easily demonstrated by differentiating Eq. 5 with respect to temperature.

First we examine the effect of the attractive interactions on the chemical potential of the solute because the chemical potential is the fundamental quantity which generates the partial molal quantities. The chemical potential of the solute X is directly obtained by differentiating Eq. 5 with respect to the number of molecules and taking the limit $n_X\to 0$,

$$\mu_X = \mu_X^{(0)} + n_S\int u^{(1)}_{SX}(r)\,g^{(0)}_{SX}(r)\,d\mathbf{r} + \frac{n_S^2}{2}\int u^{(1)}_{SS}(r)\,\frac{\partial g^{(0)}_{SX}(r)}{\partial n_X}\,d\mathbf{r}, \qquad (7)$$

where n_S and n_X are the number densities of the solvent and solute, respectively. Considering that the perturbation interactions $u^{(1)}_{SX}(r)$ and $u^{(1)}_{SS}(r)$ vary slowly compared with the short wavelength of the liquid structure, we can transform Eq. 7 into a more convienient form with a plausible approximation.

Figure 1 shows the solute–solvent radial distribution function $g^{(1)}_{SX}(r)$ and the solute-density derivative of the solvent-solvent radial distribution function, $n_S[\partial g^{(1)}_{SS}(r)/\partial n_X]$ in the hard-sphere system where $\sigma_{SS}=\sigma_{SX}$; the necessary information is available in the literature.[9]

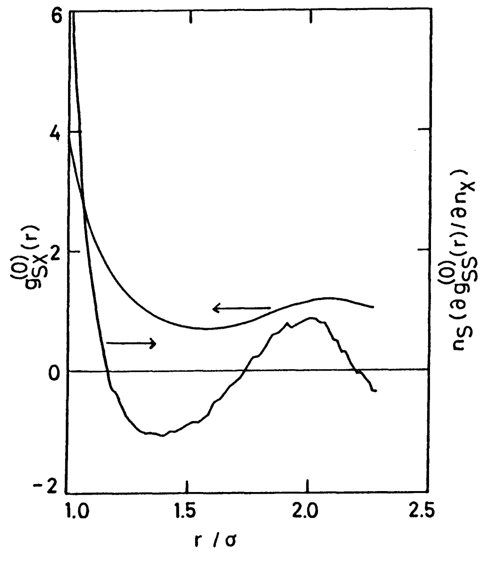

Fig. 1. The solvent(S)–solute(X) radial distribution function in the reference system, $g^{(0)}_{SX}(r)$ and the solute-density (n_X) derivative of the solvent–solvent radial distribution function, $n_S[\partial g^{(0)}_{SS}(r)/\partial n_X]$. $\sigma_{SX}=\sigma_{SS}=\sigma$; $n_S\sigma^3_{SS}=0.80$. The density derivative is obtained from the difference in the radial distribution function between $n_S\sigma^3_{SS}=0.75$ and 0.85.

The derivative of $g_{\mathrm{SS}}^{(1)}(r)$ with respect to the solute density oscillates around zero with a wavelength of the order of σ_{SS}, and fades rapidly with increasing the distance. Since the perturbation pair potential $u_{\mathrm{SS}}^{(1)}(r)$ varies slowly, the third term on the right-hand side of Eq. 7 may be ignored. On the other hand, the second term is insensitive to the number density but not negligible because $g_{\mathrm{SX}}^{(1)}(r)$ oscillates around unity with a short wavelength. To this approximation, the chemical potential is composed of the following two terms as in the case of the Helmholtz free energy, Eq. 5:

$$\mu_{\mathrm{X}} = \mu_{\mathrm{X}}^{(0)} + n_{\mathrm{S}} \int u_{\mathrm{SX}}^{(1)}(r)\, g_{\mathrm{SX}}^{(0)}(r)\, \mathrm{d}\boldsymbol{r}, \tag{8}$$

$$= \mu_{\mathrm{X}}^{(0)} + a_{\mathrm{SX}} n_{\mathrm{S}}\ , \tag{9}$$

where the integrand in the second term on the right-hand side of Eq. 7 or 8 is taken to be the constant a_{SX} because the integrand is independent of temperature and a dull function of the density as mentioned above. It is to be noted that when the third term on the right-hand side of Eq. 7 is neglected, the chemical potential of the solute becomes independent of the solvent-solvent perturbation interaction. Most of the following discussions are based on this assumption, and its limitations will be referred to later.

Equation of State of Pure Solvent. It is the equation of state of the pure solvent through that the solvent-solvent perturbation interactions affect the partial molal quantities of the solute. The equation of state is easily obtained from the Helmholtz free energy Eq. 5 by putting $N_{\mathrm{X}}=0$. Differentiating the free energy with respect to the volume, we get the expression for pressure P as[1]

$$P = P^{(0)} + \frac{a_{\mathrm{SS}}}{2} n_{\mathrm{S}}^2\ , \tag{10}$$

where $P^{(0)}$ is the pressure in the reference system. This is a generalized VDW equation of state, and a similar form of equation of state has been used for real system.[10]

Since the reference pressure $P^{(0)}$ is linearly dependent on temperature as shown by Eq. 38 in Appendix, and since a_{SS} is independent of temperature, we get the following equation for the reference pressure by differentiating Eq. 10 with respect to temperature T at constant density:

$$P^{(0)} = T\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} \tag{11}$$

It follows from Eqs. 10 and 11 that the "internal pressure" defined by $(\partial U/\partial V)_T$ is equal in magnitude to the attractive perturbation pressure with the sign opposite.

Long-Range Nature of Perturbation. The VDW theory of liquid is valid only for the short-range problem but not for the long-range one. We shall discuss this point according to Eq. 10.

The isothermal compressibility is related to the long-range part of the structure factor of liquid as follows:

$$\kappa kT = \frac{1}{n_{\mathrm{S}}} + \int [g_{\mathrm{SS}}(r) - 1]\mathrm{d}\boldsymbol{r}. \tag{12}$$

where κ denotes the isothermal compressibility, $-(\partial V/\partial P)_T/V$. Note that the right-hand side of Eq. 12 indicates the Fourier component of the infinitely large wavelength of the total correlation function $g_{\mathrm{SS}}(r)-1$. Thus the validity of the VDW picture for the long-range structure may be tested by comparing the isothermal compressibilities of the reference and the perturbed systems.

The VDW equation of state, Eq. 10, can be rewritten as

$$\frac{1}{\kappa} = \frac{1}{\kappa^{(0)}} + a_{\mathrm{SS}} n_{\mathrm{S}}^2\ , \tag{13}$$

where α is the isobaric expansibility, $(1/V)(\partial V/\partial T)_P$. At 0.1 MPa, the pressure is negligible in comparison with the reciprocal of the compressibility (usually in the order of 1000 MPa). Thus the following equation holds at 0.1 MPa:

$$\frac{1}{\kappa} = \frac{1}{\kappa^{(0)}} + 2\left(-\frac{\alpha}{\kappa}T + P\right)\ , \tag{14}$$

where $\kappa^{(0)}=-(\partial V/\partial P^{(0)})_T)/V$. Let us show that the second term on the right-hand side of Eq. 13 is not negligible at 0.1 MPa. By inserting Eq. 11 into Eq. 10 and transforming the thermodynamic variables, we have

$$\frac{\kappa}{\kappa^{(0)}} = 1 + 2\alpha T. \tag{15}$$

Since the second term on the right-hand side is usually in the range of 0.6—0.8, it cannot be neglected; e.g., the value is 0.73 for carbon tetrachloride at 25 °C and 0.1 MPa.

The marked effect of the attractive perturbation on the isothermal compressibility tells us that the simple VDW picture is very useful for treating short-range problems but not accurate enough to describe the long-wavelength component of the liquid structure. This feature of the VDW picture has to be taken into account to calculate the thermodynamic quantities in the mean field approximation.

Partial Molal Volume

The partial molal volume is the quantity which reflects a response of the volume of the system to an increase in the number of the molecules of our interest. We can understand the way of the volume response using the following scheme: (i) The introduction of the solute molecule into the solvent under isochoric conditions causes a pressure change, and (ii) the pressure change is transformed into the partial molal volume which is observed under isobaric conditions. These steps have quite different operational meanings; the second step depends on the compressibility of the whole system which is determined only by the solvent-solvent interaction, whereas the first step is characterized by the solute-solvent interaction. We show below how useful this picture is to understand the effect of perturbative interactions on the partial molal volume.

To make it easy to undestand how the partial molal volume is influenced by the attractive interactions through the pressure change, we may define a "partial molal pressure" P'_{X}[11] in the following way:

$$P'_{\mathrm{X}} = (N_{\mathrm{S}}+N_{\mathrm{X}})\left(\frac{\partial P}{\partial N_{\mathrm{X}}}\right)_{T,V,N_{\mathrm{S}}} \tag{16}$$

$$= -(N_{\mathrm{S}}+N_{\mathrm{X}})\left(\frac{\partial \mu_{\mathrm{X}}}{\partial V}\right)_{T,N_{\mathrm{S}},N_{\mathrm{X}}}, \tag{17}$$

where the factor $(N_{\mathrm{S}}+N_{\mathrm{X}})$ is introduced in order to avoid the system size dependence of the "partial molal pressure." Inserting Eq. 9 into Eq. 17, we have

$$P'_{\mathrm{X}} = P'^{(0)}_{\mathrm{X}} + a_{\mathrm{SX}} n_{\mathrm{S}}^{2}, \tag{18}$$

where we take the limit $n_{\mathrm{X}} \to 0$. Thus P'_{X} decreases with an increase in the perturbation between solute and solvent, without any influence of the solvent-solvent perturbative interaction. The exchange of the subscript S by X in Eq. 18 leads to the following expression for the "partial molal pressure" of solvent:

$$P'_{\mathrm{S}} = P'^{(0)}_{\mathrm{S}} + a_{\mathrm{SS}} n_{\mathrm{S}}^{2}. \tag{19}$$

This equation is consistent with Eq. 13 because the "partial molal pressure" of solvent is equal to the reciprocal of the isothermal compressibility of pure solvent.

The partial molal volume is directly related to the "partial molal pressure" as follows:

$$V_{\mathrm{X}} = \frac{\kappa}{n_{\mathrm{S}} + n_{\mathrm{X}}} P'_{\mathrm{X}}, \tag{20}$$

$$= \frac{\kappa}{\kappa^{(0)}} V^{(0)}_{\mathrm{X}} + a_{\mathrm{SX}} \kappa n_{\mathrm{S}}, \tag{21}$$

where the limit of infinite dilution is taken. Using Eq. 13, we rewrite Eq. 21 as

$$V_{\mathrm{X}} = V^{(0)}_{\mathrm{X}} + \kappa n_{\mathrm{S}}^{2}\,[a_{\mathrm{SX}} V^{(0)}_{\mathrm{S}} - a_{\mathrm{SS}} V^{(0)}_{\mathrm{X}}], \tag{22}$$

where we use the relation $V^{(0)}_{\mathrm{S}} = n_{\mathrm{S}}^{-1}$. This equation tells us that in contrast to P'_{X}, V_{X} is influenced by the solvent-solvent perturbative interaction through the compressibility. While P'_{X} decreases with increasing the solute-solvent perturbative interaction, κ increases with increasing the solvent-solvent perturbative interaction. The two factors compete in determining the partial molal volume.

One may expect that the perturbation effect on the partial molal volume will be small because of the presence of the competing factors in Eq. 22. This expectation is rationalized in the system where the solute molecule is identical in size with the solvent molecule in the reference system; $\sigma_{\mathrm{XS}} = \sigma_{\mathrm{SS}}$ and $g^{(0)}_{\mathrm{SX}}(r) = g^{(0)}_{\mathrm{SS}}(r)$. In this case the partial molal volume due to the attractive perturbation takes the simple form as

$$V^{(1)}_{\mathrm{X}} = V_{\mathrm{X}} - V^{(0)}_{\mathrm{X}}$$

$$= \kappa n_{\mathrm{S}}^{2} V^{(0)}_{\mathrm{X}} \int [u^{(1)}_{\mathrm{SX}}(r) - u^{(1)}_{\mathrm{SS}}(r)]\, g^{(0)}_{\mathrm{SX}}(r)\, \mathrm{d}\boldsymbol{r}. \tag{23}$$

The perturbation part of the partial molal volume arises from the difference in the attractive perturbation between solute-solvent and solvent-solvent pairs of molecules. When the solute-solvent attractive force is larger than the solvent-solvent attractive force, the partial molal volume of the solute is smaller than the reference value and vice versa. Especially when the solute-solvent interaction is identical with the solvent-solvent interaction, of course, the competing perturbations are canceled out.

Partial Molal Enthalpy and Entropy

We have shown in the preceding section that the "partial molal pressure" at constant volume has a simpler form than the partial molal volume at constant pressure. The same thing is said for the partial molal enthalpy and entropy. The partial molal energy $(U_{\mathrm{X}})_V$ and entropy $(S_{\mathrm{X}})_V$ at constant volume are given as

$$(U_{\mathrm{X}})_V = (U_{\mathrm{X}})^{(0)}_V + a_{\mathrm{SX}} n_{\mathrm{S}}, \tag{24}$$

$$(S_{\mathrm{X}})_V = (S_{\mathrm{X}})^{(0)}_V \tag{25}$$

The partial molal entropy at constant volume is unaffected by the perturbation interactions because no change in the molecular distribution over the energy states is brought about by the perturbation exerted on the reference system taken here.

As in the case of the partial molal volume discussed above, the conventional partial molal enthalpy and entropy can be derived from the corresponding partial molal quantities at constant volume as follows:

$$H_{\mathrm{X}} = (U_{\mathrm{X}})_V + \frac{\alpha}{\kappa} T V_{\mathrm{X}}, \tag{26}$$

$$S_{\mathrm{X}} = (S_{\mathrm{X}})_V + \frac{\alpha}{\kappa} V_{\mathrm{X}}. \tag{27}$$

The second term in Eq. 27 arises from the volume change due to the incorporation of the solute molecule into the solvent at constant pressure. The variation of the volume of the system actually causes a change in the probability density in the configurational phase space. This is the reason why the partial molal entropy is perturbed by the presence of the attractive forces.

Limiting Behavior of Large Solute

It is important to see the limitations of the basic assumptions used so far for deriving the expressions for the partial molal quantities. Only the partial molal volume is discussed below for this purpose.

Let us show that the expression for the partial molal volume, Eq. 21, fails to describe correctly the behavior of a large enough solute molecule. When the solute molecule is much larger than the solvent molecule, the second term in Eq. 21 may be estimated as

$$\kappa a_{\mathrm{SX}} n_{\mathrm{S}} = \kappa n_{\mathrm{S}} \int u_{\mathrm{SX}}^{(1)}(r) g_{\mathrm{SX}}^{(0)}(r)\,\mathrm{d}\boldsymbol{r},$$

$$= \kappa n_{\mathrm{S}} u_{\mathrm{SX}}^{(1)}(\sigma_{\mathrm{SX}}) g_{\mathrm{SX}}^{(0)}(\sigma_{\mathrm{SX}}) \cdot \varDelta \cdot 4\pi\sigma_{\mathrm{SX}}^{2}, \tag{28}$$

where $\varDelta$ is the length characteristic of the perturbation interaction; $\varDelta$ may be as several times as large as σ_{SS}. This indicates that in Eq. 21, the second term of the order of σ_{SX}^2 becomes negligible compared with the first term of the order of σ_{SX}^3. As a result, the partial molal volume of the solute in the perturbed system becomes larger by the factor of $\kappa/\kappa^{(0)}$ than that in the reference system. In the limit of the large solute, on the other hand, the partial molal volume should become identical with the core volume of the solute, i.e., $(\pi/6)\ \sigma_{\mathrm{XX}}^3 \simeq (4\pi/3)\sigma_{\mathrm{SX}}^3$, both in the reference and the perturbed systems. Thus Eq. 21 cannot describe the true limiting behavior of the large solute.

The limitation of Eq. 21 disclosed above is ascribed to the neglect of the third term on the right-hand side of Eq. 7. The third term is negligible only when the size of the solute molecule is not very different from that of the solvent molecule. In other words, when the solute molecule is large enough, the effect of the solute molecule on the solvent-solvent radial distribution function is really long-ranged because of its large size.

It is difficult to obtain directly the derivative of the solvent-solvent radial distribution function involved in the third term in Eq. 7. However, its asymptotic behavior can be examined using the following relation which holds for the sufficiently large spherical solute:

$$-\frac{\pi}{6}\sigma_{\mathrm{XX}}^{3}(\delta N_{\mathrm{X}})_V = (\delta V)_{N_{\mathrm{X}}}, \tag{29}$$

where $(\delta B)_Y$ denotes an infinitesimal change in quantity B at constant Y. Equation 29 shows the fact that the introduction of the macroscopic particle with volume v into the system at the constant volume has the same meaning as the shrinking of the system by the amount of v. Using Eq. 29, we evaluate the derivative involved in the third term in Eq. 7 as follows:

$$\frac{\partial}{\partial N_{\mathrm{X}}}\left[\frac{N_{\mathrm{S}}^2}{2V}\int u_{\mathrm{SS}}^{(1)}(r) g_{\mathrm{SS}}^{(0)}(r)\mathrm{d}\boldsymbol{r}\right] = \frac{\pi}{12}\ \sigma_{\mathrm{XX}}^{3} n_{\mathrm{S}}^{2}$$

$$\times\left[\int u_{\mathrm{SS}}^{(1)}(r) g_{\mathrm{SS}}^{(0)}(r)\mathrm{d}\boldsymbol{r} - V\int u_{\mathrm{SS}}^{(1)}(r)\frac{\partial g_{\mathrm{SS}}^{(0)}(r)}{\partial V}\,\mathrm{d}\boldsymbol{r}\right], \tag{30}$$

$$= \frac{\pi}{12}\ \sigma_{\mathrm{XX}}^{3} n_{\mathrm{S}}^{2} a_{\mathrm{SS}}, \tag{31}$$

where the second term on the right-hand side of Eq. 30 is neglected; note the relation

$$N_{\mathrm{S}}[\partial g_{\mathrm{SS}}^{(0)}(r)/\partial V] = -n_{\mathrm{S}}^{2}[\partial g_{\mathrm{SS}}^{(0)}(r)/\partial n_{\mathrm{S}}]$$

and recall the reason for the neglect of the third term in Eq. 7. Following the abovementioned procedure for the partial molal volume, we have the relation

$$V_{\mathrm{X}} = V_{\mathrm{X}}^{(0)} + a_{\mathrm{SS}}\kappa n_{\mathrm{S}}^{2}\left[\frac{\pi}{6}\ \sigma_{\mathrm{XX}}^{3} - V_{\mathrm{X}}^{(0)}\right], \tag{32}$$

where we neglect the term of the order of σ_{XX}^2, $a_{\mathrm{SX}}\kappa n_{\mathrm{S}}^2 V_{\mathrm{S}}^{(0)}$. This equation correctly describes the limiting behavior of the large solute molecule; in fact, the second term disappears in the limit of large solute.

Probably because of the presence of the limitation of Eq. 21, Pierotti[5,6] gave a compromising expression for the partial molal volume as

$$V_{\mathrm{X}} = \kappa kT(K_0 + K_1\sigma_{\mathrm{XX}} + K_2\sigma_{\mathrm{XX}}^2) + \frac{\pi}{6}\ \sigma_{\mathrm{XX}}^{3}{}' \tag{33}$$

where K_0, K_1, and K_2 are the parameters which are given by the scaled particle theory as a function of the number density of the solvent, and k is the Boltzmann constant. Equation 33 gives the correct partial molal volume for the reference system where the solvent-solvent perturbation interaction does not exist, and has the correct partial molal volume in the limit of large solute. However, Eq. 33 is no longer valid for the system perturbed by the attractive solvent-solvent interaction, and the last term in Eq. 33 should read as $(\kappa/\kappa^{(0)})\ (\pi/6)\sigma_{\mathrm{XX}}^3$ in the case of molecules of the common size, as pointed out by Neff and McQuarrie.[7]

Appendix

Thermodynamics of Hard-Body System. Some restrictions are imposed on the functional form of the thermodynamic quantities of the hard-body system. Such restrictions come simply from the fact that the internal energy of the hard-body system arises only from the kinetic energy of molecules and is independent of the configuration of the molecules. More explicitly, when the molecules have no internal freedom, the internal energy U is expressed by

$$U = \frac{3}{2}NkT, \tag{34}$$

where N and k are the total number of molecules and the Boltzmann constant, respectively. Thus the following equation holds for the hard-body system;

$$\left(\frac{\partial U}{\partial V}\right)_T = 0\,. \tag{35}$$

Using the thermodynamic relation, the following equations are derived from Eq. 35:

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = 0, \tag{36}$$

$$\frac{P}{T} = \left(\frac{\partial P}{\partial T}\right)_V, \tag{37}$$

$$P = Tf(n), \tag{38}$$

where the $f(n)$ is the function of the number density n and independent of temperature and pressure. Using Eqs. 37 and 38 together with the Maxwell relation, we get the following equation:

$$\left(\frac{\partial S}{\partial V}\right)_T = f(n). \tag{39}$$

Thus the entropy is expressed as

$$S = S^* + \int_{V^*}^{V} f(n)\mathrm{d}V, \tag{40}$$

where the superscript * denotes the low density state of the system in which the system can be regarded as the ideal gas, and V the volume. The temperature dependence of the entropy in the hard-body system is identical with that in the ideal gas state. This equation denotes the fact that the configuration of the molecules are independent of the temperature in the hard-body system. The isothermal compressibility and the isobaric expansibility obey the following relations:

$$\frac{1}{\kappa} = Tn\frac{\mathrm{d}f(n)}{\mathrm{d}n}, \tag{41}$$

$$\frac{1}{\alpha} = \frac{1}{\kappa f(n)}, \tag{42}$$

$$= T\frac{\mathrm{d}\ln f(n)}{\mathrm{d}\ln n}, \tag{43}$$

where $f(n)$ is the function of n and independent of temperature. It can be shown that the behavior of the partial molal quantities in the hard-body system is also restricted; e.g., the partial molal volume is independent of temperature.

References

1) H. C. Andersen, D. Chandler, and J. D. Weeks, *Adv. Chem. Phys.*, **34**, 105 (1976).

2) J. A. Barker and D. Henderson, *Rev. Mod. Phys.*, **48**, 587 (1976).

3) J. P. Hansen and I. R. McDonald, "Theory of Simple Liquids," 2nd ed, Academic, London (1986).

4) B. Sisskind and I. Kasarnowsky, *Z. Anorg. Allgem. Chem.*, **214**, 385 (1933).

5) R. A. Pierotti, *J. Phys. Chem.*, **67**, 1840 (1963).

6) R. A. Pierotti, *Chem. Rev.*, **76**, 718 (1976).

7) R. O. Neff and D. A. McQuarrie, *J. Phys. Chem.*, **77**, 413 (1973).

8) H. B. Callen, "Thermodynamics and an Introduction to Thermostatistics," 2nd ed, John Wiley, New York (1985), Chap. 20.

9) J. A. Barker and D. Henderson, *Annu. Rev. Phys. Chem.*, **23**, 439 (1972); J. A. Barker and D. Henderson, *Mol. Phys.*, **21**, 187 (1971).

10) R. L. Scott, "Physical Chemistry—an Advanced Treatise," ed by D. Henderson, Academic, New York (1971), Vol. 8A; S. Saito, "Heikobussei Suisan no Kiso (Introduction to the Evaluation of Equilibrium Properties)," Baifukan, Tokyo (1983).

11) Note that the commonly used bar over the partial molal quantities are omitted throughout this paper, and instead, pay attention to the presence of the subscript X or S for the partial molal quantities of X or S, respectively.