Formulation of Enthalpy, Entropy, and Volume Changes Accompanying Association Reaction in Solution in Terms of Molecular Distribution Functions

Yosuke Yoshimura* and Masaru Nakahara*
Department of Chemistry, Faculty of Science, Kyoto University,
Oiwake-cho, Kitashirakawa, Sakyo-ku, Kyoto 606

(Received June 27, 1986)

The equilibrium constant of the chemical reaction in solution is formulated by means of the distribution function at the semiclassical level. The equivalence of the present expression and the traditional one that is based on the standard chemical affinity is proved. The changes of the thermodynamic quantities (enthalpy, entropy, and volume) at constasnt temperature and pressure are expressed on the basis of the present formulation. They are composed of the following three terms: (i) the internal change, (ii) the translational change, and (iii) the solvation change. Each term is evaluated for the dimerization of nitrogen dioxide. It is shown that the volume change is a good measure for the solvation change because it does not contain the internal change. Since the solvation change is explicitly expressed by means of the radial distribution function and its temperature or pressure derivative in an explicit manner, it is useful for discussing the solvent effect on the chemical reaction from the point of view of the liquid structure.

Our molecular understanding of chemical reactions is much less advanced in the liquid phase than in the gas phase because of the presence of many-body interactions characteristic of the liquid phase; most fundamental theories have been developed primarily for the gas-phase reaction which is free from complicated intermolecular interactions due to solvent. It is desired to improve the situation by applying statistical thermodynamics of liquids to reacting systems. We concentrate on the molecular interpretation of the widely used thermodynamic and activation parameters, such as enthalpy, entropy, and volume changes accompanying the chemical reaction in the condensed phase; these parameters are obtainable from the application of thermodynamics and transition state theory to the experimental study on the effect of temperature and pressure on the equilibrium and rate constants for the liquid-phase reaction.1) We take advantage of the present knowledge of the liquid state at equilibrium in order to provide a theoretical framework or perspective for the molecular interpretation of the thermodynamic and activation parameters which have been used to characterize the mechanism of the reaction in solution.

It is still an open problem how the liquid structure of solvent influences the thermodynamic and activation parameters associated with chemical reactions in solution. When we consider this problem, it is of primary importance to clearly define what we mean by the solvent liquid structure. The radial distribution function is meaningful in this respect. In the previous papers,2,3) we have successfully applied the distribution function theory of liquids to the problem of reaction and activation volumes to unveil the molecular aspects of the volume properties. This potential approach is extended here to apply to enthalpy and entropy changes to have an insight into the solvent effect on these macroscopic quantities from a molecular point of view; this kind of generalization is not yet completely fulfilled after such a new direction has been suggested by Chandler and co-workers4—6) and followed by some others.2,3,7) In the present work we intend to examine the macroscopic reaction parameters mentioned above beyond the primitive view that their changes are nothing more than a difference between the reactant and the product (or transition) states.

One of the merits of the distribution function theory is the capability of continuously treating a reaction process starting just from the reactant state as in the MO calculation of the potential energy supersurface. In the present approach, the transition and product states are represented by the configuration where the coordinates of the atoms involved in the reactants are specified. Thus we can regard the chemical reaction as a continuous variation of the distribution (configuration or arrangement) of constituent atoms or groups composing the reactant molecules; in the liquid-phase reaction, not only the reactants but also the third bodies like solvent molecules have to be included in the definition of the distribution. In the distribution function theory, we define a probability (density) of finding a configuration that varies with the extent (or coordinates) of a reaction, and its equilibrium and rate constans are given in terms of such probabilities. Since the distribution function theory is applicable to both the liquid and the gas phases, it enables us to disclose the key role of solvent molecules in differentiating the liquid-phase reaction from the gas-phase one.

Molecular Model for Association Reaction in Solution

Consider a reversible association reaction in solution at infinite dilution where two spherical molecules A and B form the adduct C in an excessive

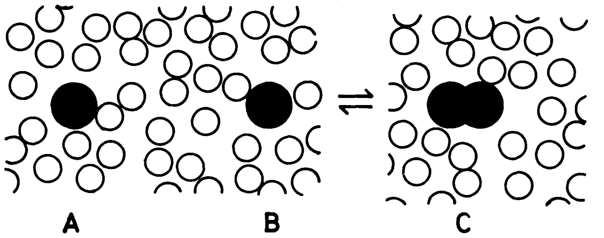

Fig. 1. Model of the bimolecular association reaction in solution illustrated in a two-dimensional way. The white circles denote the solvent molecules and the black the reactants.

amount of solvent as shown in Fig. 1. The potential energy Φ of the reaction system is assumed to be given by the pairwise additive intermolecular potentials u_{ij} as

$$\Phi = \sum u_{ij}, \tag{1}$$

where the pair potential u_{ij} is assumed to act only in the short range between the ith and jth species. The pair potential between the reactants A and B corresponds to the "potential energy supersurface" of the association reaction.

In the present paper, we neglect the quantum effect on the intramolecular behavior of the product molecule C because it is not easy to incorporate this effect into the distribution function formalism; the system is described here at the semiclassical level in the sense that the difference between the energy states is small enough compared with the thermal energy.

The behavior of the model system in the semiclassical limit can be predicted when we specify the form of the potential energy functions in the above scheme; here, however, we are concerned not with the numerical calculation but with the formalism. There remains another fundamental problem as to how to identify the product molecule C. There can be two ways to define C. One may define the product C as a molecular pair when the distance r between A and B lies between l and $l+\varepsilon$; here l and ε can be defined in an arbitrary manner independent of the environments, and l corresponds to the "bond length" when ε is in a sufficiently small range. The other may define C as a molecular pair which has the highest population at a value of r in the ensemble. We take the former definition for the sake of convenience.

Equilibrium Constant in Terms of Distribution Function

Expression for Equilibrium Constant. Since the total number N_C of the product C is the number of the molecular pair A–B which lies between l and $l+\varepsilon$ as described above, it is evaluated by using the radial distribution function $g_{AB}(r)$ as[2]

$$N_C = V\int n_A n_B g_{AB}(r)\cdot\chi(r)4\pi r^2 dr, \tag{2}$$

where V, n_A, n_B, and $\chi(r)$ denote the volume of the system, the number densities of A and B, and the characteristic function for identifying C, respectively. The explicit form of $\chi(r)$ is given here as

$$\chi(r) = \begin{cases} 1 & l \leqq r \leqq l+\varepsilon \\ 0 & r<l \text{ or } r>l+\varepsilon, \end{cases} \tag{3}$$

where ε is the distance in the range of which the molecular pair is recognized as the product C. When ε is small enough, Eq. 2 is written as

$$n_C = n_A n_B g_{AB}(l)\cdot\delta, \tag{4}$$

where n_C is the number density of C and δ is $4\pi l^2\varepsilon$. Since the concentrations of the reactants are at infinite dilution, n_C is negligibly small compared with n_A or n_B, and hence the equilibrium constant K is given as

$$\begin{aligned} K &= n_C/n_A n_B \\ &= g_{AB}(l)\cdot\delta. \end{aligned} \tag{5}$$

This simple expression is important because the molecular nature of solvent and solute molecules is taken into account in a natural manner.[8,9]

Equation 5 can be easily extended to the association between the same molecules, i.e., A=B, or the aggregation among a number of molecules. In the former case, Eq. 5 is rewritten as

$$\begin{aligned} K &= n_C/n_A^2 \\ &= \frac{1}{2}g_{AA}(l)\cdot\delta, \end{aligned} \tag{6}$$

where the factor 1/2 is necessary to avoid the double counting of the molecular pair in Eq. 2.

Radial Distribution Function in Terms of Cavity Distribution Function. Since the potential energy of the system is pairwise additive, the radial distribution function is expressed as the product of the Boltzmann factor for the "bond energy" $u_{AB}(l)$ at a fixed distance l and the cavity distribution function $y_{AB}(l)$ which is defined as[4]

$$g_{AB}(l) = \exp(-u_{AB}(l)/kT)\cdot y_{AB}(l), \tag{7}$$

where k and T are the Boltzmann constant and the temperature, respectively. The solute–solvent interactions are included in the cavity distribution function; the cavity distribution function is the radial distribution function between the hypothetical molecules which have no interactions between themselves and have interactions as usual with the solvent molecules. The cavity distribution function is introduced to represent the indirect interactions between A and B through the solvent molecules. The direct interaction $u_{AB}(l)$ between reactant molecules is separated unambiguously from the radial distribution function so that we may abstract the effect of the solvent–solvent interaction on the thermodynamic quantities of our interest.

Comparison of Distribution Function and Partition Function Expressions

Standard Chemical Affinity. The traditional scheme for treating the changes in the thermodynamic quantities is based on the standard chemical affinity A^0.[10] The standard chemical affinity is defined as

$$A^0 = -\sum \nu_i \mu_i^0, \tag{8}$$

where μ_i^0 is the standard chemical potential of species i; i runs for all the reactants ($\nu_i<0$) and the product ($\nu_i>0$); the symbol ^{0} denotes the standard state. The equilibrium constant K is related to the standard chemical affinity as follows:

$$A^0 = kT \ln K - \sum \nu_i kT \ln c^0, \tag{9}$$

where c^0 is the concentration of the standard state that is conventionally taken to be unity in most cases. The thermodynamic changes, such as enthalpy, entropy, and volume are derived by differentiating the standard chemical affinity. Furthermore, the standard chemical affinity is expressed by the partition functions Z_R^0 and Z_P^0 for the reactants and products, respectively, as

$$A^0 = kT \ln (Z_P^0/Z_R^0). \tag{10}$$

Thus we can diagnose the changes in the thermodynamic quantities by dividing into the contributions from each degree of freedom as shown below. However, the traditional treatment does not tell us the significance of the liquid structure on the chemical reaction. In this chapter, we try to find a relationship between the present and traditional schemes based on the distribution function and the partition function, respectively; remember that the liquid structure of solvent is taken into account in an explicit manner in the former approach.

Components of Standard Chemical Affinity. The standard chemical affinity of the model association reaction is composed of several factors, such as the translational, rotational, and vibrational degrees of freedom of the molecules involved in the reaction and the solute–solvent interactions. First, we briefly review the traditional formulation of the standard chemical affinity in terms of partition functions. The contributions of the solute–solvent interactions to the standard chemical potentials of A, B, and C in solution are considered to be expressed by the corresponding standard chemical potential for the process of their transfer from the ideal gas into the solvent. These are called the solvation free energies, and denoted as α_A, α_B, and α_C for A, B, and C, respectively. The internal degrees of freedom are assumed here to be unperturbed by this process. In consequence, we have the following expressions of the standard chemical potentials for species A, B, and C:

$$\mu_A^0 = kT \ln \left[\left(\frac{h^2}{2\pi m_A kT} \right)^{3/2} c^0 \right] + \alpha_A, \tag{11}$$

$$\mu_B^0 = kT \ln \left[\left(\frac{h^2}{2\pi m_B kT} \right)^{3/2} c^0 \right] + \alpha_B, \tag{12}$$

$$\mu_C^0 = -kT \ln Z_{\mathrm{int}} + kT \ln \left[\left(\frac{h^2}{2\pi (m_A+m_B) kT} \right)^{3/2} c^0 \right] + \alpha_C, \tag{13}$$

where h, and m_A, and m_B are Planck's constant and the masses of A and B, respectively, and Z_{int} is the partition function for the internal degree of freedom. Using Eqs. 11—13 we have the standard chemical affinity in the form

$$\begin{aligned} A^0 &= -\mu_C^0 + (\mu_A^0+\mu_B^0) \\ &= kT \ln Z_{\mathrm{int}} + kT \ln (\lambda^3 c^0) - \Delta\alpha, \end{aligned} \tag{14}$$

where

$$\lambda = (h^2/2\pi m_r kT)^{1/2}, \tag{15}$$

$$m_r = m_A m_B/(m_A+m_B), \tag{16}$$

$$\Delta\alpha = \alpha_C - (\alpha_A+\alpha_B). \tag{17}$$

Here we call the first term in Eq. 14 the internal contribution, the second the translational contribution, and the third the solvation contribution. Such a simple expression for the chemical affinity comes from the fact that the translational contribution is the same in the gas and liquid phases at the semiclassical level and the assumption that the internal structure of the molecule is unchanged by the solvation.

Comparison of Distribution Function and Partition Function Approaches. Although at first sight, Eqs. 5 and 14 seem to have no relation, the semiclassical expressions for the internal partition functions lead to a simple relation between them. The first term on the right-hand side of Eq. 14 comes from the following three factors; the rotational and vibrational degrees of freedom of the associated molecule C and the difference in the zero point of the energy between reactants A and B and product C. The last factor is equal to the bond energy $u_{AB}(l)$ that is negative in sign contrary to the convention. Hence it follows that

$$kT \ln Z_{\mathrm{int}} = kT \ln Z^{\mathrm{rot}} + kT \ln Z^{\mathrm{vib}} - u_{AB}(l), \tag{18}$$

where Z^{rot} and Z^{vib} denote the partition functions of the rotational and vibrational motions of C, respectively.

The rotational partition function in the semiclassical approximation is written as

$$Z^{\mathrm{rot}} = \frac{1}{s} \lambda^{-2} \cdot 4\pi l^2, \tag{19}$$

where s is the symmetry number of the associated molecule C, and the vibrational partition function as

$$Z^{\mathrm{vib}} = \lambda^{-1} \varepsilon. \tag{20}$$

In the semiclassical approximation, the rotational partition function is equivalent to the partition function of the two-dimensional translational motion for the particle of the mass m_r in an area $4\pi l^2$ (which is the surface area of the sphere of the radius l), and the vibrational partition function is equivalent to the partition function of the one dimensional translational motion of the particle in a length ε. Thus the internal partition function is written as

$$Z_{\mathrm{int}} = \frac{1}{s}\lambda^{-3}4\pi l^2\varepsilon \cdot \exp\left(-u_{\mathrm{AB}}(l)/kT\right). \tag{21}$$

When Eqs. 18—20 are used in Eq. 14 the standard chemical affinity is written as

$$A^0 = kT\ln\left(c^0 \cdot 4\pi l^2\varepsilon\right) - kT\ln s - u_{\mathrm{AB}}(l) - \Delta\alpha. \tag{22}$$

This equation can be interpreted thermodynamically by considering a process by which the associated molecule C is formed. Suppose a gas mixture of the reactants A and B at the standard state the concentration of which is c^0. The first term on the right-hand side of Eq. 22 is the change due to the compression of reactant A (or B) from the free space to the concentration $1/(4\pi l^2\varepsilon)$ in the restricted space around B (or A); $4\pi l^2\varepsilon$ is the volume where one of the reactants can move in the neighborhood of the other. If A and B are the same, only either A or B is involved in the initial gas mixture at the standard state (the concentration c^0), so that the concentration of the resultant C is one half of c^0. Therefore, it is necessary to add $kT\ln 2$ to bring the product gas C into the standard state. This correction is made through the symmetry number $s=2$. Finally, the reversible work $\Delta\alpha$ accompanying the transfer of the product from the gas phase into the solvent is added as shown in Eq. 22.

According to Eq. 9, the equilibrium constant is expressed by the standard chemical affinity and the sum of the stoichiometric number -1 ($-\nu_{\mathrm{A}}=-\nu_{\mathrm{B}}=\nu_{\mathrm{C}}=1$). Putting Eq. 22 into Eq. 9 we obtain

$$K = \frac{1}{s}\exp\left(-(u_{\mathrm{AB}}(l)+\Delta\alpha)/kT\right) \cdot 4\pi l^2\varepsilon. \tag{23}$$

Comparison of Eqs. 5 and 23 leads to the following equation:

$$y_{\mathrm{AB}}(l) = \exp\left(-\Delta\alpha/kT\right). \tag{24}$$

This equation is also derivable from the fact that $-kT\ln\, y_{\mathrm{AB}}(l)$ is equal to the reversible work accompanying the approach of A and B at a large separation to the distance l[4]; this is called the potential of mean force by the solvent molecules and equivalent to the difference of the solvation free energy $\Delta\alpha$. In the classical scheme, the change $\Delta\alpha$ due to solvation is treated as the standard chemical affinity associated with the formation or the destruction of the solvation shell. This is contained naturally in the cavity distribution function treated here.

Free Volume Theory vs. Distribution Function Theory. Let us inspect the relation between the present framework based on the distribution function theory and the old one based on the free volume theory. It has been asserted by some authors[1b,11] that the difference in the equilibrium constant between the gas and the liquid phases arises from the restriction of the translational freedom in the liquid phase, and that the "free volume" is useful as a measure of the restriction. In this framework, the chemical potential change is simply written as

$$A^0 = A^0(\mathrm{ideal}) + kT\ln\left(v^0 v_{\mathrm{C}}^{\mathrm{f}}/v_{\mathrm{A}}^{\mathrm{f}} v_{\mathrm{B}}^{\mathrm{f}}\right), \tag{25}$$

where A^0(ideal) is the standard chemical affinity without the solute–solvent interaction that is equal to the standard chemical affinity in the ideal gas, and v^0 and $v_{\mathrm{X}}^{\mathrm{f}}$ are the volume per particle $1/c^0$ and the free volume per particle X, respectively. Although the free volume is often claimed to be ambiguous, its concept can be made clear by the present molecular approach as shown below.

According to Eq. 25, the reversible work α_{X} introduced into Eqs. 11—13 is expressed as

$$\alpha_{\mathrm{X}} = -kT\ln\left(v_{\mathrm{X}}^{\mathrm{f}}/v^0\right) \cdot \tag{26}$$

Putting Eq. 26 into Eq. 24, we obtain the relation

$$y_{\mathrm{AB}}(l) = v^0 v_{\mathrm{C}}^{\mathrm{f}}/v_{\mathrm{A}}^{\mathrm{f}} v_{\mathrm{B}}^{\mathrm{f}} \tag{27}$$

$$= p_{\mathrm{C}}/p_{\mathrm{A}} p_{\mathrm{B}}, \tag{28}$$

where p_{X} is the ratio of $v_{\mathrm{X}}^{\mathrm{f}}$ to v^0. Suppose dissolution of solute X into the solvent. The probability of the allowed occupation of an arbitrary place in the solvent is assumed to be equal to the ratio p_{X} of the free volume to the total volume. The cavity distribution function at a distance l is the ratio of the probability of finding the A–B pair at the distance l to that of finding the pair without correlation between A and B; the former and the latter probabilities are given by p_{C} and $p_{\mathrm{A}}p_{\mathrm{B}}$, respectively. Thus we can explain Eq. 25 in the probabilistic manner.

Components of Changes in Thermodynamic Quantities and Their Significance

The formulation in the previous section enables us to divide the changes of the thermodynamic quantities into the following three terms in an additive manner: (i) the change due to the direct interaction between the reactants which brings about the internal degree of freedom of the product (called the "internal change"), (ii) the change due to the translational motion (called the "translational change"), and (iii) the change due to the indirect interactions between the reactants through the solvent molecules (called the "solvation change"). The term "solvation" is used here in a broad sense, whereas it is often used for strong solute–solvent interactions. In this section, we clarify the significance of each component of the enthalpy, entropy, and volume changes accompanying the association reaction proceeding under isobaric conditions. Numerical value for each component in an actual system is shown in the Appendix to see the relative importance.

Internal Contribution. The internal change in the chemical potential is represented by the first term in Eq. 14. Differentiation of the term leads to the following expressions:

$$\Delta\bar{H}^0(\text{int}) = u_{\text{AB}}(l) + \frac{3}{2}kT, \tag{29}$$

$$\Delta\bar{S}^0(\text{int}) = k\ln(\lambda^{-3}\cdot 4\pi l^2\varepsilon) + \frac{3}{2}k, \tag{30}$$

$$\Delta\bar{V}^0(\text{int}) = 0. \tag{31}$$

The internal changes are the same both in the ideal gas and in solution according to the present model. The first term in the enthalpy change is the pair potential change between the reactants. And the second term due to the energy of the internal degree of freedom of the associated molecule that is equal to $(3/2)kT$ as expected from the equipartition law of energy.[12)]

Different aspects are shown by the internal enthalpy and entropy changes. While the enthalpy change depends on the strength of the bond, $u_{\text{AB}}(l)$, the entropy change depends on the "softness" of the bond, ε. Though the semiclassical term $(3/2)kT$ in the enthalpy change arises from the internal motion which is attributed to the "softness" of the A–B bond, the contribution of the term is usually small (3.7 kJ mol^{-1} at 25 °C) compared with the bond energy. Thus the standard chemical affinity is meaningfully split into the enthalpy and the entropy changes.

It is interesting that the internal contribution does not appear in the volume change. The present result discloses that whatever the internal change takes place the volume change is not observed without the solute–solvent interactions not the direct interaction betwee the solute and the vessel. Thus the "intrinsic volume change" has no real physical meaning, as referred to previously.[3)]

Translational Contribution. The translational chemical potential change is represented by the second term in Eq. 14. Differentiation of this term leads to the following expressions:

$$\Delta\bar{H}^0(\text{trans}) = -\frac{3}{2}kT - \alpha_{\text{P}}kT^2, \tag{32}$$

$$\Delta\bar{S}^0(\text{trans}) = k\ln(\lambda^3c^0) - \frac{3}{2}k - \alpha_{\text{P}}kT, \tag{33}$$

$$\Delta\bar{V}^0(\text{trans}) = -\kappa_{\text{T}}kT, \tag{34}$$

where α_{P} and k_{T} are the isobaric expansibility and the isothermal compressibility of the solvent, respectively. Since these translational changes are determined not only by the momentum of the molecule but also by the direct interaction between the molecule and the container's walls,[11)] these equations contain the response function of the volume of the system with respect to the temperature (α_{P}) or the pressure (κ_{T}) as shown by the last term on the right hand-side of each equation.[13,14)] These terms have been treated as the "correction term" in calculating the change of the thermodynamic quantity from the equilibrium constant expressed in molarity.[1a)] The role of the last terms in Eqs. 32—34 was pointed out in a different manner in the "noninteracting solution"[11)] where the solute molecule had only the translational degree of freedom in the container. We have previously elucidated the significance of the translational volume change on the basis of the virial theorem.[3,15)]

Solvation Contribution. The solvation contribution to the standard chemical affinity is represented by the third term in Eq. 14. Differentiation of this term leads to the following expressions:

$$\Delta\bar{H}^0(\text{solv}) = kT^2\left(\frac{\partial\ln y_{\text{AB}}(l)}{\partial T}\right)_P, \tag{35}$$

$$\Delta\bar{S}^0(\text{solv}) = k\ln y_{\text{AB}}(l) + kT\left(\frac{\partial\ln y_{\text{AB}}(l)}{\partial T}\right)_P, \tag{36}$$

$$\Delta\bar{V}^0(\text{solv}) = -kT\left(\frac{\partial\ln y_{\text{AB}}(l)}{\partial P}\right)_T. \tag{37}$$

These formal expressions tell us that the solvation changes are determined by the liquid structure through the temperature or pressure derivative of the cavity distribution function. Comparison of Eqs. 29—37 reveals that the volume change is a more direct measure of the solvent effect than are the chemical affinity, and the entropy and enthalpy changes because the volume change is independent of the internal structure of the associated molecule C except for the bond length which is assumed to be unaffected by the environments.

The nature of the solvation change is more complicated than that of the internal of the translational change, which results from the fact that the cavity distribution function is determined by multibody interactions among the molecules. If the density of the solvent is small enough, the expansion of the cavity distribution function in powers of density can be truncated to the first several terms and served for a rigorous discussion of their explicit form of Eqs 35—37, an example is shown elsewhere[3)] for the volume change in the dilute gas. But such a treatment breaks down in usual liquids where multibody interactions are dominant. Hence we should explore the liquid structure in a more sophisticated manner to establish a solid basis for the treatment of the solvation effects on the chemical reaction; e.g., such "extra-thermodynamic" relationships as linear free energy relationship and the entropy–enthalpy compensation may be obtained along this line. The present-day liquid theory[16] will be useful for justifying the extra-thermodynamic rules empirically found. Our work along this line will appear in near future.

Appendix

Evaluation of the Internal, Traslational, and Solvation Contributions in an Actual System. Although the theoretical framework presented here is insufficient for understanding the molecular nature of the chemical reaction because of the complexity of the internal structure in the actual reaction system, at least, the translational and solvation contributions can be elucidated. The relative weights of the internal, translational, and solvation contributions vary from one thermodynamic quantity to another. Here, we show the significance of the three components in the changes of the thermodynamic quantities, enthalpy, entropy, and volume in an association reaction.

The dimerization of nitrogen dioxide in solution

$$2NO_2 \rightleftharpoons N_2O_4, \tag{38}$$

is a prototype association reaction studied experimentally[17–20] and theoretically[4,6] in both the gas and liquid phases. Although this reaction is complicated enough as referred to above, the translational and solvation contributions can be estimated by applying the experimental imformation in the present formulation.

We adopt the experimental data for the enthalpy and entropy changes in carbon tetrachloride which are obtained by measuring the solution susceptibility,[18] while there exists a discrepancy in the experimental data.[18,19] The isothermal compressibility and the isobaric expansibility are taken from Ref. 21.

The evaluated values for the three components at 25 °C and 1 atm (1 atm=1.013×10^5 Pa) are summarized in Table 1. The largest contribution to the entropy change comes from the translational change. If the internal freedom exists only in the associated molecule as in the present model, the internal entropy change is expected to be positive. However, since both nitrogen dioxide and dinitrogen tetroxide molecules have the internal freedom, the dimerization reaction may have the negative internal entropy change as shown in Table 1; the largest contribution to the internal entropy change comes from the rotational entropy change that is calculated here as $-55\ \mathrm{J\,K^{-1}\,mol^{-1}}$. The internal contribution plays the most important role in the enthalpy change. The volume change is dominated by the solvation change, and the translational volume change is rather small in solution, though the translational contribution to the volume change is dominant in the gas phase where the volume change amounts to $-24\ \mathrm{dm^3\,mol^{-1}}$.

Table 1. Values of the Components of Changes of the Thermodynamic Quantities Accompanying the Dimerization of Nitrogen Dioxide in Carbon Tetrachloride at 25 °C and 1 atm[a,b]

	Internal	Translational	Solvation
$\Delta\bar{H}^\circ$ (kJ mol^{-1})	−50.9	−4.6	−5.6
$\Delta\bar{S}^\circ$ (J K^{-1} mol^{-1})	−28	−116	+11
$\Delta\bar{V}^\circ$ (cm^3 mol^{-1})	0	−3	−20

a) The standard state is taken to be 1 mol dm^{-3}. b) The internal changes of the enthalpy and entropy, which are assumed to be the same in the gas and the liquid phases, are calculated from the data of the gas-phase reaction[17] by subtracting the translational changes which are obtained from Eqs. 34 and 35. The experimental data of the volume change is obtained from Ref. 20.

The entropy change has been used in the characterization of the chemical reaction in solution with such a view that the entropy change (activation entropy) reflects the "softness" or "randomness" of the product (transition state). As shown here, however, the entropy change accompanying the association reaction contains a large amount of translational contribution which is independent of the molecular parameters except for the mass. Thus we must subtrac the translational contribution before discussing the mechanism of the association or addition reaction in terms of the entropy change.

The authors are grateful for the support of the present work by the Research Grant-in-Aid from the Ministry of Education, Science and Culture (No. 61134043).

References

1) a) L. P. Hammet, "Physical Organic Chemistry," McGraw-Hill, New York (1970); b) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York (1960); c) S. G. Entelis and R. P. Tiger, "Reaction Kinetics in the Liquid Phase," translated by R. Kondor, John Wiley, New York (1976).

2) Y. Yoshimura and M. Nakahara, *J. Chem. Phys.*, **81**, 4080 (1984).

3) Y. Yoshimura and M. Nakahara, *Ber. Bunsenges. Phys. Chem.*, **90**, 58 (1986).

4) D. Chandler and L. R. Pratt, *J. Chem. Phys.*, **65**, 2925 (1976).

5) L. R. Pratt, C. S. Hsu, and D. Chandler, *J. Chem. Phys.*, **68**, 4202 (1978).

6) D. Chandler, *Faraday Discuss. Chem. Soc.*, **66**, 184 (1978).

7) B. M. Ladanyi and J. T. Hynes, *J. Am. Chem. Soc.*, **108**, 585 (1986).

8) When we ignore the ion charge in the Fuoss equation for ion-pair formation,[9] the equilibrium constant is given by

$$K = \frac{4\pi}{3}a^3,$$

where a is the center-to-center distance between the two contact spheres. This equation has no real physical meaning, and should read better as

$$K = 4\pi a^2\varepsilon,$$

which is equal to Eq. 5 when g(a) is assumed to be unity.

9) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

10) I. Prigogine and R. Defay, "Kagaku-Netsurikigaku (Chemical Thermodynamics)," translated by M. Seno, Misuzu, Tokyo (1977).

11) R. P. Bell and O. Gatty, *Phil. Mag.*, **9**, 75 (1935).

12) Since the Hamiltonian for the internal motion of C can be regarded to be independent of the coordinates, the energy partitioned is $(3/2)kT$. If the Hamiltonian depends on the coordinates, this is not the case; e.g., the harmonic oscillator shares an energy of $2kT$.

13) The translational volume change arises from the translational pressure change $(-kT/V)$ under the isochoric condition,[3] and the last terms of the translational enthalpy and entropy changes are attributed to the translational volume change. The enthalpy and entropy changes under isochoric condition are reduced to the following[14]:

$$(\Delta\bar{U}^0)_{T,V} = \Delta\bar{H}^0 - (\alpha_P/\kappa_T)T\Delta\bar{V}^0,$$
$$(\Delta\bar{S}^0)_{T,V} = \Delta\bar{S}^0 - (\alpha_P/\kappa_T)\Delta\bar{V}^0,$$

where $(\Delta\bar{U}^0)_{T,V}$ is the internal energy change under isochoric condition. When the translational volume change $\kappa_T kT$ is used in the last terms of the above equations, they become equal to the corresponding term in Eqs. 32 and 33. Thus it is verified that the last terms in Eqs. 32 and 33 are attributed to the change of the direct interaction between the molecule and the container's walls.

14) S. B. Brummer and G. J. Hills, *Trans. Faraday Soc.*, **57**, 1816 (1961).

15) Y. Yoshimura, J. Osugi, and M. Nakahara, *Ber. Bunsenges. Phys. Chem.*, **89**, 25 (1985).

16) a) J. A. Barker and D. Henderson, *Rev. Mod. Phys.*, **48**, 587 (1976); b) H. C. Andersen, D. Chandler, and J. D. Weeks, *Adv. Chem. Phys.*, **34**, 105 (1976).

17) I. C. Hisatsune, *J. Phys. Chem.*, **65**, 2249 (1961).

18) T. F. Redmond and B. B. Wayland, *J. Phys. Chem.*, **72**, 1626 (1968).

19) P. Gray and P. Rathbone, *J. Chem. Soc.*, **1958**, 3550.

20) A. H. Ewald, *Discuss. Faraday Soc.*, **22**, 138 (1956).

21) J. S. Rowlinson and F. L. Swinton, "Liquids and Liquid Mixtures," 3rd Ed., Butterworth, London (1982).