

Relationship between Boiling Temperatures and Electric Dipole Moment for Chlorofluorocarbons

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Synopsis: The boiling and critical temperatures of chlorofluorocarbons (CFCs) reduced from methane respectively fit on two parabolic curves with respect to the total dipole moment, where total dipole moment equals the addition of the permanent electric dipole moment and the induced electric dipole moment. This fact is clear and also confirmed for CFCs reduced from ethane. A theoretical description is also given for the traditional statistical mechanics procedures, since boiling and critical temperatures are macroscopic, while permanent dipole moment and polarizability of a single molecule concerned with induced dipole moment are microscopic. The simple way to provide the equation of state of the so-called van der Waals type is described. The modified van der Waals equation changed from the van der Waals' one is proposed to realize a value of ratio $P_c V_c / T_c$ close to the experimental one. The requirement to fit on a parabola is that the ratio of configuration integration against the effective volume of an atom must take the same value in a group of CFCs.

Key words: Chlorofluorocarbons, Boiling Temperature, Dipole-Dipole Interaction, van der Waals Equation.

1. Introduction

We found that the boiling temperatures of a subgroup of chlorofluorocarbons (CFCs) reduced from methane fit on a parabolic curve against the electric dipole moment as shown in Fig. 1, where electric dipole moment is defined as the total dipole moment composed of permanent and induced dipole moments. In Fig. 1, the boiling temperatures are depicted against the square values of total dipole moments to see the clear relationship. This fact is also confirmed for other reduced methane and ethane CFCs (hereinafter, reduced methane and ethane CFCs are called methane-CFCs and ethane-CFCs, respectively, and if required, the expressions $\text{CH}_x\text{F}_y\text{Cl}_{4-x-y}$ for methane-CFCs and $\text{C}_2\text{H}_x\text{F}_y\text{Cl}_{6-x-y}$ for ethane-CFCs will be used). The group of methane- and ethane-CFCs shows the square dependence of boiling temperature on dipole moment, while the group of rare gases does not exhibit the same feature. The boiling temperatures of the rare gases do not fit on a parabolic curve. We also confirmed that critical temperatures versus total dipole moments of methane-CFCs fit on two types of parabolic curves, and those of a group of ethane-CFCs stand on a parabola. The details are shown in section 2.

In the field of intermolecular forces, it is well known that dominant interaction is a

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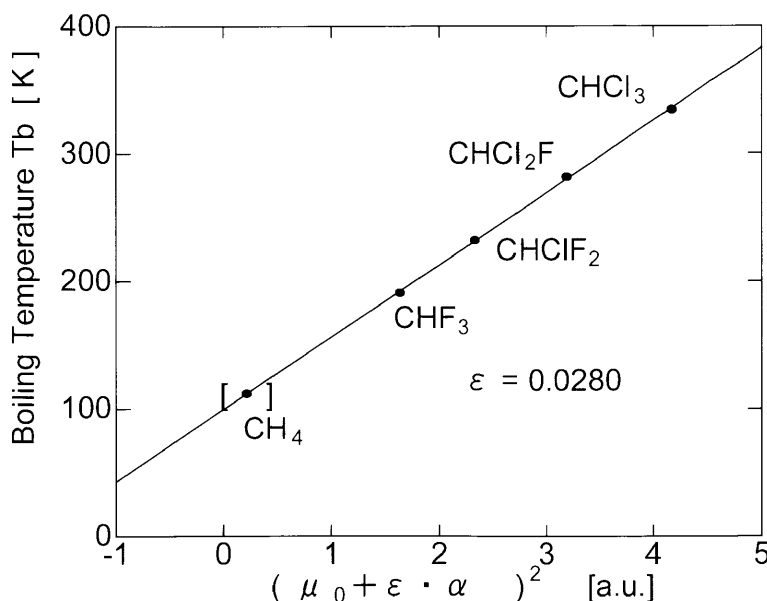


Fig. 1 Relationship between Boiling Temperature and Total Dipole Moment for Methane-CFCs
Boiling temperatures of Methane-CFCs (Chlorofluorocarbons reduced from methane) are proportional to the square value of total dipole moment. In other words, boiling temperatures stand on a parabola against the total dipole moment.

dipole-dipole interaction or a dispersion force within a system of electrically neutral molecules^{1,2}. However, this well-known fact does not immediately mean that boiling and critical temperatures in a group of molecule types depend on the square value of total dipole moment. It is possible to predict some conditions for the square dependence. To see the conditions to realize the fact considered here, we undertake the theoretical derivation of the relationships between boiling or critical temperature and total electric dipole moment. Considering the derivation process, we focus on the fact that boiling and critical temperatures are macroscopic thermodynamical quantities, whereas permanent and induced dipole moments of a molecule are microscopic quantum-chemical quantities. The quantities for binding to each other lie on quite different stages. Hence, we use the traditional method of statistical mechanics^{3,4} to derive the targeted relationships.

We use a semi-classical procedure to derive the relationships. We start from the quantum mechanical treatment of Hamiltonian, which describes the two interacting molecules. For this treatment, we expect that the Hamiltonian yields interaction energy from any pair of interacting molecules. We assume that the interaction energy given by quantum Hamiltonian is equivalent to the potential term of classical Hamiltonian. We therefore derive the targeted relationships in the statistical mechanics framework by using classical Hamiltonian. We demonstrate the derivation of the relationship that boiling and critical temperatures are proportional to the square value of the electric dipole moment. In the derivation, we assume

that molecule movements satisfy the ergodicity, and each molecule describes a typical movement expressed by a statistical average within certain deviations. Based on these assumptions, we can derive a van der Waals-type equation of state. Applying critical conditions to the equation of state, the relationship between critical temperature and electric dipole moment can be obtained. We also obtain the critical pressure and volume for the critical conditions. The relationship between boiling temperature and electric dipole moment is also obtained by use of Maxwell’s criterion to determine the phase transition from gas to liquid or reverse the transition on the equation of state. The derivations are shown in section 3.

Using the derived equations expressing the relationship between boiling or critical temperature and dipole moment, we discuss in which cases do boiling and critical temperatures fit on a parabolic curve against the total dipole moment. Only taking dipole-dipole interaction into account we obtain the expression of critical temperature versus dipole moment. This allows zero temperature when the dipole moment approaches to zero, but differs from the evidence shown in section 2. The difference will be overcome by taking higher order interactions such as quadrupole-quadrupole interactions or more higher into account, because dipole-dipole interaction is the first order approximation for electrically neutral molecules. No higher order interactions affect the derivation of the relationship between critical temperature and dipole moment.

Moreover, we require the modification of the van der Waals equation of state, since it gives different values for the ratio $P_c V_c / T_c$ from that given by the experimental values. We therefore introduce the modified van der Waals equation of state, which has the fractional volume $V^{2+\gamma}$. We call γ introduced fractional volume factor. The fractional volume factor gives a better value of ratio $P_c V_c / T_c$ close to the experimental one at $\gamma = 1/4$. These issues are discussed in section 4.

2. Evidence for the Square Dependence of Boiling and Critical Temperatures on Total Electric Dipole Moment

In the previous section, we stated that the relationship between boiling temperatures and total dipole moments from a subgroup of methane-CFCs forms a parabola as shown in Fig. 1, namely, the boiling temperature is proportional to the square value of total electric dipole moment in a subgroup of methane-CFCs. This is true for methane- and ethane-CFCs, and the same relationship can be established by replacing boiling temperature to critical temperature. It does not however mean that all the boiling and critical temperatures of CFCs lie on the same parabola. We make a set of CFCs, of which temperatures lie on the same parabola, as a group. Methane-CFCs are classified into two groups, because their boiling and critical temperatures fit on two separable parabolas with respect to the total dipole moment. This implies that some conditions exist to fit on the same parabola even if dipole-dipole interactions are dominant in electrically neutral molecules.

The physical properties of methane-CFCs are listed in Table I. The permanent dipole

Table I

molecule	μ_0	α	T_b	T_c	P_c	V_c	$P_c V_c / T_c$
CH _x F _y Cl _{4-x-y}	[a.u.]	[a.u.]	[K]	[K]	[atm]	[cm ³ /mol]	[atm·cm ³ /mol/K]
group A							
CH ₄ (50)	0.000	16.572	111.6	190.4	45.4	99.2	23.7
CHF ₃ (23)	0.818	16.500	191.0	299.3	48.0	132.7	21.3
CHClF ₂ (22)	0.666	30.742	232.4	369.3	49.0	165.6	22.0
CHCl ₂ F(21)	0.549	44.220	282.1	451.6	51.1	196.4	22.2
CHCl ₃ (20)	0.454	56.669	334.3	536.4	53.0	239.0	23.6
group B							
CF ₄ (04)	0.000	16.113	145.1	227.6	36.9	139.6	22.6
CClF ₃ (03)	0.232	30.371	193.2	302.0	38.2	180.4	22.8
CH ₃ F(31)	0.636	16.926	194.7	315.0	55.3	113.2	19.9
CH ₂ F ₂ (22)	0.803	16.883	221.5	351.6	57.5	120.8	19.8
CCl ₂ F ₂ (02)	0.143	45.045	245.2	384.9	40.9	216.7	23.0
CH ₃ Cl(30)	0.595	28.808	249.4	416.3	66.1	139.0	22.1
CH ₃ ClF(21)	0.703	30.089	264.0	426.6	55.5	158.0	20.6
CCl ₃ F(01)	0.079	58.933	296.9	471.2	43.5	247.8	22.9
CH ₂ Cl ₂ (20)	0.591	42.271	313.0	510.0	62.2	193.0	23.5
CCl ₄ (00)	0.000	71.664	349.9	556.4	45.0	275.9	22.3

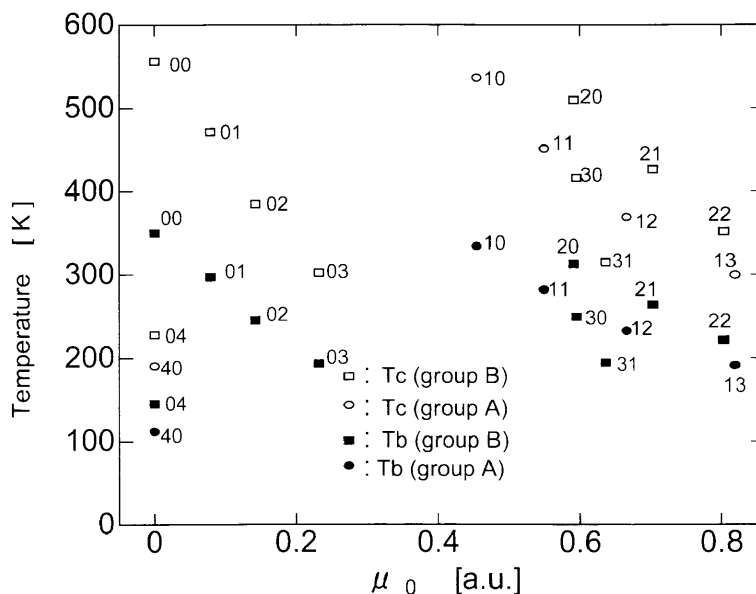


Fig. 2 Relationship between Boiling and Critical Temperatures and Permanent Dipole Moment for Methane-CFCs. A clear relationship similar to Fig. 1 cannot be found. Some types of Methane-CFCs may exist. The numbers in the figure signify (xy)s expressed in their form of CH_xF_yCl_{4-x-y}.

moments μ_0 and polarizabilities α in Table I are calculated by using the MOPAC program⁵. Boiling and critical temperatures (T_b and T_c), critical pressure P_c , and critical volume V_c of experimental values were surveyed using several data books⁶⁻¹² and papers¹³⁻¹⁹. We also show the ratios $P_c V_c / T_c$, which are referred and discussed in §4. As already mentioned above,

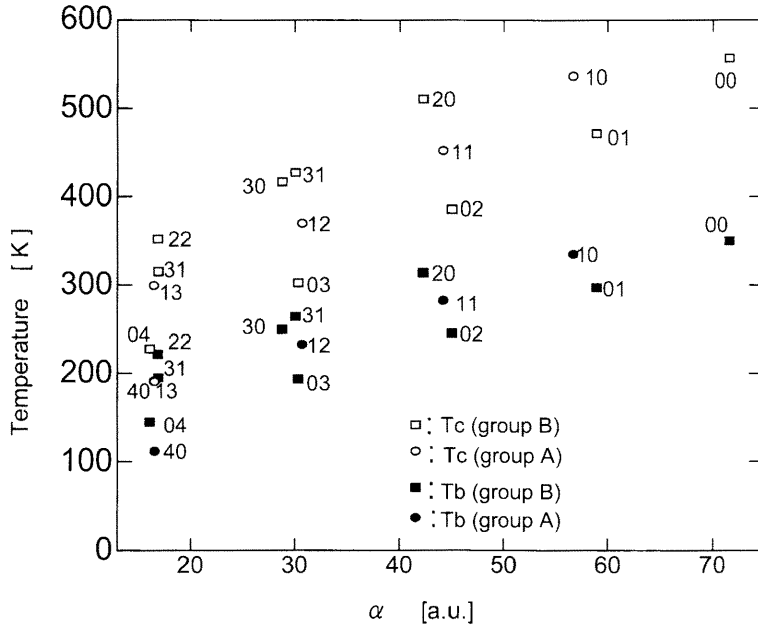


Fig. 3 Relationship between Boiling and Critical Temperatures and Electric Porlizability for Methane-CFCs. This figure cannot be found in the clear relationship shown in Fig. 1. Some types of Methane-CFCs may exist, but the meaning of this remains unknown. The numbers in the figure are the same significance as explained in Fig. 2.

methane-CFCs separate into two groups. We simply call these two groups group A and group B.

Figure 2 shows the relationship between μ_0 and (T_b or T_c) for methane-CFCs. Figure 3 shows the relationship between α and (T_b or T_c). Although these figures probably have a meaning, we cannot find clear relationship between $\mu_0 - (T_b \text{ or } T_c)$ and $\alpha - (T_b \text{ or } T_c)$, respectively. In Fig. 4, we are able to show a clear relationship between total electric dipole moment $\mu_0 + \epsilon\alpha$, and boiling or critical temperatures (T_b or T_c). Notice that $\epsilon\alpha$ means induced dipole moment. Since α is the porlizability of an atom, ϵ implies the electric field caused by atoms surrounded the considered atom. As seen from Fig. 4, the relationship between (T_b or T_c) and $\mu_0 + \epsilon\alpha$, obviously show parabolic features, and both T_b s and T_c s, respectively, lie well on different two parabolic curves. Figure 4 asserts that there are two classification groups for the methane-CFCs.

To observe evidence of square dependence of boiling and critical temperatures influencing total dipole moment, we plot T_b s and T_c s against $(\mu_0 + \epsilon\alpha)^2$ s. The results are shown in Fig. 5. On the plots in Fig. 5, a straight line means an exact parabola. As seen in Fig. 5, both members of groups A and B lie on the respective straight lines quite well.

We confirmed that the same relationship is also maintained for ethane-CFCs. We selected a class of boiling and critical temperatures of ethane-CFCs from the references⁶⁻¹⁹ for the

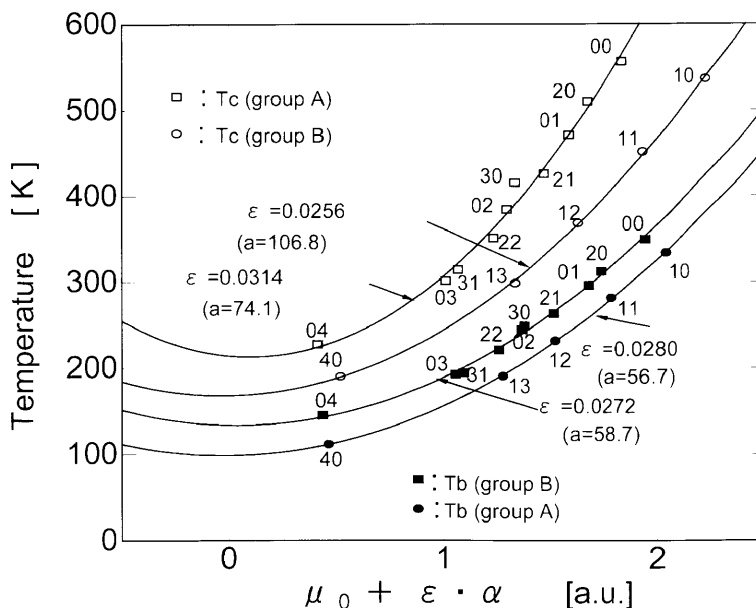


Fig. 4 Parabolic Expression for Dependence of Boiling and Critical Temperatures on the Total of Electric Dipole Moments. The relationship between boiling and critical temperatures and total electric dipole moment is shown. An obvious relationship is visible in the figure. The numbers in the figure are the same signification as explained in Fig. 2.

criterion in which experimental values given by different references agree with each other. The selected ethane-CFCs are listed in Table II with permanent dipole moments, polarizabilities, boiling temperatures, and critical temperatures. The relationship between boiling temperature and total dipole moment can be accommodated by the parabola expressed in the equation $T_b = 13.423 \cdot (\mu_0 + \epsilon\alpha)^2 + 175.32$ with deviating errors within 5%. Figure 6 shows the plotted picture of the relationship T_b s versus $(\mu_0 + \epsilon\alpha)^2$ s. We can see that boiling temperatures for ethane-CFCs are also proportional to their square values of total dipole moment.

Here, we notice that the permanent dipole moment and the polarizability of a molecule used in the present paper are microscopic quantities given by the calculation of the molecular orbital method (actual calculations were performed by the program MOPAC⁵ and some parameters for atomic properties²⁰ were used), while the boiling and critical temperatures are macroscopic quantities measured by experiments⁶⁻¹⁹. In other words, microscopic interactions of molecules appear in the macroscopic quantities which were observed in the experimental measurements.

As the result, we knew that dipole-dipole interaction or dispersion force^{1,2} (dominant interaction of electrically neutral molecules) is reflected in the boiling and critical temperatures. These facts are expected in any system of usual molecules, but actually are not general. A noteworthy point is that a group of molecular types has proportional dependence on the

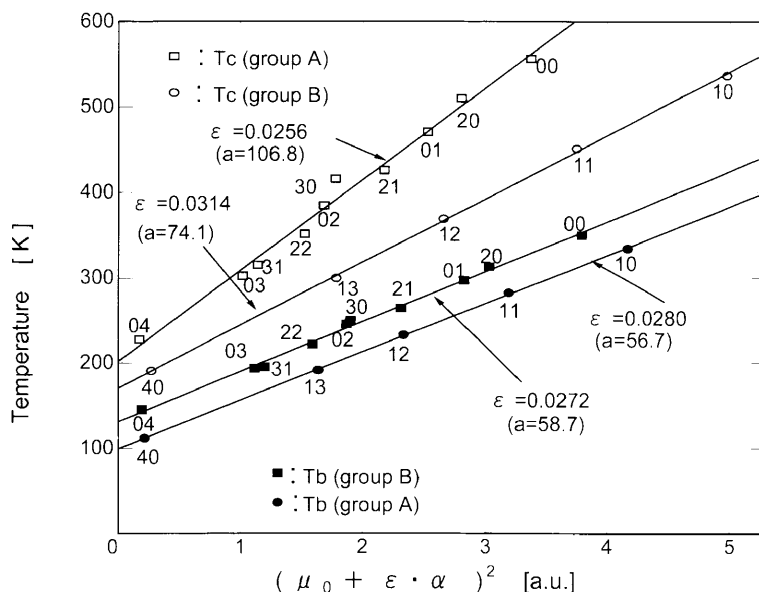


Fig. 5 Proportional Dependence of Boiling and Critical Temperatures on the Square Value of Total Electric Dipole Moment. This figure demonstrates that boiling and critical temperatures fit well on parabolic curves quite well. From the figure, we can see that Methane-CFCs are classified into two groups. These are simply named group A and group B. The numbers in the figure are the same signification as explained in Fig. 2.

Table II

molecule	μ_0	α	Tb	Tc	error
$C_2H_xF_yCl_{4-x-y}$	[a.u.]	[a.u.]	(calc.)	(exp.)	[%]
CF ₃ CF ₃	0.000	31.133	197.58	194.95	1.35
CF ₂ ClCF ₃	0.219	45.517	234.62	234.45	0.07
CHF ₂ CF ₃	0.839	30.939	235.58	224.65	4.87
CH ₃ CHF ₂	0.983	29.482	240.43	249.15	-3.50
CF ₂ ClCF ₂ Cl	0.226	59.495	272.24	276.95	-1.70
CHF ₂ CHFCl	1.026	44.089	284.33	290.15	-2.01
CF ₂ ClCHFCl	0.689	58.163	303.91	301.25	0.88
CFCI ₂ CF ₂ Cl	0.257	72.572	317.88	320.75	-0.90
CFCI ₂ CHFCl	0.640	72.471	352.95	345.65	2.11
CFCI ₂ CFCI ₂	0.174	86.468	364.18	365.75	-0.43

square value of total dipole moment $(\mu_0 + \epsilon\alpha)^2$. Presently, we see this fact for CFCs only. The rare gases do not satisfy the relationship considered here. Taking rare gases into consideration, we speculate that each type of CFCs may be similar in shape to each other, because the CFCs discussed here are reduced from the fundamental molecules CH₄ or C₂H₆ by replacing hydrogen (H) with fluorine (F) or chlorine (Cl). We mention again that the methane-CFCs

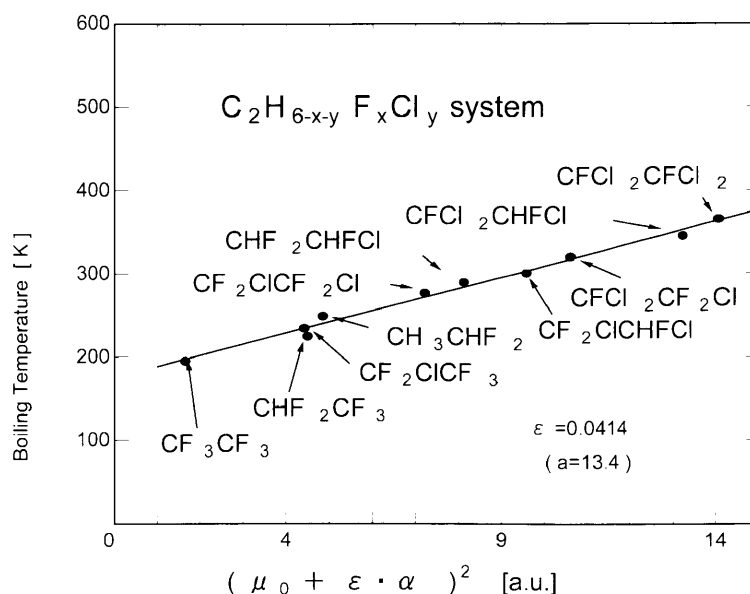


Fig. 6 Relationship between Boiling Temperature and Total Electric Dipole Moment for Ethane-CFCs
Boiling temperatures of ethane-CFCs also lie on a parabola against the total electric dipole moment.
These ethane-CFCs are selected as they correspond to experimental data from different references.

are classified into two subgroups. The particularity of group A is speculated as follows: every member of group A has a C-H bond and other bonds of a carbon are F or Cl except for methane itself.

Molecular types methane CH_4 , tetrafluoromethane CF_4 , and tetrachloromethane CCl_4 are nonpolar (see Table I), namely, these molecules have no permanent electric dipole moment. Other methane-CFCs have permanent electric dipole moments, respectively. This may be caused by an unbalanced molecular binding of F, Cl, and H to a central carbon atom. The larger permanent dipole moment comes with the combination of F and H atoms, as seen in table I. We also see in table I that the larger polarizability is caused by Cl atoms.

Hence, we briefly see that the asymmetry of a molecule results in the permanent electric dipole moment and the increase of electrons in an atom controls the polarizability of a molecule. These rough views are inferior to the evidence shown in this section, namely, the relationship of boiling and critical temperatures versus total dipole moment which form the four parabolas. We clearly understood the square dependence of boiling and critical temperatures on total dipole moment for methane- and ethane-CFCs.

3. Theoretical Description of the Relationship between Boiling and Critical Temperatures and Electric Dipole Moment

In the present section, we derive the relationship between boiling or critical temperatures

and electric dipole moment for the system where electrically neutral molecules are interacting with each other. We assume that the interaction between any two molecules is expressed by coulomb potential. The derivation scheme follows:

Let's consider a N molecule system where every molecule is electrically neutral and molecules interact with each other with coulomb interaction. The derivation is carried out under the assumptions that each molecule does not lose any electrons and that no electron exchange occurs during the interactions. We first consider the interaction energy between two molecules from the quantum chemistry viewpoint, because the calculation of permanent electric dipole moment and electric polarizability of a molecule was undertaken on the MOPAC program⁵. The obtained interaction energy is regarded as the interaction energy between any two molecules that are electrically neutral. We can treat the system described by quantum mechanics as a classical particle system where the interaction energy between any two particles is equal to that given by quantum expectation values. Regarding this point, we replace the quantum Hamiltonian of N particles system with the classical one. Using the classical Hamiltonian, we construct the partition function for the statistical ensemble of the system considered. Then the thermodynamical free energy of the system is given by a partition function using the well-known relationship in statistical mechanics^{3,4}. Moreover, an equation of state is obtained from the free energy, using the thermodynamical relationship that the pressure of a system is the negative partial derivative of free energy with respect to the temperature, with the volume remaining constant²¹. Finally, we obtain the set of equations for critical temperature, pressure, and volume, applying the critical condition that the first derivative of pressure for volume and the second derivative of that are equal to zero at the same time¹⁸. We also obtain the relationship between boiling temperature and interaction energy of molecules by using Maxwell's criterion for the change of substance phases²¹.

3.1 Interaction Energy between Two Molecules

We consider the following Hamiltonian operator to describe two interacting molecules A and B at the atomic level.

$$\hat{H} = \hat{H}_A + \hat{H}_B + V_{\text{int}} \quad (3.1)$$

$$\hat{H}_A = -\frac{1}{2} \sum_i^A \left(\nabla_i^2 - \sum_a^A \frac{Z_a}{r_{Ai}} \right) + \sum_{i \neq i'}^A \frac{1}{r_{ii'}} \quad (3.2)$$

$$\hat{H}_B = -\frac{1}{2} \sum_j^B \left(\nabla_j^2 - \sum_b^B \frac{Z_b}{r_{Bj}} \right) + \sum_{j \neq j'}^B \frac{1}{r_{jj'}} \quad (3.3)$$

$$V_{\text{int}} = -\sum_j^B \sum_a^A \frac{Z_a}{r_{aj}} - \sum_i^A \sum_b^B \frac{Z_b}{r_{bi}} + \sum_i^A \sum_j^B \frac{1}{r_{ij}} + \sum_a^A \sum_b^B \frac{Z_a Z_b}{r_{ab}}, \quad i \in A, j \in B \quad (3.4)$$

where V_{int} is energy for intermolecular interaction, H_A and H_B are intramolecule Hamiltonian operators of respective molecules A and B, suffices i, j denote electrons of each molecule (i for molecule A, j for molecule B), and suffices a, b denote nuclear of each molecule (a : molecule A, b : molecule B), Z_a and Z_b signify the nuclear charges of the respective molecules

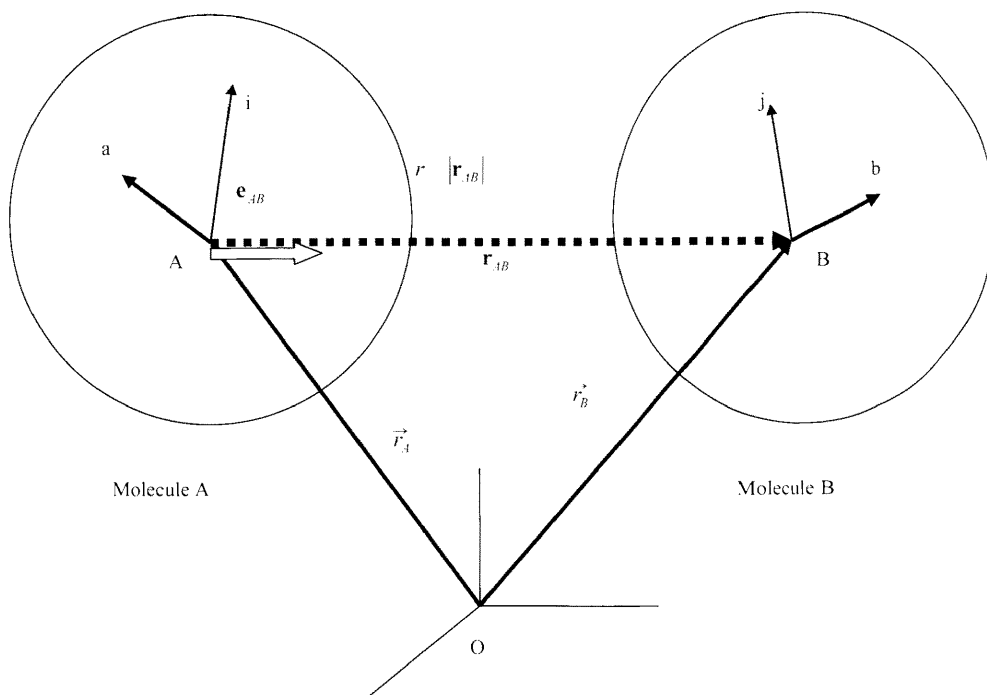


Fig. 7 Illustrated Scheme of Two Interacting Molecules
Molecules are simply expressed as A and B. Vectors to describe the relative positions of atoms are depicted briefly.

A and B. The scheme of interacting molecules A and B is briefly illustrated in Fig. 7. The laplacian terms of Hamiltonians H_A and H_B correspond to classical kinetic energies of molecules A and B. We assume that the system is stationary, so that the Hamiltonian H_{AB} satisfies the time independent Schrodinger equation, i.e.,

$$H_{AB}|\psi\rangle_{AB} = (H_A + H_B + V_{\text{int}})|\psi\rangle_{AB} = (E_A^0 + E_B^0 + E_{\text{int}})|\psi\rangle_{AB} \quad (3.5)$$

where $|\psi\rangle_{AB}$ denotes a stationary wavefunction, E_A^0 and E_B^0 are intramolecular energies of molecules A and B, and E_{int} is the energy of intermolecular interaction.

For the system of electrically neutral molecules, the potential of two interacting molecules A and B can be approximated by the perturbation method up to the second order terms^{1,2}. The approximate potential of interaction V_{int}^* becomes

$$V_{\text{int}} \approx V_{\text{int}}^* = -\frac{1}{r^3} \{3(\overline{e_{AB}} \cdot \vec{\mu}_A)(\overline{e_{AB}} \cdot \vec{\mu}_B) - \vec{\mu}_A \cdot \vec{\mu}_B\} \quad (3.6)$$

where $\overline{e_{AB}}$ denotes the unit vector describing the direction along the line between respective electrical centers of molecules A and B, which are given by following equations

$$\bar{r}_A = \frac{1}{N_A} \sum_a^A Z_a \bar{r}_a, N_A = \sum_a^A Z_a, \bar{r}_B = \frac{1}{N_B} \sum_b^B Z_b \bar{r}_b, N_B = \sum_b^B Z_b \quad (3.7)$$

$$\bar{e}_{AB} = \frac{1}{r} \bar{r}_{AB}, r = |\bar{r}_{AB}|, \bar{r}_{AB} = \bar{r}_B - \bar{r}_A \quad (3.8)$$

and μ_A, μ_B are operators of electric dipole moments for molecules A and B defined as follows:

$$\bar{\mu}_A = \sum_a^A Z_a (\bar{r}_a - \bar{r}_A) - \sum_i^A (\bar{r}_i - \bar{r}_A), \bar{\mu}_B = \sum_b^B Z_b (\bar{r}_b - \bar{r}_B) - \sum_j^B (\bar{r}_j - \bar{r}_B) \quad (3.9)$$

Notice that we use the atomic unit $\hbar = 1$, $c = 1$ and $e = 1$. The expectation values of dipole moment operators are μ_A, μ_B , respectively.

Therefore, the approximate expression for interaction energy is as follows:

$$E_{\text{int}} \approx {}_{AB} \langle \phi | V_{\text{int}}^* | \phi \rangle_{AB} \equiv f(r) \bar{\mu}_A \cdot \bar{\mu}_B \quad (3.10)$$

where we generally put the dependence of the distance r between two molecules A and B by a certain function $f(r)$, since the molecular interaction of electrically neutral molecules has the r^{-6} dependence and a higher order of correction terms^{1,2}. For homo-molecules, the intermolecular interaction energy is given by eq. (3.10) with $A = B$, namely, using the same expectation value $\mu_A = \mu_B = \mu$, the classical form of approximate interaction energy is written as

$$E_{\text{int}} \approx f(r) \mu^2 \quad (3.11)$$

where μ means the total electric dipole moment. By following Margenau and Kestner¹, symmetric molecules have only dispersion force, i.e., induced dipole moment, while asymmetric molecules have a constant independent polarizability, which corresponds to the permanent dipole moment.

3.2 Derivation of an Equation of State

In this subsection, we derive an equation of state that yields the relationship between boiling or critical temperature of a system and intermolecular interaction. We assume that electrically neutral molecules of the same types interact weakly with each other and they are in thermal equilibrium. Following the derivation scheme mentioned above, we introduce the classical Hamiltonian written as

$$H = \sum_i \frac{p_i^2}{2m} + \sum_i \varepsilon_i^0 + \sum_{i \neq j} \phi(r_{ij}) \equiv \sum_i H_i + \sum_{i \neq j} \phi(r_{ij}) \quad (3.12)$$

where p_i denotes the momentum of the i -th molecule, m is the mass of a molecule, ε_i^0 the energy of intramolecular interactions of the i -th molecule, and $\phi(r_{ij})$ the energy of intermolecular interaction for the i -th and j -th molecules, respectively. The energy of intermolecular interaction is assumed to be given as eq. (3.11) so that $\phi(r_{ij})$ has the following ap-

proximate expression

$$\phi(r_{ij}) \cong f(r_{ij})\mu^2. \quad (3.13)$$

The partition function Z for the N molecules system is given by

$$\begin{aligned} Z &= \frac{1}{N!} \frac{1}{h^{3N}} \int \cdots \int \exp \left\{ -\frac{H}{k_B T} \right\} dx_1 dy_1 dz_1 \cdots dp_{x_N} dp_{y_N} dp_{z_N} \\ &= \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \Omega(T, V) \end{aligned} \quad (3.14)$$

where h denotes Plank's constant, k_B Boltzmann's constant, T the absolute temperature of the system, and $\Omega(T, V)$ is defined as follows:

$$\begin{aligned} \Omega(T, V) &= \frac{1}{N!} \int \cdots \int \exp \left\{ -\frac{\sum \phi(r_{ij}) + \sum \varepsilon_i^0}{k_B T} \right\} dx_1 dy_1 dz_1 \cdots dx_N dy_N dz_N \\ &= \frac{1}{N!} \exp \left\{ -\frac{\sum \varepsilon_i^0}{k_B T} \right\} \int \cdots \int \exp \left\{ -\frac{\sum \phi(r_{ij})}{k_B T} \right\} dx_1 dy_1 dz_1 \cdots dx_N dy_N dz_N \\ &= \frac{1}{N!} \exp \left\{ -\frac{N\varepsilon^0}{k_B T} \right\} \int \cdots \int \exp \left\{ -\frac{\sum \phi(r_{ij})}{k_B T} \right\} dx_1 dy_1 dz_1 \cdots dx_N dy_N dz_N \end{aligned} \quad (3.15)$$

where the last expression is obtained on the assumption that intramolecular energy is independent of a molecule's position and takes the same value ε^0 for each molecule.

Now, we estimate the energy of intermolecular interactions $\sum \phi(r_{ij})$. We assume that a certain kind of ergodicity is satisfied for molecule movements, and also that a equilibrium distribution $\rho(x)$ of molecules exists. Hence, we can obtain the mean energy of intermolecular interaction which is independent of a molecule's positions as follows:

$$\begin{aligned} \sum_{i>j} \phi(r_{ij}) &= \sum_{i>j} \phi(|\bar{r}_i - \bar{r}_j|) \\ &= \iint d\bar{x} d\bar{y} \sum_{i>j} \phi(|\bar{x} - \bar{y}|) \delta(\bar{x} - \bar{r}_i) \delta(\bar{y} - \bar{r}_j) \\ &= \iint d\bar{x} d\bar{y} \phi(|\bar{x} - \bar{y}|) \sum_{i>j} \{ \delta(\bar{x} - \bar{r}_i) \delta(\bar{y} - \bar{r}_j) \} \\ &= \frac{1}{2} \iint d\bar{x} d\bar{y} \phi(|\bar{x} - \bar{y}|) \left\{ \sum_i \delta(\bar{x} - \bar{r}_i) \sum_j \delta(\bar{y} - \bar{r}_j) - \sum_i \delta(\bar{x} - \bar{r}_i) \delta(\bar{y} - \bar{r}_i) \right\} \\ &\equiv \frac{1}{2} \iint d\bar{x} d\bar{y} \phi(|\bar{x} - \bar{y}|) \rho(\bar{x}) \rho^*(\bar{y}) \\ &\approx \frac{1}{2} \iint d\bar{x} d\bar{y} \phi(|\bar{x} - \bar{y}|) \rho(\bar{x}) \rho(\bar{y}) \end{aligned} \quad (3.16)$$

where $\delta(\cdots)$ denotes Dirac's delta function, $\rho(\cdots)$ means the density distribution of molecules, and ρ^* signifies the conditional density distribution with the correction by summing up the pairs. The procedure to use the delta-measures, which converges at some kind of distribu-

tion density, follows chaos study²² and random matrix theory²³. Using the above estimation for the energy of intermolecular interactions, we can remove the energy of intermolecular interactions independently from the phase space integration. Then we obtain the following approximation of $\Omega(T, V)$, namely,

$$\begin{aligned}\Omega(T, V) &\approx \frac{1}{N!} \exp \left(-\frac{N\epsilon^0}{k_B T} \right) \int \cdots \int dx_1 dy_1 dz_1 \cdots dx_N dy_N dz_N \\ &\quad \times \exp \left\{ -\frac{1}{2k_B T} \iint d\bar{x} d\bar{y} \phi(|\bar{x} - \bar{y}|) \rho(\bar{x}) \rho(\bar{y}) \right\} \\ &= \frac{(V - Nv)^N}{N!} \exp \left(-\frac{N\epsilon^0}{k_B T} \right) \exp \left\{ -\frac{1}{2k_B T} \iint d\bar{x} d\bar{y} \phi(|\bar{x} - \bar{y}|) \rho(\bar{x}) \rho(\bar{y}) \right\} \quad (3.17)\end{aligned}$$

where V denotes the total volume of the system and v equates to the effective volume giving rise so that every molecule can approach closely to other molecules within a certain distance.

We, therefore, make a further assumption about uniform density distribution for molecules, namely,

$$\rho(x) = \rho(y) = \frac{N}{V} \quad (3.18)$$

the following calculations are performed by using not only coordinates with transformation of shift and those from Descartesian to polar one, but also the approximate form of intermolecular interaction (3.13).

$$\begin{aligned}\Omega(T, V) &\approx \frac{(V - Nv)^N}{N!} \exp \left(-\frac{N\epsilon^0}{k_B T} \right) \exp \left\{ -\frac{1}{2k_B T} \cdot \frac{N^2}{V^2} \iint d\bar{x} d\bar{y} \phi(|\bar{x} - \bar{y}|) \right\} \\ &= \frac{(V - Nv)^N}{N!} \exp \left(-\frac{N\epsilon^0}{k_B T} \right) \exp \left\{ -\frac{1}{2k_B T} \frac{N^2}{V} \int 4\pi r^2 \phi(r) dr \right\} \\ &= \frac{(V - Nv)^N}{N!} \exp \left(-\frac{N\epsilon^0}{k_B T} \right) \exp \left\{ -\frac{1}{2k_B T} \frac{N^2}{V} \int 4\pi r^2 f(r) \mu^2 dr \right\} \\ &= \frac{(V - Nv)^N}{N!} \exp \left\{ \frac{N^2 U_0 \mu^2 - 2VN\epsilon^0}{2k_B TV} \right\} \quad (3.19)\end{aligned}$$

where U_0 is defined as the following integration,

$$U_0 = - \int 4\pi r^2 f(r) dr. \quad (3.20)$$

The reason for a negative definition is to express the fact that the energy of intermolecular interaction is negative. The result (3.19) yields the following approximation of partition function Z for the system considered.

$$Z \cong \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \frac{(V - Nv)^N}{N!} \exp \left\{ \frac{N^2 U_0 \mu^2 - 2N\epsilon^0 V}{2k_B TV} \right\} \quad (3.21)$$

Using the thermodynamical relationship between the free energy of a system and partition function^{3,4}, we obtain Helmholtz's free energy F , i.e.,

$$\begin{aligned}
 F &= -k_B T \ln Z \\
 &\approx -k_B T \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \frac{(V - Nv)^N}{N!} \exp \left\{ \frac{N^2 U_0 \mu^2 - 2N\epsilon^0 V}{2k_B T V} \right\} \right] \\
 &= -k_B T \left[\frac{3N}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \{N \ln (V - Nv) - \ln N!\} + \frac{N^2 U_0 \mu^2 - 2N\epsilon^0 V}{2k_B T V} \right] \quad (3.22)
 \end{aligned}$$

We therefore give the van der Waals equation of state by use of the thermodynamical relationship²¹ $p = -(\partial F / \partial V)_T$ by applying the free energy in (3.22), i.e.,

$$\begin{aligned}
 p &= - \left(\frac{\partial F}{\partial V} \right)_T = k_B T \left[\frac{N}{V - Nv} - \frac{N^2 U_0 \mu^2}{2k_B T V^2} \right] \\
 &= \frac{nRT}{V - nN_A v} - \frac{(nN_A)^2 U_0 \mu^2}{2V^2} \quad (3.23)
 \end{aligned}$$

where P denotes the pressure of the system, $R = k_B N_A$ the gas constant, $n = N/N_A$ the molar number, respectively. As seen in the above derivation of van der Waals equation of state, we know that the van der Waals equation of state describes the mean field interaction for uniformly distributed molecules.

3.3 Critical Temperature and Boiling Temperature

Critical Temperature

The relationship between critical temperature and the energy of intermolecular interactions is obtained by applying the critical condition²¹ to the van der Waals equation of state (3.23). The critical condition of the equation of state is given by the following two partial derivatives with respect to volume V , namely,

$$\left(\frac{\partial P}{\partial V} \right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0 \quad (3.24)$$

After some calculations, critical temperature T_c , critical pressure P_c and critical volume V_c are obtained as follows:

$$T_c = \frac{4N_A U_0}{27Rv} \mu^2 \quad (3.25)$$

$$p_c = \frac{U_0}{54v^2} \mu^2 \quad (3.26)$$

$$V_c = 3nN_A v \quad (3.27)$$

As seen from eq. (3.25), it is obvious that critical temperature depends on the square value of the permanent dipole moment μ . But this does not mean that critical temperatures in a group of molecule types fit on a parabolic curve with respect to total dipole moment. We also see

that the eq. (3.25) becomes zero when dipole moment approaches zero. This is different from the evidence shown in §2. This difference is discussed in the next section and will be explained in the correction of higher order terms as an approximation for intermolecular interaction.

Boiling Temperature

The relationship between boiling temperature and the energy of molecular interaction is obtained by applying Maxwell's criterion²¹ on phase transition to the above equation of state (3.23). Maxwell's criterion on phase transition for the equation of state is illustrated in Fig. 8. Maxwell's criterion becomes the following integral relation, i.e.,

$$\int_{V_l}^{V_m} (P_a - P) dV = \int_{V_m}^{V_g} (P - P_a) dV \quad (3.28)$$

where P_a is a given pressure, V_l the volume of the liquid phase, V_g the volume of gas phase, V_m the volume at the middle point crossing the flat line P_a , which is not realized. The resulting boiling temperature is as follows:

$$T_b = \frac{\left(1 - \frac{V_l}{V_g}\right)}{nR \log \frac{V_g - nN_A v}{V_l - nN_A v}} \left\{ P_a + \frac{(nN_A)^2 U_0 \mu^2}{2V_l} \right\}. \quad (3.29)$$

As seen from eq. (3.29), the boiling temperature also depends on the square value of total dipole moment, μ^2 . It is expected that the volume of liquid state V_l is proportional to the effective volume v . If we take the relationship between V_l and v , written as $V_l = \sigma(nN_A v)$ with a certain type of proportional constant σ , and the ratio of volume of gas state over that of liquid state expressed by

$\eta = V_g/V_l$, then we can rewrite eq. (3.29) as follows:

$$T_b = \frac{\left(1 - \frac{1}{\eta}\right)}{\log \left[\frac{\eta\sigma - 1}{\sigma - 1} \right]} \left\{ \frac{P_a V_g}{nR} + \frac{N_A U_0 \mu^2}{2R\sigma v} \right\}. \quad (3.30)$$

The eq. (3.30) for boiling temperature T_b takes non-zero values at the zero dipole moment. The rewritten equation (3.30) is much easier than eq. (3.29) for comparing the relationship between boiling temperature and dipole moment with that between critical temperature and dipole moment. The term $P_a V_g/nR$ in eq. (3.30) signifies the temperature for ideal gas with volume V_g and pressure P_a .

4. Discussion

It is usual to expect that boiling and critical temperatures are governed by microscopic

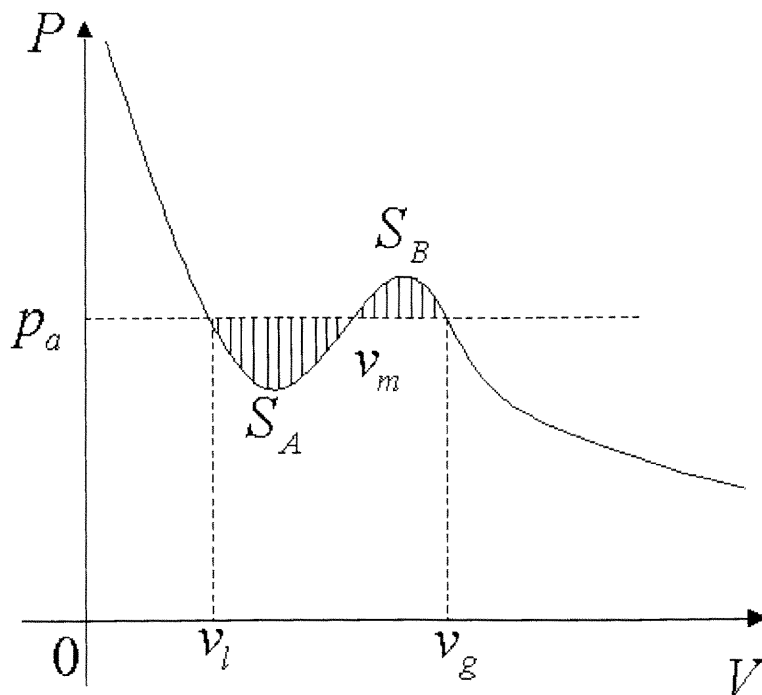


Fig. 8 Schematic Illustration of P-V Diagram.

A boiling temperature is obtained if the P-V diagram satisfies Maxwell's criterion, which means the occurrence of phase transition at the line given by the condition where areas S_A and S_B are equal, namely, $S_A = S_B$.

intermolecular interactions. As already recognized, the dominant interaction of electrically neutral molecules is the dipole-dipole type^{1,2}. This expectation does not imply that any molecular types lie on a curve with respect to electric dipole moment, as mentioned in the previous section. As seen in eqs. (3.25) and (3.30), they have the parameters U_0 and v , which are peculiar to molecular types. These equations include the parameters as a ratio U_0/v . Hence, the condition to realize the evidence that boiling and critical temperatures fit on respective parabolas with respect to the total dipole moment is that a group of molecule types has the same ratio value U_0/v . The parameter U_0 is the integration of $f(r)$ as shown in eq. (3.20). If the function $f(r)$ is the constant f_0 , then U_0 will be given as $U_0 = -f_0(4\pi r^3/3)$, which is a sphere volume multiplied by the constant $-f_0$. We interpret the parameter U_0 as the configuration integration over the space where another dipole is included. In actual molecule systems, every dipole takes an arbitrary orientation in the space so that the interaction energy changes with the orientation of each dipole. If we select any pair of interacting two dipoles, the pairs take different orientations. The function $f(r)$ implies that the effect of different orientations projects an effective value or an averaged value when any pair of dipoles takes the distance r . Therefore, ratio U_0/v means the value of distortion effect by dipole-dipole in-

interaction compared with the effective volume by packing of the non-interacting molecules.

We consider that the theoretical critical temperature has the difficulty of recording a zero temperature at the zero dipole moment. The evidence shown in section 2 requires a finite temperature at the zero dipole moment. We avoid this difficulty by taking into account higher order terms of intermolecular interaction energies in the approximation. We express the higher order terms of intermolecular interactions than dipole-dipole interaction as $g(r)\epsilon^*$ in the polar coordinates and multiplied form of polar distance function and another electric factor ϵ^* , so that the potential of intermolecular interaction between two molecules is given by the following expression in the polar coordinates, i.e.,

$$\phi(r) = g(r)\epsilon^* + f(r)\mu^2 \quad (4.1)$$

Then the equation of state is as follows:

$$P = \frac{nRT}{(V - nN_A v)} - \frac{(nN_A)^2 \{G_0\epsilon^* + U_0\mu^2\}}{2V^2} \quad (4.2)$$

where G_0 is defined by the following integration for $g(r)$, i.e.,

$$G_0 = - \int 4\pi r^2 g(r) dr. \quad (4.3)$$

The reason for a negative definition is that interaction potential between molecules takes a certain negative value in the equilibrium. By applying critical condition (3.24) to eq. (4.2), a modified critical temperature and critical pressure are obtained while the critical volume is unchanged, namely,

$$T_c = \frac{4N_A G_0}{27Rv} \epsilon^* + \frac{4N_A U_0}{27Rv} \mu^2, \quad (4.4)$$

$$P_c = \frac{G_0}{54v^2} \epsilon^* + \frac{U_0}{54v^2} \mu^2, \quad (4.5)$$

$$V_c = 3nN_A v. \quad (4.6)$$

Therefore, it is apparent in eq. (4.4) that $(4N_A G_0/27Rv)\epsilon^*$ is the temperature at zero dipole moment and $(4N_A U_0/27Rv)$ is the gradient of a straight line in the plot of temperature versus square value of dipole moment. In Fig. 5, we can obtain the ratio $(G_0/U_0)\epsilon^*$ which is $(4N_A G_0/27Rv)\epsilon^*$ divided by $(4N_A U_0/27Rv)$, namely, 2.32 [a.u.] for group A and 1.89 [a.u.] for group B.

This correction of the energy of intermolecular interaction also causes the modification of the expression for boiling temperature. The result is as follows:

$$T_b = \frac{\left(1 - \frac{1}{\eta}\right)}{\log \left[\frac{\eta\sigma - 1}{\sigma - 1} \right]} \left\{ \frac{P_a V_g}{nR} + \frac{G_0 \varepsilon^* + N_A U_0 \mu^2}{2R\sigma v} \right\}. \quad (4.7)$$

This result can explain the fact that two different parabolas exist, because $P_a V_g / nR$ is independent from the molecular types while the term $G_0 \varepsilon^* / (2R\sigma v)$ depends on the molecular types. The evidence presented in this paper lets us assert that the ratio $G_0 \varepsilon^* / \sigma v$ takes the same value in the same group. This implies some particularity of CFC molecules.

Finally, we discuss the necessity to modify the van der Waals equation of state (3.23) or (4.2). Ratio $P_c V_c / T_c$ appears in the Table I. The ratio $P_c V_c / T_c$ given by eqs. (3.23) or (4.2) is the same value $(3/8)nR$ since gases satisfy the equation of state for ideal gas, i.e., $P_c V_c = (3/8)nRT_c$. The values in Table I are for one-molar gases. If the CFC gases satisfy the van der Waals equation of state, the ratio $P_c V_c / T_c$ is $3/8R = 30.8[\text{atm} \cdot \text{cm}^3 / \text{mol} \cdot \text{K}]$ for one-molar gases. This value is roughly 50% greater than that obtained from experimental values. The actual value of ratio $P_c V_c / T_c$ is $22.15[\text{atm} \cdot \text{cm}^3 / \text{mol} \cdot \text{K}]$ averaged over the Table I values.

There are a number of equation of state types^{24,25}. But these equations of state do not give a simple equation for critical temperature. We therefore use the modified van der Waals equation of state, which has a fractional power for volume because it provides a simple form of the expression for the critical temperature.

For this purpose, we consider the term given by eq. (3.16), i.e.,

$$\iint d\bar{x} d\bar{y} \phi(|\bar{x} - \bar{y}|) \rho(\bar{x}) \rho(\bar{y}) \quad (4.8)$$

where we omit the constant 1/2 for simplicity. In eq. (4.8), the transformation of coordinates gives the volume factor V . Then the uniform density for distribution of molecules gives the factor N^2/V . It may be that the molecular distribution depends on intermolecule interactions. We can therefore expect that the density of molecular distribution to be lower than uniform case. We take this expectation for a volume with a fractional factor of power. In this situation, we assume that eq. (4.8) can be rewritten in the following form of polar coordinates, namely,

$$\iint d\bar{x} d\bar{y} \phi(|\bar{x} - \bar{y}|) \rho(\bar{x}) \rho(\bar{y}) = \lambda \frac{N^2}{V^{1+\gamma}} \int 4\pi r^2 \phi(r) dr, \quad (4.9)$$

where λ is a constant to adjust the dimension of physical quantities caused by the introduction of the fractional factor γ for the volume. This modification yields the following equation of state, i.e.,

$$P = \frac{nRT}{V - nN_A v} - \lambda (nN_A)^2 \frac{G_0 \varepsilon^* + U_0 \mu^2}{2V^{2-\gamma}} \quad (4.10)$$

where we use eq. (4.1) for $\phi(r)$ joining with definitions (4.2) and (3.20). By applying the critical condition (3.24) to the above equation of state (4.10), we can obtain the expressions for critical temperature, critical pressure, and critical volume, namely,

$$T_c = \frac{2 \frac{2+\gamma}{(1+\gamma)^2} \lambda (G_0 \varepsilon^* + U_0 \mu^2)}{R \left(\frac{2+\gamma}{1+\gamma} \right)^{3-\gamma} (N_A v)^{2-\gamma}}, \quad (4.11)$$

$$P_c = \frac{\frac{1-\gamma}{1+\gamma} \lambda}{2 \left(\frac{3+\gamma}{1+\gamma} \right)^{3-\gamma}} \frac{(G_0 \varepsilon^* + U_0 \mu^2)}{(N_A v)^{1-\gamma}}, \quad (4.12)$$

$$V_c = \frac{3+\gamma}{1+\gamma} (n N_A v). \quad (4.13)$$

For these critical expressions, the ratio $P_c V_c / T_c$ is given as,

$$\frac{P_c V_c}{T_c} = \frac{(1-\gamma)(3+\gamma)}{4(2+\gamma)} nR. \quad (4.14)$$

As seen from eq. (4.14), the ratio $P_c V_c / T_c$ changes with the value of γ . At $\gamma = 1/4$, ratio $P_c V_c / T_c$ takes the value 22.22[atm·cm³/mol·K] for one-molar gases. This value is very close to the experimental average 22.15[atm·cm³/mol·K]. This leaves us the fine value 1/4, whose meaning remains unknown at present.

References

1. H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces*, (Pergamon Press, Oxford, London, 1969).
2. J. Mahanty and B. W. Ninham, *Dispersion Forces*, (Academic Press, London, 1976).
3. D. ter Haar, *Elements of Statistical Mechanics*, (Constable & Co., London, 1954).
4. T. L. Hill, *Statistical Mechanics*, (McGraw-Hill, New York, 1956).
5. MOPAC, *Quantum Chemistry Program Exchange*, No. 455 (1983).
6. N. Itsutake, *Retrieval of Substituting Substances for Fluorocarbons*, (in Japanese, Kogyo-chosakai, 1989 1st and 1991 2nd).
7. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed. (McGraw-Hill, New York, 1987, 1990).
8. *Handbook of Chemistry*, foundation volume, (in Japanese,).
9. I. N. Levine, *Physical Chemistry*, (McGraw-Hill Book Co., New York, 1988).
10. D. R. Lide, ed., *CRC Handbook of Chemistry and Physics*, 71st ed., (CRC Press: Boca Ration, FL, 1990).
11. R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids* 3rd ed., (McGraw-Hill, New York, 1977).
12. R. C. Weast, ed., *Handbook of Chemistry and Physics*, 71st ed., (CRC Press, Ohio, 1991).
13. Y. Shibagaki, H. Orimo, M. Fukushima, and N. Itsutake, *Estimation of fundamental properties of Chlorofluorocarbons* (in Japanese), J. Chem. Industry, **12**, No5, 542 (1986).
14. K. M. Kleinczewicz and R. C. Reid, *Estimation of Critical Properties with Group Contribution Method*, AIChE J., **30**(1), 137, (1984).
15. H. H. Anderson, J. Chem. Eng. Data., **10**(2), 156, 10(4), 179, (1965).
16. M. D. Palmieri, J. Chem. Educ. **10**, A254, (1988).
17. J. S. Murray, P. Lane, T. Brinck, K. Paulsen, M. Edward Grice, and P. Politzer, J. Phys. Chem., **97**, 9369–

- 9373, (1993).
18. S. J. Grigorias, *Compt. Chem.*, **11**, 493, (1990).
 19. A. A. Radzig and B. M. Smirbov, *Chem. Phys.*, **31**, 444, (1985).
 20. N. A. Kamka, K. Mori, and R. Itoh, *Bull. Sci. Eng. Res. Lab. Waswda Univ.* **134**, 12, (1991).
 21. I. Prigogine and R. Defay, (trans. by D. H. Everett), *Chemical Thermodynamics*, Chaps.11 and 16, (Longmans Green and Co., London 1954).
 22. H. G. Schuster, *Deterministic Chaos*, 2nd ed., pp. 28–31, (VCH, Weinheim, 1989).
 23. M. L. Metha, *Random Matrices*, 2nd ed., Chap. 4, pp. 70–78, (Academic Press Sam. Diego, London, 1991).
 24. D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.*, **15**, 59, (1976).
 25. G. Soave, *Chem. Eng. Sci.*, **27**, 1197, (1972).