액체혼합물의 활동도계수의 이론적 계산

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Theoretical Calculation of Activity Coefficients of Liquid Mixtures

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요 약. 액체이론(Significant Structure Theory)를 단원자 분자로부터 다원자 분자에 이르는 여러 액체혼합물에 적용하여 전 농도 범위에서 액체 혼합물의 활동도 계수를 계산했다.

단원자 분자계(Ar-Kr, Kr-Xe)와 이원자 분자계(Ar-O₂, N₂-CO)와 메탄-크립톤계의 액체혼합물의 활동도 계수는 δE_s 수정 변수에 의해 좋은 결과를 얻었다. 아르곤-질소, 산소-질소, 그리고 메탄-프로판계에 대해서는 이 외에 δV, δn 수정 변수가 더 필요했다.

ABSTRACT. Significant structure theory was applied to some liquid mixture systems ranging from simple monatomic molecule systems to polyatomic molecule systems, and the activity coefficients γ of the liquid mixture systems were calculated over whole mole fractions using the following thermodynamic relation

$$RT\ln\gamma_i = \left(\frac{\partial A^E}{\partial N_i}\right)_{T,V,N_j}$$

where A^E represents the excess Helmholtz free energy, and N_i is the number of molecules of component i. The activity cofficients of the solutions such as monatomic molecule systems (Ar-Kr, Kr-Xe) and diatomic molecule systems (Ar-O₂, N₂-CO) and CH₄-Kr systems whose components have similar shapes for intermolecular potential curves were calculated successfully only with the δE_s correction parameter for energy E_s for mixture systems. For other systems such as Ar-N₂, O₂-N₂ and CH₄-C₃H₈ whose components have dissimilar intermolecular potential curve shapes an additional correction parameters δV and even one more paramelar δn were necessary [see Eqs. (10)~(12)].

1. INTRODUCTION

Since the Raoult theory is for an ideal liquid solution, it is customary to use it as a reference, and to express the observed behavior of real solutions as deviations from the ideal case. One

of the aims of solution theory is to predict numerical values of activity coefficients in terms of the properties which have molecular significance and which may be calculated from the properties of the pure components. Among many workable theories for liquid solutions, the significant structure theory[1,2] is one of them.

In this paper, we calculate the activity coefficients of some liquid mixtures over whole mole fractions using the significant structure theory. Some liquid mixture systems ranging from simple monatomic molecule systems to polyatomic molecule systems were studied.

2. THEORY

(1) Partition Function for a Pure Liquid.

According to significant structure theory, the partition function f of a pure liquid is written as

$$f = (f_{solid} f_{deg})^{N/X} (f_{gas})^{N(1-\frac{1}{X})} / [N(1-\frac{1}{X})]! \tag{1}$$

Here $X = V/V_s$, where V_s is the molal volume of the solid at the melting point and V is the liquid molal volume. Here f_{solid} and f_{gas} are, respectively, the partition functions of the solid-like and gas-like structures, and f_{deg} is the positional degeneracy of a solid-like molecule. N is Avogadro's number and the factorial term is due to the indistinguishability of the gas-like molecules.

For monatomic molecules such as argon, krypton and xenon which have no internal degrees of freedom, the partition function is written as;

$$f = \left[\frac{e^{E_s/RT}}{(1-e^{-\theta/T})^3} \left\{ 1+n(X-1)e^{\frac{-aE_s}{(X-1)RT}} \right\} \right]^{N/X}$$
$$\cdot \left[\frac{(2\pi m kT)^{\frac{3}{2}}}{h^3} \frac{eV}{N} \right]^{N(1-\frac{1}{X})} \tag{2}$$

For diatomic molecules such as oxygen and carbon monoxide, the solid-like molecules are

assumed to rotate freely.[3,4] Therefore, the free rotational term is included in both gas-like and solid-like parts of the partition function.

The partition function for liquids of diatomic molecules is written as;

$$f = \left[\frac{e^{E_s/RT}}{(1-e^{-\theta/T})^3} \cdot \frac{8\pi^2 I kT}{\sigma h^2} \frac{1}{1-e^{-h\nu/kT}} \right.$$
$$\left. \{1+n(X-1)e^{-\frac{aE_s}{(X-1)RT}} \} \right]^{N/X} \cdot \left[\frac{(2\pi m kT)^{\frac{3}{2}}}{h^3} \right.$$
$$\left. \frac{eV}{N} \frac{8\pi^2 I kT}{\sigma h^2} \frac{1}{1-e^{-h\nu/kT}} \right]^{N(1-\frac{1}{X})} \tag{3}$$

Especially for oxygen, the rotational term with a triplet ground state is used in the above partition function,

$$f_{O_2}^{rot} = \frac{3 \cdot (8\pi^2 I kT)}{2h^2} \tag{4}$$

For methane, a hindered rotational partition function is used for the solid-like molecule. McLaughlin and Eyring[5] introduced an approximate hindered rotational partition function, f_{HR} which is as follows:

$$f_{HR} = f_{vib}' + \exp\left(-\frac{BV_s}{(V-V_{so})RT}\right)(f_{rot} - f_{vib}') \tag{5}$$

where f_{rot} is a free rotational partition function and f_{vib}' is the restricted vibrational partition function which is approximated as unity. V_{so} is the solid volume at which a free rotation starts, and the constant B divided by the number of vacancies is taken as the barrier height. Thus the partition function for liquid methane is written as;

$$f_{CH_4} = \left[\frac{e^{E_s/RT}}{(1-e^{-\theta/T})^3} \left\{ 1+\exp\left(\frac{-BV_s}{(V-V_{so})RT}\right) \right. \right.$$
$$\left. \left(\frac{8\pi^2(8\pi^3 I^3)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{12h^3} - 1 \right) \right\} \prod_{i=1}^{9} \frac{1}{1-e^{-h\nu_i/kT}}$$
$$\left. (1+n(X-1)e^{-\frac{aE_s}{(X-1)RT}}) \right]^{N/X} \left[\frac{(2\pi m kT)^{\frac{3}{2}}}{h^3} \right.$$
$$\frac{eV}{N} \frac{8\pi^2(8\pi^3 I^3)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{12h^3}$$
$$\left. \prod_{i=1}^{9} \frac{1}{1-e^{-h\nu_i/kT}} \right]^{N(1-\frac{1}{X})} \tag{6}$$

For a rather long propane molecule which has abnormal entropy of fusion (9.854 e. u.)[6] and shows no transition in the solid state, it is assumed that a propane molecule does not rotate in solid phase. Thus, the rotational term appears only in the gas part of the partition function and a six-degree Einstein oscillator term appears in the solid part. The partition function for liquid propane is then

$$f_{C_3H_8} = \left[\frac{e^{E_s/RT}}{(1-e^{-\theta/T})^6} \left\{ 1+n(X-1)e^{-\frac{aE_s}{(X-1)RT}} \right\} \right.$$

$$\left. \prod_{i=1}^{27} \frac{1}{1-e^{-h\nu_i/kT}} \right]^{N/X} \left[\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \right.$$

$$\frac{eV}{N} \frac{8\pi^2(8\pi^3 I_A I_B I_C)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{2h^3}$$

$$\left. \prod_{i=1}^{27} \frac{1}{1-e^{-h\nu_i/kT}} \right]^{N(1-\frac{1}{X})} \qquad (7)$$

In the above equations, E_s, θ and V_s are the heat of sublimation of the solid, the Einstein characteristic temperature, and the molar volume of the solid at the melting point; a and n are dimensionless proportionality constant; I_A, I_B, and I_C are the principal moments of inertia of propane; I is the moment of inertia of the diatomic molecules and σ is the symmetry number of the molecules; ν_i is the ith mode of the internal molecular vibrational frequenies; m is the molecular mass; N is Avogadro's number.

(2) Partition Function for a Binary Mixture. Significant structure theory has been successively applied to evaluate the properties of binary mixtures[7~9] assuming the following: (a) non-random mixing may be neglected, (b) the same characteristic temperatures of vibration, θ, are retained for mixtures that were used for a pure component, (c) molecules of both components continue to possess their gaslike translational degrees of freedom, (d) the degeneracy term has the same form as for a pure liquid, (e) the parameters E_s, V_s, n, and a may be taken as suitable averages of the parameters for the pure components. Then,

the partition function of a mixture is

$$f_{mixture} = \frac{(N_1+N_2)!}{N_1!N_2!} [f_{s1}^{N_1} f_{s2}^{N_2}]^{\frac{1}{X}}$$
$$\cdot [f_{deg} \cdot e^{E_s/RT}]^{N/X} \cdot [f_{g1}^{N_1} f_{g2}^{N_2}]^{(1-\frac{1}{X})} \qquad (8)$$

N_1 and N_2 are the number of molecules of the respective species, and $N_1+N_2=N$, where N is Avogadro's number. f_{s_i} is the partition function of a solid-like molecule and f_{g_i} is that of a gas-like molecule of component i ($i=1$ or 2). f_g involves the factorial term in Eq. (1).

It is assumed that all internal degrees of freedom such as rotational and vibrational terms are the same for the pure liquid and for the solution. Besides, the following V_{so} expression in the hindered rotational partition function for the mixture is assumed:

$$V_{so} = V^1_{so}X_1 + V^2_{so}X_2 \qquad (9)$$

where V^1_{so} and V^2_{so} are the solid volumes of component "1" and "2" at which free rotation starts, and X_1 and X_2 are the mole fraction of component "1" and "2", respectively. But, the proportionality constant B is assumed to be retained for mixtures as that was used for the pure component. The parameters appeared in Eq. (8) are averages of those of pure components and are given as follows:

$$E_s = X_1^2 E_{s1} + X_2^2 E_{s2} + 2(1+\delta E_s)X_1X_2\sqrt{E_{s1}E_{s2}} \qquad (10)$$

$$V_s = X_1 V_{s1} + X_2 V_{s2} + X_1 X_2 \delta V\sqrt{V_{s1}V_{s2}} \qquad (11)$$

$$n = X_1 n_1 + X_2 n_2 + X_1 X_2 \delta n\sqrt{n_1 n_2} \qquad (12)$$

$$a = X_1 a_1 + X_2 a_2 \qquad (13)$$

The quantities δE_s, δV, and δn are correction parameters used in the cross-terms including the higher order concentration dependence.

(3) Activity Coefficient of the Liquid Mixture. Activity coefficient γ_1 of the liquid mixture is calculated using the following thermodynamic relation:

$$RT\ln\gamma_1=\left(\frac{\partial A^E}{\partial N_1}\right)_{T,V,N_2} \quad (14)$$

where,

$$A^E=A-A(\text{ideal})=A-$$
$$\{X_1A_1{}^\circ+X_2A_2{}^\circ+RT(X_1\ln X_1+X_2\ln X_2)\} \quad (15)$$

the superscript "o" indicating pure state.

Therefore, having derived the partition functions which adequately describe pure liquids and a mixture, the activity coefficient of the liquid mixture can be obtained since $A=-kT\ln f$. By a thermodynamics relation, [10] Eq. (14) is expressed as follows:

$$RT\ln\gamma_1=A^E-X_2\left(\frac{\partial A^E}{\partial X_2}\right)_{T,P} \quad (16)$$

Substituting Eq. (15) into (16) and using the relation $A=-kT\ln f_{\text{mix}}$ where f_{mix} is given by Eq. (8), the following equation is derived:

$$RT\ln\gamma_1=A-A_1{}^\circ-RT\ln(1-X_2)+kT\cdot X_2\cdot N$$
$$\left[\ln(X_1/X_2)+\frac{1}{V}\left(\frac{\partial V_s}{\partial X_2}\right)_{T,V}(X_1\ln f_{s1}+X_2\ln f_{s2})\right.$$
$$+\ln f_{\text{deg}}+E_s/RT-X_1\ln f_{g1}-X_2\ln f_{g2})$$
$$+(V_s/V)\left\{-\ln f_{s1}+\ln f_{s2}+\left(\frac{\partial\ln f_{\text{deg}}}{\partial X_2}\right)_{T,V}\right.$$
$$+(1/RT)\left(\frac{\partial E_s}{\partial X_2}\right)_{T,V}+\ln f_{g1}-\ln f_{g2}\right\}$$
$$\left.+\ln f_{g2}-\ln f_{g1}\right] \quad (17)$$

where,

$$\left(\frac{\partial\ln f_{\text{deg}}}{\partial X_2}\right)_{T,V}=\exp\left(-\frac{aE_sV_s}{(V-V_s)RT}\right)$$
$$\overline{f_{\text{deg}}}$$
$$\left[\left(\frac{\partial n}{\partial X_2}\right)_{T,V}\frac{(V-V_s)}{V_s}-n\frac{V}{V_s}\left(\frac{\partial V_s}{\partial X_2}\right)_{T,V}\right.$$
$$-\frac{naE_s}{RT}\left\{\frac{1}{a}\left(\frac{\partial a}{\partial X_2}\right)_{T,V}+\frac{1}{E_s}\left(\frac{\partial E_s}{\partial X_2}\right)_{T,V}\right.$$
$$\left.\left.+\left(\frac{1}{V_s}+\frac{1}{V-V_s}\right)\left(\frac{\partial V_s}{\partial X_2}\right)_{T,V}\right]\right]$$

$$\left(\frac{\partial E_s}{\partial X_2}\right)_{T,V}=-2X_1E_{s1}+2\cdot X_2\cdot E_{s2}$$
$$+2(1-2X_2)(1+\delta E_s)\sqrt{E_{s1}E_{s2}}$$

$$\left(\frac{\partial V_s}{\partial X_2}\right)_{T,V}=V_{s2}-V_{s1}+(1-2X_2)\sqrt{V_{s1}V_{s2}\delta V}$$

$$\left(\frac{\partial n}{\partial X_2}\right)_{T,V}=n_2-n_1+(1-2X_2)\sqrt{n_1n_2\delta n}$$

$$\left(\frac{\partial a}{\partial X_2}\right)_{T,V}=a_2-a_1$$

If hindered rotational partition function is involved in the partition function of solid-like molecules, f_r depends on mole fraction. If so, $X_1(V_s/V)(\ln f_{s1}/X_2)_{T,V}$ is added to Eq. (17) for hindered rotation of component 1, where

$$\left(\frac{\partial\ln f_{s1}}{\partial X_2}\right)_{T,V}=\left(\frac{\partial\ln f_{H\cdot R}}{\partial X_2}\right)_{T,V}$$
$$=\frac{f^1{}_{\text{rot}}-1}{f^1{}_{HR}}\exp\left(\frac{-B_1V_s}{(V-V_{so})RT}\right)$$
$$\left\{-B_1(V-V_0)\left(\frac{\partial V_s}{\partial X_2}\right)_{T,V}\right.$$
$$\left.-B_1V_s(V_{so}{}^2-V_{so}{}^1)\right\}\bigg/\left\{(V-V_{so})^2RT\right\}$$

A similar correction term is added if necessary for component 2.

3. RESULTS AND DISCUSSION

(1) **Monatomic Molecule System.** Systems of simple monatomic molecule liquid mixtures, such as argon-krypton[11] and krypton-xenon[12] liquid mixtures were studied. These two systems are the only two-component rare-gas systems which can be studied over the whole range of mole fractions. In *Table* 1, the parametric values[2] and other input values for these systems are given, and the calculated results are given in *Fig.* 1 and 2. The results obtained in this study for these liquid mixture systems are quite satisfactory. Correction parameters δV and δn were not used. Only δE_s correction parameter was used. The calculated correction parameter δE_s is 0.0050 and 0.0076 for argon-krypton system and krypton-xenon system, respectively.
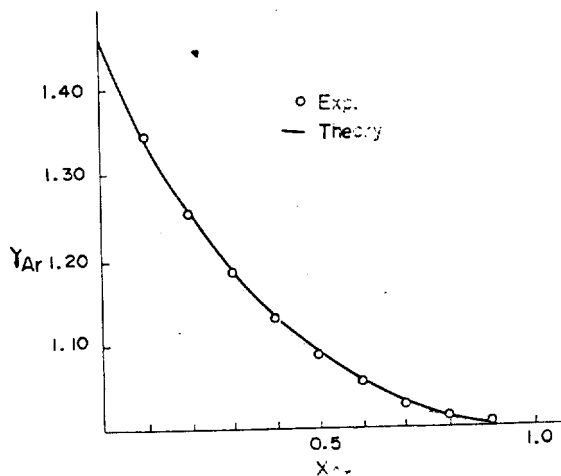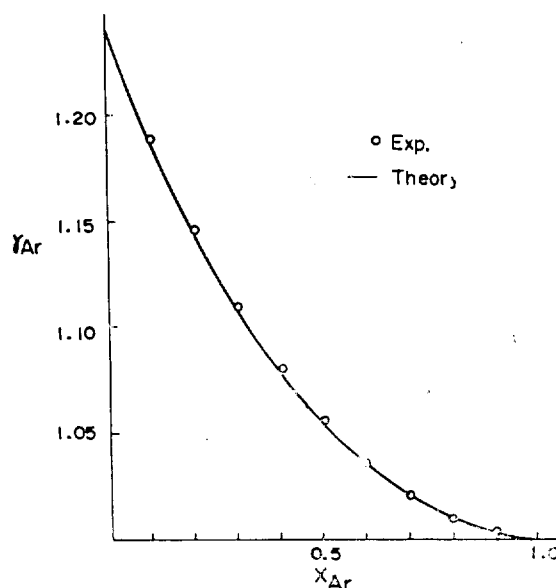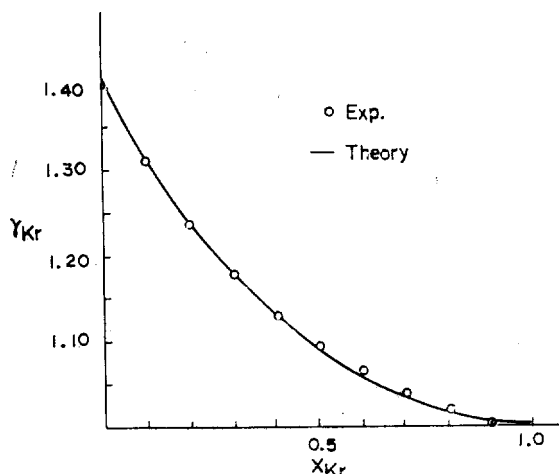
(2) **Diatemic Molecule System.** For liquid mixture systems such as argon-oxygen, nitrogen-carbon monoxide, argon-nitrogen, and nitrogen-oxygen[13] were studied. In *Table* 2, the parametric values[3,4] and other input values[2] for

Table 1. Parametric vallues and input values for argon, krypton, and xenon.

	Argon	Krypton	Xenon
E_s (cal/mole)	1888.6	2740	3898
V_s (cc/mole)	24.98	29.6	36.5
n	10.7	10.4	10.3
a	5.4×10^{-3}	7.96×10^{-3}	9.46×10^{-3}
$\theta(°K)$	60.0	45.0	39.2
m (g/molecule)	6.632×10^{-23}	1.391×10^{-22}	2.180×10^{-22}

Table 2. Parametric values and input values for nitrogen, oxygen and carbon monoxide.

	N_2	O_2	CO
E_s (cal/mole)	1530	1808	1477
V_s (cc/mole)	29.31	24.14	32.50
n	12.9	11.89	11.80
a	3.43×10^{-3}	5.89×10^{-3}	1.30×10^{-3}
$\theta(°K)$	55.94	56.02	59.62
I (g. cm^2)	13.94×10^{-40}	19.2×10^{-40}	14.318×10^{-40}
m (g/molecule)	4.652×10^{-23}	5.313×10^{-23}	4.651×10^{-23}
σ	2	2	1

Fig. 1. Activity coefficient of argon in the Ar-Kr system at 115.77°K. $E_s = 0.005$.

Fig. 2. Activity coefficient of kripton in the Kr-Xe system at 161.38°K. $E_s = 0.0076$.

Fig. 3. Activity coefficient of argon in the Ar-O$_2$ system at 83.82°K. $\delta E_s = -0.01$.

these systems are given. The calculated results are given in *Fig.* 3~6. For argon-oxygen and nitrogen-carbon monoxide system, correction parameters δE_s were calculated to be -0.010 and -0.014, respectively. However for argon-nitrogen and nitrogen-oxygen, not only E_s correction parameter but also δV correction parameter was necessary. For argon-nitrogen system $\delta E_s = -0.0053$, $\delta V = -0.0030$ and for oxygen-nitrogen system, $\delta E_s = -0.0049$ and $\delta V = 0.0007$.

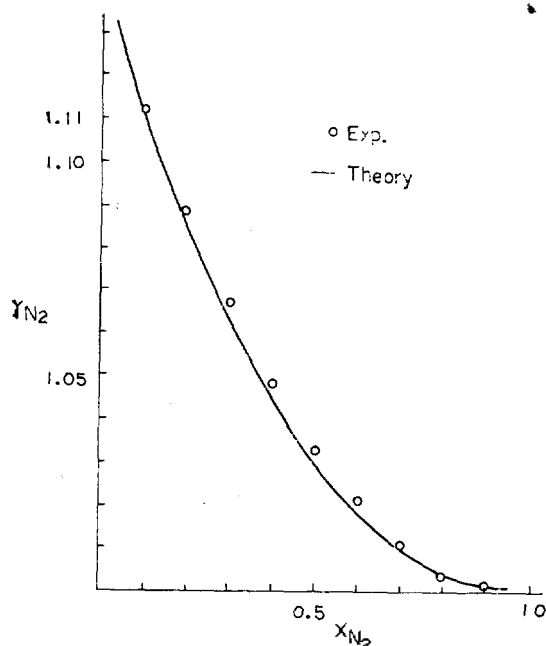**(3) Polyatomic Molecule System.** For polyatomic molecule system, methane-krypton[14] and

Fig. 4. Activity coefficient of nitrogen in the N_2-CO system at 83. 82°K. $\delta E_i = -0.014$.
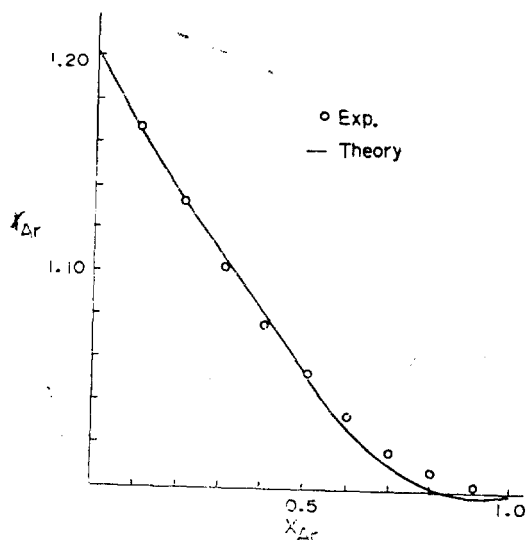

Fig. 5. Activity coefficient of argon in the Ar-N_2 system at 83. 82°K. $\delta E_i = -0.0053$, $\delta V = -0.0030$.

methane-propane[15] systems were studied. The parametric values of liquid propane were determined in this study by the Seoul Technique.[16]
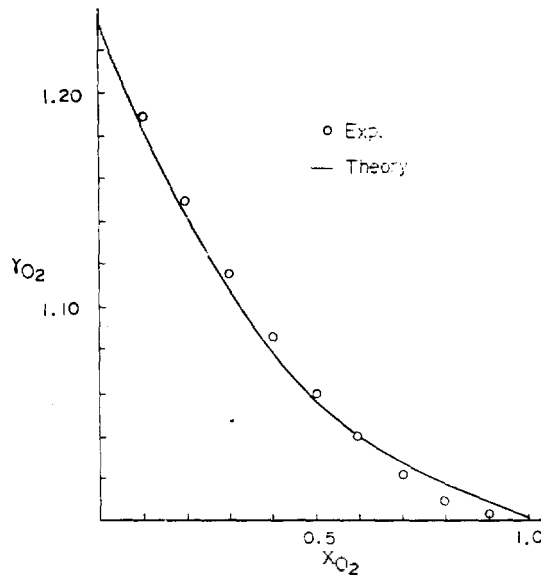

Fig. 6. Activity coefficient of oxygen in the O_2-N_2 system at 83. 82°K. $\delta E_i = -0.0049$, $\delta V = -0.0007$.

In *Table* 3 the parametric values[5] and other input values[6] are given. In determining the parameters of liquid propane, the parameteric value of n was found to be 24, which usually was taken to be 12 for ordinary liquids. The reason will be mentioned later.

The solid volume of propane at 77°K was found to be 57. 8cc/mole, and $V_s = 59.17$cc/mole seems to be acceptable. To check the validity of the obtained parameters of liquid propane, pressure, entropy, volume of liquid propane were calculated. These results are given in *Fig.* 7∼9. Due to the lack of experimental data of liquid propane[17∼19] and their inconsistency, exact comparison with experiments were difficult. But the agreement was sufficient to calculate the excess thermodynamic properties of liquid mixture system. The calculated activity coefficients for methane-krypton system and methane-propane system are given in *Fig.* 10 and 11. In methane-krypton system, only $\delta E_i = -0.0010$ gives good result over whole mole fractions. In methane-propane

Table 3. Parametric values and input values for methane and propane.

	Methane	Propane
E_s (cal/mole)	2. 200	5875
V_s (cc/mole)	31. 84	59. 16
n	10. 7	23. 97
a	5.2×10^{-3}	1.2×10^{-6}
θ (°K)	74. 63	46. 34
I_A (g·cm²)	5.47×10^{-40}	28.85×10^{-40}
I_B (g·cm²)	5.47×10^{-40}	99.12×10^{-40}
I_C (g·cm²)	5.47×10^{-40}	112.07×10^{-40}
m (g/molecule)	2.6636×10^{-23}	7.3215×10^{-23}
σ	12	2
B (cal/mole)	3. 38	
V_{so} (cc/mole)	30. 291	

Fig. 8. Entropy of liquid propane.

Fig. 9. Volume of liquid propane.

Fig. 7. Vapor pressure of liquid propane.

system whose components were much different from each other, δE_s, δV, and δn correction parameters were all necessary. $\delta E_s = 0.188$ for this system is large compared with those of ther liquid systems which are usually 0. 005 to 0. 015. This may be due to the large difference between the E_s / V_s values of each component. And in methane-propane system,
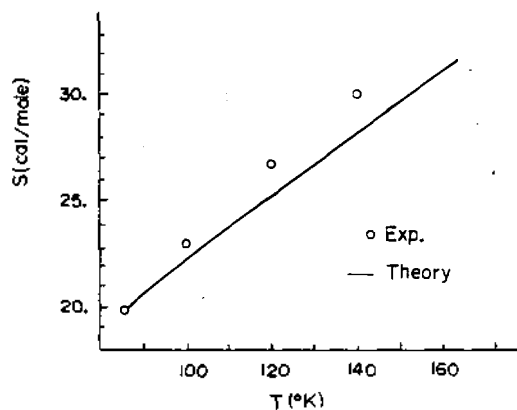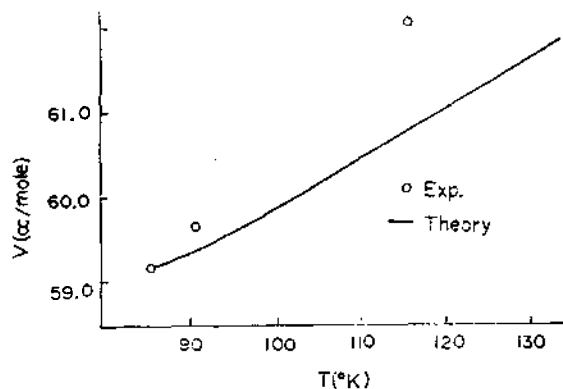
the calculation gives generally good result, but below mole fraction 0. 2 of methane, it gives rather a poor result.

The vibrational frequencies[6] for nitrogen, oxygen, carbon monoxide, methane, and propane are given in Table 4. The ν values were used for calculating each vibration partition function.

In the above, it was mentioned that the parametric value of $n(=23.97)$ is abnormally large. The reason is mentioned below.

The term n $(X-1)$ in the degeneracy factor f_{deg} [see Eq. (2)] is the number of holes around a solid-like molecule where a molecular size hole was assumed, and n is assumed to be nearly equal to Z, the coordination number. In the
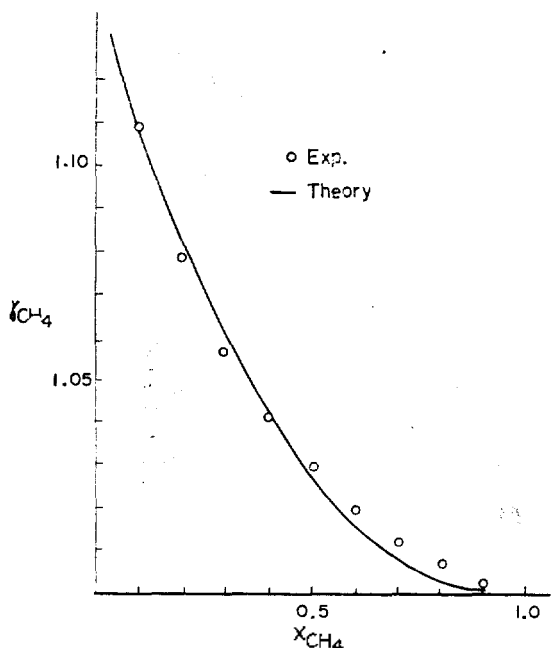
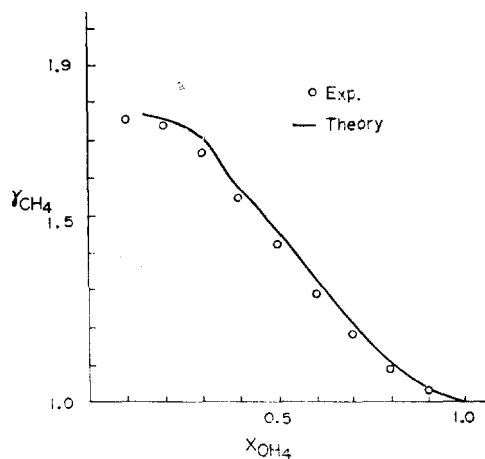*Fig.* 10. Activity coefficient of methane in the CH_4-Kr system at 115.77°K. $\delta E_s = -0.010$.

Fig. 11. Activity coefficient of methane in the CH_4-C_3H_8 system at 90.68°K. $\delta E_s = 0.1880$, $\delta V = -0.0007$, $\delta n = 0.1600$.

case of propane, the hole size is about $V_s/2$ rather than V_s. Then, the number of holes n_k around a solidlike molecules is given by

$$n_h = Z \frac{V - V_s}{V_s/2} = 2Z(X-1) = n(X-1)$$

Table 4. Vibrational frequencies of nitrogen, oxygen, carbon monoxide, metnane, and propane

	Vibrational frequencies (°K)
Nitrogen	976.66
Oxygen	2238
Carbon monoxide	3080.7
Methane	1876.6(3), 2186.0 (2), 4190, 4343(3)
Propane	539, 1248, 1514, 1661, 1352, 1326, 1076, 1924, 1695, 1970, 1977, 2085 (2), 2111, 2114, 2099, 1838, 4265, 4268 (2) 4271, 4285, 4256, 4190, 5231

where Z is 12 for hexagonal close packing, thus $n=24$. A propane molecule is long in shape. Thus, the hole will be a cylindrical shape rather than a sphere yielding $V_h \simeq V_s/2$. Because of the small sized holes, in the melting process, a large number of holes will be produced around a solidlike molecule allowing it to have large positional degeneracy. The abnormally large ΔS_m ($=9.854$ e.u) may be caused by the increase in the positional degeneracy.

ACKNOWLEDGEMENT

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