

Transient State Theory of Significant Liquid Structure Applied to A Binary Mixture of Benzene and Carbon Tetrachloride

by

DONG SIK CHOI, WOON SUN AHN*, KAK CHOONG KIM**, and SEIHUN CHANG

*Department of Chemistry, College of Liberal Arts and
Sciences, Seoul National University*

(Received October 17, 1967)

이성분 액체 혼합물(C₆H₆-CCl₄)의 통계열역학적 연구

서울대학교 문리과대학 화학과
최동식·안운선*·김각중**·장세헌
(1967. 10. 17 受理)

요 약

액체 구조에 관한 천이상태 이론을 벤젠과 사염화탄소의 이성분 액체 혼합물에 적용시켰다. 각 성분의 상태함으로부터 액체 혼합물계의 상태함을 구하고, 이것으로부터 전체압, 부분압, 몰부피, 혼합엔트로피 및 압축률 등의 열역학적 성질을 여러 온도에서 계산하였다. 계산 결과는 문헌에서 얻은 실험값과 근사적으로 일치함을 발견하였다.

Abstract

The Transient State Theory of Significant Liquid Structure is applied to a binary liquid solution of benzene and carbon tetrachloride, which gives slightly positive deviation from Raoult's law. The partition function for the solution is derived according to the proposed theory. The various thermodynamic properties such as total and partial vapor pressures, molar volumes, entropies of mixing, and compressibilities are calculated at three different temperatures, 298.15°K, 313.15°K, and 343.15°K. The calculated values agree satisfactorily with experimental data.

Introduction

Unlike the situation for gases and solids, an adequate theory to predict and explain the physical properties of liquids has been long sought for. Since the middle of nineteen thirties, two different approaches to liquid theory have been made. The one is the formal and fundamental approach; and the other is by the use of

models.

H. Eyring and his co-workers proposed the Significant Liquid Structure Theory, a model approach, and applied the theory to various liquids successfully.⁽¹⁻³⁾

S. Chang and al developed the Modified Significant Structure Theory under the basically same theoretical approach as the Significant Liquid Structure Theory.⁽⁴⁾

H. Pak, W. Ahn, and S. Chang proposed the Transient State Theory of Significant Liquid Structure,⁽⁵⁾ which is theoretically more sound and more

* Choong-Nam University, Daejeon, Korea
** The Korea University, Seoul, Korea

widely applicable than above two theories; especially noted are the applicability of this theory to more complicated liquid systems and to liquids of low vapor pressures at the triple point. This theory has been applied to various liquids including binary liquid solutions with successes⁽⁹⁾.

This paper is the further application of the Transient State Theory of Significant Liquid Structure to a binary solution of benzene and carbon tetrachloride.

Formulation of Partition Function

The partition function for benzene was written by Chang et al⁸ according to the Transient State Theory as follows:

$$F_{C_6H_6} = \frac{(N\frac{1}{x})!}{(N\frac{1}{x}\alpha)! [N\frac{1}{x}(1-\alpha)]!} \left\{ \frac{e^{E_1/RT}}{(1-e^{-\theta_1/T})^3} \right\}^{N\frac{1}{x}\alpha} \left\{ \frac{n(x-1)e^{(E_1 - \frac{\alpha E_1}{n(x-1)})/RT}}{(1-e^{-\theta_1/T})^3} \right\}^{N\frac{1}{x}(1-\alpha)} \left[\frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} \frac{\sqrt{\pi(8\pi^2 kT)^{3/2} f_{11} c^{1/3}}}{12h^3} \right]^{N(1-\frac{1}{x})} \frac{1}{\prod C_6H_6} \quad (1)$$

where, $\prod C_6H_6 = \prod_{i=1}^{\infty} (1 - e^{-h\nu_i/kT})$

Considering the basic physical properties of CCl₄ discussed by Chang et al⁸, the partition function for CCl₄ according to the Transient State Theory can be written as

$$F_{CCl_4} = \frac{(N\frac{1}{x})!}{(N\frac{1}{x}\alpha)! [N\frac{1}{x}(1-\alpha)]!} \left\{ \frac{e^{E_2/RT}}{(1-e^{-\theta_2/T})^3} \right\}^{N\frac{1}{x}\alpha} \left\{ \frac{n(x-1)e^{(E_2 - \frac{\alpha E_2}{n(x-1)})/RT}}{(1-e^{-\theta_2/T})^3} \right\}^{N\frac{1}{x}(1-\alpha)} \left[\frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} \right]^{N(1-\frac{1}{x})} \left[\frac{\sqrt{\pi(8\pi^2 kT)^{3/2}}}{12h^3} \frac{1}{\prod CCl_4} \right]^N \quad (2)$$

where, $\prod CCl_4 = \prod_{i=1}^{\infty} (1 - e^{-h\nu_i/kT})$

Here θ_2 and θ_1 are Einstein's characteristic temperatures of solid-like and of the transient molecules, respectively. E_2 is a parameter which has close value of the heat of sublimation at the melting point; " α " is proportionality constant; and " n " is the number of the nearest neighboring sites around a molecule. " α " is a fractional number which represents the portion of

solid-like molecules. The other symbols in the partition function have their usual physical meanings.

Then, the complete partition function for the solution can be given as follows in accordance with the works

by S. Chang et al⁽⁸⁾ and W. Ahn.⁽⁶⁾

$$F_{total} = \frac{(N\xi_1\frac{1}{x_1} + N\xi_2\frac{1}{x_2})}{(N\xi_1\frac{1}{x_1}\alpha_1)! (N\xi_2\frac{1}{x_2}\alpha_2)! (N\xi_1\frac{1}{x_1}(1-\alpha_1))! (N\xi_2\frac{1}{x_2}(1-\alpha_2))!} \int_{x_1}^{N\xi_1\frac{1}{x_1}\alpha_1} \int_{x_2}^{N\xi_2\frac{1}{x_2}\alpha_2} f_{11}^{N\xi_1\frac{1}{x_1}(1-\alpha_1)} f_{12}^{N\xi_1\frac{1}{x_1}(1-\alpha_1)} f_{21}^{N\xi_2\frac{1}{x_2}(1-\alpha_2)} f_{22}^{N\xi_2\frac{1}{x_2}(1-\alpha_2)} \frac{1}{(N\xi_1(1-\frac{1}{x_1}))!} \frac{1}{N\xi_2(1-\frac{1}{x_2})!} \quad (3)$$

where $x_i = \frac{V - V_s + V_{si}^0}{V_{si}^0}$ and $V_s = \xi_1 V_{s1}^0 + \xi_2 V_{s2}^0$

Here, f_{11} , f_{12} , f_{21} and f_{22} , f_{11} , f_{12} , f_{21} , f_{22} represent partition functions for degrees of freedom of solid-like, transient, and gas-like of components 1 and 2, respectively. " ξ_i " is the mole fraction of i -th component.

Parameter Determination

The parameters for benzene are determined by the method developed by Chang et al.⁽⁸⁾

The parameters for carbon tetrachlorides are determined according to the same method except that the experimental value for compressibility at the temperature under consideration is used in order to avoid arbitral choosing of one of the parameters.

The parameters for the both components, thus determined, are shown in Table 1.

Table 1. The Parametric Values

	θ_2 (°K)	θ_1 (°K)	α	E_2 (cal./mole)	n
Benzene	56.515	49.041	0.04524	1,035.0	10.585
Carbon Tetrachloride	57.300	54.539	0.02047	8,743.3	11.483

Calculation of Thermodynamic Properties

From the fact that the free energy of a system becomes minimum at an equilibrium, the following relationship can be obtained.

$$\alpha_1 = \frac{f_{11}}{f_{11} + f_{12}} \quad \text{and} \quad \alpha_2 = \frac{f_{22}}{f_{22} + f_{21}} \quad (4)$$

Substituting equation (4) into equation (3)

$$F_{total} = \frac{[N\xi_1 \frac{1}{x_1} + N\xi_2 \frac{1}{x_2}]!}{[N\xi_1 \frac{1}{x_1}]! [N\xi_2 \frac{1}{x_2}]!} \quad (5)$$

$$f_{i1}^{N\xi_1 \frac{1}{x_1}} f_{i2}^{N\xi_2 \frac{1}{x_2}} f_{i1}^{N\xi_1 (1-\frac{1}{x_1})} f_{i2}^{N\xi_2 (1-\frac{1}{x_2})}$$

where

$$F_{i1} = \frac{e^{E_{i1}/RT}}{(1 - e^{-E_{i1}/RT})^6} \left\{ 1 + \lambda_1(x_1 - 1) e^{-\frac{\sigma_1 E_{i1}}{n_1(x_1-1)RT}} \right\} \frac{1}{\prod C_s H_s}$$

$$F_{i2} = \frac{e^{E_{i2}/RT}}{(1 - e^{-E_{i2}/RT})^6} \left\{ 1 + \lambda_2(x_2 - 1) e^{-\frac{\sigma_2 E_{i2}}{n_2(x_2-1)RT}} \right\} \frac{1}{\prod C_s H_s}$$

$$F_{s1} = \frac{(2\pi m_1 k T)^{3/2}}{h^3} \frac{e^{(V - V_s + V_{s1}^0)}}{N\xi_1} \frac{\sqrt{\pi} (8\pi^2 I k T)^{3/2}}{12h^3} \frac{1}{\prod C_s H_s}$$

$$F_{s2} = \frac{(2\pi m_2 k T)^{3/2}}{h^3} \frac{e^{(V - V_s + V_{s2}^0)}}{N\xi_2} \frac{\sqrt{\pi} (8\pi^2 I k T)^{3/2}}{12h^3} \frac{1}{\prod C_s H_s}$$

Here, $\lambda = n \left\{ \frac{1 - \exp(-\theta_i/T)}{1 - \exp(-\theta_i/T)} \right\}^3$ (b_1/b_2). where, b represents the partition function for rotational and vibrational degrees of freedom. Subscripts, t and s stand for transient and solid-like molecules, respectively.

The heat of sublimation of solid-like molecules of component "i" in the mixture can be expressed

$$E_{si} = \frac{1}{2} n_i \xi_i \phi_{ii} + \frac{1}{2} n_i \xi_j \phi_{ij} = \xi_i E_{si}^0 + \xi_j E_{sij}$$

where ϕ_{ii} and ϕ_{ij} are the molar binding energies between the pair of similar molecules and that of dissimilar molecules, respectively. " n_i " and " n_j " are the coordination number for a molecule of component "i" assuming that the surrounding molecules are of i-th component alone and assuming that the surrounding molecules are of j-th component alone, respectively. E_{sij} can be determined by the method developed by Ahn⁶. The calculated values at three different temperatures are shown in Table 2.

Table 2. Calculated E_{sij} Values

Tem. ($^{\circ}K$)	ΔE_{mix} (cal./mole)	E_{sij} (cal./mole)
298.15	29.4	9,487.9
313.15	27.1	9,492.5
343.15	23.8	9,499.1

By using the basic thermodynamic data, thus obtained, the thermodynamic properties are calculated

at temperatures 298.15° K, 313.15° K, and 345.15° K.

(A) Total Pressures and the Molar Volumes

Using the expression,

$$A = -kT \ln F_{total}(T, V, \xi_1, \xi_2) \quad (6)$$

the curve for Helmholtz free energy vs volume is plotted at constant temperature. Then, as expressed by the well known thermodynamic relationship

$$P = -(dA/dV)_{T, \xi_1, \xi_2} \quad (7)$$

the negative slope of the common tangential line between liquid region and the gaseous region will give the total vapor pressure of the system in equilibrium with its own vapor. And the tangential point at the liquid region will give the molar liquid volume.

The calculated values for total pressures and molar liquid volumes are shown in second and third columns, respectively, in Tables 3, 4, and 5.

(B) Partial Vapor Pressures:

Since the ideal behavior of vapor is assumed for this work, the partial pressures of the component "i" can be calculated following relationship

$$\mu_i^* = \mu_i^0 + kT \ln(p_i/p_i^0) \quad (8)$$

where, μ_i^* and μ_i^0 are chemical potentials of component "i" in the mixture and in the pure state, respectively.

Determining μ_i^* and μ_i^0 from the expression,

$$\mu_i = (dA/dN_i)_{T, V, N_{j \neq i}} \quad (9)$$

partial pressure, p_i , can be calculated.

The partial pressures, thus obtained, are shown in the fourth columns of Table 3, 4, and 5.

(C) Entropies of Mixing

The entropies of mixing are calculated using the thermodynamic relationships.

$$S = -(dA/dT)_{V, \xi_1, \xi_2} \quad (10)$$

and

$$\Delta S_{mix} = S_{total} - (\xi_1 S_1^0 + \xi_2 S_2^0) \quad (11)$$

The calculated values for the entropies of mixing are shown in the seventh (the last) column of Tables 3, 4, and 5.

(D) Compressibilities

The compressibilities are calculated for the equimolar mixture, using the following equation

$$\beta = -\frac{1}{V} \left(\frac{dV}{dP} \right)_{T, \xi_1, \xi_2} \quad (12)$$

The calculated values are tabulated in Table 5.

Table 3. Thermodynamic Properties at 298.15 °K

	Molar Volume (cc)	P_{Total} (mm)	P_1 (mm)	P_2 (mm)	P_1+P_2 (mm)	S_{mix} (e. u.)
0.0	96.69	113.3	0	113.3	113.3	0
0.1	96.13	113.0	10.5	102.9	113.3	0.685
0.2	95.42	112.3	20.3	92.3	112.7	1.041
0.3	94.79	111.2	29.9	81.9	111.9	1.290
0.4	94.01	109.7	39.1	71.4	110.6	1.408
0.5	93.23	107.9	48.3	60.7	108.9	1.446
0.6	92.45	105.8	57.4	49.5	106.9	1.406
0.7	91.59	103.3	66.4	38.1	104.6	1.265
0.8	90.77	100.8	75.7	26.1	101.8	1.039
0.9	89.91	97.8	85.1	13.4	98.5	0.677
1.0	88.97	94.7	94.7	0	94.7	0

Table 4. Thermodynamic Properties at 313.15 °K

	Molar Volume (cc)	P_{Total} (mm)	P_1 (mm)	P_2 (mm)	P_1+P_2 (mm)	S_{mix} (e. u.)
0.0	98.19	213.7	0	213.7	213.7	0
0.1	97.59	212.1	19.6	193.8	213.4	0.666
0.2	96.94	210.8	38.4	173.9	211.4	1.057
0.3	96.24	208.9	56.7	154.1	210.8	1.248
0.4	95.47	206.4	74.5	134.0	208.5	1.360
0.5	94.68	203.4	92.2	113.5	205.6	1.386
0.6	93.85	199.9	109.8	92.5	202.2	1.327
0.7	92.99	196.0	127.4	70.8	198.1	1.178
0.8	92.11	191.6	145.2	48.2	193.4	0.928
0.9	91.20	186.9	160.3	29.1	189.4	0.546
1.0	90.27	181.8	181.8	0	181.8	0

Table 5. Thermodynamic Properties at 343.15 °K

	Molar Volume (cc)	P_{Total} (mm)	P_1 (mm)	P_2 (mm)	P_1+P_2 (mm)	S_{mix} (e. u.)
0.0	101.56	624.6	0	624.6	624.6	0
0.1	100.89	622.1	57.5	565.7	623.2	0.675
0.2	100.17	618.5	113.6	506.9	620.6	1.045
0.3	99.40	613.6	168.6	447.7	616.3	1.271
0.4	98.60	607.5	222.9	388.0	610.9	1.400
0.5	97.75	600.3	276.8	327.3	604.1	1.441
0.6	96.88	592.1	330.6	265.5	596.1	1.396
0.7	95.98	583.1	384.6	202.2	586.8	1.263
0.8	95.06	572.0	439.0	137.1	576.1	1.031
0.9	94.11	562.0	494.1	69.8	563.9	0.666
1.0	93.14	550.2	550.2	0	550.2	0

Results and Discussions

As illustrated in Figure 1, the calculated values of molar volumes show good agreement with observed values. The deviation from the observed values, which is noticeable at the higher temperature, are about same as that in the theoretical values of each component liquid in the pure state. However, by

Table 5. Compressibilities of Equimolar Mixture

Temp (°K)	Obsd. (atm ⁻¹)	Calcd. (atm ⁻¹)	Percent Deviation
298.15	1.060×10^{-4}	0.805×10^{-4}	23%
313.15	1.172×10^{-4}	0.892×10^{-4}	24%
343.15	1.510×10^{-4}	1.126×10^{-4}	25%

looking at the shape of the curve, the calculated excess volumes seem to be slightly larger than the experimental values.

As shown in Figures 2, 3, 4, and 5, the calculated values for the total and partial pressures agree very well with the observed values (less than 1% at the highest deviation). As stated in the previous chapter, the ideal behavior of the vapor is assumed in calculating the partial pressure. In view of good agreement between calculated and observed values, the assumption seem to be a well valid one.

As shown in Figure 6, the calculated compressibility values show comparatively high deviation (about 25% at the highest) from the observed values. This again is about the same percent deviation shown in a pure liquid of either component.

The calculated entropies are slightly larger than the ideal mixing entropies. Since the behavior of the system is not perfectly ideal, this deviation can be expected. The difference between the calculated and the ideal mixing entropies, shown in Figure 7, are the excess entropies.

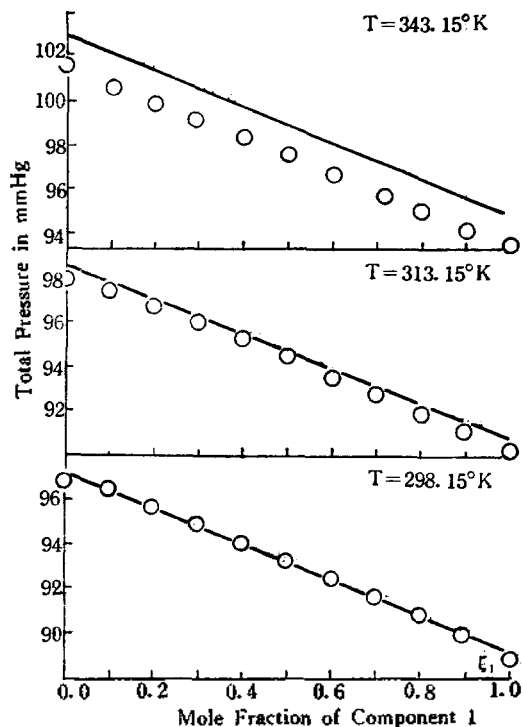


Figure 1. Molar Volumes of Solution
 ○ Calcd. — Obsd.

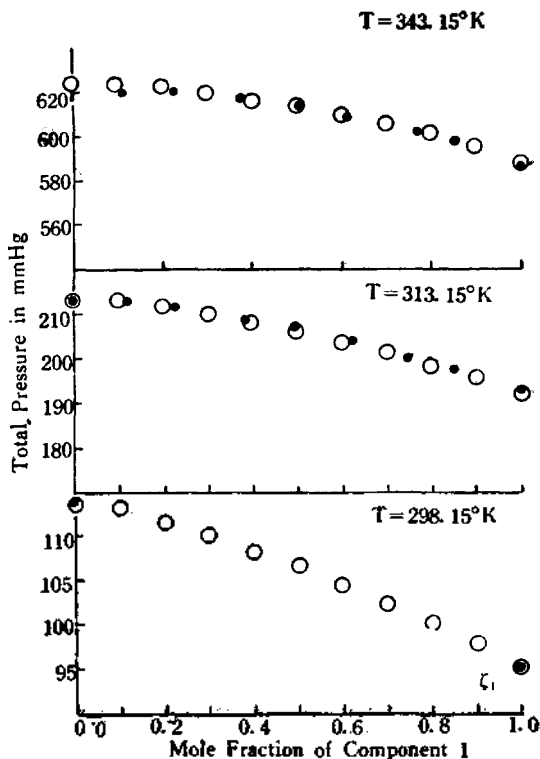


Figure 2. Total Pressures of the Solution
 ○ Calcd. ● Obsd.

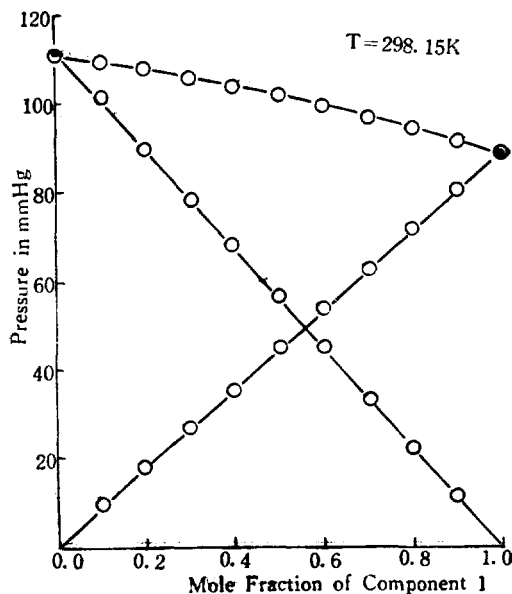


Figure 3. Partial Pressures of Each Component at 298.15°K
 ○ Calcd. ● Obsd.

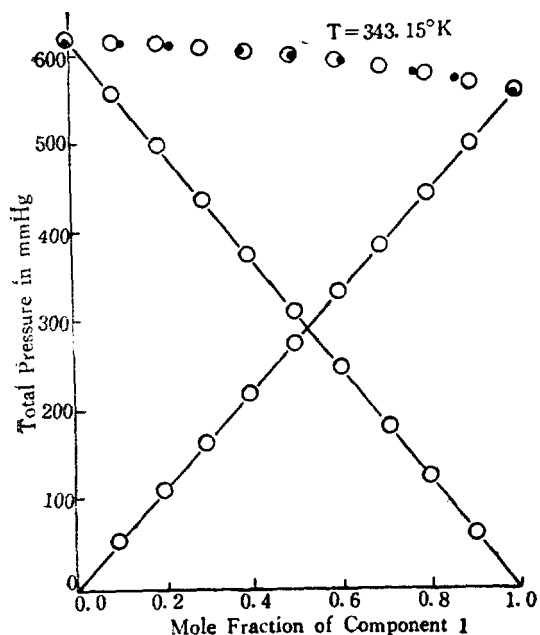


Figure 5. Partial pressure of Each Component at 343.15°K
○ Calcd. ● Obsd.

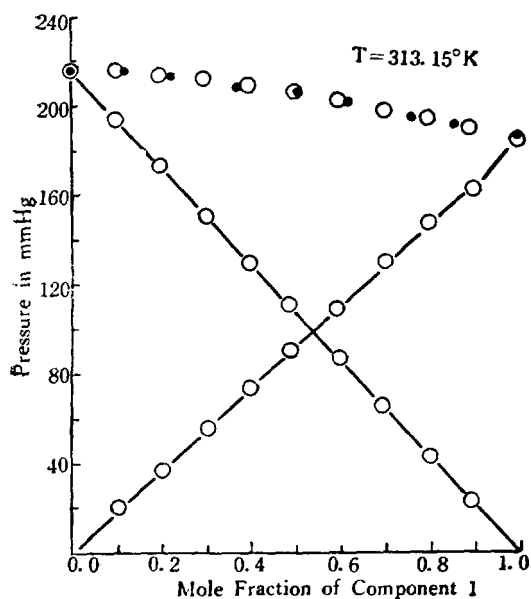


Figure 4. Partial Pressures of Each Component at 313.15°K
○ Calcd. ● Obsd.

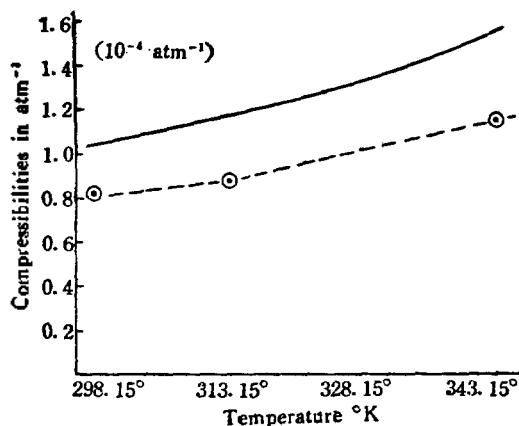


Figure 6. Compressibilities
— Obsd. --- Calcd.

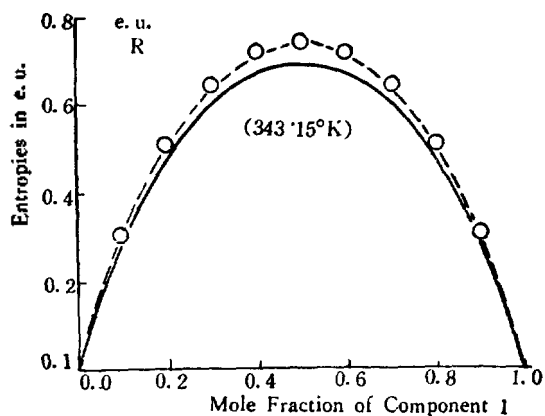


Figure 7. Entropies of Mixing
— Ideal. --- Calcd.

This work is a further proof of the general applicability of the Transient State Theory of the Significant Liquid Structure to liquid mixtures, in view of the fact that the calculated values do not deviate from the observed values any more than the deviations observed in pure liquids.

It is especially noted that no additional parameter is used for mixing, as is used in the theoretical work on liquid mixtures by other workers. ^(12,13)

References

- (1) Henry Eyring, Taikyu Ree and H. Hiral *Proc. Nat. Acad. Sci.*, **44**, 683 (1958)
- (2) E. J. Fuller, T. Ree and H. Eyring, *Ibid.*, **45**, 45 (1959)
- (3) H. Eyring and T. Ree, *Ibid.*, **47**, 526 (1961)
- (4) Seihun Chang and al, *J. of Korean Chem. Soc.*, **8**, 33 (1964)
- (5) H. Pak, W. Ahn and S. Chang, *Ibid.* **10**, 18 (1966)
- (6) W. Ahn, *Ibid.* **10**, 136 (1966)
- (7) W. Paik and S. Chang, *Ibid.*, **8**, 29 (1964)
- (8) W. Ahn, H. Pak and S. Chang, *Ibid.*, **9**, 215 (1965)
- (9) Scott E. Wood and James p. Brusie, *J. Am. Chem. Soc.*, **65**, 1889 (1943)
- (10) L. Liang, H. Eyring and R. Marchi, *Proc. Nat. Acad. Sci.*, **52**, 1107 (1964)
- (11) S. Ma and H. Eyring, *J. Chem. Phys.*, **42**, 1920 (1965)