Transient State Theory of Significant Liquid Structure applied to Binary Mixture, Benzene-Cyclohexane

by

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이성분 액체 혼합물의 통계열역학적 연구

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요 약

벤젠—시클로헥산 이성분 용액에다 Transient State Theory of Significant Liquid Structure 를 확장 적용시켰다. 상태합을 구하고 이것으로부터 계의 전체압, 부분압, 몰부피 그리고 과량의 엔트로피와 같은 열역학적 양을 303. 15°, 313. 15° 및 343. 15°K 에서 계산하였다. 이와 같이 구한 계산치들은 실측치와 대단히 잘 맞았다.

Abstract

The Transient State Theory of Significant Liquid Structure has been successfully extended to binary mixture, benzene-cyclohexane system, which gives positive deviation from Raoult's law. The partition function has been derived, and from it various thermodynamic properties, such as total and partial vapor pressures, molar volumes, and excess entropies have been calculated at the temperatures 303. 15°, 313. 15°, and 343. 15° K. The calculated values agree satisfactorily with the experimental data.

Introduction

The Significant Liquid Structure Theory proposed by H. Eyring and his coworkers[1,4] works very well when applied to various classes of liquids; however, it has some theoretical defects and is hardly applicable to the liquids which have very low vapor pressures near the melting point. To eliminate the theoretical defects of the theory, S. Chang et al[5] have recently proposed Transient State Theory of Significant Liquid Structure and shown that it can be applicable to various classes of liquids including those which have very low vapor pressures near the melting point.

The forms of the partition functions derived from the Transient State Theory are similar to those derived from the original Significant Liquid Structure Theory although there is a fundamental difference between the two theories. The difference appearing in the partition functions derived from the two theories is that in the partition function according to the former theory the coordination number, n, is replaced by λ which stands for $n\left(\dfrac{1-e^{-\theta_s/T}}{1-e^{-\theta_t/T}}\right)^3\dfrac{b_t}{b_s}$, where b_t and b_s represent the partition functions for degrees of freedom of molecular rotation and intramolecular vibrations of transient state molecules and those of soid-like molecules, respectively.

S. Chang et al extended the Significant Liquid Structure Theory to an ideal binary mixture of benzene and ethylenechloride. [6] They successfully formulated the partition function and calculated various thermo-

dynamic properties of the liquid mixture from the partition functions of the pure components without using extra parameters. In view of the fact that the partition functions derived from the two theories resemble each other, Transient State Theory should also be applied to binary mixtures in the similar way. K. Liang, H. Eyring, R. Marchi and S. Ma have, also, extended the Significant Liquid Structure Theory to solutions in a different manner by introducing considerable number of parameters[7,8]. Introducing extra parameters gives considerable complications for the calculations of thermodynamic properties besides being theoretically unsound. According to the Significant Liquid Structure Theory, a liquid molecule possesses both the solid-like and gas-like degrees of freedom.

A molecule around the vacant hole in the liquid possesses the gas-like degree of freedom when it jumps into the hole. Considering the high liquid densities and strong interactions among the molecules in liquid, it is hardly imaginable that the transition of the degrees of freedom from solid-like to gas-like would occur directly. S, Chang et al proposed in the Transient State Theory that a definite portion of the bonded molecules have solid-like degree of freedom while the remaining portion have transient state degree of freedom and are ready to take gas-like degree of freedom. The transient state molecules are supposed to be in a higher energy state compared with the solid-like molecules due to the strain energy which is proportional to the ground state energy and inversely proportional to the number of vacant sites around a molecule. The partition functions for benzene and for cyclohexane have been derived previously according the Transient State Theory as follows:[5,9]

$$F_{C_6H_6} = \frac{\left(N\frac{1}{x}\right)!}{\left(N\frac{1}{x}\alpha\right)! \left[N\frac{1}{x}(1-\alpha)\right]!} \left\{\frac{e^{E_s/RT}}{(1-e^{-\theta_s/T})^6}\right\}^{N\frac{1}{x}\alpha} \cdot$$

$$\left\{\frac{n(x-1)e^{(E_s-\frac{aE_s}{n(x-1)})/RT}}{(1-e^{-\theta_t/T})^6}\right\}^{N\frac{1}{x}(1-\alpha)} \cdot \left\{\frac{(2\pi mkT)^{3/2}}{h^3}\right.$$

$$\left. \frac{eV}{N} \frac{\sqrt{\pi}(8\pi^2kT)^{3/2}I_AI_C^{1/2}}{12h^3}\right\}^{N(1-\frac{1}{x})} \frac{1}{\Pi C_6H_6} \cdots\cdots(1)$$

$$F_{C_6H_{12}} = \frac{\left(N\frac{1}{x}\right)!}{\left(N\frac{1}{x}\alpha\right)! \left[N\frac{1}{x}(1-\alpha)\right]!} \left\{\frac{e^{E_s/RT}}{(1-e^{-\theta_s/T})^3}\right.$$

$$\left. \frac{\sqrt{\pi}(8\pi^2kT)^{3/2}(I_AI_BI_C)^{1/2}}{6h^3} \frac{1}{\Pi C_6H_{12}}\right\}^{N\frac{1}{x}\alpha} \cdot$$

$$\left\{\frac{n(x-1)e^{(E_s-\frac{aE_s}{n(x-1)})/RT}}{1-e^{-\theta_t/T})^3}\right.$$

$$\left. \frac{\sqrt{\pi}(8\pi^2kT)^{3/2}(I_AI_BI_C)^{1/2}}{6h^3} \frac{1}{\Pi C_6H_{12}}\right\}^{N\frac{1}{x}(1-\alpha)} \cdot$$

$$\left\{\frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} \frac{\sqrt{\pi}(8\pi^2kT)^{3/2}(I_AI_BI_C)^{1/2}}{6h^3}\right.$$

$$\left. \frac{1}{\Pi C_6H_{12}}\right\}^{N(1-\frac{1}{x})} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

$$\left.\begin{array}{l} \Pi C_6H_6 = \prod_{i=1}^{30}(1-e^{-h\mu i/RT}) \\[2mm] \Pi C_6H_{12} = \prod_{i=1}^{43}(1-e^{-h\nu i/TR}) \end{array}\right\} \cdots\cdots\cdots\cdots\cdots\cdots (3)$$

where E_s, θ_s and θ_t are parameters corresponding to the heat of sublimation at the melting point and Einstein characteristic temperatures of the solid-like and transient state molecules, respectively. The proportionality constant, a, in the strain energy term, $aE_s/n(x-1)$, is also a parameter. V_s is the molar volume of the solidlike molecules at the melting piont, and its ratio to the liquid molar volume, denoted by $1/x$, is taken as the fraction of the bonded molecules. "n" is the number of the nearest neighboring sites around a molecule. The values of the parameters were determined as shown in Table I [5,9]. The remaining symbols in the partition function, R, K, N, T, and h have their usual physical meanings. I_A, I_B and I_C are the three principal moment of inertia. The i-th internal frequencies are denoted by μ_i and ν_i for benzene and cyclohexane, respectively.

Table I The Parameters

	$\theta_s{}^\circ K$	$\theta_t{}^\circ K$	$\frac{E_s}{\text{cal/mole}}$	a	n
C_6H_6	55. 515	49. 041	10, 350	0. 04524	10. 585
C_6H_{12}	76. 271	75. 146	8823. 16	0. 03187	11. 301

Partition Function

In formulating the complete partition function for the mixture, we have assumed that the molecules mix in a random manner, and that the parameters θ_s, θ_t, a and n are independent of the composition of the mixture. The molar volumes of the solid-like molecules of the components are also assumed to be independent of the composition. Accordingly, the total molar volume of the solid-like molecules of the mixture can be given as follows;

$$V_s = \xi_1 V_{s1}{}^0 + \xi_2 V_{s2}{}^0 \cdots\cdots\cdots\cdots\cdots\cdots\cdots(4)$$

where ξ is the mole fraction of a component, and the superscript zero denotes the pure state. The subscript

1 and 2 represent benzene (component one) and cyclohexane (component tow), respectively.

The number of holes around a molecule of component one can be given by

$$\frac{V-V_s}{V_{s1}{}^\circ}=x_1-1$$

Likewise, for the second component it can be given by

$$\frac{V-V_s}{V_{s2}{}^\circ}=x_2-1$$

The relation between x_1 and x_2 can be obtained from the above two equations

$$x_2-1=(x_1-1)V_{s1}{}^\circ/V_{s2}{}^\circ$$

Accordingly, the fraction of the gas-like molecules of the component one can be given by

$$\frac{x_1-1}{(x_1-1)+1}=1-\frac{1}{x_1}$$

and that of the second component is $1-\dfrac{1}{x_2}$

The complete partition function for the mixture consists of combinatorial factor, two solid-like parts, two transient state parts, and two gas-like parts;

$$F_t=\frac{\left(N\xi_1\frac{1}{x_1}+N\xi_2\frac{1}{x_2}\right)!}{\left(N\xi_1\frac{1}{x_1}\alpha_1\right)!\ \left(N\xi_2\frac{1}{x_2}\alpha_2\right)!\left[N\xi_1\frac{1}{x_1}(1-\alpha_1)\right]!}$$

$$\frac{}{\left[N\xi_2\frac{1}{x_2}(1-\alpha_2)\right]!}f_{s1}^{N\xi_1\frac{1}{x_1}\alpha_1}f_{s2}^{N\xi_2\frac{1}{x_2}\alpha_2}f_{t1}^{N\xi_1\frac{1}{x_1}(1-\alpha_1)}$$

$$f_{t2}^{N\xi_1\frac{1}{x_2}(1-\alpha_2)}f_{g1}^{N\xi_1(1-\frac{1}{x_1})}\frac{1}{\left[N\xi_1\left(1-\frac{1}{x_1}\right)\right]!}$$

$$f_{g2}^{N\xi_2(1-\frac{1}{x_2})}\frac{1}{\left[N\xi_2\left(1-\frac{1}{x_1}\right)\right]!}\ \cdots\cdots\cdots\cdots\cdots (5)$$

The combinatorial factor introduced in the complete partition function is due to the random mixing of the solid-like and transient state molecules, as we have assumed. The solid-like, transient state, and gas-like parts of the partition function for the two components are given by;

$$f_{s1}=\frac{e^{Es_1/RT}}{(1-e^{-\theta s_1/T})^6}\ \frac{1}{\overline{\Pi}\,c_6H_6}$$

$$f_{s2}=\frac{e^{Es_2/RT}}{(1-e^{-\theta s_2/T})^3}\ \frac{\sqrt{\pi}(8\pi^2kT)^{3/2}(I_A'I_B'I_C')^{1/2}}{6h^3}$$

$$\frac{1}{\overline{\Pi}\,c_6H_{12}}$$

$$f_{t1}=\frac{n_1(x_1-1)e^{(Es_1-a_1Es_1/n_1(x_1-1))/RT}}{(1-e^{-\theta t_1/T})^6}\ \frac{1}{\overline{\Pi}\,c_6H_6}$$

$$f_{t2}=\frac{n_2(x_2-1)e^{(Es_2-a_2Es_2/n_2(x_2-1))/RT}}{(1-e^{-\theta t_2/T})^3}\ .$$

$$\frac{\sqrt{\pi}(8\pi^2kT)^{1/2}(I_A'I_B'I_C')^{1/2}}{6h^3}\ \frac{1}{\overline{\Pi}\,c_6H_{12}}$$

$$f_{g1}=\frac{(2\pi m_1kT)^{3/2}(V-V_s)}{h^3}\ .$$

$$\frac{\sqrt{\pi}(8\pi^2kT)^{3/2}I_AI_C^{1/2}}{12h^3}\ \frac{1}{\overline{\Pi}\,c_6H_6}$$

$$f_{g2}=\frac{(2\pi m_2kT)^{3/2}(V-V_s)}{h^3}$$

$$\frac{\sqrt{\pi}(8\pi^2kT)^{3/2}(I_A'I_B'I_C')^{1/2}}{6h^3}\ \frac{1}{\overline{\Pi}\,c_6H_{12}}$$

To derive the thermodynamic properties from the partition function, it is necessary to evaluate the $\alpha's$ and $E_s's$. In the equilibrium distribution of the molecules, the values of the $\alpha's$ should minimize the free energy of the system.

Therefore

$$\left(\frac{\partial A}{\partial \alpha_1}\right)_{T,\,V,\,\xi_1,\,\xi_2}=-kT\left(\frac{\partial \ln F_t}{\partial \alpha_1}\right)_{T,\,V,\,\xi_1,\,\xi_2}=0\cdots\cdots (6)$$

$$\left(\frac{\partial A}{\partial \alpha_2}\right)_{T,\,V,\,\xi_1,\,\xi_2}=-kT\left(\frac{\partial \ln F_t}{\partial \alpha_2}\right)_{T,\,V,\,\xi_1,\,\xi_2}=0\cdots\cdots (7)$$

Above conditions will give the following relationships,

$$\alpha_1=\frac{f_{s_1}}{f_{s_1}+f_{t_1}},\quad \alpha_2=\frac{f_{s_2}}{f_{s_2}+f_{t_2}}\cdots\cdots\cdots\cdots\cdots\cdots (8)$$

Combining equations (5) and (8), we can eliminate the $\alpha's$ and obtain

$$F_t=\frac{\left(N\xi_1\frac{1}{x_1}+N\xi_2\frac{1}{x_2}\right)!}{\left(N\xi_1\frac{1}{x_1}\right)!\ \left(N\xi_2\frac{1}{x_2}\right)!}F_{s1}^{N\xi_1\frac{1}{x_1}}F_{s2}^{N\xi_2\frac{1}{x_2}}F_{g1}^{N\xi_1(1-\frac{1}{x_1})}$$

$$F_{g2}^{N\xi_2(1-\frac{1}{x_2})}\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (9)$$

where

$$F_{s1}=\frac{e^{Es_1/RT}}{(1-e^{-\theta s_1/T})^6}\left\{1+\lambda_1(x_1-1)e^{-\frac{a_1Es_1}{n_1(x_1-1)RT}}\right\}\frac{1}{\overline{\Pi}\,c_6H_6}$$

$$F_{s2}=\frac{e^{Es_2/RT}}{(1-e^{-\theta s_2/T})^3}\ \frac{\sqrt{\pi}(8\pi^2kT)^{3/2}(I_A'I_B'I_C')^{1/2}}{6h^3}$$

$$\left\{1+\lambda_2(x_2-1)e^{-\frac{a_2Es_2}{n_2(x_2-1)RT}}\right\}\frac{1}{\overline{\Pi}\,c_6H_{12}}$$

$$F_{g1}=\frac{(2\pi m_1kT)^{3/2}}{h^3}\ \frac{e(V-V_s+V_{s1})}{N\xi_1}$$

$$\frac{\sqrt{\pi}(8\pi^2kT)^{3/2}I_AI_C^{1/2}}{12h^3}\ \frac{1}{\overline{\Pi}\,c_6H_6}$$

$$F_{g2}=\frac{(2\pi m_2kT)^{3/2}}{h^3}\ \frac{e(V-V_s+V_{s2})}{N\xi_2}$$

$$\frac{\sqrt{\pi}(8\pi^2kT)^{3/2}(I_A'I_B'I_C')^{1/2}}{6h^3}\ \frac{1}{\overline{\Pi}\,c_6H_{12}}$$

The heat of sublimations of the solid-like molecules of the components in the mixture are determined as follows;

$$E_{s1}=\frac{1}{2}n_1\xi_1\phi_{11}+\frac{1}{2}n_1'\xi_2\phi_{12}$$

$$= E_{s1}{}^0\xi_1 + \frac{1}{2}n_1'\xi_2\phi_{12} \cdots\cdots\cdots\cdots\cdots\cdots(10)$$

where ϕ_{11} and ϕ_{12} are molar binding energies between the molecules of the component one and that between the molecules of the two different types, respectively. When the molecules of different dimensions are coordinated, the coordination number may change its value and therefore it is distinguished by prime. Likewise for the second component it can be expressed as

$$E_{s2} = E_{s2}{}^0\xi_2 + \frac{1}{2}n_2'\xi_1\phi_{21} \cdots\cdots\cdots\cdots\cdots (11)$$

The mean heat of sublimation of the solid-like molecules in the mixture can be given by;

$$E_s = E_{s1}\xi_1 + E_{s2}\xi_2 \cdots\cdots\cdots\cdots\cdots\cdots\cdots(12)$$

combining equations (10), (11) and (12), it follows;

$$E_s = E_{s1}{}^0\xi_1{}^2 + E_{s2}{}^0\xi_2{}^2 + \frac{1}{2}\xi_1\xi_2 n_1'\phi_{12} + \frac{1}{2}\xi_1\xi_2 n_2'\phi_{21}$$

The contribution to the E_s of 1-2 and 2-1 binding should always be the same; therefore the following relationships can be established

$$\frac{1}{2}\xi_1\xi_2 n_1'\phi_{12} = \frac{1}{2}\xi_1\xi_2 n_2'\phi_{21} \equiv \xi_1\xi_2 E_{s12}$$

and

$$E_s = E_{s1}{}^0\xi_1{}^2 + E_{s2}{}^0\xi_2{}^2 + 2\xi_1\xi_2 E_{s12} \cdots\cdots\cdots\cdots(13)$$

On the other hand, since the total energy of the system should be conserved, the mean heat of sublimation can be given as

$$E_s = E_{s1}{}^0\xi_1 + E_{s2}{}^0\xi_2 + \Delta E_{mix} \cdots\cdots\cdots\cdots\cdots\cdots(14)$$

From the knowlidge of the mixing energy, E_{s12} can be determined by combining equations (13) and (14). Using Scatchard's empirical formula, [10] S. E. Wood and A. E. Austin [11,12] calculated equimolal mixing energy for the binary system under the cosdideration. Their calculated values are;

 −123. 5 cal/mole   at 303. 15°K
 −124. 8 cal/mole   at 313. 15°K
 −128. 7 cal/mole   at 343. 15°K

With the data, E_{s12} are calculated to be

 9339. 6 cal/mole   at 303. 15°K
 9337. 0 cal/mole   at 313. 15°K
 9329. 2 cal/mole   at 343. 15°K

Calculation

It is possible to calculate the Helmholtz's free energy and other thermodynamic properties, since all the parameters appearing in the partition function are known and the partition function is related to the Helmholtz free energy as

$$A = -kT\ln F_t(T, V, \xi_1, \xi_2) \cdots\cdots\cdots\cdots\cdots\cdots(18)$$

The calculations are performed at the temperatures 303. 15°, 313. 15° and 343. 15°K.

1) Total Vapor Pressures and Molar Volumes; The Helmholtz free energy versus molar volume is plotted for different values of molar volume of the system to utilize the well known thermodynamic relation

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T, \xi_1, \xi_2}$$

The negative slope of the common tangential line between the liquidous portion and the gaseous portion gives the total vapor pressure of the system in equilibrium with its own vapor, as it is done in one component system. The tangential point at the liquidous portion gives the molar volume of the liquid. The calculated values are given in the second and third columns of the Table II, III, and IV.

2) Partial Vapor Pressures; Assuming ideal behavior of the vapor, the partial pressures of the component one are calculated from the relation

$$\mu_1{}^* = \mu_1{}^0 + kT\ln\frac{P_1}{P_1{}^0}$$

where $\mu_1{}^*$ and $\mu_1{}^0$ are the chemical potentials of component one in the mixture and in the pure state. They are deduced from the thermodynamic relation

$$\mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T, V, N_{j\neq i}}$$

The partial pressures of the second component are also calculated in the exactly same manner. The results are given in the fourth and fifth columns of the Table II, III and IV.

3) Excess Entropies; The excess entropies are calculated using thermodynamic relations

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V, \xi_1, \xi_2}$$

and

$$\Delta S^E = S_{mix} - (\xi_1 S_1{}^0 + \xi_2 S_2{}^0) - (-\xi_1\ln\xi_1 - \xi_2\ln\xi_2)$$

The calculated values are recorded in the seventh column of the Table II, III and IV.

Discussion

The total and partial vapor pressures are graphically represented in Fig. 1, 2, and 3. The calculated values are in a good agreement with experimental data, though they give slight positive deviations in general. The maximum deviations of the total vapor pressure

Table Ⅱ Various Thermodynamic Properties Calculated at 303.15° K.

ξ_1	P_{total}	M. V.	P_1	P_2	P_1+P_2	ΔS^E
	atm.	cc.	atm.	atm.	atm.	eu.
0.0	0.1591	110.21	0.0000	0.1591	0.1591	0.0000
0.1	0.1690	108.65	0.0262	0.1456	0.1718	0.1024
0.2	0.1771	106.87	0.0468	0.1331	0.1799	0.1625
0.3	0.1828	104.86	0.0633	0.1214	0.1847	0.1771
0.4	0.1861	102.85	0.0777	0.1097	0.1874	0.1948
0.5	0.1869	100.84	0.0911	0.0973	0.1884	0.2153
0.6	0.1852	98.60	0.1030	0.0843	0.1873	0.1861
0.7	0.1811	96.35	0.1151	0.0692	0.1843	0.1577
0.8	0.1747	94.04	0.1275	0.0512	0.1787	0.1117
0.9	0.1663	91.72	0.1411	0.0288	0.1699	0.0657
1.0	0.1561	89.32	0.1561	0.0000	0.1561	0.0000

Table Ⅲ Various Thermodynamic Properties Calculated at 313.15° K.

ξ_1	P_{total}	M. V.	P_1	P_2	P_1+P_2	ΔS^E
	atm.	cc.	atm.	atm.	atm.	eu.
0.0	0.2417	111.51	0.0000	0.2417	0.2417	0.0000
0.1	0.2566	109.88	0.0393	0.2209	0.2602	0.0909
0.2	0.2683	107.95	0.0702	0.2017	0.2719	0.1154
0.3	0.2770	105.94	0.0957	0.1837	0.2794	0.1479
0.4	0.2820	103.93	0.1181	0.1654	0.2835	0.1726
0.5	0.2834	101.76	0.1380	0.1461	0.2841	0.1674
0.6	0.2811	99.52	0.1567	0.1270	0.2837	0.1470
0.7	0.2753	97.36	0.1761	0.1035	0.2796	0.1444
0.8	0.2660	95.04	0.1955	0.0762	0.2717	0.1085
0.9	0.2540	92.64	0.2161	0.0432	0.2593	0.0548
1.0	0.2392	90.24	0.2392	0.0000	0.2392	0.0000

Table Ⅳ Various Thermodynamic Properties Calculated at 343.15° K.

ξ_1	P_{total}	M. V.	P_1	P_2	P_1+P_2	ΔS^E
	atm.	cc.	atm.	atm.	atm.	eu.
0.0	0.7207	115.72	0.0000	0.7207	0.7207	0.0000
0.1	0.7610	113.89	0.1130	0.6571	0.7701	0.0686
0.2	0.7939	111.80	0.2046	0.5981	0.8027	0.0968
0.3	0.8184	109.79	0.2833	0.5417	0.8250	0.1397
0.4	0.8332	107.55	0.3510	0.4861	0.8371	0.1441
0.5	0.8385	105.30	0.4135	0.4285	0.8420	0.1492
0.6	0.8337	102.99	0.4727	0.3666	0.8393	0.1409
0.7	0.8195	100.51	0.5299	0.2982	0.8281	0.1039
0.8	0.7956	98.12	0.5903	0.2173	0.8076	0.0803
0.9	0.7634	95.72	0.6548	0.1211	0.7759	0.0559
1.0	0.7240	93.17	0.7240	0.0000	0.7240	0.0000

arise near the equi-molar mixture portions, and are less than 4 per cent at 303.15° and 313.15°K and 6 per cent at 343.15°K. If the mixing energy becomes less negative, E_s will be increased and accordingly the vapor pressure will be decreased. Considering the errors which may probably be included in ΔE_{mix}, the above results are satisfacotry.
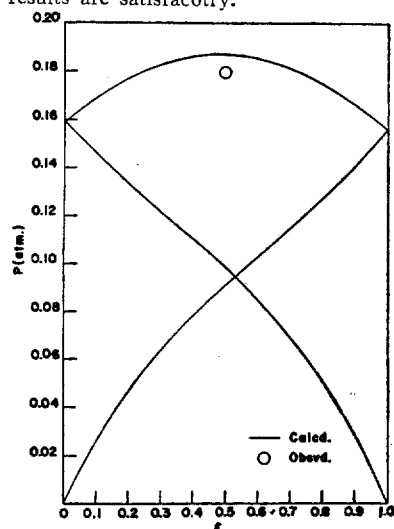

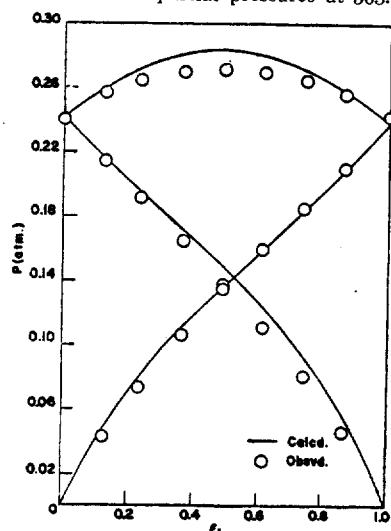**Fig.** I Total and partial pressures at 303.15°K

Fig. II Total and partial pressures at 313.15°K

As shown in Fig. 4, the molar volume curves are in good agreement with the experimental values.

The excess entropies are calculated by S. E. Wood and A. E. Austin using Scatchard's empirical formulas. [10,11,12]. They obtained the values of 0.161, 0.171, and 0.197 eu. for the equi-molal slutoins at 303.15°, 313.15°, and 343.15°K, respectively, showing an
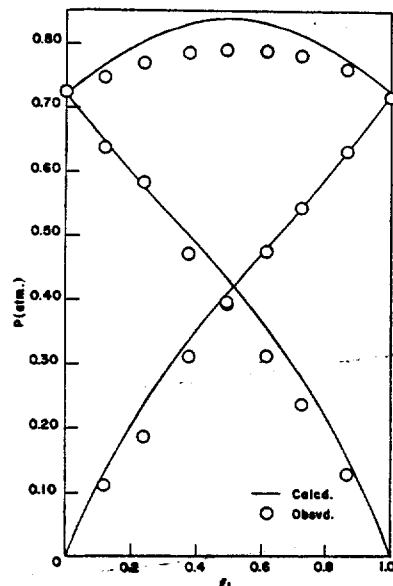

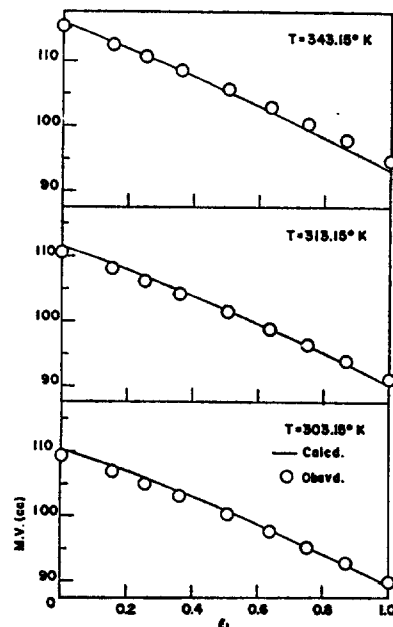**Fig,** III Total and partial pressures at 343.15°K

Fig. IV Molar volumes

increasing tendency with the temperature. With the other Scatchard's formula they obtained the values 0.234, 0.215, and 0.153 eu. at the respective temperatures, which shows decreasing tendency. The excess entropies calculated from the partition function lie between the above two sets of data, showing a decreasing tendency. The comparison of our calculated values with the values calculated by the use of Scatchard's formulas does not seem to have any physical significance.

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