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Statistical Thermodynamics of Liquid Mixtures

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A statistical thermodynamic theory of binary liquid mixtures has been worked out on the basis of the equivalent free volume defined without use of lattice model. A liquid mixture is regarded as a mixture of hard spheres immersed in a uniform background potential. The total free energy is expressed as the sum of terms given by the analytical solution of the generalized Percus-Yevick equation for the hard sphere mixture and the term resulting from the uniform background potential. Thermodynamic functions are in a simple form convenient for practical applications. The nature of the equivalent free volume for the mixture which consists of molecules differing in size is elucidated. The energy interaction parameters and excess thermodynamic functions for eight binary mixtures composed of nonpolar molecules are calculated, and the results are discussed.

Since the designation of "regular solution" by Hildebrand and Scott[1)] attempts have been made to develop a statistical theory of liquid mixtures. The most remarkable theories are those presented by Prigogine and co-workers,[2)] and Flory.[3)] Prigogine *et al.* presented the theories based on the average potential model, and Flory introduced the interactions between surface-sites of molecules, using the corresponding state theorem. These theories have been used by many workers during the last two decades.[4)] However, the basic assumptions underlying the theories seem to require further examination.

The most important problem in the statistical theories of liquid mixtures is to estimate the "entropy of mixing" for the mixtures composed of molecules differing in size. A cell or lattice model has been used for estimation, but no rigorous treatment has been given so far. The solution for mixtures of hard spheres was first given by Lebowitz,[5)] who succeeded in obtaining an analytical and explicit solution of the generalized Percus-Yevick equation.

Snider and Herrington[6)] made a direct application of the Lebowitz solution to binary mixtures on the basis of the Longuet-Higgins and Widom model[7)] which was proposed first for pure fluids. For the excess thermodynamic functions of binary mixtures of nonpolar molecules, they obtained good agreement between the calculated and experimental values. Marsh and others tested Snider and Herrington's treatment for several binary mixtures[8)] and Kreglewski *et al.* carried out a statistical thermodynamic treatment along the same line.[9)] However, the physical nature of those theories remains unclarified.

The equivalent free volume for mixtures of hard spheres has been defined on the basis of the Lebowitz solution without assuming any specified lattice.[10)] We indicate in the present work that all molecules constituting a liquid mixture hold the same magnitude of the "equivalent free volume" in spite of their different sizes. A simple and convenient formulation of thermodynamic functions for liquid mixtures is attempted in terms of equivalent free volume.

For calculation, molecular parameters for each component are usually determined from the thermodynamical data for pure species. However, the energy interaction parameter between different species, which is necessary for the calculation of various excess thermodynamic functions, can not be obtained directly. The data for one of excess functions are used to determine the parameter. Excess enthalpy or excess Gibbs free energy has been used so far for the determination of the parameter. Snider and Herrington[6)] calculated the energy interaction parameter for binary mixtures from the experimental values of excess Gibbs free energy. We have determined it from the observed values of excess volume obtained more easily than for the other thermodynamic functions such as excess heat *etc.* The results are satisfactory. Their significance is discussed in this paper.

Theory

The Liquid Model. For the formulation of the theory, the liquid mixture consisting of various species of molecules is regarded as a mixture of hard spheres immersed in a uniform background potential resulting from the attractive forces between molecules. Longuet-Higgins and Widom[7)] applied the model to liquid Argon. The model has later been applied to pure liquid and solutions by several workers[6,9–11)] including the present authors.

The Free Energy and Entropy. In the liquid model, the translational part of the total partition function for the mixture becomes identical with the partition function for the mixture of hard spheres with no attraction between themselves. In a previous paper,[10)] an analytical expression was given on the translational partition function for mixtures of hard spheres on the basis of the Lebowitz solution for the Percus-Yevick equation. A partition function Z_0 at a given volume V and temperature T for an assembly of r components is expressed as

$$Z_0 = \frac{N!}{\prod\limits_{i=1}^{r} N_i!} \prod_{i=1}^{r} \left[\left(\frac{2\pi m_i kT}{h^2}\right)^{3/2}\left(e\frac{Vf_m}{N}\right)\right]^{N_i}. \tag{1}$$

The Helmholtz free energy F_0 becomes

$$F_0 = -kT\sum_{i=1}^{r} N_i \ln\left(\frac{2\pi m_i kT}{h^2}\right)^{3/2} - NkT\ln\left(e\frac{Vf_m}{N}\right) - T\Delta S_{\mathrm{id.mix.}}. \tag{2}$$

The equivalent free volume fraction f_m is given by

$$f_m = (1-\xi)\exp\left[-\frac{9}{\pi}\frac{V}{N}\frac{1}{(1-\xi)^2}(2XY-2XY\xi+X^3)\right], \tag{3}$$

and the packing fraction for the mixture, ξ, by

$$\xi = \sum_{i=1}^{r} \frac{\pi}{6} \frac{N_i}{V} R_i^3, \tag{4}$$

where N_i is the number of molecules, m_i the mass, R_i the diameter of hard spheres for i-th species, $N(=\sum_{i=1}^{r} N_i)$ the total number of molecules, and

$$X = \sum_{i=1}^{r} \frac{\pi}{6} \frac{N_i}{V} R_i^2, \quad Y = \sum_{i=1}^{r} \frac{\pi}{6} \frac{N_i}{V} R_i. \tag{5}$$

The ideal entropy of mixing $\Delta S_{\text{id. mix.}}$ is

$$\Delta S_{\text{id.mix.}} = k \ln[N!/\prod_{i=1}^{r} N_i!]. \tag{6}$$

Equation 2 (or Eq.1) is seen to have a form which is identical with that given in the usual free volume theories. Thus we have the "equivalent free volume,"

$$v_f = V f_m / N. \tag{7}$$

Hence, f_m has been defined as the "equivalent free volume fraction,"[10] which is an extension of the case of a one-component fluid[11] to mixtures. No cell or lattice model is presupposed in the definition of the equivalent free volume.

Equation 2 indicates that the equivalent free volume v_f is the same for all the species in the mixture, in spite of their different sizes. The physical meaning of this remarkable fact will be discussed, in comparison with the interpretation of "free volume" made in the usual free volume theories of solutions.[12]

Let us assume that the attractive forces give rise to a uniform background potential, taking the liquid model proposed by Longuet-Higgins and Widom[7] into consideration. A uniform background potential is given by $U_{\text{BG}} = -N^2(\sum_{i=1}^{r}\sum_{j=1}^{r} x_i x_j a_{ij})/V$, where $x_i(=N_i/N)$ is the mole fraction of i-th species, a_{ii} the energy constant for the pure component, and $a_{ij}(i \neq j)$ the additional one for the mixture.[13] Thus, the free energy is written as

$$F = F_0 - \frac{N^2}{V}(\sum_i \sum_j x_i x_j a_{ij})$$

$$= F_{\text{id,m}} - NkT \ln(f_m) - \frac{N^2}{V}(\sum_i \sum_j x_i x_j a_{ij}), \tag{8}$$

where $F_{\text{id, m}}$ is the free energy of the mixture of ideal gases which is given by[14]

$$F(V, T, N_1 \cdots N_r)_{\text{id,m}} = -NkT \sum_i x_i \ln\left(\frac{2\pi m_i kT}{h^2}\right)^{3/2} - NkT \ln\left(e\frac{V}{N}\right) - T\Delta S_{\text{id.mix.}}. \tag{9}$$

The first term $F_{\text{id, m}}$ in the right-hand side of Eq. 8 is the ideal term, the second one $-NkT\ln(f_m)$ is the contribution from the repulsive interaction between molecules in the fluctuational thermal motions, and the third one is that from the uniform background potential in which the molecules constituting the mixture are immersed.

The entropy S is expressed as

$$S = S_{\text{id,m}} + Nk \ln(f_m), \tag{10}$$

where $S_{\text{id, m}}$ is given by

$$S(V, T, N_1 \cdots N_r)_{\text{id,m}} = Nk \sum_i x_i \ln\left(\frac{2\pi m_i kT}{h^2}\right)^{3/2} + \frac{3}{2} Nk + Nk \ln\left(e\frac{V}{N}\right) + \Delta S_{\text{id.mix.}}. \tag{11}$$

The Equation of State. Differentiating Eq. 8 with respect to V at constant T, we have

$$pV = NkT + NkT \frac{V}{f_m}\left(\frac{\partial f_m}{\partial V}\right)_{T,N} - \frac{N^2}{V}(\sum_i \sum_j x_i x_j a_{ij}) \tag{12}$$

$$= NkT \chi_m(\xi) - \frac{N^2}{V}(\sum_i \sum_j x_i x_j a_{ij}), \tag{13}$$

where

$$\chi_m(\xi) = \frac{1}{(1-\xi)^3}\left[(1-\xi)^2 + \frac{18}{\pi}\frac{V}{N}(XY - XY\xi + X^3)\right]. \tag{14}$$

$\chi_m(\xi)$ is the compressibility factor given by Lebowitz.[5]

Excess Thermodynamic Functions. Various excess molar quantities are given in the following. The excess volume V^E is given by

$$V^E = V - \sum_i x_i V_i, \tag{15}$$

where V_i and V are the molar volume for the pure fluid of i-th species and that for the mixture, respectively.

The excess free energy F^E is given by

$$F^E = F - \sum_i x_i F_i + T\Delta S_{\text{id.mix.}}, \tag{16}$$

where F_i is the free energy for the pure fluid of i-th species. Thus F^E is derived as follows by means of Eq. 8.

$$F^E = -N_A kT \sum_i x_i \ln\left(\frac{f_m V}{f_i V_i}\right) - \left[\frac{N_A^2}{V}\sum_i \sum_j x_i x_j a_{ij} - \sum_i x_i \frac{N_A^2}{V_i} a_{ii}\right], \tag{17}$$

where f_i is the equivalent free volume fraction for the pure fluid of i-th species and N_A Avogadro's number.

For the excess entropy, using Eq. 10 we obtain

$$S^E = S - \sum_i x_i S_i - \Delta S_{\text{id.mix.}}$$

$$= N_A k \sum_i x_i \ln\left(\frac{f_m V}{f_i V_i}\right). \tag{18}$$

Ignoring the difference between the energy and enthalpy of a liquid at ordinary pressure, we obtain the excess enthalpy H^E from Eqs. 17 and 18.

$$H^E = F^E + TS^E = -\left[\frac{N_A^2}{V}\sum_i \sum_j x_i x_j a_{ij} - \sum_i x_i \frac{N_A^2}{V_i} a_{ii}\right]. \tag{19}$$

Eqs. 17 and 19 can be expressed in terms of ξ, using the equation of state at vanishing pressure.[11,15] Equating the right-hand side of Eq. 13 to zero, we obtain

$$(N_A^2/V)\sum_i \sum_j x_i x_j a_{ij} = N_A kT \chi_m(\xi) \quad \text{(for a mixture)}, \tag{20}$$

$$(N_A^2/V) a_{ii} = N_A kT \chi(\xi_i) \quad \text{(for a pure fluid)}, \tag{21}$$

where ξ_i is the packing fraction for the pure fluid of species i. $\chi(\xi_i)$ is the compressibility factor for a one-component fluid of hard spheres.[16] Eqs. 17 and 19 are rewritten as follows:

$$F^E = -N_\mathrm{A}kT\sum_i x_i \ln\left(\frac{f_m V}{f_i V_i}\right) - N_\mathrm{A}kT[\chi_m(\xi) - \sum_i x_i\chi(\xi_i)], \tag{22}$$

and

$$H^E = -N_\mathrm{A}kT[\chi_m(\xi) - \sum_i x_i\chi(\xi_i)]. \tag{23}$$

The f_i[11] and $\chi(\xi_i)$[16] are given as

$$f_i = (1-\xi_i)\exp\left[-\frac{3\xi_i(2-\xi_i)}{2(1-\xi_i)^2}\right] \tag{24}$$

and

$$\chi(\xi_i) = \frac{(1+\xi_i+\xi_i^2)}{(1-\xi_i)^3}, \tag{25}$$

respectively, where

$$\xi_i = \frac{\pi}{6}\frac{N_\mathrm{A}}{V_i}R_i^3. \tag{26}$$

It is confirmed that the free energy of a pure fluid of species i is derived from Eq. 8 for the mixture when $x_i=1$ and all $x_j=0$ for $i\neq j$. For the case of a one-component fluid, we see that f_m (Eq. 3) is reduced to f_i (Eq. 24) and that U_BG for the mixture becomes $U_\mathrm{BG}=-N_\mathrm{A}^2 a_{ii}/V_i$, which is the uniform background potential for a pure fluid.[7]

Calculation and Results

The binary liquid mixtures chosen in this work consist of nonpolar molecules which are regarded as approximately spherical. Calculations have been made for equimolar mixtures.

Determination of a_{ii} for a Pure Component. The energy parameter a_{ii} for a pure fluid is determined from the observed values of molar volume V_i and those of the heat of vaporization $\Delta H_\text{vap.}$ at a given temperature, using the relation

$$a_{ii} = (V_i/N_\mathrm{A}^2)(\Delta H_\text{vap.} - N_\mathrm{A}kT). \tag{27}$$

The values of $\chi(\xi_i)$, ξ_i, and f_i are calculated by means of Eqs. 21, 26, and 24, respectively.

For the determination of a_{ii}, we have used the observed values of $\Delta H_\text{vap.}$ and of V_i at 25 °C, except for the case of neopentane for which boiling-point data have been used. Experimental data of V_i and $\Delta H_\text{vap.}$, and the calculated values of a_{ii} are given in Table 1, where a_{ii} is expressed in kcal cm³/mol². All the experimental data refer to ordinary pressure.

Calculation of the Energy Interaction Parameter between Different Species, a_{12}, and Excess Thermodynamic Functions.

Experimental data and calculated values are given in Table 2. For a binary mixture we have

$$\xi = (x_1\xi_1V_1 + x_2\xi_2V_2)/V, \tag{28}$$

and

$$a_{12} = \left[N_\mathrm{A}kT\chi_m(\xi)\frac{V}{N_\mathrm{A}^2} - (x_1^2a_{11} + x_2^2a_{22})\right]\frac{1}{2x_1x_2}. \tag{29}$$

By means of Eq. 28, ξ is calculated from the observed value of excess volume V^E at 25 °C (at 0°C for the systems including neopentane). a_{12} is then obtained by means of Eqs. 29, 14, and 5.

Table 1. Energy parameter a_{ii} for pure components

	T (°C)	$V_{i,\text{obsd}}$ (cm³/mol)	$\Delta H_\text{vap.}$ (kcal/mol)	a_{ii} (kcal cm³/mol²)
CCl_4	25	97.09[a]	7.83[b]	$702._7$
C_6H_6	25	89.41[a]	8.09[a]	$670._4$
c-C_6H_{12}	25	108.75[a]	7.89_6[a]	$794._3$
$C_6H_5CH_3$	25	106.85[a]	9.08[a]	$906._9$
$C(CH_3)_4$	9.5	119.67[a]	5.44[c]	$583._8$

a) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publ. Co., Amsterdam (1950, 1965). b) See Ref. 1. c) N. A. Lange, "Lange's Handbook of Chemistry," McGraw-Hill, New York (1973).

The calculated values of H^E are obtained by Eqs. 23, 14, and 21, those of TS^E being obtained by Eqs. 18, 3, and 24. The agreement between the calculated and observed values is good.

The values of a_{12} calculated from the observed values of excess enthalpy H^E are also given in Table 2 for a comparison with those obtained from the excess volume. In calculating ξ from H^E_obsd, Eq. 23 has been used replacing V by $(x_1\xi_1V_1+x_2\xi_2V_2)/\xi$. The agreement between the values of a_{12} from V^E_obsd and those from H^E_obsd is very good.

Other excess functions V^E_calcd and TS^E_calcd obtained from H^E_obsd are also given.

Equivalent Free Volume Fraction. We have calculated the values of equivalent free volume fraction f_i and f_m using Eqs. 24 and 3. The values of f_i (the free volume fraction for the pure liquid i), packing fraction ξ_i and equivalent free volume are given in Table 3. A free volume refers to $V_if_i(=Nv_f(\text{cm}^3/\text{mol}))$. The values of f_m which are identical for all components constituting the mixture, ξ and Vf_m are given in Table 4.

Discussion

Equivalent Free Volume Fraction for Mixtures. The concept of the equivalent free volume fraction was investigated for the case of a one-component hard-sphere fluid.[11] The same argument is applied to the case of mixtures.

As shown in Eqs. 1, 2, and 8, the free volume available for the molecule within the liquid mixture is Vf_m. The equivalent free volume fraction f_m given by Eq. 3 consists of a factor $(1-\xi)$ and an exponential factor. The former is equal to the fraction of void space for the total volume V, and the latter is supposed to come from the volume exclusion effect of hard sphere molecules in their thermal motions, similar to the case of a one-component fluid.[11]

The further problem is associated with the fact that the molecules constituting a mixture differ in size. We see from Eq. 2 that Vf_m is identical for all species of molecules included in the mixture, where f_m is determined from the diameters and number densities of all the constituents (Eq. 3). In other words, the same magnitude of the equivalent free volume, $v_f=Vf_m/N$, is as-

TABLE 2. ENERGY INTERACTION PARAMETER a_{12} AND EXCESS THERMODYNAMIC FUNCTIONS FOR EQUIMOLAR MIXTURES AT 25°C (AT 0 °C FOR $CCl_4+C(CH_3)_4$ AND $C_6H_6+C(CH_3)_4$)
a_{12} is in kcal cm^3/mol^2, V^E in cm^3/mol, and H^E and TS^E in cal/mol.

	Observed			Calculated from V^E_{obsd}			Calculated from H^E_{obsd}		
	V^E_{obsd}	H^E_{obsd}	TS^E_{obsd} a)	a_{12}	H^E_{calcd}	TS^E_{calcd}	a_{12}	V^E_{calcd}	TS^E_{calcd}
$CCl_4+C_6H_6$	0.01 b)	27 (±1) c,d,e)	6 b)	$685._5$	12	4	$683._5$	0.07	9
$CCl_4+c\text{-}C_6H_{12}$	0.16 f)	40 c,g)	23 h)	$741._9$	41	14	$742._1$	0.15	13
$C_6H_6+c\text{-}C_6H_{12}$	0.65 i)	192 j)	118 k)	$706._9$	185	59	$706._0$	0.68	62
$CCl_4+C_6H_5CH_3$	−0.04 l)	10 l)		$798._2$	−1	−2	$796._6$	0.00	1
$C_6H_6+C_6H_5CH_3$	0.06 l)	15 (±1) l,m,n)		$778._3$	14	7	$778._1$	0.07	7
$c\text{-}C_6H_{12}+C_6H_5CH_3$	0.56 (±0.01) j,m,o)	146 (±4) j,m,n,p)		$823._1$	172	46	$827._1$	0.45	39
$CCl_4+C(CH_3)_4$	−0.53 q)	75 r)	−3 q)	$623._6$	202	42	$641._8$	−1.22	2
$C_6H_6+C(CH_3)_4$*	−0.5 q)	(135) q,r)		$601._0$	(236)	73	$621._4$	−1.27	27

a) Estimated from the observed values of excess Gibbs free energy and H^E_{obsd}. b) G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Am. Chem. Soc.*, **62**, 712 (1940). c) J. R. Goates, R. J. Sullivan, and J. Bevan, *J. Phys. Chem.*, **63**, 589 (1959). d) J. A. Larkin and M. L. McGlashan, *J, Chem. Soc.*, **1961**, 3425. e) C. G. Savini, D. R. Winterhalter, L. H. Kovack, and H. C. van Ness, *J. Chem. Eng. Data*, **11**, 40 (1966). f) S. E. Wood and J. A. Gray, *J. Am. Chem. Soc.*, **74**, 3729 (1952); M. D. Peña and M. L. McGlashan, *Trans. Faraday Soc.*, **57**, 1511 (1961). g) H. Kehlen and H. Sackmann, *Z. Physik. Chem. (Frankfiurt)*, **50**, 135, 144 (1966). h) G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Am. Chem. Soc.*, **61**, 3206 (1939). i) S. E. Wood and A. E. Austin, *J. Am. Chem. Soc.*, **67**, 480 (1945). j) A. E. P. Watson, I. A. Mclure, J. E. Bennett, and G. C. Benson, *J. Phys. Chem.*, **69**, 2753 (1965). k) G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Phys. Chem.*, **43**, 119 (1939). l) R. P. Rastogi, J. Nath, and J. Misra, *J. Phys. Chem.*, **71**, 1277 (1967). m) A. R. Mathieson and J. C. J. Thynne, *J. Chem. Soc.*, **1956**, 3708. n) Kuei-Yen Hsu and H. L. Clever, *J. Chem. Thermodyn.*, **7**, 435 (1975). o) S. A. Sanni, C. J. D. Fell, and H. P. Hutchison, *J. Chem. Eng. Data*, **16**, 424 (1971). p) G. W. Lundberg, *J. Chem. Eng. Data*, **9**, 193 (1964). q) V. Mathot and A. Desmyter, *J. Chem. Phys.*, **21**, 782 (1953). r) A. Englert-Chwoles, *J. Chem. Phys.*, **23**, 1168 (1955).
* For $C_6H_6+C(CH_3)_4$ system, the values in bracket are those of excess Gibbs free energy, and the values given in columns 8—10 are calculated from excess Gibbs free energy.

TABLE 3. EQUIVALENT FREE VOLUME FRACTION f_i, FREE VOLUME V_f (cm^3/mol) AND PACKING FRACTION ξ_i FOR PURE LIQUIDS AT 25 °C

	$f_i\times10^3$	V_f	ξ_i
CCl_4	8.96	0.87	0.48_1
C_6H_6	7.94	0.71	0.48_6
$c\text{-}C_6H_{12}$	8.69	0.94	0.48_2
$C_6H_5CH_3$	5.11	0.55	0.50_3
$C(CH_3)_4$ a)	22.23	2.62	0.43_7

a) Calculated for 0 °C.

TABLE 4. EQUIVALENT FREE VOLUME FRACTION f_m, FREE VOLUME $V_{f,m}$ (cm^3/mol) AND PACKING FRACTION ξ FOR MIXTURES AT 25 °C

	$f_m\times10^3$	$V_{f,m}$	ξ
$CCl_4+C_6H_6$	8.48	0.79	0.48_3
$CCl_4+c\text{-}C_6H_{12}$	9.00	0.93	0.48_1
$C_6H_6+c\text{-}C_6H_{12}$	9.07	0.90	0.48_1
$CCl_4+C_6H_5CH_3$	6.74	0.69	0.49_3
$C_6H_6+C_6H_5CH_3$	6.41	0.63	0.49_5
$c\text{-}C_6H_{12}+C_6H_5CH_3$	7.17	0.78	0.49_0
$CCl_4+C(CH_3)_4$ a)	12.42	0.69	0.46_6
$C_6H_6+C(CH_3)_4$ a)	12.26	0.66	0.46_7

a) Calculated for 0 °C.

signed to all the molecules included in a liquid mixture in spite of the difference in their diameters.

In the usual free volume theories of solutions, it is important to know how the available total free volume is shared between molecules differing in size. However, the determination whether the free volume is shared equally between the molecules or shared unequally between them is made with some *ad hoc* assumptions.[2,12,17] The present treatment starting from Eqs. 2 and 8, considered to be equivalent to the free volume theory of fluids, suggests that the available total free volume for a fluid mixture is shared equally between the molecules.

We see from Tables 3 and 4 that the values of the equivalent free volume fraction are in the range 5—9×10^{-3} in most cases of pure fluids and mixtures, and that the values of free volume are in the range 0.55—0.93 cm^3/mol. We obtain $f_1<f_m<f_2$ in most cases, where subscripts 1 and 2 refer to pure components constituting the mixture. The values of packing fraction ξ are in the range 0.48—0.50 and we have $\xi_1<\xi<\xi_2$. The values for the systems including neopentane differ considerably from those shown above. This might be attributed to the fact that the temperature of measurement is near the boiling point of $C(CH_3)_4$.

The Generalized van der Waals Equation of State and the Longuet-Higgins and Widom Model. Longuet-Higgins and Widom[7] proposed the following equation of state for pure fluids.

$$pV = p_0V - aN^2/V, \tag{30}$$

where p_0 is the pressure exerted by hard cores taken to be the true 3-dimentional hard-sphere pressure rather than the value $NkT/(V-b)$ as in the original van der Waals theory.

The equation of state Eq. 13, which was presented for binary mixtures by Snider and Herrington,[6] is an extention of the generalized van der Waals equation of state Eq. 30 to mixtures.

The liquid model of Longuet-Higgins and Widom rests on the following view for fluid. The repulsive forces between molecules play the most important role in determining the short range behavior of molecules in a liquid, the attractive forces merely maintaining the liquid density. This view seems to be essentially correct, as stated also by Leland, Rowlinson and Sather[13]. The Lebowitz solution is an analytical solution of the generalized Percus-Yevick equation for hard sphere mixtures, giving the "entropy of mixing" for mixtures on the theoretically more sound ground than the lattice theories of fluids.[18] Snider and Herrington used the equation of state of hard spheres obtained from the Lebowitz solution, but they did not elucidate the nature of the Lebowitz solution, giving very lengthy expressions untractable for practical use.[20]

Energy Parameters and Excess Functions. The values of a_{12} from V^E_{obsd} are in extremely good agreement with those from H^E_{obsd} (fifth and eighth columns, Table 2). The values do not differ from each other by more than about 0.5%, except in the case of the systems including neopentane. The energy interaction parameter a_{12} between different species has been introduced for extending a uniform background potential for pure fluids to mixtures ($U_{\text{BG}}=-N_A^2\sum_i\sum_j x_ix_ja_{ij}/V$). The striking agreement between the values of a_{12} from V^E_{obsd} and those from H^E_{obsd} shows the reality of that parameter and the effectiveness of the present treatment.

In order to determine a_{12}, data for one of excess thermodynamic functions must be used. Usually, the experimental data of H^E or that of the excess Gibbs free energy is used. The results shown in Table 2 permit us to calculate the values of a_{12} from the measured values of V^E (or density). This is very useful in practical applications since the density can be measured more easily than other thermodynamic quantities such as excess heat.

The agreement between the values of H^E calculated from V^E_{obsd} and the experimental values is fairly good. This is ascribed to the good agreement between the values of a_{12} from V^E_{obsd} and those from H^E_{obsd}. Reasonable values of H^E and S^E as well as a_{12} can be obtained from V^E_{obsd}.

In the present treatment, a_{ii} has been regarded as unchanged with the variation of temperature. In order to determine the values, the observed values of $\Delta H_{\text{vap.}}$ and V_i at 25 °C were used. The values of a_{ii} for C_6H_6 calculated from the data of $\Delta H_{\text{vap.}}$ and V_i at various temperatures are given in Table 5. The standard deviation of errors in the values of a_{ii} is about 7 kcal cm^3/mol^2 (about 1.1% to the mean values) in the range 10—50 °C. The values of a_{ii} can be regarded to be constant in this range. In the range, 0—80.1 °C (boiling point), it is about 14.4 kcal cm^3/mol^2 (about 2.2%).

Temperature Dependence of Excess Functions and Energy Parameters. The calculation of excess functions for the binary mixtures of CCl_4, C_6H_6 and c-C_6H_{12} at 20—

TABLE 5. VALUES OF a_{ii} AT VARIOUS TEMPERATURES FOR C_6H_6

T (°C)	$V_{i,\text{obsd}}$ (cm^3/mol)	$\Delta H_{\text{vap.}}$ (kcal/mol)	a_{ii} (kcal cm^3/mol^2)
0	86.78[a]	8.35_8[b]	$678._2$
10	87.82[c]	8.21_7[c]	$672._2$
25	89.41[c]	8.09_0[c]	$670._4$
50	92.26[c]	7.75_6[c]	$656._3$
80.1	95.90[c]	7.35_3[c]	$638._0$

a) S. E. Wood and J. P. Brusie, *J. Am. Chem. Soc.*, **65**, 1891 (1943). The value was estimated by extrapolation. b) See Table 1, footnote b. c) See Table 1, footnote a.

TABLE 6. EXCESS THERMODYNAMIC FUNCTIONS FOR EQUIMOLAR MIXTURES AND ENERGY INTERACTION PARAMETER a_{12} AT 20, 30, AND 40 °C

V^E is in cm^3/mol, H^E and TS^E in cal/mol, and a_{12} in kcal cm^3/mol^2.

T (°C)	Observed			Calculated from V^E_{obsd}			Calculated from H^E_{obsd}		
	V^E_{obsd}	H^E_{obsd}	TS^E_{obsd}[a]	a_{12}	H^E_{calcd}	TS^E_{calcd}	a_{12}	V^E_{calcd}	TS^E_{calcd}
$CCl_4+C_6H_6$									
20	0[b]	24[c]	4[d]	$685._8$	9	3	$684._1$	0.05	8
30	0.02[b]	28[c]	9[d]	$685._2$	14	5	$683._5$	0.07	9
40	0.04[b]	31[c]	12[d]	$684._7$	19	6	$683._1$	0.09	10
CCl_4+c-C_6H_{12}									
20	0.16[e]	40[c,e]	23[f]	$741._6$	42	14	$742._1$	0.15	13
30	0.16[e]	40[c,e]	23[f]	$742._0$	40	13	$742._2$	0.16	14
40	0.16[e]	40[c,e]	23[f]	$742._3$	39	14	$742._0$	0.17	14
C_6H_6+c-C_6H_{12}									
20	0.65[g]	197[h]	121[i]	$706._4$	189	59	$705._5$	0.68	62
30	0.66[g]	190[h]	116[i]	$707._1$	183	59	$705._9$	0.70	61
40	0.66[g]	180[h]	109[i]	$708._3$	175	58	$707._5$	0.68	60

a) See Table 2, footnote a. b) See Table 5, footnote a. c) See Table 2, footnote c. d) See Table 2, footnote b. e) See Table 2, footnote g. f) See Table 2, footnote h. g) See Table 2, footnote i. h) Estimated from the heats of mixing as reported in the following works: G. Scatchard, L. B. Ticknor, J. R. Goates, and E. R. McCartney, *J. Am. Chem. Soc.*, **74**, 3721 (1952); R. Thacker and J. S. Rowlinson, *Trans. Faraday Soc.*, **50**, 1036 (1954); W. R. Moore and G. E. Styan, *Trans. Faraday Soc.*, **52**, 1556 (1956); see also Table 2, footnote j. i) See Table 2, footnote k.

40 °C has been carried out (Table 6). For the values of V_i and V^E we used the observed ones at each temperature. Concerning the values of a_{ii}, we used those given in the fifth column of Table 1 regarding as unchanged with the variation in temperature. The results obtained from the data of H^E_{obsd} are also included in Table 6.

We see that the calculated values for the various excess functions reproduce the trend of the temperature dependence in the observed values, but not necessarily the absolute magnitude. The values of the energy parameter a_{12}, which has been treated as a constant, are practically constant in the range 20—40 °C.

Concluding Remarks

A statistical thermodynamic theory of binary liquid mixtures has been worked out using the notion of the equivalent free volume fraction.

(a) The total free energy is expressed as the sum of three terms: the translational term of an ideal-gas mixture, the term resulting from the equivalent free volume fraction, and the energy term resulting from the uniform background potential.

(b) The equivalent free volume fraction is found to be identical for all species of molecules constituting the mixture, *viz.*, the same magnitude of equivalent free volume is assigned to all the molecules in spite of their different sizes, which is in sharp contrast to the cases in usual free volume theories.

(c) Concerning the energy parameter of mixtures, the form of a quadratic sum of a_{ij} has been used. The values of the energy interaction parameter a_{12} calculated from the values of V^E_{obsd} are found to be in good agreement with those from H^E_{obsd}. This result shows the reality of a_{12} and permits us to calculate the values of a_{12} from V^E_{obsd}.

(d) The agreement between the experimental and calculated values of various excess thermodynamic functions is found to be good on the whole, except for the case of the systems including neopentane.

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