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Statistical Thermodynamics of Binary Liquid Mixtures

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By means of the cell method and using the Sutherland type potential function for pair interactions between molecules, a statistical theory was formulated for binary liquid mixtures consisting of rigid spherical molecules differing in size. A formula was derived for cohesive energy as a function of the volume of liquid, and studied in combination with the radial distribution function. The applicability of the square-well type potential function within a cell was also examined. Formulas for excess thermodynamic functions were derived and their applicability investigated. For 22 binary systems consisting of nearly spherical molecules, excess thermodynamic functions were calculated and compared with data in literature. The results show that the theory is applicable to the mixtures.

The present paper deals with the statistical theory of non-electrolyte solutions. The principal problem in the statistical thermodynamics of liquid mixtures is to calculate the thermodynamic properties of mixtures from the forces between molecules. Many attempts have been made since the designation of "regular solutions" by Hildebrand[1] and Scott.[1,2] The following theories are remarkable: "strictly regular solution theory" based on the lattice model developed by Guggenheim[3] and Rushbrooke,[4] the "conformal solution" theory by Longuet-Higgins,[5] theories by the cell method developed mainly by Prigogine and co-workers,[6-9] by Salsburg and Kirkwood,[10] and by Scott,[11] theories based on the explicit combination of the cell method and the "corresponding state theorem" developed by Prigogine and coworkers[12] and by Scott,[11] and the significant structure theory by Eyring and coworkers.[13]

Recently, Flory and Abe have presented a simple corresponding state theory of liquid mixtures of nonpolar molecules,[14] which is applicable to mixtures of molecules differing in size, based on Prigogine's treatment of r-mer molecules.[15]

Theories based on the radial distribution function, which have been developed by Kirkwood, Born, Green, and others,[16] are more rigorous than the theories described above, but they are mathematically laborious, and inconvenient for practical use.

The present statistical theories of solutions are unsatisfactory as a whole, as the agreement between calculated and observed values is only qualitative, and the underlying assumptions need further examination.

The authors present a statistical theory of binary liquid mixtures by the cell method in combination with the radial distribution function, where the interaction potential between molecules is assumed to be of Sutherland type.

Part I. Theory

Formulation of the Partition Function. *Mean*

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[1] J. H. Hildebrand and R. L. Scott, "The Solubility of Non-electrolyte," 3rd Ed., Reinhold, New York (1953) p. 46.

[2] R. L. Scott, *Discuss. Faraday Soc.*, **15**, 44 (1953).

[3] E. A. Guggenheim, *Proc. Roy. Soc.*, *Ser. A* **148**, 304 (1935); *ibid.*, **A183**, 203, 213 (1944). R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge Univ. Press Inc. (1939) p. 351.

[4] G. S. Rushbrooke, *Proc. Roy Soc.*, *Ser. A* **166**, 296 (1938).

[5] H. C. Longuet-Higgins, *ibid.*, *Ser. A* **205**, 247 (1951).

[6] I. Prigogine and V. Mathot, *J. Chem. Phys.*, **20**, 49 (1952).

[7] V. Mathot and A. Desmyter, *ibid.*, **21**, 782 (1953).

[8] I. Prigogine and A. Bellemans, *ibid.*, **21**, 561 (1953).

[9] I. Prigogine and A. Bellemans, *Discuss. Faraday Soc.*, **15**, 80 (1953).

[10] Z. W. Salsburg and J.G. Kirkwood, *J. Chem. Phys.*, **21**, 2169 (1953).

[11] R. L. Scott, *ibid.*, **25**, 193 (1956).

[12] I. Prigogine, A. Bellemans and A. Englert-Chowles, *ibid.*, **24**, 518 (1956).

[13] H. Eyring, A.T. Ree and N. Hirai, *Proc. Nat. Acad. Sci. U.S.*, **44**, 683 (1958); S. Ma and H. Eyring, *J. Chem. Phys.*, **42**, 1920 (1965).

[14] P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1833 (1965); A. Abe and P.J. Flory, *ibid.*, **87**, 1838 (1965).

[15] I. Prigogine, A. Bellemans and C. Naar-Colin, *J. Chem. Phys.*, **26**, 751 (1957).

[16] J. G. Kirkwood and E.M. Boggs, *ibid.*, **10**, 394 (1942). J.G. Kirkwood and F.P. Buff, *ibid.*, **19**, 774 (1951). M. Born and H. S. Green, *Proc. Roy. Soc.*, **A188**, 10 (1946). G.J. Throop and R. J. Bearman, *J. Chem. Phys.*, **44**, 1423 (1966). H. S. Chung and W.F. Espensheid, *ibid.*, **47**, 219 (1967).

Field for a Molecule within a Cell. In the following treatment we assume that molecules are rigid spheres, and the potential of interaction between two molecules is a function of the intermolecular separation. As the potential function for two molecules a distance a apart, a Sutherland type function, $\varepsilon(a)$, is used,[17] where a is the average distance between the centers of nearest neighbors.

$$\varepsilon(a)=\begin{cases}-\varepsilon^*\left(\dfrac{r^*}{a}\right)^6 & \text{for } a>r^* \\ \infty & \text{for } a<r^*\end{cases} \tag{1}$$

where ε^* is an energy constant. For a pure liquid, a molecule with a diameter r^* is assumed to be wandering in a spherical cell of radius a. The average potential function of mutual interaction, $\bar{\varepsilon}(r)$, in the cell is evaluated according to the same averaging procedure as made by Lennard-Jones and Devonshire,[18] where r is the distance from the center of the cell.[*1].

$$\bar{\varepsilon}(r)=\frac{1}{2}\int_0^\pi \varepsilon((r^2+a^2-2ar\cos\theta)^{1/2})\sin\theta\mathrm{d}\theta$$

$$=\begin{cases}-\varepsilon^*(r^*/a)^6 & \text{for } r=0 \\ -\varepsilon^*\dfrac{r^{*6}(a^2+r^2)}{(a^2-r^2)^4} & \text{for } r<a-r^* \\ \infty & \text{for } r>a-r^*\end{cases} \tag{2}$$

The shape of the function is of nearly square-well type.

We have calculated the magnitude of $\bar{\varepsilon}(a-r^*)/\bar{\varepsilon}(0)$ (the ratio between the depth of the potential at the center and that at its periphery) in order to investigate the extent of deviations of the potential function $\bar{\varepsilon}(r)$ from the perfect square-well type. The results are given in Table 1 for various magnitudes of (a/r^*). In ordinary liquids, the ratio $(a/r^*)^3$ is believed to be not larger than 1.3.

Thus the function $\bar{\varepsilon}(r)$ could be approximated by a perfect square-well type whose depth is given in Eq. (2)

TABLE 1. POTENTIAL FIELD WITHIN A CELL

a/r^*	$(a/r^*)^3$	$\bar{\varepsilon}(a-r^*)/\bar{\varepsilon}(0)$
1.05	1.16	1.01
1.1	1.33	1.04
1.2	1.73	1.15

In order to obtain the average potential, $\omega(r)$, for a wandering molecule within a cell for $r<a-r^*$, the influence of the outer neighbors is taken into account, and the following integration has been made, where $g(l)$ is the radial distribution function[16,19] at distance l in the liquid consisting of N molecules and occupying a volume V.

$$\omega(r)=\int_{r^*}^\infty \bar{\varepsilon}(r)\cdot 4\pi l^2\frac{Ng(l)}{V}\mathrm{d}l$$

$$=-\int_{r^*}^\infty \varepsilon^*\frac{r^{*6}(l^2+r^2)}{(l^2-r^2)^4}\cdot\frac{4\pi l^2}{V}Ng(l)\mathrm{d}l$$

$$=-\gamma\varepsilon^*\left(\frac{N\cdot\frac{4}{3}\pi r^{*3}}{V}\right)$$

$$\times\left[1+3\left(\frac{\gamma'}{\gamma}\right)\left(\frac{r}{r^*}\right)^2+\mathrm{O}\left(\left(\frac{r}{r^*}\right)^4\right)\right] \tag{3}$$

where

$$\left.\begin{aligned}\gamma&=\int_{r^*}^\infty\frac{g(l)}{l^4}\mathrm{d}l\Big/\int_{r^*}^\infty\frac{\mathrm{d}l}{l^4}\\ \gamma'&=\int_{r^*}^\infty\frac{g(l)}{l^6}\mathrm{d}l\Big/\int_{r^*}^\infty\frac{\mathrm{d}l}{l^6}\end{aligned}\right\} \tag{4}$$

As described above, $r/r^*\lesssim 0.1$ for ordinary liquids, and γ and γ' are of the same order (Table 2). Therefore, $\omega(r)$ can be approximated by the first term in Eq. (3), similar to the case of the mutual potential energy $\bar{\varepsilon}(r)$. Throughout the present calculations the potential energy function $\omega(r)$ of square-well type, as given in the following, is used for a wandering molecule within a cell.

$$\omega(r)=\begin{cases}-\gamma\varepsilon^*\left(\dfrac{\frac{4}{3}\pi r^{*3}N}{V}\right) & \text{for } r<a-r^* \\ \infty & \text{for } r>a-r^*\end{cases} \tag{5}$$

The wandering molecule behaves like a gas molecule within a cell. The depth of the potential well, $\omega(0)$, is related to the heat of vaporization ΔH_V for the liquid as shown by

$$-\frac{N}{2}\omega(0)=\frac{2}{3}\pi N^2\gamma\varepsilon^* r^{*3}\frac{1}{V}=\Delta H_V-\boldsymbol{R}T, \tag{6}$$

where $\boldsymbol{R}$ is gas constant and T temperature.

Partition Function for a Binary Liquid Mixture. Thermodynamic properties of a solution consisting of N_A molecules of species A and N_B molecules of species B, are derived from the following partition function Z formulated by the cell method assuming the square-well type potential within each cell in the solution.

$$Z=\frac{N!}{N_A!N_B!}f_A^{N_A}f_B^{N_B}$$

$$\times\exp\left[-\frac{1}{2kT}(N_A\omega_A(0)+N_B\omega_B(0))\right]$$

$$f_A=\frac{4\pi}{3}(a_A-r_A^*)^3 j_A,\quad f_B=\frac{4\pi}{3}(a_B-r_B^*)^3 j_B \tag{7}$$

where j_A(T) and j_B(T) are internal partition functions for each molecule of species A and B, and

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[17] J. O. Hirshfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gasses and Liquids," Wiley, New York (1954), p. 32.

[18] J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc.*, **A163**, 53 (1937), **A165**, 1 (1938).

[*1] Readers should refer to "Theory of Liquids," A. Harashima (Iwanami), pp. 41—42, Fig. 8—1 (1954).

[19] J. G. Kirkwood, E. K. Maun and B. J. Alder, *J. Chem. Phys.*, **18**, 1040 (1950).

$\omega_A(0)$ and $\omega_B(0)$ are the depth of the potential well for the molecules of species A and B in each cell, respectively. a_A and a_B are the radius of the spherical cell for each species in the solution. They are related to the volume per molecule v by the formula

$$\frac{V}{N} = v(a_A, a_B) = x_A\beta a_A{}^3 + x_B\beta a_B{}^3, \tag{8}$$

where x_A and x_B are the mole fraction for each species. The applicability of the common packing parameter β is assumed. $r_A{}^*$ and $r_B{}^*$ are the collision diameter of the molecule within each cell. They are assumed to be related to the diameters of each species in the pure state $r_{AA}{}^*$ and $r_{BB}{}^*$ by the formula

$$r_A{}^* = x_A r^*_{AA} + x_B r^*_{AB}, \quad r_B{}^* = x_A r^*_{AB} + x_B r^*_{BB}, \tag{9}$$

where

$$r^*_{AB} = \frac{1}{2}(r^*_{AA} + r^*_{BB}).$$

The energy $\omega_A(0)$ and $\omega_B(0)$ for the molecules within cell, and $\omega_A{}^\circ(0)$ and $\omega_A{}^\circ(0)$ for the molecules within cells in each pure liquid, are given by

$$\omega_A(0) = -\gamma\varepsilon_A{}^*\left(\frac{\frac{4}{3}\pi r_A{}^{*3}}{v}\right),$$

$$\omega_B(0) = -\gamma\varepsilon_B{}^*\left(\frac{\frac{4}{3}\pi r_B{}^{*3}}{v}\right),$$

$$\omega_A{}^\circ(0) = -\gamma\varepsilon^*_{AA}\left(\frac{\frac{4}{3}\pi r^{*3}_{AA}}{v_A{}^\circ}\right),$$

$$\omega_B{}^\circ(0) = -\gamma\varepsilon^*_{BB}\left(\frac{\frac{4}{3}\pi r^{*3}_{BB}}{v_B{}^\circ}\right) \tag{10}$$

according to Eq. (5), where $v_A{}^\circ$ and $v_B{}^\circ$ are the volume per molecule in each pure state. The energy parameters $\varepsilon_A{}^*$ and $\varepsilon_B{}^*$ are given by

$$\varepsilon_A{}^* = x_A\varepsilon^*_{AA} + x_B\varepsilon^*_{AB}, \quad \varepsilon_B{}^* = x_A\varepsilon^*_{AB} + x_B\varepsilon^*_{BB}, \tag{11}$$

where $\varepsilon_{AB}{}^*$ is the energy parameter of the Sutherland type pair interaction between species A and B (Eq. (1)) in the solution.

Determination of Parameters a_A and a_B, and the Equation of State. The two parameters a_A and a_B, which are the radius of the spherical cell for each species in the solution, are determined by the minimization of the Helmholtz energy A under the condition of a given volume (Eq. (8)) as well as that of vanishing external pressure by procedures similar to those adopted by Prigogine and Bellemans.[9]

$$A = A(a_A, a_B, T) = A(a_A, v, T) = -kT\ln Z \tag{12}$$

$$\left(\frac{\partial A}{\partial a_A}\right)_{v,T} = \left(\frac{\partial A}{\partial a_A}\right)_{a_B,T} + \left(\frac{\partial A}{\partial a_B}\right)_{a_A,T}\left(\frac{\partial a_B}{\partial a_A}\right)_v = 0 \tag{13}$$

$$-p = \left(\frac{\partial A}{\partial v}\right)_{T,a_A} = \left(\frac{\partial A}{\partial a_B}\right)_{a_A,T}\left(\frac{\partial a_B}{\partial v}\right)_{a_A} = 0 \tag{14}$$

Combinining Eqs. (13) and (14), we obtain

$$\left(\frac{\partial A}{\partial a_A}\right)_{a_B,T} = \left(\frac{\partial A}{\partial a_B}\right)_{a_A,T} = 0. \tag{15}$$

From Eqs. (7) and (12), the Helmholtz energy A is expressed as follows.

$$\begin{aligned} A = {} & \frac{N}{2}(x_A\omega_A(0) + x_B\omega_B(0)) \\ & + NkT(x_A\ln x_A + x_B\ln x_B) \\ & - NkT(x_A\ln f_A + x_B\ln f_B) \end{aligned} \tag{16}$$

Introducing Eq. (16) into Eq. (15), and assuming $(\partial\gamma/\partial v)=0$,*2 we obtain

$$\begin{aligned} a_A{}^2(a_A - r_A{}^*) &= a_B{}^2(a_B - r_B{}^*) \\ &= \frac{3v^2kT}{2\pi\gamma\beta(x_A\varepsilon_A{}^* r_A{}^{*3} + x_B\varepsilon_B{}^* r_B{}^{*3})}. \end{aligned} \tag{17}$$

In principle, we can determine the magnitude of a_A and a_B from Eq. (17). However, it is difficult to obtain analytical solutions of a_A and a_B because Eq. (17) is 3rd power with respect to a_A and a_B. Thus putting

$$\frac{a_A - r_A{}^*}{r_A{}^*} = \rho_A, \quad \frac{a_B - r_B{}^*}{r_B{}^*} = \rho_B \tag{18}$$

and using the conditions $\rho_A < 1$, $\rho_B < 1$ for ordinary liquids, we obtain the following relation, where Eq. (8) is used and higher order terms than the first with respect to ρ_A and ρ_B are ignored.

$$\frac{v - \beta(x_A r_A{}^{*3} + x_B r_B{}^{*3})}{v^2} = \frac{9kT}{2\pi(x_A\gamma\varepsilon_A{}^* r_A{}^{*3} + x_B\gamma\varepsilon_B r_B{}^{*3})} \tag{19}$$

$$\rho_A = \frac{3v^2kT}{2\pi\beta r_A{}^{*3}(x_A r_A{}^{*3}\gamma\varepsilon_A{}^* + x_B r_B{}^{*3}\gamma\varepsilon_B{}^*)}$$

$$\rho_B = \frac{3v^2kT}{2\pi\beta r_B{}^{*3}(x_A r_A{}^{*3}\gamma\varepsilon_A{}^* + x_B r_B{}^{*3}\gamma\varepsilon_B{}^*)}. \tag{20}$$

Excess Thermodynamic Functions of the Binary Liquid Mixture. Various excess thermodynamic functions can be obtained from the equations described above. The excess Helmholtz energy $A_E = A - x_A A_A{}^\circ - x_B A_B{}^\circ - T\Delta S^{\mathrm{id.}}_{\mathrm{mix}}$ is given in Eq. (21) from Eq. (16).

$$\begin{aligned} A_E = {} & \frac{N}{2}\{x_A(\omega_A(0) - \omega_A{}^\circ(0)) + x_B(\omega_B(0) - \omega_B{}^\circ(0))\} \\ & - NkT\left(x_A\ln\frac{f_A}{f_A{}^\circ} + x_B\ln\frac{f_B}{f_B{}^\circ}\right) \end{aligned} \tag{21}$$

where $\omega_A(0)$, $\omega_B(0)$, $\omega_A{}^\circ(0)$, $\omega_B{}^\circ(0)$, f_A, and f_B are given in Eqs. (7) and (10). The superscript ° represents the values for pure liquids. The excess

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*2 As will be discussed later, γ is slightly dependent on volume. However, in the present treatment γ is replaced by its average value.

energy $E_E=E-x_AE_A{}^\circ-x_BE_B{}^\circ$ is obtained from Eq. (21) and the thermodynamical relations, assuming $(\partial\gamma/\partial T)_V=0$ and the invariance of internal partition function by the transfer from pure liquid to solution.

$$E_E=\frac{N}{2}\{x_A(\omega_A(0)-\omega_A{}^\circ(0))+x_B(\omega_B(0)-\omega_B{}^\circ(0))\} \tag{22}$$

Introducing Eq. (10) into Eq. (22), we obtain

$$E_E=-\frac{2\pi N}{3}\left\{\frac{1}{v}(x_Ar_A{}^{*3}\gamma\varepsilon_A{}^*+x_Br_B{}^{*3}\gamma\varepsilon_B{}^*)-\left(\frac{x_Ar_{AA}^{*3}\gamma\varepsilon_{AA}^*}{v_A{}^\circ}+\frac{x_Br_{AA}^{*3}\gamma\varepsilon_{BB}^*}{v_B{}^\circ}\right)\right\} \tag{22'}$$

The excess entropy $S_E=S-x_AS_A{}^\circ-x_BS_B{}^\circ-\Delta S_{\text{mix}}^{\text{id.}}$ is obtained as follows.

$$\begin{aligned}S_E&=-3Nk\left(x_A\ln\frac{a_A{}^\circ-r_{AA}^*}{a_A-r_A{}^*}+x_B\ln\frac{a_B{}^\circ-r_{BB}^*}{a_B-r_B{}^*}\right)\\&=-3Nk\left(x_A\ln\frac{\rho_A{}^\circ r_{AA}^*}{\rho_Ar_A{}^*}+x_B\ln\frac{\rho_B{}^\circ r_{BB}^*}{\rho_Br_B{}^*}\right)\end{aligned} \tag{23}$$

The excess volume $V_E=V-x_AV_A{}^\circ-x_BV_B{}^\circ$ is obtained from Eq. (19)

$$V_E=N\left[\beta\{x_A(r_A{}^{*3}-r_{AA}^{*3})+x_B(r_B{}^{*3}-r_{BB}^{*3})\}+\frac{9kT}{2\pi}\left\{\frac{(x_Av_A{}^\circ+x_Bv_B{}^\circ)^2}{x_A\gamma\varepsilon_A{}^*r_A{}^{*3}+x_B\gamma\varepsilon_B{}^*r_B{}^{*3}}-\frac{x_Av_A{}^{\circ2}}{\gamma\varepsilon_{AA}^*r_{AA}^{*3}}-\frac{x_Bv_B{}^{\circ2}}{\gamma\varepsilon_{BB}^*r_{BB}^{*3}}\right\}\right]\Bigg/\left[1-\frac{9kT}{\pi}\left(\frac{x_Av_A{}^\circ+x_Bv_B{}^\circ}{x_A\gamma\varepsilon_A{}^*r_A{}^{*3}+x_B\gamma\varepsilon_B{}^*r_B{}^{*3}}\right)\right]. \tag{24}$$

From Eq. (19) we obtain the following equation, when $x_A=1$ and $x_B=0$.

$$\gamma\varepsilon_{AA}^*=\frac{9kT}{2\pi}\cdot\frac{v_A{}^\circ}{r_{AA}^{*3}}\cdot\frac{v_A{}^\circ}{v_A{}^\circ-\beta r_{AA}^{*3}} \tag{25}$$

Introducing Eqs. (10) and (25) into Eq. (22), the approximate relation between E_E and V_E is derived.

$$\frac{E_E}{3NkT}=\left\{\left(\frac{x_Av_A{}^\circ}{v_A{}^\circ-\beta r_{AA}^{*3}}+\frac{x_Bv_B{}^\circ}{v_B{}^\circ-\beta r_{BB}^{*3}}\right)-\left(\frac{\bar v_0}{\bar v_0-\bar v^*}\right)\right\}+\left\{\frac{\bar v^*}{(\bar v_0-\bar v^*)^2}\right\}v_E \tag{26}$$

where $\bar v_0=x_Av_A{}^\circ+x_Bv_B{}^\circ$ and $\bar v^*=x_A(\beta r_{AA}{}^{*3})+x_B(\beta r_{BB}{}^{*3})$, and the conditions $v_E\ll\bar v_0$ and $v_E\ll\bar v_0-\bar v^*$ are satisfied.

Discussion on the Potential $\omega(r)$ and the Physical Meaning of the Parameter γ. *Volume Dependency of the Potential within a Cell.* For the volume dependency of the potential energy the inverse first power relation has been proposed by Hildebrand *et al.*,[20] and adopted by Flory and Abe[14] in their solution theory. Assuming that the energy is proportional to V^{-n}, Hildebrand and co-workers showed the power n for various organic liquids to be not far from unity. Their result was confirmed experimentally by Beninga and Scott.[21]

We have derived the average potential as a function of the volume of liquid on the basis of the Sutherland type interaction, and have obtained an explicit representation of the potential with molecular parameters using the radial distribution function $g(l)$.

In the derivation of the equation of state, Eq. (17), from Eq. (15), we have assumed that γ is independent of volume. The potential function $\omega(r)$ (Eq. (5)) within a cell is found to be proportional to $(1/V)$ in accordance with the earlier results.[20,21] The value of γ is maintained to be 2.0 within the range of fluctuation of 0.1 for ordinary liquids (Table 3 and Appendix). The underlying assumption is regarded to be reasonable as an approximation. However, as seen in Table 2 γ decreases gradually with volume. This means that $n>1$. Recently, it has been found experimentally that n is 1.4 for alkanes which are non-spherical in molecular shape.[22]

Temperature Dependence of the Parameter γ. Using the values of $g(l)$ calculated by Kirkwood *et al.*[19] for liquids consisting of rigid spherical molecules, we have determined the magnitude of γ (Table 2) for various magnitudes of a parameter λ which is related to density.[19]

TABLE 2. VALUES OF PARAMETER γ

	Rigid sphere with no attractive forces*[19]				
λ	5	10	20	27.4	33
V/V^*	5.15	3.20	2.10	1.73	1.53
γ	1.19	1.36	1.59	1.72	1.82
γ'	1.29	1.50	1.81	1.99	2.13
	Lennard-Jones fluid,(Kirkwood *et al.*[23])				
	$\lambda=27.4$		$V/V^*=1.73$		
kT/ε	0.833		1.111		1.667
γ	1.63		1.69		1.78
	Lennard-Jones fluid (Verlet[24])				
			$V/V^*=1.885$		
kT/ε	0.827				1.304
γ	1.49				1.49
			$V/V^*=1.663$		
kT/ε	0.719		0.880		1.273
γ	1.60		1.60		1.57

* $V^*=N\beta r^{*3}$

As seen from Eq. (4), γ is dependent on temperature through the temperature dependence of $g(l)$. In the derivation of Eq. (22) the temperature dependence of γ is ignored. Taking the temperature dependence into account, the excess energy E_E is obtained as

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20) Ref. 17, p. 280; Ref. 1, Chapter V.

21) H. Beninga and R. L. Scott, *J. Chem. Phys.*, **23**, 1911 (1955).

22) V. Fried and G. B. Schneider, *J. Phys. Chem.*, **72**, 4688 (1968).

$$E_E = \frac{\partial(A_E/T)}{\partial(1/T)_V} = E_E^\circ\left(1-\left(\frac{\partial \log \gamma}{\partial \log T}\right)_V\right), \quad (27)$$

where E_E° is the excess energy given in Eq. (22), and the same temperature dependence of γ is assumed for all species.

According to the Kirkwood-Born-Green theory[16,19] the temperature dependence of the radial distribution function g for a fluid of rigid spheres with no attraction comes from that of a parameter λ, which is related to only density, and thus, only from the temperature dependence of (V^*/V). Thus, for a fluid consisting of rigid spherical molecules with no attractive pair interactions, we have

$$(\partial g/\partial T)_V = 0$$

and

$$(\partial \ln \gamma/\partial \ln T)_V = 0. \quad (28)$$

Thus Eq. (27) reduces to Eqs. (22) and (22′). In all the theories based on a cell model, the number of nearest neighbors was always assumed to be constant. This is equivalent to the assumption that γ is independent of temperature.

When attractive forces act between molecules, it is difficult to calculate $(\partial \log \gamma/\partial \log T)_V$ analytically. The values of γ are calculated numerically for fluids in which the interaction potential between molecules is of Lennard-Jones type, using the values of g given by Kirkwood *et al.*[23] and Verlet.[24] The results are given in Table 2. It is seen that the temperature dependence of γ, is very small. Thus, the application of condition (28) is justified.

Recently Fried and Schneider[22] have reported from experimental grounds that the parameter a (the cohesive energy is given by $-a/V^n$ in their paper) is slightly temperature-dependent at ordinary temperatures, and that the variation of a is less than 3% over a wide range of temperature. The parameter a is supposed to be proportional to our parameter γ. Thus, their results seem to support our result with respect to the temperature dependence of γ.

Estimation of Parameters λ and γ. The values of parameter λ are determined for liquids consisting of rigid spherical molecules with no attractive interactions, by means of the formula[16]

$$\lambda = 3((2\Delta H_V)/(NkT) - \log(V_g/V_l)) \quad (29)$$

where V_l and V_g are the volume of liquid and gas respectively.[16] It is difficult to determine λ for fluids in general. Thus, we use Eq. (29) as an approximate formula for the determination of λ. Values of λ for various liquids are given in Table 3, together with values of γ determined by extrapolation along the γ *vs.* λ curve given in Fig. 1. It is shown in the appendix[25,26] that the estimation of γ is reasonable.

TABLE 3. VALUES OF PARAMETERS λ AND γ FOR VARIOUS LIQUIDS

	T (°K)	V^l (cm^3)	ΔH_v (cal/mol)	λ	γ
A	87	28	1560	35.9	1.84
N_2	77	35	1330	36.2	1.86
CH_4	112	38	1960	36.1	1.86
CCl_4	298	97	7830	62.3	2.1
C_6H_6	298	89	8090	64.6	2.1
	353	96	7350	45.4	1.9_5
c-C_6H_{12}	298	109	7900	63.3	2.1
	354	116	7190	43.5	1.9_5

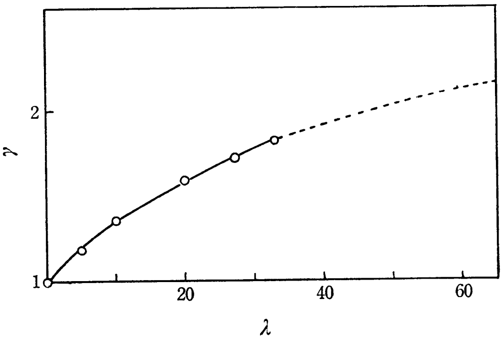

Fig. 1. The values of parameter γ for the liquid composed of rigid spherical molecules with no attractive forces.

Part II. Numerical Computations.

We present here with an analysis of excess functions V_E, E_E, and S_E for binary liquid mixtures. The binary systems consist of pairs of molecules which are approximately spherical and not greatly different in size. Random mixing is assumed. The excess thermodynamic functions for 22 binary liquid mixtures are calculated.

Procedure of Calculation. *Excess Thermodynamic Function.* Combining Eq. (22) with Eqs. (19) and (25), we have

$$E_E = 3\boldsymbol{R}T\left\{\left(\frac{x_A v_A^\circ}{v_A^\circ-\beta r_{AA}^{*3}}+\frac{x_B v_B^\circ}{v_B^\circ-\beta r_{BB}^{*3}}\right)\right.$$
$$\left.-\frac{v}{v-\beta(x_A r_A{}^{*3}+x_B r_B{}^{*3})}\right\}. \quad (30)$$

For the excess volme V_E, we obtain from Eq. (30)

$$\frac{V_E}{N} = \beta(x_A r_A{}^{*3}+x_B r_B{}^{*3})\left(\frac{K-E_E}{K-E_E-3\boldsymbol{R}T}\right) - \bar{v}_0 \quad (31)$$

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23) J. G. Kirkwood, V. A. Lewinson and B. J. Alder, *J. Chem. Phys.*, **20**, 929 (1952).

24) L. Verlet, *Phys. Rev.*, **165**, 201 (1968).

25) A. Harashima, "Theory of Liquids," Iwanami (1954), p. 42.

26) A. Eisenstein and N. S. Gingrich, *Phys. Rev.*, **62**, 261 (1942).

where

$$K = 3\boldsymbol{R}T\left\{\left(\frac{x_A v_A{}^{\circ}}{v_A{}^{\circ}-\beta r_{AA}^{*3}}\right)+\left(\frac{x_B v_B{}^{\circ}}{v_B{}^{\circ}-\beta r_{BB}^{*3}}\right)\right\}.$$

From Eqs. (19), (20) and (23), we obtain the following equation for TS_E.

$$TS_E = 3\boldsymbol{R}T\left[x_A \ln\left\{\left(\frac{v_A{}^{\circ}-\beta r_{AA}^{*3}}{v-\beta(x_A r_A{}^{*3}+x_B r_B{}^{*3})}\right)\left(\frac{r_A{}^{*}}{r_{AA}^{*}}\right)^2\right\} + x_B \ln\left\{\left(\frac{v_B{}^{\circ}-\beta r_{BB}^{*3}}{v-\beta(x_A r_A{}^{*3}+x_B r_B{}^{*3})}\right)\left(\frac{r_B{}^{*}}{r_{BB}^{*}}\right)^2\right\}\right] \tag{32}$$

Determination of Parameters for Pure Components. From Eq. (17) we obtain the following equation for $\gamma\varepsilon_{AA}{}^{*}$ of pure component A, when $x_A=1$ and $x_B=0$.

$$N\gamma\varepsilon_{AA}^{*} = \frac{3NkT}{2\pi}\left(\frac{v_A{}^{\circ}}{r_{AA}^{*3}}\right)\left(\frac{v_A{}^{\circ\,1/3}}{v_A{}^{\circ\,1/3}-(\beta r_{AA}^{*3})^{1/3}}\right) \tag{33}$$

$\gamma\varepsilon_{AA}{}^{*}$ is related to the heat of vaporization $\varDelta H_V$ in Eq. (6). Eq. (25) is regarded as an approximate representation of Eq. (33).

Differentiating Eq. (33) with respect to temperature assuming that $(\mathrm{d}\gamma/\mathrm{d}T)_V=0$, we obtain

$$v_A{}^{*} = \beta r_{AA}^{*3} = v_A{}^{\circ}\left(\frac{1+\alpha_A T}{1+\frac{4}{3}\alpha_A T}\right)^3, \tag{34}$$

where α_A is the thermal expansion coefficient for pure component A. Eq. (34) is found to be similar to that given by Abe and Flory.[14] This may be due to the similarity in the volume dependence of energy.

By means of Eq. (34), $\beta r_{AA}{}^{*3}$ is obtained from thermal expansion coefficient. $N\gamma\varepsilon_{AA}{}^{*}$ is determined using Eq. (33). When $\varDelta H_V$ is known, we can obtain $N\gamma\varepsilon_{AA}{}^{*}$ directly by means of Eq. (6). The results are given in Table 4 for 15 liquids. The values given in column 7 are calculated by means of Eq. (33) and those in column 8 by means of Eq. (6). The values in column 7 and those in column 8 are in good agreement with each other. This shows applicability of the present theory. For the calculation of excess thermodynamic functions the values in column 7 are used.

Calculation of Excess Thermodynamic Functions for Equimolar Binary Mixtures. Substituting the observed values of excess energy[*3] given in Table 5

TABLE 4. MOLECULAR PARAMETERS OF PURE LIQUIDS

Substance	T (°C)	V (cc/mol)	$\alpha\times10^3$ (deg^{-1})	βr^{*3} (cc/mol)	$\varDelta H^v$ (kcal/mol)	$N\gamma\varepsilon^{*}$[1] (kcal/mol)	$N\gamma\varepsilon^{*}$[2] (kcal/mol)
CCl_4	0	94.21	1.191	74.42	8.09	3.07	3.23
	20	96.49	1.219	74.97	7.85	3.14	3.16
	25	97.08	1.229	75.10	7.79	3.15	3.14
	40	98.91	1.265	75.43	7.64	3.19	3.11
	70	102.88	1.363	76.00	7.29	3.25	3.02
$SiCl_4$	20	114.64	1.415	86.67		2.92	
	25	115.47	1.442	86.71	7.19	2.92	2.97
$TiCl_4$	20	109.80	1.026	87.88		3.43	
$SnCl_4$	20	116.92	1.171	91.50		3.20	
$C(Me)_4$	0	118.03	1.811	86.24	5.61	2.53	2.34
Ar	84°K	28.20	4.370	22.11	1.56(87°K)	0.92	0.60
O_2	77°K	26.50	3.960	21.16		0.90	
	84°K	27.28	4.270	21.18		0.90	
N_2	77°K	34.62	5.670	25.92	1.33	0.75	0.53
	84°K	36.10	6.320	26.00		0.76	
C_6H_6	20	88.86	1.214	69.11		3.14	
	25	89.40	1.223	69.21	8.09	3.16	3.27
	40	91.07	1.256	69.54		3.20	
	70	94.69	1.346	70.13		3.27	
$C_6H_5CH_3$	25	106.83	1.055	84.21	9.08	3.33	3.64
c-C_5H_{10}	25	94.73	1.390	71.63	6.84	2.97	2.79
c-C_6H_{12}	25	108.75	1.217	84.27	7.84	3.17	3.16
	40	110.79	1.264	84.51	7.69	3.19	3.13
	70	115.25	1.365	85.12	7.31	3.24	3.03
c-C_7H_{14}	25	121.62	1.000	97.47	9.19	3.50	3.62
C_6H_5F	40	96.04	1.197	73.97		3.28	
$C_2H_4Cl_2$	20	78.99	1.132	62.55		3.33	

1) The values calculated by means of Eq. (33)
2) The values calculated by means of Eq. (6)

[*3] They are excess enthalpy, not excess energy. However, the difference is very small, and can be ignored.

TABLE 5. EXCESS THERMODYNAMIC QUANTITIES OF EQUIMOLAr MIXTURES

System A–B	T (°C)	H_E (cal/mol)	V_E (cc/mol)		TS_E (cal/mol)		$\theta\times10^3$	$\theta_{\mathrm{disp}}\times10^3$	$V_{E,\,\mathrm{size}}$ (cc/mol)	$V_{E,\,\mathrm{int}}$ (cc/mol)	$E_{E,\,\mathrm{calc}}$ (cal/mol)
		Obsd	Obsd	Calcd	Obsd	Calcd					
CCl_4–$C(Me)_4$	0	75[a]	−0.50[a]	−0.76	−1[a]	3	−9.2	−3.3	−0.21	−0.55	−98
CCl_4–$SiCl_4$	25	36[b][c]	0.02[d]	−0.19	16[e]	9	−1.9	−0.5	−0.20	0.01	4
CCl_4–$TiCl_4$	20	42[c]	0.08[f]	−0.01		9	−8.1	−0.9	−0.22	0.21	24
CCl_4–$SnCl_4$	20	69[c]	0.46[f]	0.03		22	−5.0	0	−0.37	0.4	121
$SiCl_4$–$TiCl_4$	20	38[c]	−0.36[f]	−0.24	(15)[g]	−4	−11.7	−2.8	0	−0.24	−88
$SiCl_4$–$SnCl_4$	20	64[c]	0.13[f]	0.18		15	−14.3	−0.8	−0.03	0.21	28
$TiCl_4$–$SnCl_4$	20	45[c]	0.08[f]	0.05		9	−7.2	−0.5	−0.02	0.07	22
Ar–O_2	84°K	14[h]	0.14[h]	0.05	5[h]	4	−2.2	−0.1	0	0.05	41
Ar–N_2	84°K	12[h]	−0.18[h]	−0.33	4[h]	−3	1.5	−3.5	−0.08	−0.25	−33
O_2–N_2	77°K	11[i]	−0.21[j]	−0.27	1[i]	−1	−1.7	−2.8	−0.11	−0.16	−46
CCl_4–c-C_6H_{12}	25	35[k]	0.16[l]	0.05	18[k]	11	−4.3	0	−0.12	0.17	42
	40	34[k]	0.16[l]	0.06	18[k]	12	−4.0	0	−0.12	0.18	39
	70	30[k]	0.17[l]	0.06	16[k]	12	−2.9	0	−0.14	0.2	34
CCl_4–C_6H_6	25	26[m]	0.01[n]	0.05	6[m]	8	−5.5	0	−0.06	0.11	3
	40	31[m]	0.04[n]	0.07	12[m]	10	−6.1	0	−0.06	0.13	11
	70	(41)[m]	0.11[n]	0.14	(23)[m]	15	−7.2	0	−0.06	0.15	25
CCl_4–$C_6H_5CH_3$	25	10[o]	−0.04[o]	−0.04		2	−2.8	−0.3	−0.12	0.06	−11
C_6H_6–c-C_5H_{10}	25	150[p]	0.30[p]	0.50		45	−30.7	−0.3	−0.01	0.51	80
C_6H_6–c-C_6H_{12}	25	195[q]	0.65[r]	0.50	117[q]	61	−32.1	0	−0.34	0.84	178
	40	180[q]	0.66[r]	0.49	109[q]	60	−28.0	0	−0.35	0.84	166
	70	155[q]	0.67[r]	0.49	95[q]	59	−21.9	0	−0.39	0.87	142
C_6H_6–c-C_7H_{14}	25	181[p]	0.67[p]	0.02		52	−25.0	−1.2	−1.06	1.08	202
$C_6H_5CH_3$–c-C_5H_{10}	25	87[p]	0.08[p]	0.15		20	−18.9	−1.2	−0.24	0.39	21
$C_6H_5CH_3$–c-C_6H_{12}	25	149[p]	0.57[p]	0.53		41	−25.1	−0.2	0	0.53	154
$C_6H_5CH_3$–c-C_7H_{14}	25	141[p]	0.53[p]	0.37		37	−22.8	−0.3	−0.21	0.58	156
C_6H_6–$C_6H_5CH_3$	25	14[o]	0.07[o]	0.14		5	0.5	−0.3	−0.33	0.19	21
C_6H_{12}–C_6H_5F	40	212[s]	0.71[s]	0.71	98[s]	67	−36.7	0.1	−0.17	0.88	180
C_6H_6–$C_2H_4Cl_2$	20	17[t]	0.25[t]	−0.07	9[u]	4	5.2	−0.3	−0.07	0	88

a) A. Englert-Chwoles, *J. Chem. Phys.*, **23**, 1168 (1955).
b) R. D. Vold, *J. Amer. Chem. Soc.*,**59**, 1515 (1937).
c) A. Kolbe and H. Sackmann, *Z. Phys. Chem.*, **31**, 281 (1962).
d) A. Hildebrand and J. M. Carter, *J. Amer. Chem. Soc.*, **54**, 3592 (1932).
e) S. E. Wood, *ibid.*, **59**, 1510 (1937).
f) H. Sackmann and H. Arnold, *Z. Electrochem.*, **63**, 565 (1959).
g) R. B. Crookston and L. N. Canjar, *J. Chem. Eng. Data*, **8**, 544 (1963).
h) R. A. H. Pool, G. Saville, T. M. Herrington, B. D. C. Shields and L. A. K. Staveley, *Trans. Faraday Soc.*, **58**, 1692 (1962).
i) C. M. Knobler, R. J. J. Van Heijningen and J. J. M. Beenakker, *Physica*, **27**, 296 (1961).
j) H. F. P. Knaap, M. Knoester and J. J. M. Beenakker, *ibid.*, **27**, 309 (1961).
k) D. S,. Adock and M. C. McGlashan, *Proc. Roy. Soc.*, (London), **A226**, 266 (1954).
l) S. E. Wood and J. A. Gray, *J. Amer. Chem. Soc.*, **74**, 3729 (1952).
m) J. R. Goates, R. J. Sullivan and J. B. Ott, *J. Phys. Chem.*, **63**, 589 (1959).
n) S. E. Wood and J. P. Brusie, *J. Amer. Chem. Soc.*, **65**, 1891 (1943).
o) R. P. Rastogi, J. Nath and J. Misra, *J. Phys. Chem.* , **71**, 1277 (1967).
p) A. E. P. Watson, I. A. McLure, J. E. Bennett and G. C. Benson, *ibid.*, **69**, 2753 (1965).
q) A. Abe and P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1838 (1965).
r) S. E. Wood and A. E. Austin, *ibid.*, **67**, 480 (1945).
s) A. V. Anantaraman, S. N. Bhattacharyya and S. R. Palit, *Trans. Fraday Soc.*, **59**, 1101 (1963).
t) L. H. Ruiter, *Rec. Trav. Chim. Pays-Bas*, **74**, 1131 (1955).
u) L. Sieg, J. L. Crützen and W. Jost, *Z. Phys. Chem.*, **198**, 18 (1951).

into Eq. (31), the excess volume V_E for 22 equimolar binary mixtures is calculated. From the values of V_E calculated and those of $\beta r_{AA}{}^{*3}$ given in Table 4, the values of TS_E are calculated using Eqs. (32) and (9). The values obtained are given in Table 5, and compared with the observed values.

The agreement between calculated and observed values for V_E and TS_E in satisfactory, as seen in Table 5. The standard deviation of the calculated values from the observed values with respect to V_E, is calculated to be 0.12_5 cc/mol*4 for the binary mixtures given in Table 5.

It is seen that the calculated entropy is less than the value observed. This is especially remarkable for the systems which include aromatic species as a constituent.

From the observed values of E_E and V_E, substituting the values of $\gamma\varepsilon_{AA}{}^*$ and $\gamma\varepsilon_{BB}{}^*$ given in Table 4 into Eq. (22′), we can determine the magnitude of the parameter θ defined as follows.

$$\theta = (\varepsilon^*_{AB} - (\varepsilon^*_{AA} + \varepsilon^*_{BB})/2)/\varepsilon^*_{AA} \tag{35}$$

The values of θ thus obtained are given in column 8 of Table 5, together with those of θ_{disp}, in column 9 which are calculated by assuming the Bertholet relation

$$\varepsilon^*_{AB} = (\varepsilon^*_{AA}\varepsilon^*_{BB})^{1/2}. \tag{36}$$

It is observed that for nearly all systems given in Table 5, the sign of θ is negative and $\theta < \theta_{\mathrm{disp}}$. This means that the mutual interactions between different species are less attractive than those within each species in the systems, and that the interactions between molecules can not be ascribed only to dispersion forces.

From Eq. (24) we can divide the excess volume V_E into two terms,[27] $V_{E,\mathrm{size}}$ and $V_{E,\mathrm{int}}$, where $V_{E,\mathrm{size}}$ corresponds to the first term in the numerator in Eq. (24) and $V_{E,\mathrm{int}}$ to the second term:

$$V_E = V_{E,\mathrm{size}} + V_{E,\mathrm{int}}. \tag{37}$$

The values of $V_{E,\mathrm{size}}$ and $V_{E,\mathrm{int}}$ are calculated using the values of θ in Table 5, and are also given in Table 5. The formula for $V_{E,\mathrm{size}}$ is transformed as follows.

$$\begin{aligned} V_{E,\mathrm{size}} &= \beta N\{x_A(r_A{}^{*3} - r^{*3}_{AA}) + x_B(r_B{}^{*3} - r^{*3}_{BB})\} / \\ &\quad \left[1 - \frac{9kT}{\pi}\left(\frac{x_A v_A{}^{\circ} + x_B v_B{}^{\circ}}{x_A \gamma\varepsilon_A{}^* r_A{}^{*3} + x_B \gamma\varepsilon_B{}^* r_B{}^{*3}}\right)\right] \\ &= -\frac{\beta N}{4} x_A x_B (r^*_{AA} - r^*_{BB})^2 \left[\left(4 + \frac{3x_A - x_B}{2}\right) r^*_{AA} \right. \\ &\quad \left. + \left(4 + \frac{3x_B - x_A}{2}\right) r^*_{BB}\right] \Big/ \\ &\quad \left[1 - \frac{9kT}{\pi}\left(\frac{x_A v_A{}^{\circ} + x_B v_B{}^{\circ}}{x_A \gamma\varepsilon_A{}^* r_A{}^{*3} + x_B \gamma\varepsilon_B{}^* r_B{}^{*3}}\right)\right] \end{aligned} \tag{38}$$

As is evident in Eq. (38), we have

$$\begin{aligned} V_{E,\mathrm{size}} &< 0 \quad \text{for} \quad r^*_{AA} \neq r^*_{BB} \\ &= 0 \quad \text{for} \quad r^*_{AA} = r^*_{BB} \end{aligned} \tag{39}$$

where the denominator in Eq. (38) has turned out to be always positive for the systems. The values of $V_{E,\mathrm{size}}$ and $V_{E,\mathrm{int}}$ calculated are given in columns 10 and 11 of Table 5.

The numerator in Eq. (38) is regarded to represent the excess volume for the mixture of rigid spherical particles with no mutual attraction. Thus, the fact that the values of $V_{E,\mathrm{size}}$ can not be positive means that the excess volume for the mixture of rigid spherical particles with no attractive forces is always negative or zero. This is supported by the experimental results reported by Westman and Huggil.[28]

The values of $V_{E,\mathrm{int}}$ are observed to be positive or negative. This term is regarded as the excess volume which occurs from an interaction*5 between molecules.

In order to investigate the relation between E_E and V_E, the second term in Eq. (26) which is taken for the part of E_E apparently attributable to V_E, is calculated using the observed values of V_E, and given in column 12 of Table 5.

Comparison with Other Theories. The calculated values of various excess thermodynamic functions for three equimolar mixtures, benzene-carbon tetrachloride, carbon tetrachloride-cyclohexane and cyclohexane-benzene are given in Table 6(a), and those for equimolar mixtures of aromatic-alicyclic systems in Table 6(b) for comparison with calculated values from other theories. In Table 6(a) the values calculated by means of various theories which were reported previously,[5,9,10,11,14,16] are given together with our results. The Bertholet relation has been assumed in the calculation given in rows (a) to (d), but not in rows (e) to (g) where the calculation was made using the observed values of H_E.

There is not such a large difference in the calculated quantities, A_E, E_E and TS_E by various theories. The difference in the values of V_E is found to the most remarkable. Thus, it seems that the excess volume gives the most sensitive test to the applicability of the theory. With respect to excess volume, the results of Salsburg and Kirkwood,[10] and those of Chung and Espensheid[16] are too large. The results of Scott,[11] Abe and Flory[14] and the authors are of the same order of magnitude compared with the observed values.

In Table 6(b) the values of V_E and θ, calculated

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*4 The value for the system C_6H_6–c-C_7H_{14} is excluded, where an extraordinary large deviation is observed.

27) R. K. Nigam and P. P. Singh, *Trans. Faraday Soc.*, **65**, 950 (1968); R. P. Rastogi, J. Nath and J. Mishra, *J. Phys. Chem.*, **71**, 1278 (1967).

28) A. E. R. Westman and H. R. Huggil, *J. Amer. Cer. Soc.*, **13**, 767 (1930); E. Manegold, R. Hofmann and K. Solf, *Kolloid Z.*, **56**, 142 (1931).

*5 The designation of $V_{E,\mathrm{size}}$ and $V_{E,\mathrm{int}}$ is conventional, as an interaction parameter $\varepsilon_{AB}{}^*$ is included in the common denominator of the two parts of V_E.

TABLE 6. (a) COMPARISON WITH THE RESULTS PREVIOUS THEORIES (25°C)

System	Ref.	A_E	H_E (cal/mol)	TS_E	V_E/V (%)
C_6H_6-CCl_4	Obsd	20	27±1	7	0.01
	(a)	25	37	12	0.10—0.2
	(b)	26	30	4	0.25
	(c)	10	16	6	0.09
	(d)	(19)	30	11	0.09
	(e)	20	(27)	7	0.08
	(f)	25	42.7	17.7	0.70
	(g)	18	(26)	8	0.05
CCl_4-*c*-C_6H_{12}	Obsd	17	35	18	0.16
	(a)	12	18	6	0.05—0.15
	(b)	44	52	8	0.46
	(c)	23	38	15	0.28
	(d)	(17)	27	10	0.09
	(e)	26	(35)	9	0.12
	(f)	15.4	27.4	12	0.54
	(g)	24	(35)	11	0.05
C_6H_6-*c*-C_6H_{12}	Obsd	78	195	117	0.63
	(a)	65	100	35	0.20—0.35
	(b)	146	171	25	1.32
	(c)	63	105	42	0.68
	(d)	(74)	116	42	0.36
	(e)	142	(195)	53	0.63
	(f)	79.2	133.7	54.5	2.45
	(g)	134	(195)	61	0.50

a) I. Prigogine, A. Bellemans, *Disscuss. Faraday Soc.*, **15**, 80 (1953).
b) Z. W. Salsburg and J. G. Kirkwood, *J. Chem. Phys.*, **21**, 2169 (1953).
c) R. L. Scott, *ibid.*, **25**, 193 (1956).
d) H. C. Longuet-Higgins, *Proc. Roy. Soc.*, *Ser. A* **205**, 247 (1951).
e) A. Abe and P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1838 (1965).
f) H. S. Chung and W. F. Espensheid, *J. Chem. Phys.*, **44**, 1433 (1966).
g) Present work.

TABLE 6(b). COMPARISON WITH THE RESULT OF OTHER THEORY (Aromatic-Alicyclic Systems at 25°C)

Systems	$H_{E,\text{obs}}$ (cal/mol)	$V_{E,\text{obs}}$ (cal/mol)	$V_{E,\text{calc}}$ (cm³/mol)		$\theta \times 10^3$	
			(a)	(b)	(a)	(b)
C_6H_6-*c*-C_5H_{10}	151	0.30	0.41	0.50	−25.3	−30.7
C_6H_6-*c*-C_6H_{12}	195	0.65	0.98	0.50	−12.4	−32.1
C_6H_6-*c*-C_7H_{14}	181	0.67	2.10	0.02	31.8	−25.0
C_6H_6-*c*-C_8H_{16}	181	0.58	3.82	−0.42	87.9	−22.8
$C_6H_5CH_3$-*c*-C_5H_{10}	87	0.08	0.70	0.15	1.2	−18.9
$C_6H_5CH_3$-*c*-C_6H_{12}	149	0.57	0.36	0.53	−22.9	−25.1
$C_6H_5CH_3$-*c*-C_7H_{14}	141	0.53	0.59	0.37	−12.8	−22.8
$C_6H_5CH_3$-*c*-C_8H_{16}	148	0.51	1.41	0.15	11.7	−21.7

(a) I. Prigogine, "The Molecular Theory of Solution," North Holland Pub. Co., Amsterdam (1957), Chaps. 10, 11.
(b) Present work

for equimolar mixtures of aromatic-alicyclic systems by Benson and co-workers[29] using Prigogine's theory[9,30] are compared with our results. we see

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[29] L. A. McLure, J. E. Benett, A. E. P. Watson and G. C. Benson, *J. Phys. Chem.*, **69**, 2759 (1965).

[30] I. Prigogine "The Molecular Theory of Solutions," North Holland Pub. Co., Amsterdam (1957), Chapts. 10, 11.

that the agreement between calculated and observed values is better in the present theory than in Prigogine's theory. The present theory gives slightly smaller values than the observed, while Prigogine's theory gives larger values.

Discussion on the Results of Numerical Computations. In Table 5 the values of θ which are calculated for the observed values of E_E and V_E are compared with those obtained from the Bertholet relation. The former are larger than the latter in absolute magnitude.

In Table 5 appreciable differences are observed between the systems containing an aromatic constituent and other systems. For aromatic-alicyclic systems the values of $|\theta|$ are 0.02—0.03, and are seen to be larger by one order than those of other systems. Benson and coworkers have reported[29] that the values of $|\theta|$ calculated using Scatchard-Hildebrand theory[31] and Barker's quasi-lattice theory[32] are about 0.03 for aromatic-alicyclic systems. Their results agree with our results. The values of θ calculated by Prigogine's theory, shown in column 6, Table 6(b) (cited from Benson *et al.*[29]) vary greatly. This is unreasonable when the similar properties of these systems are taken into account.

For the aromatic-alicyclic systems the observed values of H_E are positive and large compared with those of other systems in Table 5, which correspond to fairly large values of $|\theta|$. We see that the excess entropy calculated is larger for the aromatic-alicyclic systems than for the other systems, and that the observed values of excess entropy for the systems are larger than for the calculated values. A certain ordered arrangement seems to be present in liquid benzene and disturbed by the addition of non-aromatic constituents.[14]

For aromatic-carbon tetrachloride systems the values of $|\theta|$ and those of TS_E are very small. It seems that the systems are to some extent ideal from a thermodynamical point of view, compared with the non-ideal behavior of aromatic-alicyclic systems.

For the benzene-ethylene dichloride system,[33] the situation is different, compared with other systems containing one aromatic constituent. In spite of some positive values of V_E observed, the value of TS_E is small, and the value of θ is positive. The calculated values given in column 12, Table 5, are seen to be fairly larger than the observed value of H_E in column 3. For the aromatic-alicyclic systems in Table 5, the values in column 3 are nearly equal to those in column 12. From the results it seems that an ordered arrangement between benzene and ethylene dichloride molecules occurs in the mixture, and that it reduces the magnitude of TS_E and H_E in spite of the observed positive value of V_E. This explains the fact that the value of V_E calculated from the observed value of H_E is fairly smaller than the observed value of V_E.

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Appendix

Estimation of the Number of Nearest Neighbors for Pure Liquid. From Eq. (5) we can estimate the effective number of nearest neighbors, $Z_{\mathrm{eff.}}$ for pure liquid, as follows.

$$\omega(0) = \gamma\varepsilon^* - \left(\frac{N\cdot\frac{4}{3}\pi r^{*3}}{V}\right) = -\gamma\left(\frac{4\sqrt{2}\pi}{3}\right)\left(\frac{r^*}{a}\right)^3\varepsilon^* \tag{40}$$

where

$$V = Na^3/\sqrt{2}.$$

On the other hand we can put

$$\omega(0) = -Z_{\mathrm{eff.}}\varepsilon^*\left(\frac{r^*}{a}\right)^6 \tag{41}$$

where $Z_{\mathrm{eff.}}$ is the effective number of nearest neighbors, which includes the influence of outer neighbors.

Equating Eq. (40) and Eq. (41), we have

$$Z_{\mathrm{eff.}} = \gamma\left(\frac{4\sqrt{2}\pi}{3}\right)\left(\frac{a}{r^*}\right)^3 = \gamma\left(\frac{4\sqrt{2}\pi}{3}\right)\left(\frac{V}{V^*}\right) \tag{42}$$

where V^* is a "hard core volume"[14] and is taken to be equal to $N\beta r^{*3}$.

The influence of outer neighbors is estimated to increase the potential energy within a cell by about 20%, compared with the potential occuring from the first nearest neighbors only.[18,25] Thus, we can estimate the number of the first nearest neighbors approximately equal to $Z = Z_{\mathrm{eff.}}/1.2$.

From the values of γ given in Table 3, estimating the values of (V/V^*) to be 1.3 for ordinary conditions of liquids, we can determine the values of Z to be 11.8 for liquid argon and to be 12.8 for C_6H_6, c-C_6H_{12}, and CCl_4. The values are supposed to be of reasonable magnitudes, though slightly larger than the observed.[26] This seems to support the adequacy of the present theory.

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