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Statistical Thermodynamic Study of Liquid Organic Compounds

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A statistical thermodynamic study of liquid organic compounds has been worked out on the basis of a liquid model: a liquid is regarded as an assembly of particles immersed in a uniform background potential resulting from the attractive forces between molecules. In the model the equation of state is expressed as a sum of the term derived from the analytical solution of the Percus-Yevick equation and that from the background potential. Calculations of thermodynamic functions for five liquids (benzene, carbon tetrachloride, toluene, chloroform, cyclohexane) have been performed. The results show the effectiveness and reasonableness of the theory with the evidence of coincidence of calculated values and observed ones.

Statistical thermodynamic calculations for organic liquids such as benzene, toluene, carbon tetrachloride, and others are scarce and, still now, nearly untractable, especially from the practical point of view. Needs for those calculations are now increasing also in the fields of chemical engineering. One of the authors proposed an approach[1–3] to the calculations on the basis of the integral equation theory (the Percus-Yevick equation).[4–6] And then, along the line proposed, we intend here to perform an overall statistical thermodynamic calculation for five organic liquids (benzene, toluene, carbon tetrachloride, chloroform, and cyclohexane), which are considered as typical examples of liquids composed of nonpolar or weak-polar molecules with compact and nearly spherical shape.

Theoretical

The Liquid Model. In the formulation of the total partition function, we assume that attractive forces between molecules give rise to a uniform background potential,[1–3,7] and then a liquid is considered to be an assembly of particles immersed in the uniform background potential. Within the liquid a molecule is regarded as a free rotor and, with respect to vibrational motions, intramolecular modes only are taken into consideration.

The Partition Function and the Equation of State. For the model used the total partition function Z is expressed as a product

$$Z = Q_{\text{trans.}}\, Q_{\text{rot.}}\, Q_{\text{vib.}}\, Q_{\text{BG}}, \tag{1}$$

in terms of the translational, rotational, vibrational, and background potential contribution, respectively.

With respect to $Q_{\text{trans.}}$ and Q_{BG}, a molecule is considered to be a hard sphere particle moving freely within the uniform background potential, and the equation of state of the liquid is derived from the translational and the background potential contribution only. Thus, in the formulation of $Q_{\text{trans.}}$ as well as of the equation of state, we can use the analytical solution of the Percus-Yevick equation for hard sphere fluids which was given by Wertheim and Thiele.[8]

Concerning $Q_{\text{trans.}}$, one of the authors and others gave a compact form,[1–3] which was derived from the Wertheim's expression,[8] and $Q_{\text{trans.}}$ becomes, in the combined form with Q_{BG},

$$Q_{\text{trans.}} \cdot Q_{\text{BG}} = \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} efv\right]^N (\exp -\langle V_N\rangle_{\text{av.}}/kT), \tag{2}$$

and

$$f \equiv (1-\xi)\exp\left[-\left(\frac{3\xi(2-\xi)}{2(1-\xi)^2}\right)\right], \tag{3}$$

$$\xi = N\pi a^3/6V = \pi a^3/6v, \tag{4}$$

$$\langle V_N\rangle_{\text{av.}} = -a_{\text{ii}}/V, \tag{5}$$

where N is the number of molecules, f the effective free volume fraction,[1–3] a the (effective) hard sphere diameter, and a_{ii} the energy parameter of the liquid.

The rotational contribution as a three dimentional free rotor, $Q_{\text{rot.}}$, is expressed as

$$Q_{\text{rot.}} = \left[\frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 kT}{h^2}\right)^{3/2} (I_A I_B I_C)^{1/2}\right]^N, \tag{6}$$

where I_A, I_B, I_C, and σ are the moment of inertia and the symmetry factor, respectively.

The vibrational contribution $Q_{\text{vib.}}$ is expressed as

$$Q_{\text{vib.}} = \left[\prod_{j=1}^{r}\left\{\frac{\exp(-h\nu_j/2kT)}{1-\exp(-h\nu_j/kT)}\right\}\right]^N, \tag{7}$$

where r is the number of intramolecular vibrational modes.

The equation of state is, here, expressed as follows:[1]

$$pV = NkT\left(\frac{1+\xi+\xi^2}{(1-\xi)^3}\right) - V\frac{\partial\langle V_N\rangle_{\text{av.}}}{\partial V}, \tag{8}$$

where ξ is the volume fraction of hard sphere molecules, p pressure, V volume, T temperature, and $\langle V_N\rangle_{\text{av.}}$ the uniform background potential. The first term in Eq. 8 is the hard sphere term given by Wertheim and Thiele. The determination of the parameters, a and a_{ii}, are important in this treatment and the procedures are given in details in the later section. Using the expression Eq. 5 for the uniform background potential, the equation of state is rewritten as follows:

$$pV=NkT\left(\frac{1+\xi+\xi^2}{(1-\xi)^3}\right)-\frac{a_{\mathrm{ii}}}{V}. \tag{9}$$

For the isothermal compressibility κ_{T} of liquid, we can derive the following formula from Eqs. 3 and 8.

$$\kappa_{\mathrm{T}}=\left[\frac{1}{\kappa_0}-\frac{2}{V}(\Delta H_{\mathrm{vap.}}-RT)\right]^{-1}, \tag{10}$$

where κ_0 is the isothermal compresibility for the liquid of hard spheres and expressed by

$$\kappa_0=\left(\frac{V}{NkT}\right)\left[\frac{(1-\xi)^2}{(1+2\xi)}\right]^2. \tag{11}$$

Thermodynamic Functions. Thermodynamic functions as free energy F, entropy S, and internal energy U are calculated from partition function Z as follows:

$$F=-kT\ln Z, \tag{12}$$

$$\begin{aligned}S&=-\frac{\partial F}{\partial T}=S_{\mathrm{trans.}}+S_{\mathrm{rot.}}+S_{\mathrm{vib.}}\\&=\left(k\ln Q_{\mathrm{trans.}}+\frac{3}{2}R\right)+\left(k\ln Q_{\mathrm{rot.}}+\frac{3}{2}R\right)\\&\quad+\left(k\ln Q_{\mathrm{vib.}}+kT\frac{\partial}{\partial T}\ln Q_{\mathrm{vib.}}\right),\end{aligned} \tag{13}$$

$$U_{\mathrm{trans.}}=U_{\mathrm{rot.}}=\frac{3}{2}RT, \tag{14}$$

$$U_{\mathrm{vib.}}=kT^2\frac{\partial\ln Q_{\mathrm{vib.}}}{\partial T}, \tag{15}$$

$$U_{\mathrm{BG}}=\langle V_N\rangle_{\mathrm{av.}}=-\frac{a_{\mathrm{ii}}}{V}, \tag{16}$$

$$U_{\mathrm{total}}=U_{\mathrm{trans.}}+U_{\mathrm{rot.}}+U_{\mathrm{vib.}}+U_{\mathrm{BG}}. \tag{17}$$

Numenical Computations

Determination of Energy Parameter a_{ii} and a. The energy parameter a_{ii} for a liquid is obtained from the heat of vaporization $\Delta H_{\mathrm{vap.}}$ as follows:[1,2]

$$a_{\mathrm{ii}}=V(\Delta H_{\mathrm{vap.}}-RT). \tag{18}$$

For the determination of the hard sphere diameter a, we must first obtain ξ from the equation of state (9), using the value of a_{ii} determined from Eq. 18, and then, can determine a from ξ at a given volume V.

$$a=(6\xi N/\pi V)^{1/3}. \tag{19}$$

In calculation of ξ through the equation of state, we can safely ignore the term pV as follows:

Table 1. Energy Parameter a_{ii} and Equivalent Hard Sphere Diameter a for Pure Components

	$\Delta H_{\mathrm{vap.}}$	T	V	a_{ii}	a
	kJ mol^{-1}	°C	cm^3 mol^{-1}	kJ cm^3 mol^{-2}	Å
C_6H_6	34.61[a,b]	10	87.81[b]	2832	5.17
	34.08	20	88.86	2812	5.17
	33.85	25	89.40	2805	5.16
	33.51	30	89.94	2787	5.16
	33.00	40	91.08	2768	5.15
	32.45	50	92.26	2746	5.15
	31.90	60	93.47	2723	5.14
$C_6H_5CH_3$	39.48[c,d]	0	104.1[b]	3873	5.56
	38.89	10	105.1	3840	5.55
	38.32	20	106.3	3814	5.55
	37.99	25	106.8	3793	5.54
	37.73	30	107.4	3781	5.54
	37.20	40	108.6	3757	5.54
	36.66	50	109.8	3731	5.53
	36.12	60	111.1	3705	5.53
CCl_4	33.58[e,f]	0	94.22[b]	2950	5.30
	33.13	10	95.34	2934	5.29
	32.67	20	96.50	2917	5.29
	32.41	25	97.08	2906	5.28
	32.20	30	97.68	2899	5.28
	31.71	40	98.88	2878	5.27
	31.22	50	100.14	2857	5.27
	30.71	60	101.44	2834	5.26
$CHCl_3$	32.3_5[g]	0	78.21[j]	2352	4.96
	31.8_7	10	79.18	2337	4.95
	31.4_0	20	80.17	2322	4.95
	31.1_6	25	80.69	2314	4.95
	30.9_2	30	81.21	2306	4.94
	30.4_4	40	82.29	2291	4.94
	29.9_6	50	83.41	2275	4.93
	29.4_9	60	84.59	2260	4.93
c-C_6H_{12}	33.03[h,i]	25	108.7[b]	3321	5.50
	32.76	30	109.4	3308	5.49
	32.18	40	110.7	3274	5.49
	31.62	50	112.1	3243	5.48
	31.05	60	113.6	3213	5.47

a) J. F. Connolly and G. A. Kandalic, *J. Chem. Eng. Data,* **7**, 137 (1962). b) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publ. Co., Amsterdam (1950). c) B. D. Smith and R. Srivastava, "Thermodynamic Data for Pure Compounds. Part A. Hydrocarbons and Ketones," Elsevier, Amsterdam (1986), p. 242 d) D. W. Scott, G. B. Guthrie, J. F. Messerly, S. S. Todd, W. T. Berg, I. A. Hossenlopp, and J. P. McCullough, *J. Phys. Chem.,* **66**, 911 (1962). e) V. Majer, L. Šváb, and V. Svoboda, *J. Chem. Thermodynam.,* **12**, 843 (1980). f) D. L. Hildebrand and R. A. McDonald, *J. Phys. Chem.,* **63**, 1521 (1959). g) "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," ed by E. W. Washburn, McGraw-Hill, New York (1926), Vol. V, p. 138. h) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa. (1953). i) W. Kozicki and B. H. Sage, *Chem. Eng. Sci.,* **15**, 270 (1961). j) Foot note g, Vol. III, p. 28.

Table 2. Calculated Values of Volume Fraction ξ, Molecular Diameter a and Energy Parameters a_{ii}

	T	ξ	a	a_{ii}
	°C		Å	kJ cm^3 mol^{-2}
C_6H_6	25	0.4857	5.16	2805
$C_6H_5CH_3$	25	0.5032	5.54	3793
CCl_4	25	0.4789	5.28	2906
$CHCl_3$	25	0.4728	4.95	2314
c-C_6H_{12}	25	0.4819	5.50	3321

Table 3. Molecular Parameters I_A, I_B, I_C, σ

		I_A	I_B	I_C	σ
		10^{-40} g cm^2	10^{-40} g cm^2	10^{-40} g cm^2	
C_6H_6	a)	145.3	145.3	291	12
$C_6H_5CH_3$	b)	154.3	330.5	482.0	1
CCl_4	a)	486	486	486	12
$CHCl_3$	a)	259	259	501	3
c-C_6H_{12}	a)	$I_A \cdot I_B \cdot I_C = 12583 \times 10^{-117}$ g cm^2			6

a) "Landolt-Börnstein Tabellen", 6 Aufl. II Band, 4 Teil, S. 424-444, Springer-Verlag, Berlin, Göttingen, Heidelberg (1961). b) Determined from molecular structure (molecular dimension was adopted from F. A. Keidel and S. H. Bauer, *J. Chem. Phys.*, **25**, 1218 (1956)).

$$\frac{1+\xi+\xi^2}{(1-\xi)^3}=\frac{a_{ii}/V}{RT}. \tag{20}$$

The values of a_{ii} and a determined from experimental data of $\Delta H_{\text{vap.}}$ and V using Eqs. 18—20 are given in Table 1 at each temperature. As clearly seen in the table, the magnitudes of those parameters are nearly kept constant at all temperatures for each liquid. Then, in the calculation below, we used the values of a_{ii} and a determined from the experimental data at 25 °C, assuming those to be kept constant at all temperatures throughout. The values of a_{ii} and a thus assigned to each liquid are given in Table 2, together with the values of ξ at 25 °C. The magnitudes of ξ obtained for these five liquids are seen to be consistent with the value by Hoover and Ree's Monte Carlo determination[9] for hard-sphere fluids.

Molecular Parameters I_A, I_B, I_C, σ, ν_J. The molecular parameters I_A, I_B, I_C can be determined either by molecular spectra or direct calculation from molecular structure ($I_A=\sum_{i=1}^{s} m_i r_{iA}^2$ etc., where m_i is the mass of the i-th atom and r_{iA} is the distance of the i-th atom from the A-axis of the molecule. s is the number of atoms of the molecule.) Symetry number σ can be determined from the symetry character of the molecule. The molecular parameters which were determined as mentioned above are shown in Table 3.

To calculate vibrational partition function by Eq. 7, ν_J's are necessary and all ν_J's corresponding to the degrees of freedom of intramolecular vibration were counted in.[10,11] (Degrees of freedom of intramolecular vibration are 30 for C_6H_6, 39 for $C_6H_5CH_3$, 9 for CCl_4, 9 for $CHCl_3$, 48 for c-C_6H_{12}.)

Calculations of Thermodynamic Variables. The computations of thermodynamic variables, F, U, S, and isothermal compressibility κ_T were carried out for each temperature, using the values of $(-a_{ii}/V)$ as background potential U_{BG}. As can be seen from Eq. 17, there remains $(-a_{ii}/V)$ at 0 K when the terms $U_{\text{trans.}}$, $U_{\text{rot.}}$ and $U_{\text{vib.}}$ tend to zero at 0 K except for the zero-point vibration energy in $U_{\text{vib.}}$. Thus, $-\langle V_N\rangle_{\text{av.}}$ at 0 K corresponds the heat of sublimation at 0 K from the definition $-\langle V_N\rangle_{\text{av.}}$ $(=\Delta H_{\text{vap.}} - RT)=\Delta H_{\text{vap.}}$ Heat of sublimation at 0 K can be estimated from Eq. 21

$$\Delta H_{\text{sub}} \text{ at } 0\text{ K}=(\Delta H_{\text{vap, 298 K}}+\Delta H_{0\to 298\text{ K}})_{\text{condensed phase}} -(\Delta H_{0\to 298\text{ K}})_{\text{gaseous phase}}. \tag{21}$$

The calculated values of F, U, S, κ_T are shown in Figs. 1a through 5c together with observed values.

Discussion

Overall Behaviors of Thermodynamic Functions. From Figs. 1a, 1b through 5a, 5b , it can be seen that calculated values of F, U, S coincide well with observed values on the whole.

From the overall coincidence between calculated

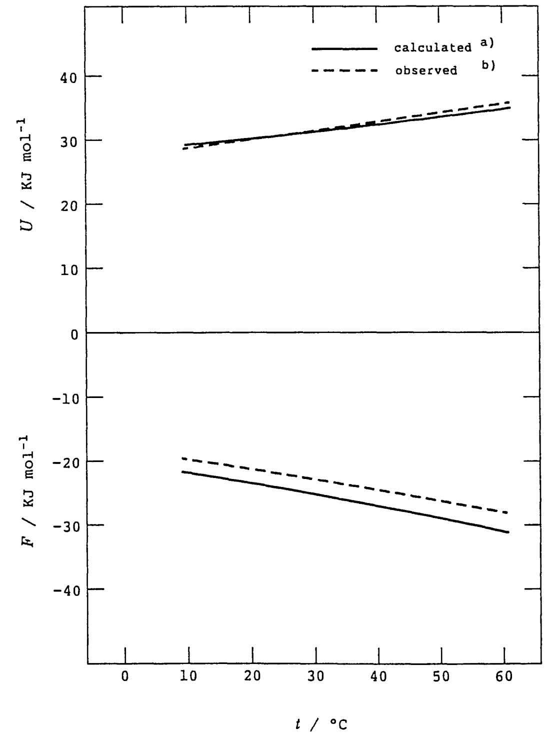

Fig. 1a. Temperature dependence of U and F for liquid C_6H_6.
a) 49.73 kJ mol^{-1} (ΔH_{sub} at 0 K) has been added to U.
b) "Landolt-Börnstein Tabellen," 6 Aufl. II Band, 4 Teil, S. 427. Springer-Verlag, Berlin, Göttingen, Heidelberg (1961).

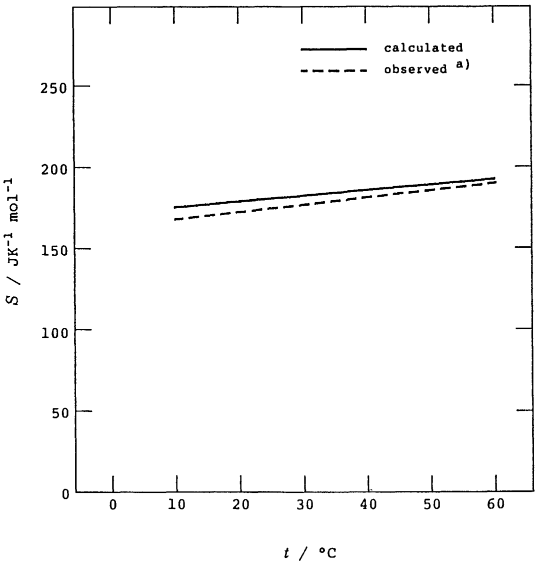

Fig. 1b. Temperature dependence of S for liquid C_6H_6.
a) See Fig. 1a. Footnote b.

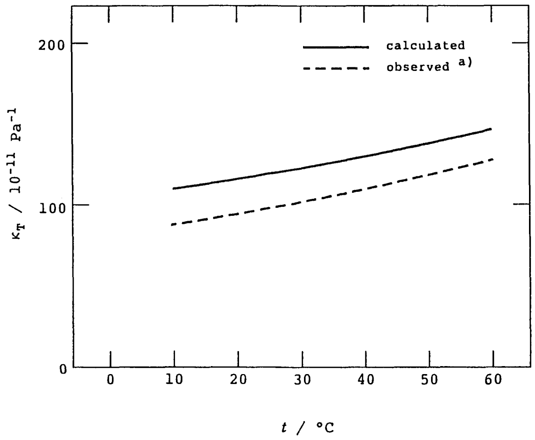

Fig. 1c. Temperature dependence of κ_T for liquid C_6H_6.
a) D. Tyrer, *J. Chem. Soc.*, **105**, 2534 (1914), L. A. K. Staveley, W. I. Tupman, and K. R. Hart, *Trans. Faraday Soc.*, **51**, 323 (1955).

and observed values of F, U, S for five liquids, in spite of the comparatively small departure between those, it can be safely said that this statistical thermodynamic calculation procedure is practically useful to have insight into liquid structure. This fact shows the reasonableness of the present liquid model.

Calculated κ_T are about 20% larger than observed values, which shows that the equation of state which is derived from Percus-Yevick theory (Eq. 8) gives some departure for such higher order differentiated values as κ_T.

In Table 4, contributions of $U_{kin.}$ $(=U_{trans.}+U_{rot.})$, $U_{vib.}$, and U_{BG} are shown for C_6H_6. To calculate U_{total}, the sublimation energy at 0 K (49.73 kJ mol^{-1}) has been added to calculated values as explained before.

As seen in the table, the contributions from U_{BG} is found to occupy about 60% of U_{total}, which is considered to be reasonable.

Behaviors of Entropy. As shown in Figs. 1b through 5b, the calculated values of S_{total} are found to coincide well with the observed data on the whole. To proceed into more detailed considerations on

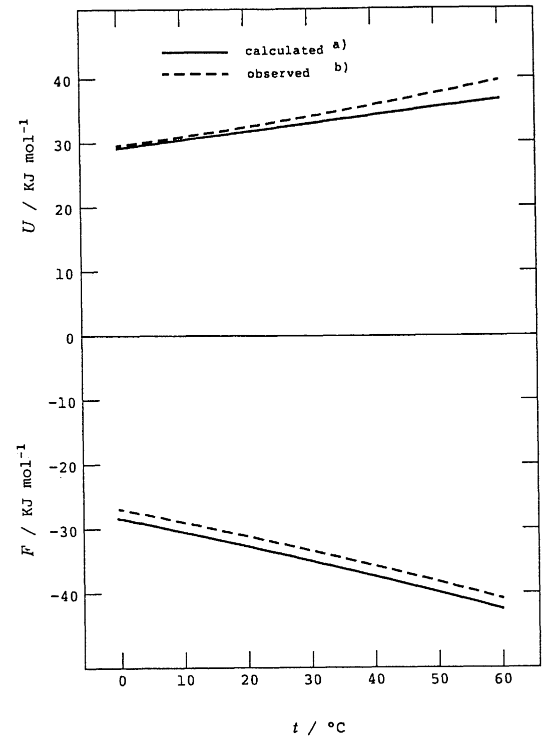

Fig. 2a. Temperature dependence of U and F for liquid $C_6H_5CH_3$.
a) 53.43 kJ mol^{-1} (ΔH_{sub} at 0 K) has been added to U.
b) See Table 1. Footnote d.

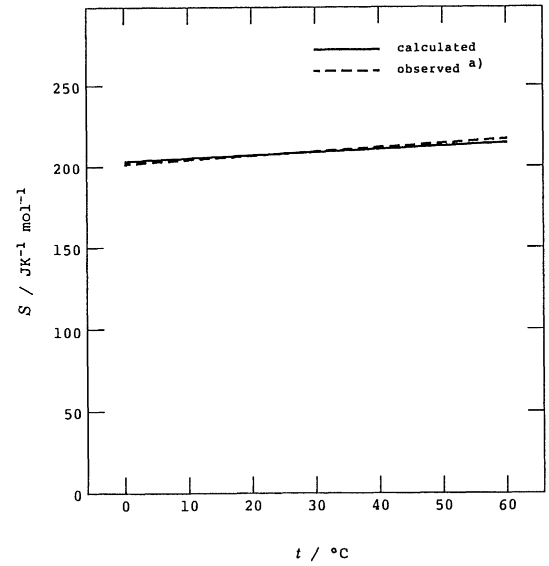

Fig. 2b. Temperature dependence of S for liquid $C_6H_5CH_3$.
a) See Table 1. Footnote d.

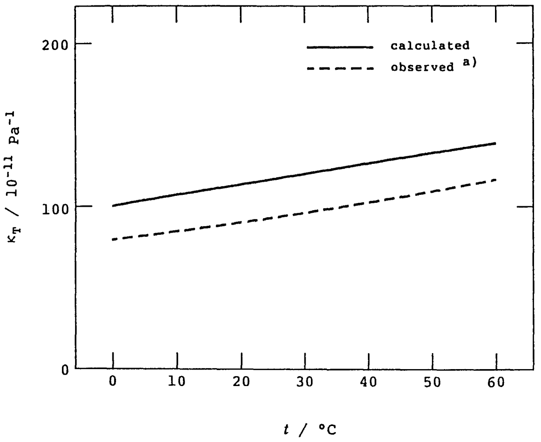

Fig. 2c. Temperature dependence of κ_T for liquid $C_6H_5CH_3$.

a) J. S. Shraiber, *Isr. J. Chem.*, **13**, 185 (1975), E. B. Freyer, J. C. Hubbard, and D. H. Andrews, *J. Am. Chem. Soc.*, **51**, 759 (1929).

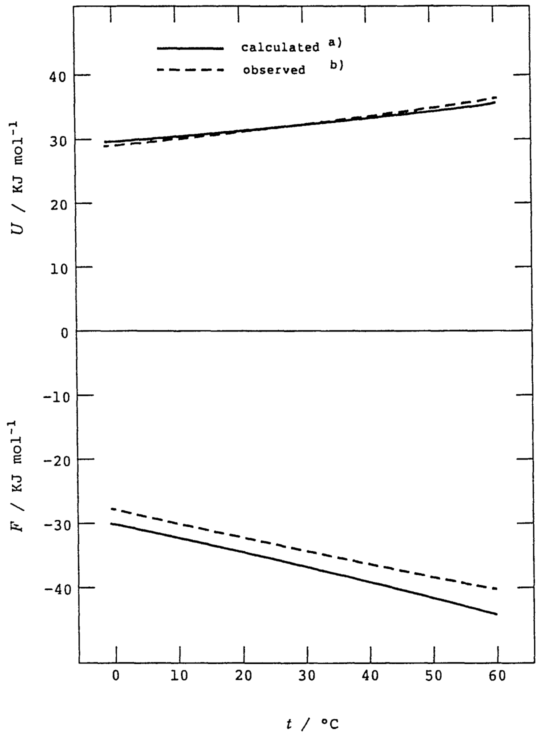

Fig. 3a. Temperature dependence of U and F for liquid CCl_4.

a) 46.90 kJ mol^{-1} (ΔH_{sub} at 0 K) has been added to U.

b) Values at 25 °C were taken from D. L. Hildebrand and R. A. McDonald, *J. Phys. Chem.*, **63**, 1521 (1959). Other values were calculated from heat capacity data (J Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam (1950), p. 228).

entropy, each contribution from translational, rotational, and vibrational degrees of freedom is given in Tables 5 through 9 for five liquids.

It can be seen in these tables that the contributions from $S_{rot.}$ occupy the largest portion and reach about

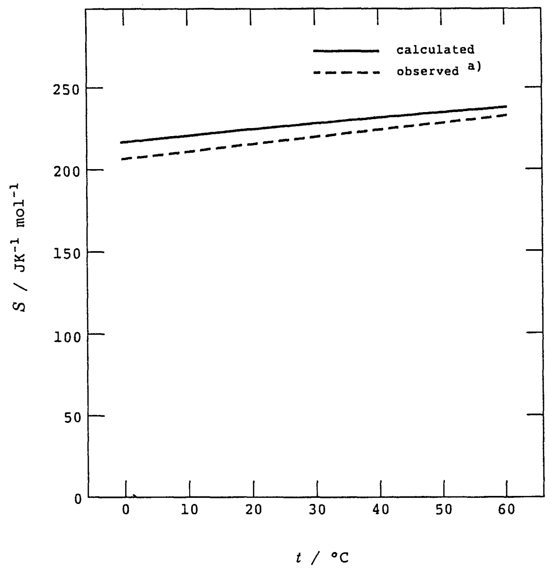

Fig. 3b. Temperature dependence of S for liquid CCl_4.

a) See Fig. 3a. Footnote b.

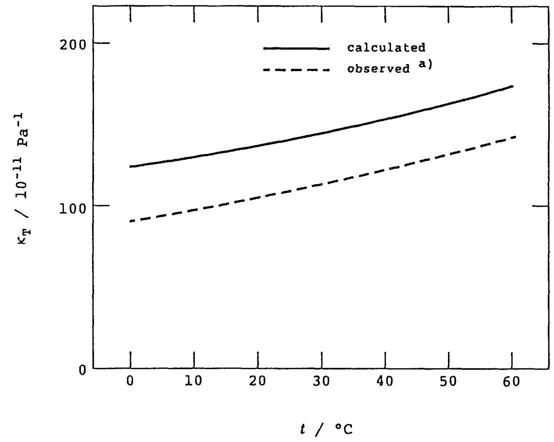

Fig. 3c. Temperature dependence of κ_T for liquid CCl_4.

a) L. A. K. Staveley, W. I. Tupman, and K. R. Hart, *Trans. Faraday Soc.*, **51**, 323 (1955), E. B. Freyer, J. C. Hubbard, and D. H. Andrews, *J. Am. Chem. Soc.*, **51**, 759 (1929).

Table 4. Calculated Values of Various Terms in Eq. 14 for C_6H_6 (kJ mol^{-1})

Temp / °C	$U_{kin.}$	$U_{vib.}$	U_{BG}	U_{total}
10	7.06	3.59	17.79	28.44
20	7.31	4.04	18.17	29.52
25	7.43	4.28	18.36	30.07
30	7.56	4.53	18.55	30.64
40	7.81	5.05	18.94	31.80
50	8.06	5.59	19.33	32.98
60	8.31	6.18	19.73	34.22

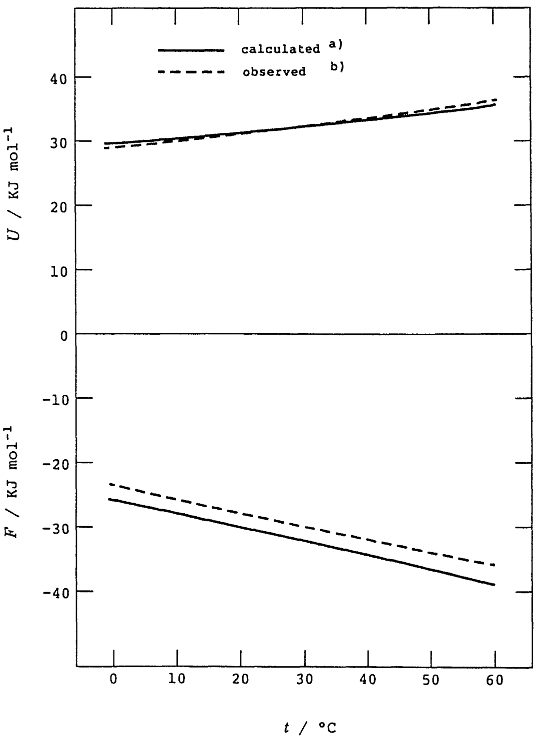

Fig. 4a. Temperature dependence of U and F for liquid $CHCl_3$.

a) 48.99 kJ mol^{-1} (ΔH_{sub} at 0 K) has been added to U.

b) Entropy at 25 °C was taken from "Landolt-Börnstein Tabellen," 6 Aufl, Band II, Teil 4. S. 293, Springer-Verlag, Berlin. Göttingen, Heidelberg (1961). The other values were calculated from both heat capacity of the liquid (Y. S. Touloukian and C. Y. Ho, "Thermophysical Properties of Matter," IFI/Plenum, New York (1970), p. 162) and estimated solid heat content.

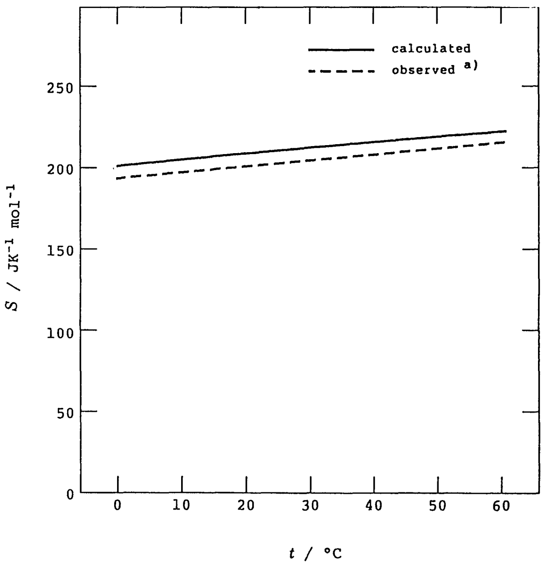

Fig. 4b. Temperature dependence of S for liquid $CHCl_3$.

a) See Fig. 4a. Footnote b.

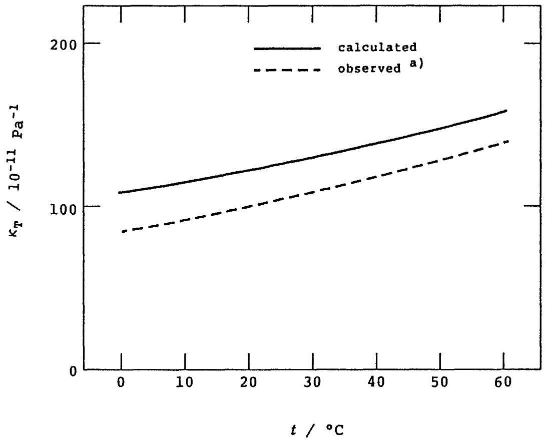

Fig. 4c. Temperature dependence of κ_T for liquid $CHCl_3$.

a) See Fig. 3c., Footnote a, and D. Tyrer, *J. Chem. Soc.*, **105**, 2534 (1914).

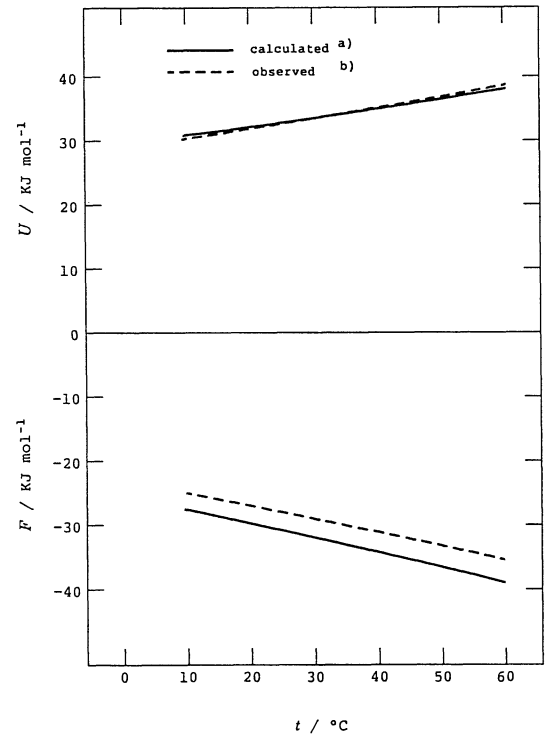

Fig. 5a. Temperature dependence of U and F for liquid c-C_6H_{12}.

a) 48.03 kJ mol^{-1} (ΔH_{sub} at 0 K) has been added to U.

b) Entropy at 25 °C and heat capacity data to calculate the other values were taken from J. G. Aston, G. J. Szasz, and H. L. Fink, *J. Am. Chem. Soc.*, **65**, 1135 (1943).

40—50% of S_{total}, which is found as a common feature among five liquids. In addition to this, the overall coincidence of the calculated S_{total} with $S_{obs.}$ supports the idea in the present liquid model that the molecules within the liquid behave as free rotors moving under the uniform background potential.

To see further in details, we compare Table 5 for

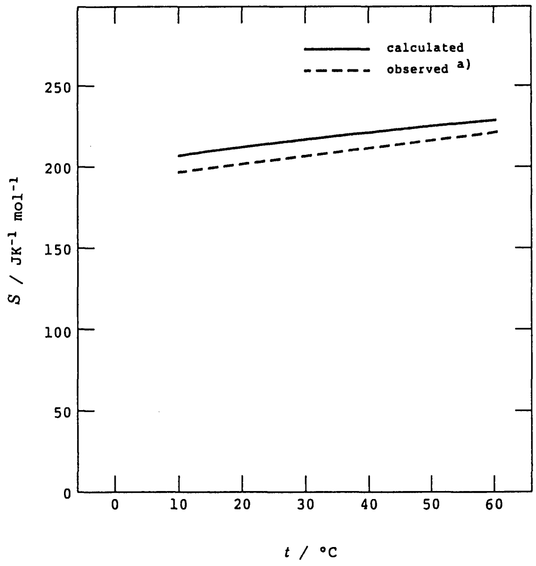

Fig. 5b. Temperature dependence of S for liquid c-C_6H_{12}.
a) See Fig. 5a. Footnote b.

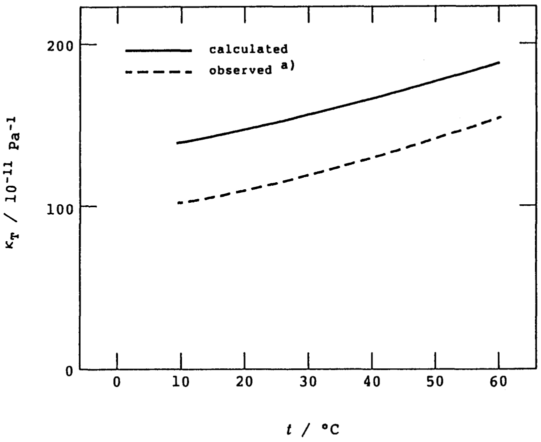

Fig. 5c. Temperature dependence of κ_T for liquid c-C_6H_{12}.
a) M. L. Huggins, *Colloid Polym. Sci.*, **258**, 477 (1980).

Table 5. Calculated Values of Various Terms of Entropy for C_6H_6 (J K^{-1} mol^{-1})

Temp / °C	$S_{trans.}$	$S_{rot.}$	$S_{vib.}$	S_{total}	S_{obsd}
10	73.4	85.9	16.2	175.5	166
20	75.3	86.3	17.6	179.2	171
25	76.2	86.5	18.2	180.9	173
30	77.2	86.7	18.9	182.8	175
40	78.9	87.1	20.3	186.3	180
50	80.6	87.5	21.6	189.7	184
60	82.3	87.9	23.0	193.2	189

Table 6. Calculated Values of Various Terms of Entropy for $C_6H_5CH_3$ (J K^{-1} mol^{-1})

Temp / °C	$S_{trans.}$	$S_{rot.}$	$S_{vib.}$	S_{total}	S_{obsd}
0	71.2	111.9	27.5	210.6	207
10	73.2	112.3	29.6	215.1	213
20	75.2	112.8	31.8	219.8	218
25	76.1	113.0	32.8	221.9	221
30	77.0	113.2	34.0	224.2	224
40	78.8	113.6	36.2	228.6	229
50	80.5	114.0	38.5	233.0	234
60	82.2	114.3	40.9	237.4	239

Table 7. Calculated Values of Various Terms of Entropy for CCl_4 (J K^{-1} mol^{-1})

Temp / °C	$S_{trans.}$	$S_{rot.}$	$S_{vib.}$	S_{total}	S_{obsd}
0	82.2	97.6	35.2	215.0	205
10	83.9	98.6	36.9	219.4	209
20	85.8	98.5	38.7	223.0	214
25	86.7	98.7	39.5	224.9	216
30	87.6	98.9	40.3	226.8	218
40	89.3	99.3	42.0	230.6	223
50	91.0	99.7	43.6	234.3	227
60	92.6	100.1	45.3	238.0	231

Table 8. Calculated Values of Various Terms of Entropy for $CHCl_3$ (J K^{-1} mol^{-1})

Temp / °C	$S_{trans.}$	$S_{rot.}$	$S_{vib.}$	S_{total}	S_{obsd}
0	78.5	104.0	19.4	201.9	193
10	80.4	104.5	20.5	205.4	197
20	82.3	104.9	21.6	208.8	201
25	83.2	105.1	22.1	210.4	203
30	84.1	105.3	22.6	212.0	205
40	85.8	105.7	23.7	215.2	209
50	87.4	106.1	24.8	218.3	212
60	89.0	106.5	25.9	221.4	216

Table 9. Calculated Values of Various Terms of Entropy for c-C_6H_{12} (J K^{-1} mol^{-1})

Temp / °C	$S_{trans.}$	$S_{rot.}$	$S_{vib.}$	S_{total}	S_{obsd}
10	76.7	94.6	35.9	207.2	196
20	78.6	95.1	38.3	212.0	201
25	79.5	95.3	39.6	214.4	204
30	80.5	95.5	40.8	216.8	206
40	82.2	95.9	43.4	221.5	212
50	83.8	96.3	46.1	226.2	217
60	85.5	96.7	48.7	230.9	222

C_6H_6 with Table 6 for $C_6H_5CH_3$. The magnitude of S_{total} of $C_6H_5CH_3$ is found to be larger than that of C_6H_6, which mainly comes from the increase in $S_{rot.}$ for $C_6H_5CH_3$ as well as from that in $S_{vib.}$, compared with those for C_6H_6. The increase in $S_{rot.}$ for $C_6H_5CH_3$ is attributed to the smaller symmetry number σ and the larger moment of inertia I_A, I_B, and I_C as seen in Table 3.

In the comparison between Tables 7 and 8, the circumstances are the more impressive. That is to say, in the case of $CHCl_3$ the contribution from $S_{rot.}$ is found to reach about 50% of S_{total} and to be larger than that for CCl_4 in its absolute magnitude in spite of the smaller moments of inertia for $CHCl_3$ than CCl_4. The main cause of this is clearly attributed to the smaller σ of $CHCl_3$.

In Table 9, contributions of each term of S for c-C_6H_{12} are shown. In this case, $S_{rot.}$ is about 10% larger than that of C_6H_6 and this comes from larger I_A, I_B, I_C, and smaller σ than those of C_6H_6.

Liquid Model. As discussed in above paragraphs, the picture of liquid composed of hard sphere and uniform background potential are considered to be reasonable in the first approximation from the fact that the calculated values of thermodynamic quantities coincide well with observed values. And, further, it can be totally mentioned that free rotor picture of molecules in these liquids has been clarified from this calculation, though, from the small departure of S_{calcd} from S_{obsd}, there may be some small restriction for free rotor.

The adequacy of the free rotor picture means that the motion of the molecules within the liquids may be regarded as completely orientationally-uncorrelated. This appears as a common feature for these five liquids at least in the thermodynamic sense. And further, different aspects among these liquids, such as exemplified in the latter half of the preceding item, emerge in addition to the common feature.

Concluding Remarks

The statistical thermodynamic equivalent free volume theory of liquids based on the combination of the Percus-Yevick integral equation approach and the uniform background model was applied effectively to estimate thermodynamic functions of five organic liquids.

The usefulness of present approach supports the idea that the overall thermodynamic behaviors of these liquids are represented in the first approximation by the liquid picture which is constituted by the freely-rotating hard sphere molecules with some effective diameter moving within the uniform backgound potential.

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