Fusion and State Equation of Simple Liquids. II. Critical Data and Fusion Parameters

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1. Numerical Calculations of State Equation and Critical Data

The numerical calculations of state equation (21) were performed using the upper limit $Z=12$ and the lower limit $Z=4$ for the summations in expressions (22). $Z=12$ was selected in accordance with the closest packing arrangement. The selection of the value of lower limit is arbitrary to a certain extent since it gives only a small effect on Eq. (21). The left side of Eq. (21) contains ζ in the terms of X, X_z, Y and Y_z. Therefore the value of ζ for the given value of R and ξ must be obtained by the successive approximation. The results obtained for the case of $\delta=0.10$ and 0.12 are shown in Table 1. The P–V diagram deduced from these values shows van der Waals' type condensation and the critical constants are determined by a graphical method. The critical constants obtained for three different values of δ are shown in Table 2 in which the com-

Table 1

Values of ζ Calculated from Eq. (21)

	$\delta=0.10$ ξ at				$\delta=0.12$ ξ at			
R^{-6}	0	0.05	0.10	0.15	0	0.05	0.10	0.15
0.1	1.419	1.286	1.174	1.080	1.392	1.263	1.156	1.064
0.2	1.178	1.084	1.003	0.933	1.163	1.071	0.992	0.923
0.25	1.144	1.036	0.980	0.913	1.134	1.048	0.973	0.908
0.3	1.128	1.043	0.970	0.905	1.121	1.038	0.964	0.900
0.4	1.098	1.019	0.950	0.889	1.107	1.027	0.957	0.895
0.5	1.086	1.010	0.942	0.882	1.109	1.030	0.960	0.898
0.6	1.127	1.046	0.974	0.909	1.175	1.089	1.012	0.943
0.7	1.265	1.168	1.081	1.004	1.332	1.227	1.130	1.051
0.8	1.541	1.410	1.294	1.192	1.716	1.561	1.427	1.309
0.9	2.196	1.965	1.774	1.612	2.662	2.338	2.075	1.865

parison is done between calculated and empirical values for noble gases and few other gases. Following the variation of δ, the proper values of g are selected to adjust the calculated and experimental values. The agreements are rather good when we take into consideration on the rough approximation of v_f and Ψ for the large value of T and small value of Z.

Table 2 .

Calculated and Observed Critical Data

	δ	g	R^{-6}	$[Z]_{AV}$	$\zeta_c = \frac{\varepsilon_0}{kT_c}$	$\frac{P_c r_0^3}{\varepsilon_0}$	$\frac{v_c}{r_0^3}$	$\frac{RT_c}{PV_c}$
Calc.	0.08	1.1	0.3	9.7	0.99	0.19	1.9	2.8
	0.10	1.0	0.3	9.7	1.02	0.17	1.8	3.0
	0.12	0.9	0.2	9.6	1.04	0.15	1.8	3.4
Obs.	Argon				0.79	0.166	2.22	3.44
	Nitrogen				0.76	0.185	2.06	3.45
	Neon				0.80	0.157	2.36	3.47
	Hydrogen				0.93	0.108	3.04	3.27

Souces: Critical data-Int. Crit. Tab.
ε_0 and r_0-from the Table in R.H. Fowler E.A. Guggenheim, "Statistical Thermodynamics," 285 (1939).

2. Equilibrium between Solid and Liquid States

When we assume that the essential difference between solid and liquid states consists only in the irregularity in the molecular arrangements, then the free energy of solid states of a face centered crystalline state may be given by the equation (9) in which $\delta=0$ and all of the values of $P(Z)$ is zero except in the case of $Z=12$. The free energy expression thus obtained is identical to that given by Lennard-Jones and Devonshire for liquid state lacking the additional term of kT. The Gibbs' free energy for solid state may then be written as follows,

$$\mu_s = -\frac{\varepsilon_0}{\zeta}\Big[(\ln[(2\pi m\varepsilon_0/\zeta)^{3/2}\Big/h^3] + \ln J - \frac{\zeta}{2\varepsilon_0}\psi(R_s,\,12) + \ln v_f(R_s,\,12)\Big] + P_s v_s, \tag{23}$$

$v_s = \gamma R_s^3 r^3$; ($\gamma = 2^{-1/2}$ in the case of a face centered cubic lattice.)

where $\psi(R_s,\,12)$ and $v_f(R_s,\,12)$ are respectively given by Eqs. (7) and (5) substituting R_s for R and 12 for Z. R_s which corresponds to R in the solid state is given as a function of ζ and ξ by the state equation for solid state, *i. e.*

$$\begin{aligned} &12\,R_s^{-3}\xi_s\zeta \\ &= -\zeta\left(28R_s^{-6} - 24R_s^{-2} - 4R_s\frac{\mathrm{d}M}{\mathrm{d}R_s} + 4R_s^{-6}\right) \\ &\quad + 1 - 2\,l_1R_s^{-6} - 2\beta_1R_s^{-6}/[1+\exp(-\alpha \\ &\quad - 12\beta\zeta)], \end{aligned} \tag{24}$$

which is deduced from Eq. (21) with $[Z]_{AV}=12$ and $\delta=0$.

To compare the free energy of liquid state with that of solid state we rewrite the term A in Eq. (19) using the Eqs. (18), (5), (20) and (22).

$$A^{-1} = 2\pi(r_0R)^3(X+e^{\alpha}Y)\exp(l_0 + l_1R^{-6} + 2(1+4.2\,\delta^2)\zeta R^{-6}).$$

Therefore

$$-\ln A = \ln v_f(R,\,12) + \ln(X+e^{\alpha}Y) - \ln(1+e^{\alpha+12\beta\zeta}) - \frac{\zeta}{2}\Psi(R,\,12) + 12\,\xi\zeta R^{-3} - 12\,\rho\zeta.$$

Then the Gibbs' free energy of liquid state obtained by Eq. (19) is as follows,

$$\mu_l = -\frac{\varepsilon_0}{\zeta}\Big[\ln[(2\pi m\varepsilon_0/\zeta)^{3/2}\Big/h^3] + \ln J - \frac{\zeta}{2}\Psi(R,\,12) + \ln v_f(R,\,12) + \ln(X+e^{\alpha}Y) - \ln(1+e^{\alpha+12\beta\zeta}) + 12\xi\zeta R^{-3} - 12\rho\zeta - [Z]_{AV}R^{-3}\xi\zeta\Big] + Pv. \tag{25}$$

The condition for equilibrium between solid and liquid phases with the same temperature and pressure is

$$\begin{aligned} 0 &= (\mu_l - \mu_s)/\varepsilon_0 \\ &= \frac{1}{\zeta}\Big[\frac{\mathrm{d}G}{\mathrm{d}R_s}\Delta R + (6\times15.6\,R^{-12} - 14\times4.2\,R^{-6})\delta^2 \\ &\quad - \ln[(X+e^{\alpha}Y)e^{-12\rho\zeta}\Big/(1+e^{\alpha+12\beta\zeta})]\Big] \\ &\quad + P(v-v_s)/\varepsilon_0 - (12-[Z]_{AV})\xi R^{-3}, \end{aligned} \tag{26}$$

where

$$G = \frac{\zeta}{2\varepsilon_0}\psi(R_s,\,12) - \ln v_f(R_s,\,12),$$

$$\Delta R = R - R_s.$$

In the solid state pressure is obtained from the expression of free energy given by Eq. (23)

$$P = -\frac{\partial(\mu_s - Pv_s)}{\partial v_s} = -\frac{\varepsilon_0}{\zeta}\frac{R_s^{-2}}{3\gamma r_0^3}\frac{\mathrm{d}G}{\mathrm{d}R_s}.$$

Therefore

$$\frac{\varepsilon_0}{\zeta}\frac{\mathrm{d}G}{\mathrm{d}R_s}\varDelta R = -Pr_0{}^3\gamma 3R_s{}^2\varDelta R$$
$$\doteqdot Pr_0{}^3\gamma(R_s{}^3-R^3)\,.$$

Using the above equation, we can simplify the terms regarding the volume change in Eq. (26) as follows,

$$\begin{aligned} &Pr_0{}^3\gamma(R_s{}^3-R^3)+P(v-v_s)\\ &\quad -(12-[Z]_{AV})\varepsilon_0\,\xi R^{-3}\\ &=Pv\left(2-[Z]_{AV}\frac{\gamma}{g}-12/[Z]_{AV}\right)\\ &=-(\xi R^{-3}\varepsilon_0/12)(12-[Z]_{AV})^2\,,\end{aligned}$$

where we used the relation $12\gamma=g$ which may hold near the melting point. From this equation we can obtain the condition for melting as following,

$$\begin{aligned} 0&=(\mu_l-\mu_s)\zeta/\varepsilon_0\\ &=\ln[(X+e^{\alpha}Y)e^{-12\rho\zeta}/(1+e^{\alpha+12\beta\varepsilon})]\\ &\quad+(\xi\zeta R^{-3}/12)(12-[Z]_{AV})^2\\ &\quad+(14\times 4.2\,R^{-6}-6\times 15.6\,R^{-12})\,\delta^2\,. \quad (27)\end{aligned}$$

3. Fusion Parameters

From the above equation we can obtain the melting temperature for the given value of ξ, substituting the value of R determined as a function of ζ and ξ by the state equation (21). The pressure dependence of melting point obtained from this method in the case of $\delta=$ 0.1 and 0.12 are shown in Figure 1. Too large theoretical value of ζ_m (see Table 3) was reduced by the use of ζ_c given by Table 2 which are also too large compared with experimental values. Therefore the calculated values in Figure 1 fairly agree with experimental values. The values of melting point derived by this method depend on δ, and ζ_m increases with decreasing values of δ. The variation of n in the expression of the molecular interaction energy gives greater influence on the melting temperature. In the general case of the molecular interaction expressed by Eq. (1), the condition for melting temperature is given by Eq. (27) with the alteration of the last term to the following expression,

$$(29.4\,nR^{-6}-3.6\,n(n+1)R^{-n})\frac{\delta^2}{n-6}\,. \quad (28)$$

To obtain the melting point for the general cases, we have to calculate R for the given ζ and ξ using the state equation (21) and expression for ρ in (22) with different numerical constants. Also the free volume v_f given by Eq. (5) needs revision which corresponds to the change of n, and this revision may result the changes of numerical values in expression (6′). The change of melting point by this revision may not be of a negligible order, however we may see the inclination of change in the melting point with different values of n by the calculation using the same numerical values in expression (6′). The result obtained is shown in Figure 2 in the case of $\delta=0.12$. With higher value of δ the curve in Figure 2 shifts downward. It is easily supposed that the melting point has a strong dependence on n since the molecular distances of nearest neighbors at the melting point are so short that the repulsive force plays an important role. To reduce

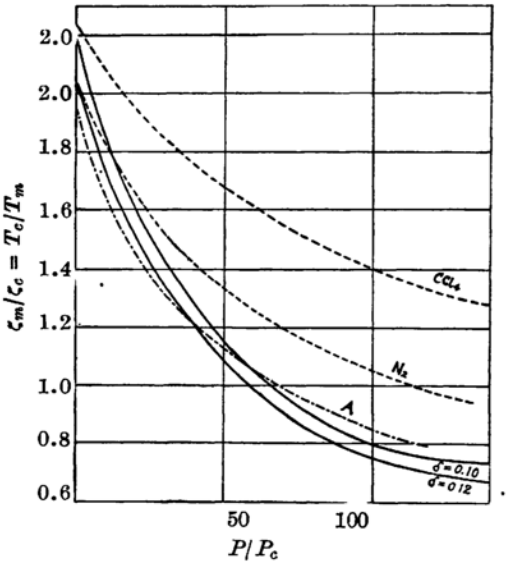

Fig. 1.

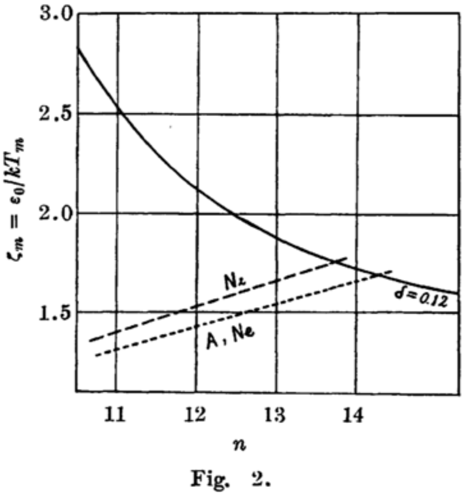

Fig. 2.

the observed melting temperature T_m to $\zeta_m = \mathcal{E}_0/kT_m$ we have determined the values of $\mathcal{E}_0$. Lennard-Jones and Buckingham have determined the values of $\mathcal{E}_0$ for argon, neon and nitrogen, etc. using the results of exact measurements on isotherms of these gases. These results show a linear dependence of $\mathcal{E}_0$ on n. Estimated values of ζ_m using these values are shown in Figure 2 by the dotted line for argon, neon and nitrogen. The cross points of full line and dotted lines indicate proper values of n with which the calculated melting point agree with the observed values. Therefore we may obtain a rough estimation of the relative values of n for simple molecules by this method. If we assume that the relation $T_c = 4\mathcal{E}_0/3k$ holds for $n=12$ and also $\mathcal{E}_0$ changes with n in a similar way as illustrated for A, Ne and N, we can obtain the relative values of n from the critical and melting temperature. When molecules have an attractive force proportional to r^{-6} we may conclude that the lower value of the ratio T_c/T_m corresponds to a higher value of n. The noble gases have the highest value of n and other molecules having more complex structures show lower values of n.

The volume change Δv by fusion is obtained from the values of R_s, R and $[Z]_{AV}$ at the melting point which are presented in Table 3. R_s is obtained by the solid state equation (24) at the melting temperature and pressure. Using the relation (10) we get

$$\Delta v = v_l - v_s = v_{so}\left[\frac{12}{[Z]_{AV}}\left(\frac{R}{R_{so}}\right)^3 - \left(\frac{R_s}{R_{so}}\right)^3\right] \quad (29)$$

as a volume change from a liquid state to a face centered crystalline state, where v_{so} is a volume per molecule and R_{so} is R in a solid at $P=0$, $T=T_m$.

The entropy of fusion per molecule may be written using the following thermodynamic relation,

$$\Delta S = \left(\frac{\partial \Delta\mu}{\partial T}\right)_p = \zeta_m k\left(\frac{\partial \Delta\mu/\mathcal{E}_0}{\partial\zeta}\right)_p. \quad (30)$$

From Eq. (27) though we may obtain the derivative of the right side in Eq. (30), it is easier to make numerical or graphical calculation using the following relation,

$$\left(\frac{\partial \Delta\mu/\mathcal{E}_0}{\partial\zeta}\right)_p = \left(\frac{\partial \Delta\mu/\mathcal{E}_0}{\partial\zeta}\right)_\xi + \left(\frac{\partial \Delta\mu/\mathcal{E}_0}{\partial\xi}\right)_\zeta \times \frac{\xi\left(\frac{\partial(R^6[Z]_{AV}^{-2}}{\partial\zeta}\right)_\xi}{R^6[Z]_{AV}^{-2} - \xi\left(\frac{\partial(R^6[Z]_{AV}^{-2})}{\partial\xi}\right)_\zeta}.$$

The theoretical fusion parameters $\Delta v/v_{so}$ and ΔS thus obtained in the case of $\delta=0.10$ and 0.12 are also given in Table 3. The observed values at high pressure in Table 3 is obtained by the interpolation of Bridgman's measurements, where the values used for P/P_c are the same as those in the case of $\delta=0.10$. At ordinary pressure, calculated fusion parameters agree remarkably well to experimental values in the case of $\delta=0.10$. On the other hand, though the pressure dependence of fusion parameters ΔS and $\Delta v/v_{so}$ agree moderately well with experiments for argon, but the agreement is rather poor when compared with that of the

Table 3

Calculated and Observed Fusion Parameters

	ξ	P/P_c	ζ_m	$[Z]_{AV}$	R^{-6}	R_s^{-6}	$\Delta v/v_{so}$	ΔS, cal./mol
Calc. $\delta=0.12$	0	0	2.124	11.19	0.853	1.005	0.164	3.8
	0.15	13.3	1.715	11.22	0.878	1.009	0.136	3.5
	0.5	48.4	1.175	11.40	0.947	1.055	0.108	3.1
	1.0	109.1	0.769	11.40	1.069	1.173	0.096	2.4
Calc. $\delta=0.10$	0	0	2.208	11.34	0.902	1.010	0.121	3.4
	0.15	12.5	1.776	11.40	0.928	1.022	0.104	3.1
	0.5	45.7	1.239	11.47	1.002	1.080	0.083	2.7
	1.0	103.5	0.817	11.47	1.134	1.209	0.073	2.2

	Obs. for argon				Obs. for nitrogen			
P/P_c	T_m	ζ_m	$\Delta v/v_{so}$	ΔS	T_m	ζ_m	$\Delta v/v_{so}$	ΔS
0	83.7	1.433	0.125	3.34	63.1	1.53	0.069	3.45
12.5	97.6	1.229	0.101	2.80	71.8	1.34	0.062	3.38
45.7	131.1	0.915	0.063	2.11	91.8	1.05	0.050	3.17
103.5	180.2	0.666	0.037	1.52	121.0	0.80	0.034	2.72

Sources: ϵ_0 and r_0 are same as in Tab. 2.
Observed values are from Randolt, and Bõrnstein, "Physik.-Chem. Tab. Eg. III$_c$," 2687, 2689.

pressure dependence of melting temperature.

The molecular arrangements at high pressure will become more likely similar to the solid state arrangements. And it may be expected that the higher the pressure becomes, the steeper the distribution of the distances between two nearest neighbors becomes, and also the shorter these distances become. From the general inclination of change of fusion parameter with the change of δ we can expect that a better agreement may be obtained between calculated and observed values of ΔS and $\Delta v/v_{s0}$ when we assume smaller values of δ at higher pressure.

The quantitative agreements between theoretical and experimental values of fusion parameters may be expected when we take into consideration the pressure dependence of the value of δ and a revision regarding a calculation of the free volume which was performed with a model of too restricted molecular motion in this paper. We may therefore conclude that the experimental confirmation of assumption on the molecular arrangements as well as the procedure of the construction of partition function is adequate. To know the behavior of the liquid state and liquid-solid equilibrium at the pressure higher than $P/P_c \sim 100$ we have to check the correctness of the approximate formula for free volume expressed by Eq. (6), since at such pressure R^{-6} and R_s^{-6} becomes arger than 1.2.

4. Summary

The molecular arrangements in liquid state may be characterized by assignement of the number of nearest neighbors on each molecule, and distances between two nearest neighbors. The assumption is made on the distribution of distances r between the two nearest neighbors which does not take a definite value as in the crystalline state but is distributed over the region of $[r(1+\delta),\ r(1-\delta)]$. The partition function and state equation are deduced under these assumptions using proper values of δ expected by X-ray diffraction on liquid argon. The critical constants for a simple liquid are determined which agree well with experimental values. The condition for the equilibrium between liquid and solid crystalline states is obtained on the basic assumptions that the essential differences of liquid and solid states consist in the difference of values of δ and the number of nearest neighbors around each molecule. The calculated melting temperature, volume and entropy inerements by fusion and pressure dependences of these fusion parameters agree well with experimental values.

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