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Fusion curves and thermodynamic properties of carbon tetrachloride, chloroform, bromoform and silicon tetrachloride at pressure up to 3500 MPa*

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The fusion temperature as a function of pressure for carbon tetrachloride, chloroform, bromoform and silicon tetrachloride at pressures up to 3500MPa has been determined. The experimental data were fitted by the equation $T_{\rm fus} = T_0(1 + \Delta p/a_1)^{a_2}\exp(-a_3\Delta p)$ and the changes of the molar enthalpy and molar internal energy on fusion were calculated using the parameters of the fitted equation. Comparisons with the data from the literature show that the experimental data, parameters of fitted equations, changes of the molar enthalpy and molar internal energy are reliable.

Keywords: fusion curve, molar entropy change, molar internal energy change, high pressure
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1. Introduction

Some substances show unusual physical properties at high pressures, therefore the studies on the properties of substance at high pressure are attracting increasing interest. Theoretical calculation indicates that, at sufficiently high pressures, all matter is converted to a metallic form. This has been verified for I_2 and CsI.[1]

Fusion transition can be useful for calibration of pressure devices since the transition is quite sharp (small hysteresis) and can be detected easily by using either direct or indirect methods. Methods used to detect phase transition include measurement of electrical resistance, volume, refractive index, absorption reflectance, x-ray diffraction, neutron diffraction, differential thermal analysis, magnetic properties and capacitance. Bridgman[2–4] investigated the melting curves of a number of organic substances at pressures up to 1200MPa. Osugi *et al*[5] determined the high pressure liquid–solid transitions of benzene, chlorobenzene and toluene at 298K. Crawford and Daniel,[6] Strong and Bundy,[7] Akella and Kennedy[8] determined the melting curves of Kr, Ne, He and some metallic elements such as copper, gold, silver and iron, etc.

This paper describes the experimental method which was developed for determining fusion temperatures and pressures of carbon tetrachloride, chloroform, bromoform and silicon tetrachloride between 226 and 915K at pressures up to 3500MPa. Equations for the pressure dependence of the fusion temperature, based on thermodynamic principles, were obtained. Changes of the molar entropy and molar internal energy during freezing were calculated using the parameters of fitted equations and changes of the molar volume.

2. Theoretical models

There are two basically different approaches used to solve the fusion problem.

(i) Fusion is considered as an ordinary first-order phase transition (the two-phase approach to melting). In accordance with the thermodynamic theory, the fusion occurs when the Gibbs free energies of the liquid and solid are equal at a given temperature and pressure. The thermodynamic relationship for liquid–solid equilibrium is given by the Clapeyron equation:[9]

$$\frac{{\rm d}\ln T_{\rm fus}}{{\rm d}p_{\rm fus}} = \frac{\Delta_{\rm fus}V}{\Delta_{\rm fus}H}, \tag{1}$$

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where $T_{\rm fus}$ is the absolute fusion temperature and $\Delta_{\rm fus}H = T_{\rm fus}\Delta_{\rm fus}S$ is the fusion enthalpy, $\Delta_{\rm fus}S$ is the entropy change during fusion. $\Delta_{\rm fus}V = V_{\rm liq} - V_{\rm sol}$ is the volume change during fusion. This approach can be used in thermodynamic calculation through different approximations of the equation of state for the solid and liquid phases.[10,11]

(ii) Another widespread theory for fusion based on the lattice instability is the Lindemann criterion of fusion.[12] In differential form, the Lindemann equation of fusion can be written as

$$\frac{\mathrm{d}\ln T_{\rm fus}}{\mathrm{d}p_{\rm fus}} = \frac{\Gamma_{\rm fus}}{B_{\rm fus}}. \tag{2}$$

Here $\Gamma_{\rm fus} = -(\mathrm{d}\ln T/\mathrm{d}\ln V)_{\rm fus} = 2(\gamma_{\rm fus} - 1/3)$, $\gamma_{\rm fus} = -(\mathrm{d}\ln\Theta/\mathrm{d}\ln V)_{\rm fus}$ is the Grüneisen fusion parameter, Θ is the characteristic temperature of solid on fusion. $B_{\rm fus}$ is the bulk modulus of solid along the fusion curves, $B_{\rm fus} = -(\mathrm{d}P/\mathrm{d}\ln V)_{\rm fus} = B_{\rm T}[1 + 2(\gamma_{\rm fus} - 1/3)\alpha T_{\rm fus}]$, with $\alpha = -(\mathrm{d}\ln V/\mathrm{d}T)_P$ being the volume coefficient of thermal expansion and $B_{\rm T}$ the isothermal bulk modulus at melting temperature. For the rising fusion curves $B_{\rm fus} > B_{\rm T}$, for the falling curve $B_{\rm fus} < B_{\rm T}$, and at the curve maximum $B_{\rm fus} = B_{\rm T}$.

Since it is evident that the dependence of the right-hand-side parts of Eqs.(1) and (2) on pressure are identical, this dependence can be written as a fractional form function performing Padé $[L/M]$ approximation. The fractional form function approximates a very wide class of functions. Hence Eqs.(1) and (2) can be written in a unified form as

$$\frac{\mathrm{d}\ln T_{\rm fus}}{\mathrm{d}p} = \frac{c_0 + c_1\Delta p + \cdots + c_L(\Delta p)^L}{b_0 + b_1\Delta p + \cdots + b_M(\Delta p)^M}, \tag{3}$$

where $\Delta p = p - p_0$, p_0 is some reference (for example, triple point) pressure; c_0, c_1, ..., c_L and b_0, b_1, ..., b_M are constants. Equation (3) combines both one-phase and two-phase approaches to fusion. Integration of Eq.(3) with respect to pressure leads to the fusion curve equation $T_{\rm fus} = F_{[L/M]}(x)$.

For M=1

$$T_{\rm fus} = F_{[0/1]}(x) = T_0(1+x)^{a_2}, \tag{4}$$

$$T_{\rm fus} = F_{[1/1]}(x) = F_{[0/1]}(x)\exp(-a_3x), \tag{5}$$

$$T_{\rm fus} = F_{[L/1]}(x) = F_{[0/1]}(x)\exp\left(-\sum_{k=1}^{L} a_{k+2}x^k\right). \tag{6}$$

For M=2

$$T_{\rm fus} = F_{[0/2]}(x) = F_{[0/1]}(x)(1+a_3x)^{-a_2}, \tag{7}$$

$$T_{\rm fus} = F_{[1/2]}(x) = F_{[0/1]}(x)(1+a_3x)^{-a_4}, \tag{8}$$

$$T_{\rm fus} = F_{[2/2]}(x) = F_{[1/2]}(x)\exp(-a_5x), \tag{9}$$

$$T_{\rm fus} = F_{[L/2]}(x) = F_{[1/2]}(x)\exp\left(-\sum_{k=2}^{L} a_{k+3}x^{k-1}\right). \tag{10}$$

Here $x = \Delta p/a_1$ is the reduced pressure, a_1 has the dimensionality of pressure, and the other parameters are dimensionless. The parameters a_k in Eqs.(4)–(11) can be expressed in term of c_k and b_k and vice versa.

Similar to Eqs.(5)–(10), the fusion equations have the same structure

$$T_{\rm fus} = F_{[0/1]}(x)D_{\rm fus}(x). \tag{11}$$

Function $F_{[0/1]}(x)$ is the Simon–Glatzel empirical equation for fusion, which can be written in the form[13]

$$T_{\rm fus} = T_0(1 + \Delta p/a)^{1/c}, \tag{12}$$

where T_0 is the temperature at the triple point and $\Delta p = p - p_0$.

Expanding Eq.(3) at point $\Delta p = p - p_0$ up to the second order, one obtains

$$\frac{\mathrm{d}\ln T_{\rm fus}}{\mathrm{d}p} = y \approx y_0 + y_0'\Delta p + \frac{1}{2}y_0''(\Delta p)^2, \tag{13}$$

where single and double primes denote the first- and second-order derivatives, respectively, with respect to pressure. Performing the Padé approximation to the right-hand side of Eq.(13) we obtain

$$\frac{\mathrm{d}\ln T_{\rm fus}}{\mathrm{d}p} = \frac{1 - \beta\Delta p}{\sigma(\alpha + \Delta p)}, \tag{14}$$

where the parameters α, β and σ are given by

$$\begin{aligned} \alpha &= -y_0'/y_0'', \\ \beta &= y_0''/2y_0' - y_0'/y_0, \\ \sigma &= -y_0''/2y_0y_0'. \end{aligned} \tag{15}$$

By integrating Eq.(14) with respect to pressure, one obtains the equation for pressure dependence of fusion temperature in the following form:

$$T_{\rm fus} = T_0(1 + \Delta p/a_1)^{a_2}\exp(-a_3\Delta p), \tag{16}$$

where $a_1 = \alpha$, $a_2 = (1 + \alpha\beta)/\sigma = y_0'\alpha^2$ and $a_3 = \beta/\sigma = -y_0'\alpha - y_0$.

Note that the fusion curves can be predicted if the thermodynamic values at the reference pressure are known.

3. Experiment

3.1. Materials and their purities

Since impurities lower the freezing temperature of a solvent, all reagents were purified. Carbon tetrachloride, chloroform, bromoform and silicon tetrachloride were fractionally recrystallized 5 times. A mass-spectroscopic analysis of all reagents showed that all the purified ones can reach above 99.99 mass percentage. The samples used were degassed for 4h at a temperature of 1 or 2K below their respective normal fusion temperatures.

3.2. Experimental apparatus and accuracy

Since pressure transfer in solids is very slow and difficult and the determination of a freezing curve is fairly straightforward, the fusion temperatures of a pure material are obtained by measurement of its freezing temperatures. Experiments were performed in a high-pressure autoclave with a movable piston which has been described previously.[14] The tube-like autoclave was made of austenitic manganese steel, which a length of 300mm and the outer and inner diameters of 120 and 20mm, respectively. The piston was modified for high pressure and operated with a 3rd-order multiplying pressure function. After the samples were introduced into the autoclave, the temperature was changed while maintaining a constant pressure, which was achieved by adjusting the movable piston. Temperatures were decreased stepwise at a rate of 2K/h until the estimated freezing temperature was reached.

The system pressures were measured with a strain gauge dilating-cylinder pressure transducer. A detailed description had been reported by Jäger and Wanninger.[15] For this device, the ratio of the external to internal diameters of the cylinder, κ, is equal to 5.0. The output, $I(p)$, from the gauge for either rising or falling pressure showed a reproducibility of 0.03% of full scale. The estimated maximum uncertainty for high pressure was about ±2.0MPa. In order to achieve isothermal condition for this dilating cylinder, a water jacket (at 273K) was used to stabilize the casing temperature and great care was exercised to avoid pressure-induced temperature change in the pressure transmitting fluid. The $I--p$ curve was calibrated using the mercury melting-point curve. For this gauge the maximum deviation of pressure from linearity was 2.67MPa due to hysteresis effect. The temperature of the vessel was measured with a platinum resistance thermometer with an estimated maximum uncertainty of ± 0.02K.

3.3. Experimental procedure

One way to experimentally determine a solid–liquid equilibrium temperature (fusion temperature) at constant pressure is to use thermal analysis. The temperature of a system will remain constant at the freezing temperature, although slight dip below the freezing temperature can occur due to supercooling. In order to reduce the supercooling effect, nanometre-sized SiO_2 were added to the samples. Prior to introducing the sample into the autoclave, the equipment was dried, evacuated and flushed with pure sample. For temperatures below 173K, the cooling medium in the autoclave jacket was liquid nitrogen. In the range of 173 to 273K, the cooling medium was ethanol cooled by a mixture of liquid nitrogen and dry ice. For 273–353K, water was used. For temperatures greater than 353K, anhydrous glycerine was used.

During the cooling process, the volume decreased, therefore a movable piston was used to keep the pressure constant. The above procedure was repeated at other pressures to obtain the $p--T$ fusion curves.

4. Results and discussion

Most substances freeze at a higher temperature when subject to pressure, as if the pressure is preventing the formation of solid phase from the less dense liquid phase. Exceptions to this behaviour include water, for which the liquid is denser than the solid. We can rationalize the response of fusion temperature to pressure as follows. The variation of the chemical potential with pressure is expressed as

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_{\mathrm{m}}. \tag{17}$$

This equation shows that the slope of chemical potential against pressure is equal to the molar volume of the substance. An increase in pressure raises the chemical potential of any pure substance (because $V_{\mathrm{m}} > 0$). In most cases, $V_{\mathrm{m}}(\mathrm{l}) > V_{\mathrm{m}}(\mathrm{s})$ and the equation predicts that an increase in pressure increases the chemical potential of the liquid more than that of the solid. The effect of pressure in such a case is to raise the freezing temperature slightly.

Table 1 gives the fusion temperatures ($T_{\rm fus}$), changes of molar volume ($\Delta_{\rm fus}V_{\rm m}$) from references, changes of molar enthalpy ($\Delta_{\rm fus}H_{\rm m}$) and changes of molar internal energy ($\Delta_{\rm fus}U_{\rm m}$) on fusion at pressures up to 3500MPa for carbon tetrachloride, chloroform, bromoform and silicon tetrachloride. Changes of molar enthalpy are computed from Clapeyron's equation. Change of molar internal energy differs from that of molar fusion enthalpy only by the external work ($p\Delta_{\rm fus}V_{\rm m}$) on fusion. Changes of the molar volume on fusion become less with increasing pressure because of the intrinsic shapes of the molecules at high pressures. As pressure rises, the unoccupied space left by the uncoordinated motion of the molecules of the liquid would be expected to become smaller.

Table 1. The fusion temperatures ($T_{\rm fus}$), molar volume changes ($\Delta_{\rm fus}V_{\rm m}$), taken from Refs.[3, 4], molar enthalpy changes ($\Delta_{\rm fus}H_{\rm m}$), molar internal energy changes ($\Delta_{\rm fus}U_{\rm m}$) on fusion for carbon tetrachloride, chloroform, bromoform and silicon tetrachloride.

	carbon tetrachloride				chloroform			
p/MPa	$T_{\rm fus}$/K	$\Delta_{\rm fus}V_{\rm m}$ /(cm^3·mol^{-1})	$\Delta_{\rm fus}H_{\rm m}$ /(kJ·mol^{-1})	$\Delta_{\rm fus}U_{\rm m}$ /(kJ·mol^{-1})	$T_{\rm fus}$ / K	$\Delta_{\rm fus}V_{\rm m}$ /(cm^3·mol^{-1})	$\Delta_{\rm fus}H_{\rm m}$ /(kJ·mol^{-1})	$\Delta_{\rm fus}U_{\rm m}$ /(kJ·mol^{-1})
100	289.05	3.0764	2.5451	2.2374	226.40			
200	321.45	2.5508	2.6447	2.1345	243.03			
300	352.45	2.1496	2.6803	2.0354	263.46	5.9443	10.2789	8.3876
400	380.05	1.8248	2.6596	1.9297	278.44	5.5807	10.7255	8.3580
500	403.55	1.5465	2.5807	1.8074	291.03	5.2273	11.0717	8.2998
600	428.15	1.3055	2.4549	1.6716	305.62	4.8997	11.3566	8.2387
700	450.25	1.1034	2.3091	1.5367	322.56	4.6048	11.6098	8.1912
800	470.85	0.9417	2.1712	1.4179	331.87	4.3437	11.8514	8.1661
900	490.75	0.8081	2.0356	1.3084	348.81	4.1096	12.0801	8.1576
1000	505.85				354.76	3.9058	12.3214	8.1790
1500	590.05				413.44			
2000	666.67				460.81			
2500	730.22				502.28			
3000	788.94				535.63			
3500	837.21				570.87			

	bromoform				silicon tetrachloride			
p/MPa	$T_{\rm fus}$/K	$\Delta_{\rm fus}V_{\rm m}$ /(cm^3·mol^{-1})	$\Delta_{\rm fus}H_{\rm m}$ /(kJ·mol^{-1})	$\Delta_{\rm fus}U_{\rm m}$ /(kJ·mol^{-1})	$T_{\rm fus}$ / K	$\Delta_{\rm fus}V_{\rm m}$ /(cm^3·mol^{-1})	$\Delta_{\rm fus}H_{\rm m}$ /(kJ·mol^{-1})	$\Delta_{\rm fus}U_{\rm m}$ /(kJ·mol^{-1})
100	302.74	8.9517	11.6316	10.7364	238.44			
200	326.77	8.1177	12.1693	10.5458	265.93	4.0596	3.8124	3.0005
300	345.02	7.3519	12.5107	10.3051	291.25	3.6620	3.9539	2.8553
400	365.41	6.6872	12.7537	10.0788	320.85	3.3316	4.0681	2.7355
500	385.61	6.0908	12.8857	9.8403	345.07	3.0464	4.1531	2.6299
600	408.90	5.5449	12.9033	9.5763	369.15	2.8598	4.3076	2.5917
700	420.30	5.0875	12.9303	9.3690	393.25	2.6957	4.4482	2.5612
800	437.24	4.7109	12.9987	9.2300	417.52	2.5653	4.6040	2.5518
900	452.98	4.4076	13.1357	9.1688	440.06	2.4629	4.7787	2.5620
1000	465.60	4.1473	13.2898	9.1425	465.96	2.3770	4.9598	2.5828
1500	538.38				568.73			
2000	595.62				666.85			
2500	645.88				752.73			
3000	684.38				833.67			
3500	723.65				915.32			

Figure 1 presents experimental data points of this work, previously published data and the least-squares fitting curves using Eq.(16) for carbon tetrachloride, chloroform, bromoform and silicon tetrachloride. The equation provides a good description for the experimental results and the data from Refs.[3] and [4]. The four fusion curves show in a striking way that the shapes of curves are with no maximum temperatures as Tammann[16] had supported.

Table 2 lists the parameters T_0, a_1, a_2 and a_3 in Eq.(16) obtained using a nonlinear least-squares fitting procedure as well as the average deviations between the measured and calculated values. For the four substances, p is on the order of magnitude of billions of Pa and p_0 is hundred of Pa, and hence, p_0 could be neglected. In all cases the fits are as good as the experimental data.

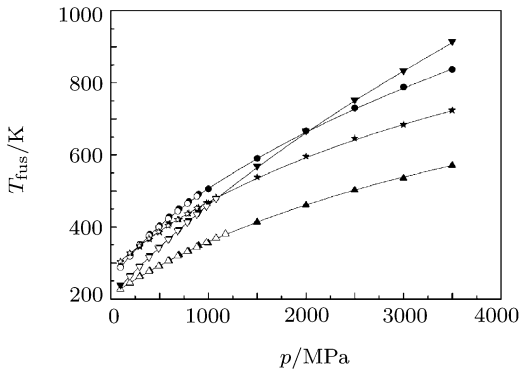


Fig.1. The fusion curves of carbon tetrachloride, chloroform, bromoform and silicon tetrachloride. Lines are the fitted curves. Silicon tetrachloride: ▼, this work; ▽, Ref.[3]. Bromoform: ★, this work; ☆, Ref.[3]; Carbon tetrachloride: ●, this work; ○, Ref.[4]; Chloroform: ▲, this work; △, Ref.[4].

Table 2. The least-squares fitting parameters used in Eq.(16).

substance	T_0/K[17]	a_1/GPa	a_2	a_3/GPa	δ/K[a]
carbon tetrachloride	250.61	0.2975	0.4830	0.0064	2.03
chloroform	209.70	0.6846	0.6567	0.0536	1.79
bromoform	280.91	0.58661	0.5538	0.0370	2.43
silicon tetrachloride	205.02	0.4829	0.7412	0.0206	2.10

[a]Average deviation: $\delta = \overline{|T_{fus}(exp) - T_{fus}(cal)|}$

Figures 2 and 3 show the computed values of $\Delta_{fus}H_m$ and $\Delta_{fus}U_m$. $\Delta_{fus}H_m$ increases slightly with increasing pressure, but $\Delta_{fus}U_m$ slightly decreases and would be constant at high pressures. $\Delta_{fus}U_m$ of chloroform is close to 8.16kJ·mol^{-1}, that of silicon tetrachloride 2.56kJ·mol^{-1}, and that of bromoform 9.14kJ·mol^{-1}. For carbon tetrachloride, however, there is no consistent value of $\Delta_{fus}U_m$. Hence, more experimental data are necessary. This phenomenon may be related to the intrinsic shapes of the molecules, which will limit the motion of the molecules. For carbon tetrachloride, chloroform, bromoform and silicon tetrachloride, the computed $\Delta_{fus}H_m$ and $\Delta_{fus}U_m$ and values reported in the literature are basically consistent. So these computed data of $\Delta_{fus}H_m$ and $\Delta_{fus}U_m$ on fusion are reliable.

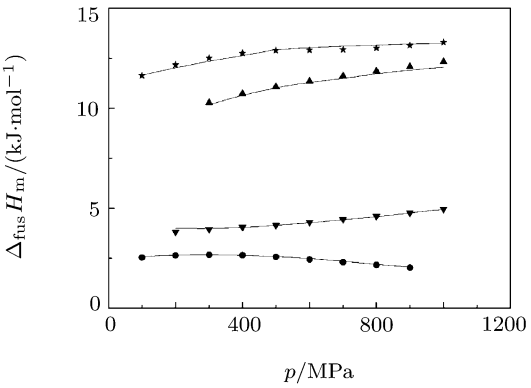


Fig.2. The computed molar enthalpy changes on fusion of silicon tetrachloride (▼), bromoform (★), carbon tetrachloride (●) and chloroform (▲). Lines show values from Refs.[3] and [4]. Data points show computed values.

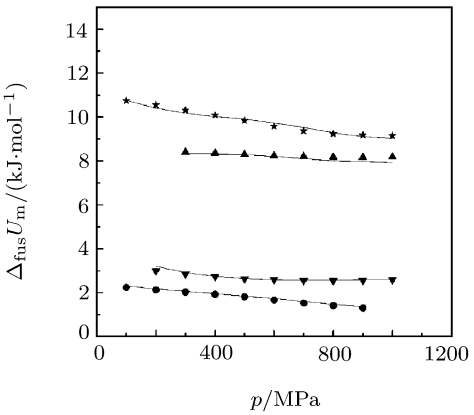


Fig.3. The computed molar internal energy changes on fusion of silicon tetrachloride (▼), bromoform (★), carbon tetrachloride (●) and chloroform (▲). Lines show the values reported in Refs.[3] and [4]. Data points show the computed values.

5. Conclusions

We have described a method of measuring the fusion temperatures at high pressures and reported the fusion curves of carbon tetrachloride, chloroform, bromoform and silicon tetrachloride at pressures up to 3500MPa. The data of the four substances point conclusively to only one conclusion, namely the four fusion curves have no maximum temperatures as Tammann had supposed. The fusion equations based on the two- and one-phase approaches were used to fit the experimental data. The changes of the molar enthalpy and molar internal energy on fusion were calculated using the parameters of the fitted equation. Comparisons with previously published data show that experimental and calculated results are in reasonable agreement.

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