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Author(s)	Osugi, Jiro; Shimizu, Kiyoshi; Onodera, Akifumi
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LIQUID-SOLID TRANSITION AT HIGH PRESSURE

— Benzene, Monochlorobenzene and Toluene —

BY JIRO OSUGI, KIYOSHI SHIMIZU AND AKIFUMI ONODERA

Among the pioneering works of P. W. Bridgman in high pressure research, the studies on the compressibility of liquids and on the liquid-solid transition are remarkable.

The object of this paper is to present the results of the high pressure liquid-solid transitions of benzene, monochlorobenzene and toluene.

Transition pressure was observed as a discontinuity in the volume at increasing or decreasing pressures. The method of volume discontinuity gave the results, not only for the temperature and pressure of transition, but also for the change of volume during transition. By reading transition pressures at different temperatures, it was possible to determine the ordinary parameters which characterize the thermodynamics of transition.

Pressures up to about $10,000 \text{ kg/cm}^2$ are transmitted by liquids and measured by a bourdon gauge. For the calibration of the bourdon gauge the freezing point of liquid mercury, the "mercury point" found by Bridgman, has been used. Thus, liquid-solid transition, and also solid-solid transition which occurs in a very high pressure region, have great significance in relation to pressure calibration. Discussions are made about benzene, monochlorobenzene and toluene as to the pressure calibration.

The samples used in these experiments were chemically pure, which had been distilled three times.

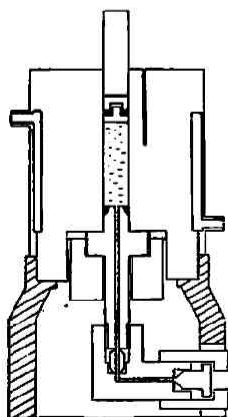
Benzene : $80.0\text{--}80.5^\circ\text{C}$ Monochlorobenzene : $131.0\text{--}131.3^\circ\text{C}$ Toluene : $110.5\text{--}110.7^\circ\text{C}$ 

Fig. 1 Schematic diagram of high pressure vessel

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The sample was placed in the cylinder which is schematically shown in Fig. 1, and this cylinder was kept at a specified temperature by circulating water or refrigerant liquid of a definite temperature through its over-jacket. The volume of the sample in the cylinder was about 40 cm^3 .

The temperature of the sample was measured with a calibrated iron-constantan thermocouple which was inserted into the cylinder wall. Temperatures were determined with a precision of $\pm 0.2^\circ\text{C}$.

A force was applied to the piston by means of a compression member which was attached to the hydraulic press. The ratio of the force generated by the press (calculated from its ram area and the oil pressure) and the area of the sample gave the pressure of the sample.

Pressure was increased by pressing the piston, and the piston position was plotted against the pressure.

For the volume change of the sample with pressure, the displacement of the piston in the cylinder was measured by means of the dial gauge which was graduated to 0.01 mm .

In order to freeze the liquid sample completely, the excess load was at first needed by a few hundred (for benzene) or thousand (for monochlorobenzene and toluene) kilograms beyond the freezing pressure, and because of the contraction of volume due to the liquid-solid transition the pressure decreased to the freezing pressure after a few minutes. This operation was repeated until the transition was completed. After the sample had been frozen by increasing pressure, readings were repeated with decreasing pressure.

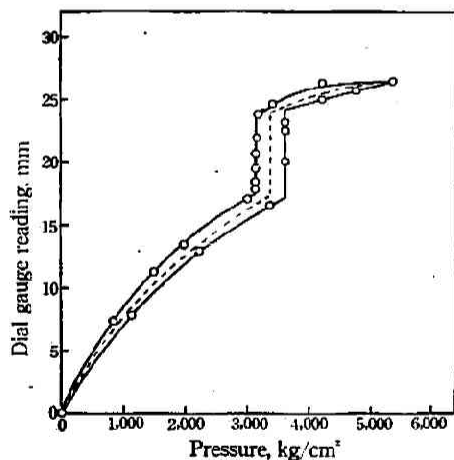


Fig. 2 A typical experimental curve
 —○—: Data as taken
 - - - - : Data corrected for friction

A typical experimental curve is shown in Fig. 2. The difference between the increasing and decreasing pressure curves may be due to friction, and the true curve is the mean of these curves, under the assumption that friction is approximately the same on the up- and down-stroke.

The experimental data which were obtained fall into two separate parts, those which refer to the thermodynamic parameters of the liquid-solid transition, and those which refer to the high pressure calibration points.

In Fig. 3, the transition temperature is shown as a function of pressure. The transition tempera-

ture rises with increasing pressure, corresponding to the fact that the liquid has a larger volume than the solid. The transition pressure of benzene was found to increase linearly with temperature from 425 kg/cm² at 15.0° to 785 kg/cm² at 25.0°. For monochlorobenzene and toluene the linearity is also seen. In series C₆H₆, C₆H₅Cl, C₆H₅CH₃, the transition pressure increases in the order given. The smoothed values for the transition pressure and temperature are given in Table 1.

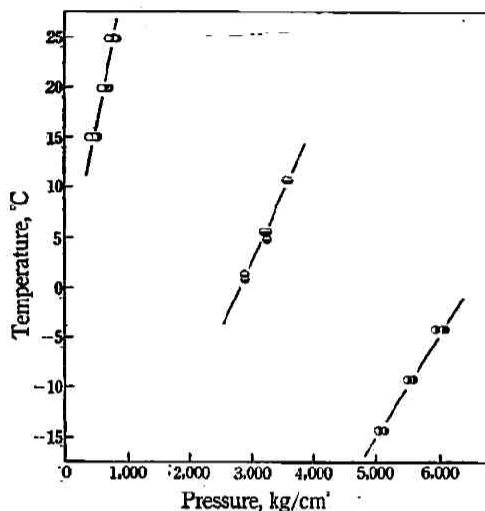


Fig. 3 Transition point curves of benzene monochlorobenzene, and toluene.

○: Benzene
◐: Monochlorobenzene
●: Toluene

Table 1 Smoothed values of transition pressure and temperature.

	T °C	p kg/cm ²
Benzene	15.0	425
	20.0	605
	25.0	785
Monochlorobenzene	0.0	2,790
	5.0	3,150
	10.0	3,510
Toluene	-15.0	4,980
	-10.0	5,460
	-5.0	5,950

The fractional change of volume on transition is shown in Fig. 4 as a function of pressure and in Fig. 5 as a function of temperature. ΔV decreases with increasing pressure and temperature.

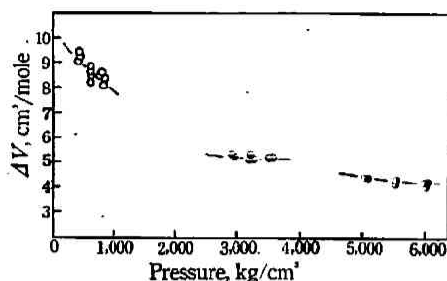


Fig. 4 The volume changes at the transition as a function of pressure

○: Benzene
◐: Monochlorobenzene
●: Toluene

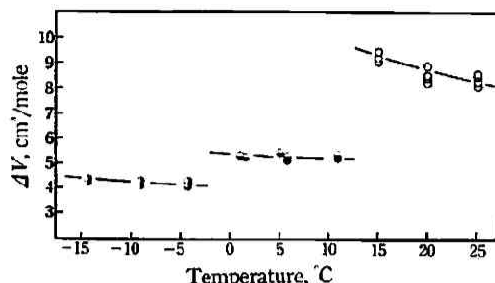


Fig. 5 The volume changes at the transition as a function of temperature

○: Benzene
◐: Monochlorobenzene
●: Toluene

The decrease of ΔV with temperature, and also with pressure, could be understood from the following equation given by Zhokhowski¹⁾

$$\Delta V = \Delta V_0 e^{-\kappa(T-T_0)} \quad (1)$$

where κ is empirical constant, T_0 , and ΔV_0 being the corresponding values at the triple point.

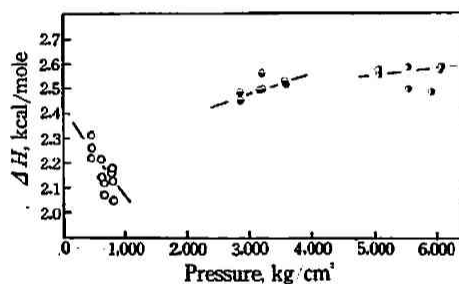


Fig. 6 Latent heat of the transition as a function of pressure

○: Benzene
◐: Monochlorobenzene
●: Toluene

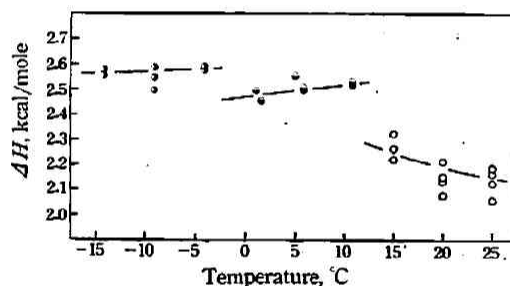


Fig. 7 Latent heat of the transition as a function of temperature

○: Benzene
◐: Monochlorobenzene
●: Toluene

In Fig. 6, the latent heat is shown as a function of pressure along the transition curve, in units of kcal per mole, calculated from the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = \frac{\Delta S}{\Delta V} \quad (2)$$

ΔH decreases with pressure only in benzene, while monochlorobenzene and toluene do not show such tendency. This difference is due to the large decrease in ΔV against the small increase in T with pressure in benzene. In Fig. 7, the latent heat is shown as a function of temperature.

Fig. 8 shows the entropy change during the transition as a function of pressure, in entropy unit (e.u.). ΔS decreases with pressure. In Fig. 9, ΔS is shown as a function of temperature.

The freezing point of mercury at 0°C (7,640 kg/cm² by Bridgman²⁾, and more recently 7,717 kg/cm² by Johnson and Newhall³⁾) has been useful as a calibration point up to about 10,000 kg/cm². These

1) M. K. Zhokhowski, *Zhur. fz. Khim.*, 38, 33 (1964)

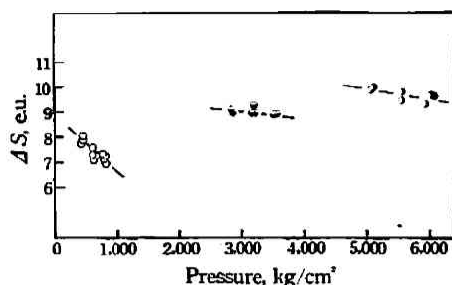


Fig. 8 The entropy change of the transition as a function of pressure

○: Benzene
◐: Monochlorobenzene
●: Toluene

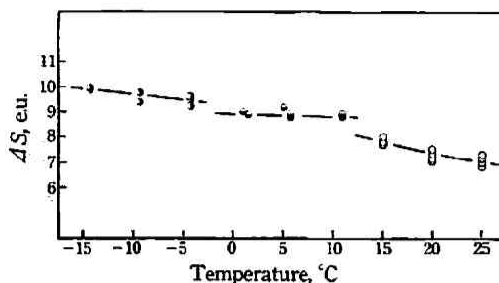


Fig. 9 The entropy change of the transition as a function of temperature

○: Benzene
◐: Monochlorobenzene
●: Toluene

three organic compounds were examined whether they are useful as calibration materials in the pressure range under the "mercury point".

Table 2 Values of $\frac{dp}{dT}$ and $\frac{1}{p} \cdot \frac{dp}{dT}$

		p kg·cm ⁻²	$\frac{dp}{dT}$ kg·cm ⁻² ·deg ⁻¹	$\frac{1}{p} \cdot \frac{dp}{dT}$ deg ⁻¹
Benzene	at 15.0°C	425	36.5	0.09
Benzene (Bridgman ²⁾)	at 15°C	355	36.9	0.10
Monochlorobenzene	at 10.0°C	3,510	72.3	0.021
Monochlorobenzene (Bridgman ²⁾)	at 16.7°C	4,000	75.3	0.019
Toluene	at -5.0°C	5,950	97.0	0.016
Mercury (Bridgman ²⁾)	at 10°C	9,630	198.3	0.021

In Table 2, the values of $\frac{dp}{dT}$ and $\frac{1}{p} \cdot \frac{dp}{dT}$ obtained from these experiments are shown, with the values quoted from Bridgman's data^{2,4,5)}.

During the transition the temperature moved by $\pm 0.2^\circ\text{C}$. The smaller the value of $\frac{1}{p} \cdot \frac{dp}{dT}$ the better is the reproducibility of the transition point. Toluene and monochlorobenzene have the values of $\frac{1}{p} \cdot \frac{dp}{dT}$ comparable to that of mercury.

On the other hand, the large value of $\frac{dp}{dT}$ is favorable where the setting of temperature was varied in order to obtain various transition pressures about a certain compound. In this view, toluene is superior to the other two compounds.

Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University Kyoto, Japan

2) P.W. Bridgman. *Proc. Amer. Acad. Arts. Sci.*, **47**, 347 (1912)

3) D. P. Johnson and D. H. Newhall. *Trans. Amer. Soc. mech. Engrs.*, **75**, 301 (1953)

4) P. W. Bridgman, *Phys. Rev.*, **3**, 153 (1914)

5) P. W. Bridgman, *Phys. Rev.*, **6**, 1 (1915)