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LIQUID-SOLID TRANSITION AT HIGH PRESSURE III

Benzene, Monochlorobenzene and Toluene at 25°C

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New and accurate measurements were made on the liquid-solid transition pressures of benzene, monochlorobenzene and toluene at 25°C. Pressures were directly measured with a free piston gauge of controlled-clearance type in the static state of no leak and no friction. Transitions were detected by differential thermal analysis, the thermoelements of semiconductors being used. The values obtained were 706.5 ± 0.5 kg/cm² for benzene, $4,650.2 \pm 1.0$ kg/cm² for monochlorobenzene, and $8,598.9 \pm 1.9$ kg/cm² for toluene.

Introduction

As part of continuing effort¹⁾²⁾ to establish fixed points of pressure, new and accurate measurements on the liquid-solid transition pressures of benzene, monochlorobenzene and toluene at 25°C are presented here. Pressures were measured directly with a free piston gauge of controlled-clearance type in the static state of no leak and no friction. Transitions were detected from the temperature changes caused by latent heat using the thermoelements of semiconductors.

No previous work concerned with the melting curve of toluene is known to the present authors. In this paper, the results of the authors' previous publications¹⁾²⁾ and the present work are summarized.

Experimentals

Materials

Benzene, monochlorobenzene and toluene were purified by refluxing (over sodium hydride for benzene and toluene) followed by careful fractional distillation. Gas chromatography indicated the presence of moisture only as impurities. The samples of benzene fractionally crystallized twelve times were also used, and they gave the successful results as noted later.

Apparatus

The details of the apparatus have been described elsewhere²⁾⁻⁵⁾. A general survey of the instru-

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1) J. Osugi, K. Shimizu and A. Onodera, *This Journal*, **34**, 97 (1964)

2) J. Osugi, K. Shimizu, K. Yasunami and A. Onodera, *ibid.*, **37**, 10 (1967)

mental setup is shown in Fig. 1. The apparatus was composed of the transition pressure generating

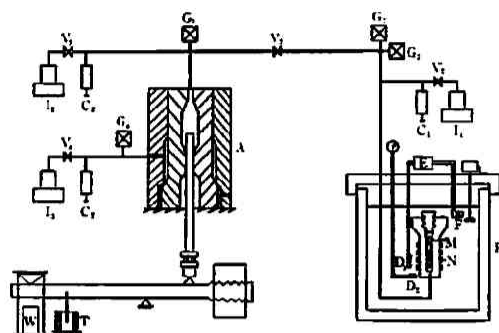


Fig. 1 General arrangement

- A piston cylinder assemblies of controlled clearance type
- B bath
- $C_1 \sim C_3$ volume change regulators
- D_1 temperature detector for control
- D_2 detector for temperature measurement
- E bridge and power supply
- F heater
- G_1 semiconductor strain pressure gauge
- $G_2 \sim G_4$ wire strain pressure gauges
- $I_1 \sim I_3$ pressure intensifiers
- M pressure vessel and sample holder
- N thermoelements
- T differential transformer
- $V_1 \sim V_4$ stop valves
- W dead weights

system and the free piston gauge which were separated by a stop valve V_2 . The sample to be studied was contained in the pressure vessel M. On the outer surface of the vessel, the thermoelements of semiconductors N were stuck in order to detect the heat of the transition, compression and expansion of the sample.

The temperature of the bath B was regulated by a proportional control method. As the regulator served a thermistor of semiconductors D_1 placed near the vessel in the bath. This thermistor formed a part of one component of a Wheatstone bridge, which was set at a balance to give the desired temperature. With the amplified output voltage of the bridge, the power supply for the heater F was controlled proportionally to the difference between the bath temperature and the set temperature. Thus the temperature was controlled within $\pm 0.002^\circ\text{C}$. The temperature was measured with another thermistor D_2 , whose resistance change was calibrated with the triple point cells of acetophenone and diphenyl ether. They were confirmed to present the definite temperatures of 19.636°C and 26.870°C , respectively, by use of Pt thermometer.

The absolute pressure was measured with a free piston gauge of controlled-clearance type³⁾⁻⁵⁾. The state of no leak and no friction was realized by use of the volume change regulators C_2 and C_3 , and detected by the measurement of the displacement of the lever.

Experimental procedure

A detailed description of the experimental methods²⁾⁴⁾ will not be repeated here. In brief, the procedure was as follows. A sample volume of about 3cc was contained in a sample holder. In the present work three sorts of sample holder were used: a stainless-steel cylinder as shown in Fig. 2, a bottle made of polyethylene, or a package of aluminum foil laminated with polyethylene and poly-

3) K. Yasunami, *Proc. Japan Acad.*, **43**, 310 (1967)

4) K. Yasunami, *This Journal*, **37**, 1 (1967)

5) K. Yasunami, *Metrologia*, **4**, 168 (1968)

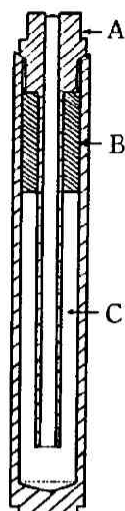


Fig. 2 Sample holder
 A. stainless-steel
 B. sample
 C. mercury

ester on either side. The sample holder was placed in the high pressure vessel. With the valve V_2 closed, the pressure on the sample was increased. Freezing was indicated by a sudden rise in the curve of the voltage of the thermoelements. When the system reached the equilibrium state, the free piston gauge was then connected with the transition pressure generating system. Weights were added to and removed from the pan of the free piston gauge in sequence, until the equilibrium load was obtained. All the indicated pressures obtained by dividing the load by the effective area of the free piston were converted to the absolute values after all corrections.

Results and considerations

The equilibrium pressures determined at 25°C in several runs are listed in Table 1. The final

Table 1 Pressures of liquid-solid transition of benzene, monochlorobenzene and toluene at 25°C

Benzene	Monochlorobenzene	Toluene
706.4	4,651.8	8,601.2
706.0	4,649.6	8,598.7
707.0	4,649.2	8,597.0
707.6	4,650.0	8,601.2
705.4	4,651.0	8,598.7
	4,649.8	8,596.5
	4,649.9	
$706.5 \pm 0.5 \text{ kg/cm}^2$	$4,650.2 \pm 1.0 \text{ kg/cm}^2$	$8,598.9 \pm 1.9 \text{ kg/cm}^2$

values and their uncertainties, including those due to the piston gauge and the bath, are shown in the last row. The transition pressure of benzene (706.5 kg/cm^2) is rather lower than that obtained by other

investigators, for example 724 kg/cm² by Bridgman⁶⁾, 728 kg/cm² by Deffet⁷⁾ and 723.3 kg/cm² by Kubota, Ueda and Makita⁸⁾. In the present work it was noticed that the impurities, which could not have been detected with gas chromatography and infrared spectroscopy, greatly affect the transition pressure of benzene. Even when one-half of the sample had melted, the recovery of pressure after the small change of volume was not adequate. Only the samples which had been fractionally crystallized twelve times showed successful result. In this case, however, the pressure recovery to the equilibrium state after the small change of volume was shown merely when more than 60% of the sample had melted. The discrepancy of the present result from the work of other investigators may be attributed to the fact that in the latter the transition might be determined under the conditions of more than one-half of the sample frozen.

In Table 2 are listed the liquid-solid transition pressures of benzene, monochlorobenzene and toluene at 0°C²⁾ and 25°C. The freezing point of benzene at atmospheric pressure is 5.5°C. The linear

Table 2 Pressures of liquid-solid transition of benzene, monochlorobenzene and toluene at 0°C and 25°C in unit of kg/cm²

	0°C	25°C
Benzene	—	706.5±0.5
Monochlorobenzene	2,799.0±1.2	4,650.2±1.0
Toluene	6,440.4±1.2	8,598.9±1.9

temperature coefficients of the transition pressure between 0°C (5.5°C for benzene) and 25°C of benzene, monochlorobenzene and toluene are 36, 74, and 86 kg·cm⁻²·deg⁻¹, respectively.

No work concerning the melting curve of toluene is known to the present authors. Only Bridg-

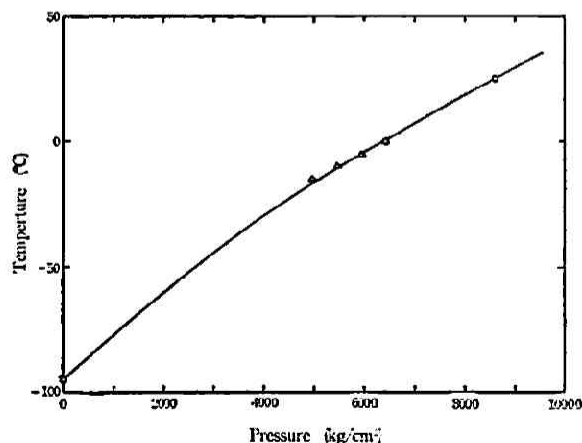


Fig. 3 The melting curve of toluene
○ : free piston gauge
△ : force to piston area ratio
□ : normal melting point

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

7) L. Deffet, *Bull. Soc. Chim. Belg.*, **44**, 41 (1935)

8) H. Kubota, K. Ueda and T. Makita, *Preprint of the 9th Symposium on High Pressure in Japan (Nagoya)*, p. 119 (1967)

man⁹⁾ reported the freezing pressure of 9,600 kg/cm² at 30°C, presumably on the superpressed sample. In Fig. 3 are summarized the results of the authors' previous publications¹⁾²⁾ and the present work. In general, most organic compounds do not show a linear relationship between melting temperatures and pressures. Simon and Glatzel¹⁰⁾ suggested an empirical equation for a melting curve. The Simon equation is written by

$$P - P_0 = a \left\{ \left(\frac{T}{T_0} \right)^c - 1 \right\}, \quad (1)$$

where a is closely related to the internal pressure, c is the positive constant, T_0 is the normal melting point, and P_0 is the pressure corresponding to the temperature T_0 . Applying equation (1) to the results, the following values are obtained for the constants: a is 4.7×10^3 bars, and c is 2.0. It is likely that these values are reasonable in comparison with those of benzene and some monosubstituted aromatic compounds listed in Table 3, quoted from the data of Babb¹¹⁾. For the more accurate determination of the parameters on toluene, experiments over a wide temperature range are needed.

Table 3 Parameters in Simon equation

	a (bars)	c
Benzene*	3,600	2.60
Aniline*	5,352	2.339
Monobromobenzene*	4,800	2.46
Monochlorobenzene*	4,980	2.42
Nitrobenzene*	6,100	1.93
Benzonitrile*	10,800	1.18
Toluene**	4,700	2.0

* Ref. 11)

** Present work

In the previous paper¹⁾ the authors presented some remarks on fixed points of pressure. Here a few additional remarks are presented in the following. At present, the freezing point of mercury at 0°C is used almost alone as a fixed point in the pressure range up to about 10,000 kg/cm². Mercury, however, is not the ideal pressure calibrant in view of the fact that it has a large temperature coefficient of the transition pressure. In toluene, dP/dT is nearly one-half of that of mercury. In benzene and monochlorobenzene, the temperature coefficients are much smaller than toluene. Pressure calibrations are generally operated at 25°C or near so. It is felt, therefore, the transition pressures of toluene and monochlorobenzene are of practical use as well as the 0°C mercury point. A continuous pressure calibration could be performed using these two calibrants, the transitions of which occur in succession.

9) P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, **59**, 141 (1923)10) F. E. Simon and G. Glatzel, *Z. Anorg. Allgem. Chem.*, **178**, 309 (1929)11) S. E. Babb, Jr., *Rev. Mod. Phys.*, **35**, 400 (1963)

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