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# LIQUID-SOLID TRANSITION AT HIGH PRESSURE II

## Monochlorobenzene and Toluene at 0°C

BY JIRO OSUGI, KIYOSHI SHIMIZU, KAZUO YASUNAMI AND AKIFUMI ONODERA

New and more accurate measurements were made on the liquid-solid transition pressures of monochlorobenzene and toluene at 0°C. Pressures were measured directly with a controlled-clearance type free piston gauge 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 2799.0 $kg/cm^2$ for monochlorobenzene and 6440.4 $kg/cm^2$ for toluene, each with uncertainty of $\pm 1.2\,kg/cm^2$.

## Introduction

Liquid-solid transition of organic substances at high pressure has been reported in voluminous literature. In the pressure range up to about 10,000 $kg/cm^2$, where liquids are used as pressure transmitting media, most experiments are performed in the piston-cylinder apparatus. The transitions are detected by the volume change, the electrical resistance, and the thermal conductivity, etc. The pressures of the transition are generally determined from the ratio of the force generated by the press and the area of the sample, as reported previously by the authors[1]. For the accurate determination of the transition pressure, however, the pressure of the sample should be measured directly by means of primary pressure standards. In this sense it is believed clever to connect a free piston gauge directly with the high pressure system.

This paper reports new and more accurate measurements on the liquid-solid transition pressures of monochlorobenzene and toluene at 0°C. Pressures were measured directly with a controlled-clearance type free piston gauge in the static state of no leak and no friction. Transitions were detected by means of temperature changes due to latent heat using thermoelements of semiconductors.

## Experimentals

### Materials

Monochlorobenzene and toluene were cleaned with acid and freshly distilled.

### Apparatus

The details of the apparatus have been described elsewhere[2][3]. It was composed of the transition

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1) J. Osugi, K. Shimizu and A. Onodera, *This Journal*, **34**, 97 (1964)
2) K. Yasunami, *Proc. Japan Acad.*, **43**, 310 (1967)
3) K. Yasunami, *This Journal*, **37**, 1 (1967)

pressure generating system and the free piston gauge which were separated by a stop valve. The sample to be studied was contained in the pressure vessel. On the outer surface of the vessel, the thermoelements of semiconductors ($Bi_2Te_3$) were stuck in order to detect the heat of the transition, compression and expansion of the sample. One piece of the thermoelements was composed of eight pairs of $p$, $n$, semiconductors having the power of about 400$\mu$V/deg. The temperature of the ice-bath was checked by the triple point of water. The temperature was controlled within ±0.001°C. The hydraulic fluid employed was a mixture of glycerine-water. Pressure was developed with intensifiers.

The absolute pressure was measured with a controlled-clearance type free piston gauge[2)3)]. The state of no leak and no friction was realized by use of the volume change regulator (VCR), and detected by the measurements of the displacement of the lever. The volume change regulator had the capacity to change the volume up to 0.45 cc with 7.25 revolutions. The sensitivity of this instrument is better than 2 parts in 100,000; the accuracy in absolute value of the readings 3 parts in 10,000.

## Experimental procedure

A sample volume of about 5 cc was contained in a sample holder made of 18-8 stainless-steel cylinder as shown in Fig. 1, or in a bottle made of polyethylene. In Fig. 1, mercury was used to separate the sample from the pressure transmitting medium. It was confirmed by IR spectra that both silicone rubber and polyethylene did not solve into the sample. Experiments on toluene were made only in the polyethylene bottle, because it was expected that mercury in Fig. 1 would freeze at lower pressure than toluene would. The sample holder was placed in the high pressure vessel. The vessel was then immersed into the ice-bath. The transition pressure generating system was at that time separated from the free piston gauge.

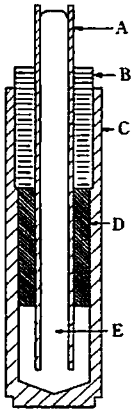

Fig. 1 Sample holder
A. Stainless steel tube
B. Silicone rubber
C. Stainless steel vessel
D. Sample
E. Mercury

With the ice-bath set up for a sufficient time for temperature stability to be reached, the pressure on the sample was first slowly increased. After every increase of pressure it was necessary to wait about 40 minutes for the dissipation of the heat of compression to the surrounding bath. Pressure was increased beyond the freezing point sufficiently to ensure complete freezing. Freezing was indicated by a sudden rise in the curve of the voltage of the thermoelements. To find the equilibrium pressure, the pressure on the solid phase was lowered until the melting to the liquid state started, and then by the work at the volume change regulator the pressure was adjusted so that the sample was in a state of equilibrium, the changes of pressure being too small to measure on the ordinary gauge. That the equilibrium was reached was ascertained by comparing the curve of the voltage of thermoelements with that of the liquid or solid state alone.

The pressure balancing was made as follows. The weights on the free piston gauge was adjusted to the approximately correct value for equilibrium. The free piston gauge was then connected with transition pressure generating system. Weights were added to and removed from the pan of the free piston gauge in sequence. In practice, the steps of about 0.2 kg/cm$^2$ were adopted. A pressure step of this magnitude on either side of the equilibrium point was found to give rise almost instantaneously to a recognizable drift of the curve of the voltage of the thermoelements, corresponding to a slow increase or decrease in the fraction of the sample frozen according to the direction of the pressure change. Eventually, two loads were recorded, one of which displaced the curve of the voltage of the themoelements in one direction, while the other allowed it to move in the opposite direction. The mean load was then tested for equilibrium. If no departure from equilibrium was observed, the mean load was taken as equilibrium load.

The force exerted by the various weight loading was corrected for air buoyancy. Slight corrections for the ratio of the lever and for the heights of mercury and of glycerine-water mixture were made. All the indicated pressures obtained by dividing the force by effective area were converted to the absolute values by addition of the barometric pressure.

Pressures, temperatures, the voltage of the thermoelements and the lever displacement were automatically recorded by means of electronic recorder in each experiment. A semiconductor strain pressure gauge made of Ge-Si alloy was also used. The semiconductor gauge was sensitive enough to be used to recognize the state of the sample together with the thermoelements.

## Results and Considerations

Freezing was indicated by a sudden rise of the curve of the voltage of the thermoelements. A typical example is shown in Fig. 2. Freezing occurred during the compression or during the dissipation of heat after the compression.

The liquid-solid equilibrium state could easily be distinguished from the liquid or solid state alone, by comparing the curve of the voltage of the thermoelements caused by one revolution of the volume change regulator. With both phases present, the latent heat of the phase change is large, and relatively high peaks in the curve of the voltage of the thermoelements were recorded. In Fig. 3, the pressure changes recorded by the semiconductor gauge are also shown. The state of the sample could be recognized; the recovery of the pressure was observed in the equilibrium state after each step of the pressure change, while it was not observed if only one phase was present, whether liquid or solid.

The equilibrium pressures found at 0°C in several runs are shown in Table 1, with uncertainty

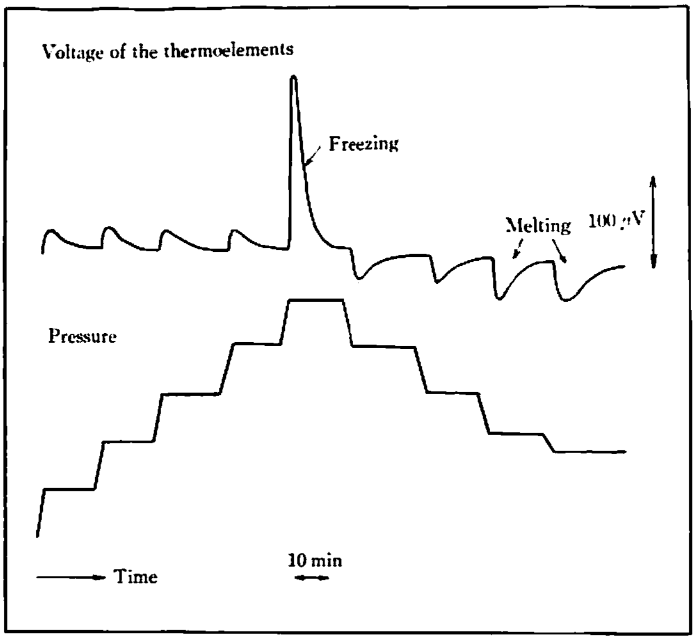

Fig. 2 Typical experimental data showing freezing and melting

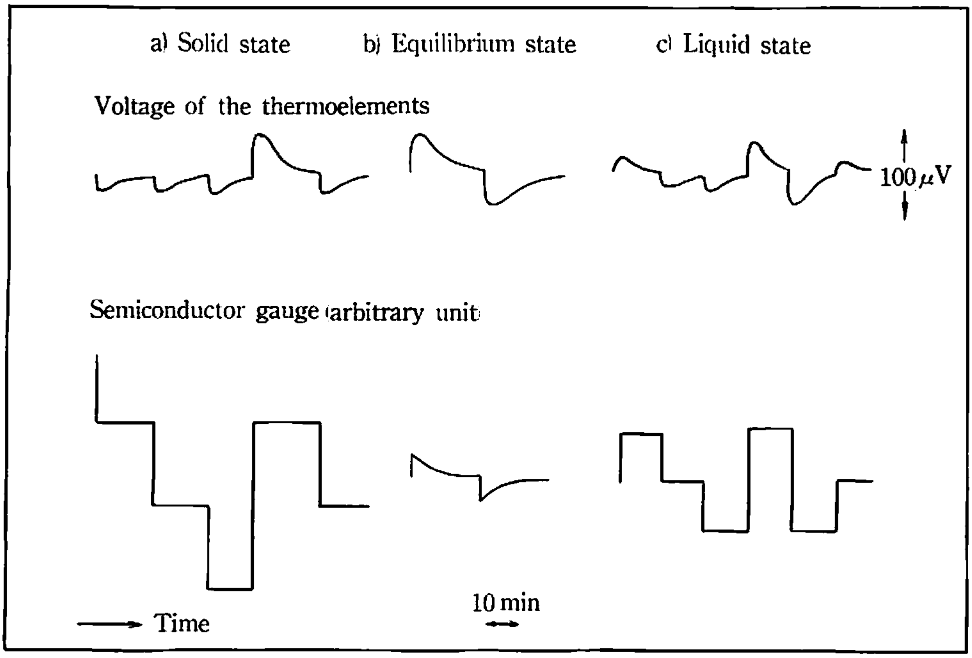

Fig. 3 Solid, liquid and equilibrium states

Table 1 Pressures of the liquid-solid transition of monochlorobenzene and toluene with uncertainty of ± 1.2 kg/cm²

| Monochlorobenzene | Toluene |
|---|---|
| 2799.8 | 6441.0 |
| 2799.6 | 6440.5 |
| 2799.2 | 6439.8 |
| 2798.4 | 6440.1 |
| 2798.5 | 6440.4 |
| 2799.8 | |
| 2798.3 | |
| 2798.2 | |
| 2799.0 kg/cm² | 6440.4 kg/cm² |

of ±1.2 kg/cm². The average values are in excellent agreement with the values extrapolated from the previously reported data by the authors1). From this, it may be said that the pressure in the piston-cylinder apparatus should be measured as the mean of the up- and down-stroke.

One way of pressure calibration in the piston-cylinder apparatus where liquids are used as pressure transmitting media is proposed in the following. In the usual experiments the sample pressure is calculated from the ratio of the force on up-stroke generated by the press and the area of the sample. The calculated pressure on up-stroke is much higher than the true pressure. The amount of the pressure difference1) is approximately 200 kg/cm² at 3,000 kg/cm², and 300 kg/cm² at 5,000 kg/cm², respectively. The amount is equal to the value $\Delta P = P_f - P_e = P_e - P_m$, where subscripts represent freez-

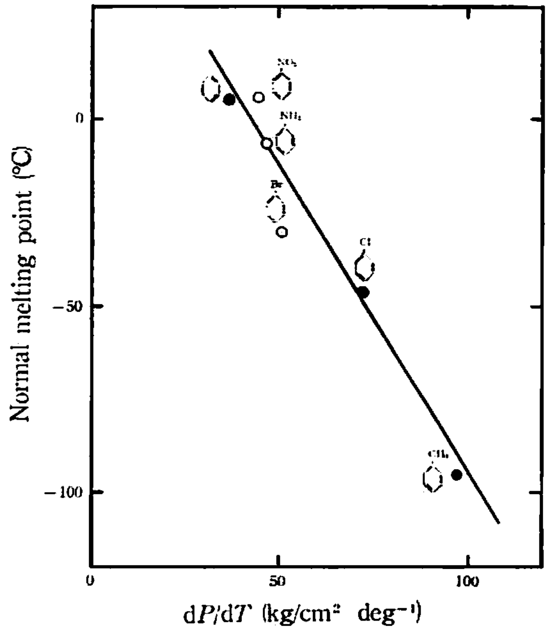

Fig. 4 Plots of normal melting point against d$P$/d$T$

ing, melting and equilibrium. $\Delta P$'s are intrinsic for every apparatus if the friction of the piston is kept in the same state. From the calibration curve of $P_f$ plotted against $\Delta P$, the estimation of the pressure $P_e = P_f - \Delta P$ could be made.

The transition pressures of benzene, monochlorobenzene and toluene, which are investigated in this work and in the previous work$^{1)}$, are the linear functions of temperature in the short range covered. It is interesting to note that a plot of $dP/dT$ against the normal melting temperature for these compounds yields an approximately linear relation as shown in Fig. 4. Points of other monosubstituted aromatic compounds quoted from the literature$^{4)}$ are also shown. They are located near the line. Although these correlations are empirical and of uncertain meaning in the absence of a detailed theory, they may be useful in estimating the melting relations for the other aromatic compounds not yet investigated experimentally.

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

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4) S. D. Hamann, "Physico-Chemical Effects of Pressure", p. 223, Butterworths, London (1957)