Thermochimica Acta, 25 (1978) 1–10

QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS UNDER HIGH PRESSURES

K. TAKAMIZAWA

Department of Applied Science, Faculty of Engineering, Kyushu University 36, Hakozaki, Higashi-ku, Fukuoka 812 (Japan)

(Received 1 August 1977)

ABSTRACT

A high pressure differential thermal analysis (DTA) apparatus is described which is capable of operation in the pressure range up to 500 MPa and at temperatures from 25 to 300 °C. The requirements for quantitative DTA are examined. The apparatus enables the determination of heat of transition under high pressure by using small samples.

INTRODUCTION

Differential thermal analysis is a sensitive and convenient means for studying phase transitions under high pressure. Several designs of high pressure DTA cell suitable to study organic compounds and polymers have been described in the literature[1–6]. These systems were designed to be operated at pressure up to about 0.8 GPa and temperatures from 300 to 700 K. Recent developments in high pressure DTA enabled measurements to be made on small samples, of the order of mg[2–4]. This gave satisfactory resolution of thermal events under high pressure. Melting and rotational transition peaks of *n*-alkanes were resolved[7], and the complicated behavior of melting and crystallization of polyethylene were elucidated[3, 8]. The author also obtained, by using high pressure micro-DTA[3], the pressure dependence of melting temperatures of polyethylene fractions[9] and higher *n*-alkanes[10].

In order to understand thoroughly phase transition at high pressures, it is necessary to know not only the melting temperature but also the magnitude of the heat of transition as a function of pressure and temperature. Up to the present, the heat of transition under high pressure has been obtained through the Clausius-Clapeyron equation from dilatometric measurements. The experimental determination by this method is connected with some difficulties. The number of the data available remains inconsiderable since P. W. Bridgman's time. It is desirable to develop a quantitative, dynamic thermal method under high pressure. As far as the author is aware, no quantitative DTA under high pressure has ever been reported. Although there were attempts to operate a differential scanning calorimeter under high pressure[11, 12], it seems that in the determination of the heat of transition of any substance, some problems remain to be solved.

Ozawa proposed the conditions of DTA cell design to be satisfied for the quantitative determination of heat evolved or absorbed, on the basis of the heat transfer equation for cylindrical cells, and he verified his theory experimentally[13-16]. The design requirements are the placement of a thermal barrier between the sample and the heating block and temperature measurement at the sample surface. The same conclusion was later presented by McIntosh et al.[17]. It seemed that the high pressure DTA cell used by Takamizawa et al.[9] could be easily modified to a quantitative one, in which pressure-transmitting fluid plays a role as the thermal barrier and the temperature is measured beneath a metal cup containing the sample. It is the object of this paper to describe this apparatus which is capable of operation under pressures up to 0.5 GPa and at temperatures from 250 to 550 K. Results obtained on several substances will be presented. From these we could suggest future development of DTA under high pressure.

EXPERIMENTAL

Description of apparatus

A schematic diagram of the high pressure DTA system employed is illustrated in Fig. 1. A hand oil pump and an intensifier were used to generate hydrostatic pressure in dimethyl silicone oil (TSF 451, 10 cStoke, Toshiba Silicone Co., Ltd.); the pressure was fed to the DTA vessel and a container for a manganin coil gauge. In order to avoid temperature correction for the gauge, the intensifier and the gauge vessel, together with a bridge box, were thermostated. The gauge was calibrated through the relation between melting point and pressure for mercury, as previously described in detail[15].

The high pressure DTA cell is shown in Fig. 2(a) and (b). A vessel for DTA (A) was made of stainless steel (SUS 27B) with 10 mm inner and 70 mm outer diameter. The vessel, wound non-inductively with two sheathed heaters (500 W × 2), (K) was

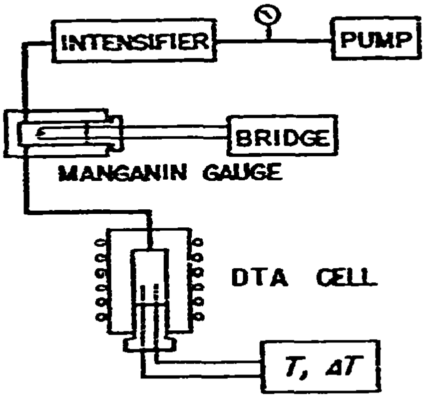


Fig. 1. Schematic diagram of high pressure DTA system.

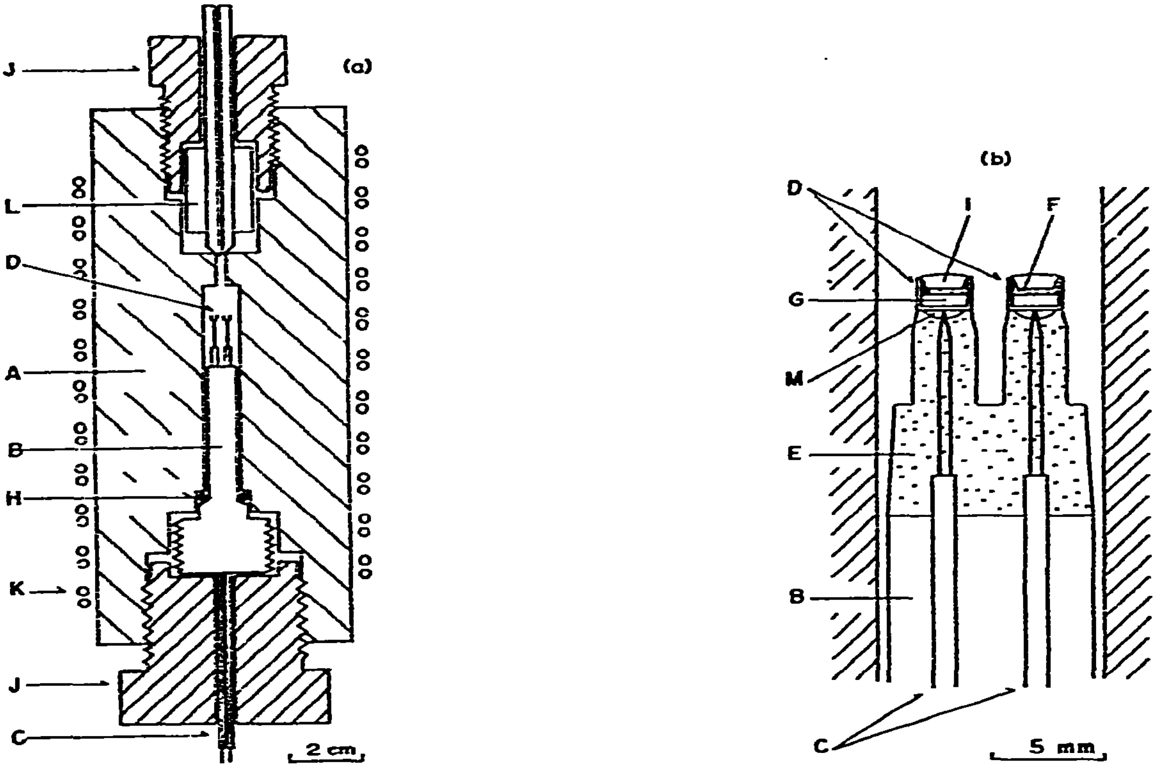


Fig. 2. (a) Drawing of high pressure DTA cell. (b) Details of cell arrangement. A, High pressure vessel (furnace); B, DTA plug; C, sheathed thermocouples; D, sample and reference cup; E, high temperature resistant epoxy resin; F, fast-curing epoxy resin; G, sample and reference substances; H, SBR O-ring with armored ring; I, RTV silicone rubber; J, threaded plug; K, heaters; L, collar and pipe; M, solder.

used as a heating block. The heating rate was controlled manually by adjusting the voltage supplied to the heaters. This method allowed a linear heating rate up to about 8 K/min over the measured temperature range. Two sheathed thermocouples of Alumel–Chromel (2ABAc10, Philips) (C) were soldered to a plug (B) and used as an open type. The bare portion of the thermocouple wires was about 8 mm long. The sample and reference containers consisted of 1.2 or 2 mm by 2 mm in diameter platinum cups (D) soldered to the thermojunctions. Sealing for the filler of the sheathed tube and fixing of the position of the cups were done with heat resistant epoxy resin (Epicote 828) (E), which provided a satisfactory performance at high temperature and pressure. The tight seal of the plug (B) was obtained by the use of a SBR O-ring (H) with an armored ring of phosphor bronze.

The sample temperature was measured with a reference voltage unit (type 3109, Yokogawa Electric Works, Ltd.) and a two-pen recorder (VP-654B, Matsushita Communication Industrial Co., Ltd.). The temperature difference was amplified with a d.c. amplifier (AM-1002B, Ohkura Electric Co., Ltd.) and recorded on the same chart as the temperature.

Materials

The substances used for the high pressure measurements were gallium, indium, bismuth (each of purity above 99.99%, Wako Pure Chemical Industries, Ltd.), *n*-octadecane (purity above 99%, Tokyo Kagaku Seiki Co., Ltd.) and *n*-tetracosane (Tokyo Kasei Kogyo Co., Ltd.). The *n*-octadecane was used without further purification and the *n*-tetracosane was purified by treating it several times with conc. sulfuric acid at 120°C, followed by crystallization from *n*-pentane solution. These *n*-alkanes respectively gave a sharp and single peak on the gel permeation chromatography chart. In addition, tin (purity 99.999%, Wako Pure Chemical Industries, Ltd.) and *n*-hexacontane were used for the measurements at atmospheric pressure only. The preparation and purification of the latter were briefly described elsewhere[10].

Temperature calibration

Each DTA thermocouple used was calibrated in the temperature range to be measured against a standard thermocouple. This was a sheated thermocouple of insulated closed-type, which had been calibrated on the basis of the melting points of four substances, naphthalene, benzoic acid, In and Sn. The two organic compounds used were purified by a zone-melting technique. The effect of pressure on the e.m.f. of the thermocouple could not be detected up to 0.5 GPa within ± 0.002 mV.

Experimental procedure

The sample setting procedure was basically the same; a sample that had been shaped to fit the cup and weighed on a microbalance was placed in the sample cup and thinly covered by epoxy resin (fast-curing type at room temperature): the resin was further covered by RTV silicone rubber (Silastic 731, Dow Corning Corp.). The epoxy resin was used to fix the sample during the operation of raising or lowering the pressure and also to protect the alkanes from dissolution by the pressure-transmitting liquid. The alkane was closely fitted to the cup by pushing down it by a Teflon rod and was covered by an aluminum foil before fixing by epoxy resin. A small amount of silicone grease was used to give a good contact between the metallic sample and the bottom of the cup. Since bismuth was found to react with platinum on melting at high pressure, the cup was protected with a thin, matched liner made of Teflon film. A similar amount of lead was placed in the reference cup with the same procedure as that described above.

After the plug with the DTA sensors was installed, the pressure in the system was adjusted to a level below the measuring pressure. Once the pressure was stabilized, the heating was begun and the sample and the differential temperatures were recorded. A heating rate of 4 K/min was normally employed. There was an increase in pressure as a result of heating the cell. An amplified output signal of the pressure bridge was recorded, where one division deflection on the chart amounted to about 0.5 MPa. During the heating, the pressure was readjusted to attain the desired measuring pressure at melting within ± 1 MPa. The pressure was taken at the moment melting started. The change during the melting was from 0.3 to 0.5 MPa.

The area between an endothermic peak and a linear base line was determined by a weighing method; its standard deviation was within about 1%.

RESULTS AND DISCUSSION

Quantitative DTA has to satisfy the following requirements: (a) the peak area, A, is proportional to the heat absorbed or evolved in a sample

$$\Delta H\, m = K\, A \tag{1}$$

where K is the proportionality coefficient, ΔH the heat of transition per unit mass, and m the weight of the sample; (b) the coefficient does not depend on the thermal characteristics of the sample. For the cell design proposed by Ozawa, the coefficient was given approximately by the relation[13]

$$K = 2\pi\, l\, \lambda \ln\left(\frac{R_i}{R_o}\right) \tag{2}$$

where λ is the thermal conductivity of the thermal barrier, l the length of the sample container, R_i its radius, and R_o the outer radius of the thermal barrier. The coefficient is a function of pressure and temperature in terms of λ of a given thermal barrier. The present cell design does not strictly satisfy the conditions necessary to derive eqn. (2). Then, it needs to prove empirically the quantitativity of the cell.

Figure 3 shows a chart of a DTA run on 4.128 mg of Bi at 500 MPa at a heating rate of 4 K/min, indicating the ΔT signal at low noise level. The area and shape of the peaks were reproducible on repeated runs. These results allowed accurate measurements of peak area. The peak area decreased with an increase in pressure whereas the difference in temperature between peak and intersection was almost constant. Both temperatures were determined within ± 0.2 K for the metallic samples and ± 0.4 K for the n-alkanes, irrespective of measuring pressure and sample size. The pressure dependences of melting point for these samples were in good agreement with those

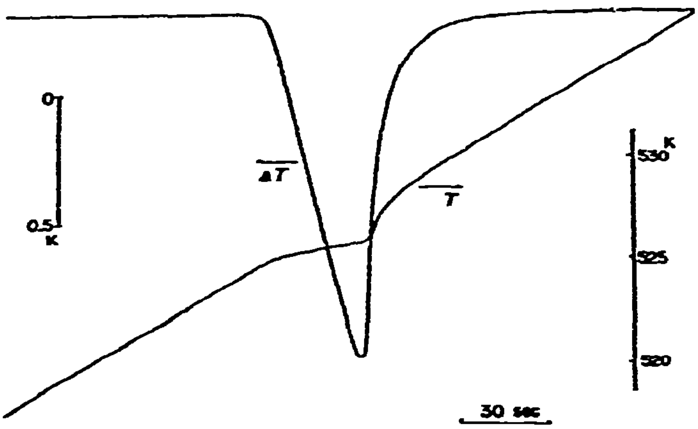
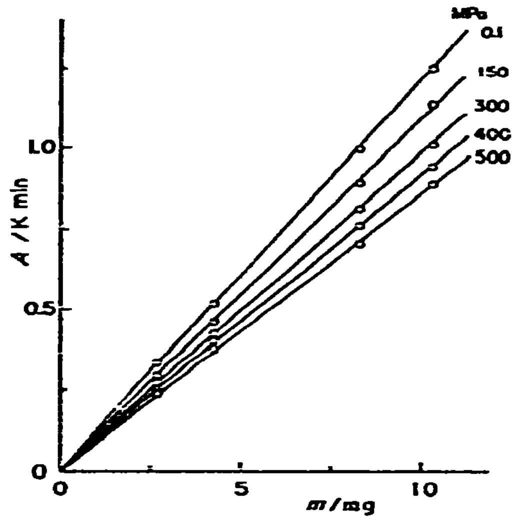


Fig. 3. DTA chart for melting of 4.128 mg Bi at 500 MPa at a heating rate of 4 K min^{-1}.



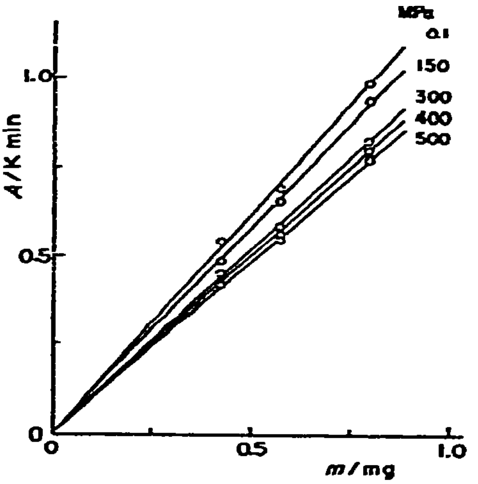


Fig. 4. Peak area at various pressures vs. sample size for indium. Numerals indicate pressure.

Fig. 5. Peak area at various pressures vs. sample size for *n*-tetracosane. Numerals indicate pressure.

reported. Moreover, it was excellent in the resolution of solid–solid transition and melting peaks for n-$C_{24}H_{50}$, observed at atmospheric pressure, because of the small sample size.

Relation between peak area and sample size at various pressures are shown in Figs. 4 and 5 for In and n-$C_{24}H_{50}$, respectively. The pressures were controlled within ± 0.7 MPa at 150, 300, 400, and 500 MPa. For In and Bi, DTA measurements at atmospheric pressure could not be made. It was necessary to apply a slight pressure of below 2 MPa to suppress the evolution of bubbles in the silicone oil used as the thermal barrier and to prevent the effect of its thermal convection. This slight pressure has scarcely any effect on the melting points and heats of melting. The results, as shown in Figs. 4 and 5, indicate that requirement (a) for quantitative DTA is satisfied irrespective of pressure. The ratio A/m was determined within a standard deviation of ± 0.7% for In and of ± 1.5% for n-$C_{24}H_{50}$. The large value for the latter is partly due to slight uncertainty in the drawing of a base line and also to weighing errors. A similar degree of error was observed for the other substances. It is here pointed out that the depth of the sample cup manifested an influence on the ratio of peak area at 150 MPa to that at atmospheric pressure. The data in Figs. 4 and 5 were obtained using a cell of 1.2 mm depth, whereas one of 2 mm gave almost the same areas. This may be ascribed to the effect of convection in the thermal barrier in the low pressure region.

In order to calculate K as a function of pressure and temperature, it is necessary to use known values of the heat of melting under pressure, ΔH. We have data on the melting of Bi and Ga by Bridgman[19], and of n-alkanes by Nelson et al.[20]. Before using these data, some revisions were needed. Although Bridgman's data have been presented as smoothed relations of ΔH against pressure, his pressure scale is different from a present one. Correction was made according to the recommendations given by Babb[21, 22]. Furthermore, the value of the heat of melting at atmospheric pressure, ΔH_0, for Ga was lower by 4.5% than the literature value[23], 80.2 Jg^{-1}. Using this ΔH_0 and assuming that the pressure coefficient of ΔH given by Bridgman remains constant, we corrected his relation. Similar correction was also applied to the data for n-$C_{18}H_{35}$. Because the data for n-$C_{24}H_{50}$ was significantly scattered, its pressure coefficient of ΔH was assumed to be the same as that for n-$C_{18}H_{38}$. As ΔH_0 for both n-alkanes, calorimetric data[24] were used. Although indium is suitable for use as a standard substance for DTA, its ΔH under pressure has not been reported. A calculated dependence of ΔH on pressure[25] was utilized. In this way, used values of ΔH under pressure have some uncertainty.

Measurements on Sn and n-$C_{60}H_{122}$ were done only at atmospheric pressure. A literature value of ΔH_0 for Sn[23] was used. For the latter, ΔH_0 was determined by means of a Perkin-Elmer DSC-1B and through the Clausius–Clapeyron equation. An average value of 238 ± 2 Jg^{-1} was used.

The proportionality coefficients at various pressures are plotted against temperature in Fig. 6. A good, smooth curve can be drawn through the data at atmospheric pressure. This clearly shows that the present cell, in which a liquid thermal barrier having a large λ is used, satisfies requirement (b) for the quantitativity, at least for measurements at atmospheric pressure. On the basis of this result, we may obtain K at each high pressure as a function of temperature only despite the small number of data points and their scatter. This scatter is partly due to the uncertainty in the value of ΔH used. Thus, we can have a thermal mean for the determination of heats of transition under high pressure.

When we know λ for the silicone oil as a function of pressure and temperature, the behavior of K is approximately predicted according to eqn. (2). The functional form of its λ, however, has not been reported except at atmospheric pressure. In general, the thermal conductivity of liquids at atmospheric pressure has a negative

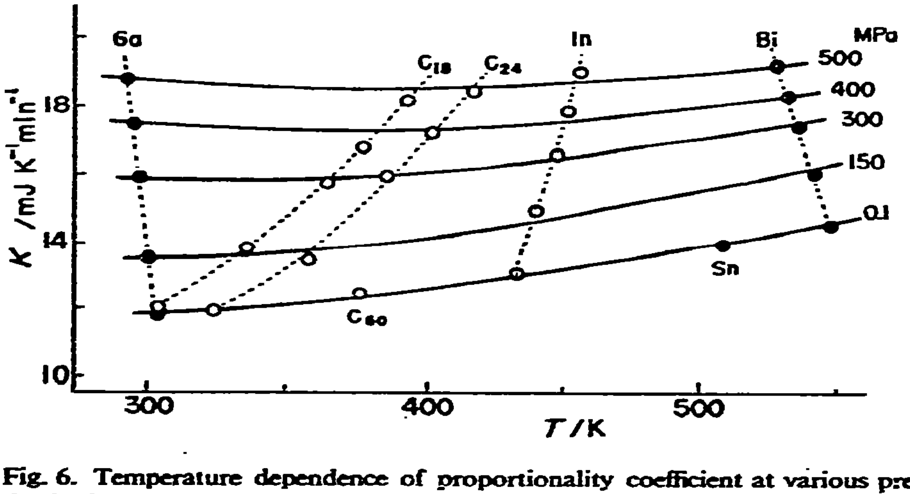


Fig. 6. Temperature dependence of proportionality coefficient at various pressures. C_{18}, C_{24}, and C_{60} indicate n-octadecane, n-tetracosane, and n-hexacontane, respectively.

TABLE 1

COMPARISON OF THE PRESSURE DEPENDENCE OF THE PROPORTIONAL COEFFICIENT WITH THAT OF THERMAL CONDUCTIVITY OF ORGANIC LIQUIDS

(*K* is the proportional coefficient at 30°C, λ the mean values of thermal conductivity of 13 simple organic liquids at 30°C[26]. Subscripts indicate pressures in MPa.)

p (MPa)	K_p/K_{500}	λ_p/λ_{500}
400	0.93	0.95 ± 0.01
300	0.85	0.89 ± 0.01
150	0.72	0.78 ± 0.03
0.1	0.64	0.61 ± 0.05

temperature coefficient. It is known that at higher pressure the temperature coefficient is reversed, and this occurs at about 300 MPa[26]. Due to such complexity, we cannot examine exactly the behavior of *K* in terms of λ, but the following may be said. For the silicone oil at atmospheric pressure, λ at 200°C is lower by about 10% than that at 30°C[27]. Increase in *K* at atmospheric pressure, as shown in Fig. 6, is ascribed to the effect of convection in the thermal barrier. That is, the temperature gradient within it developed during melting is diminished by convection. Its effect may become smaller in the low temperature and high pressure region. Next, we examine the effect of pressure on *K* in this region. Ratios of *K* at 30°C at each pressure to that at 500 MPa

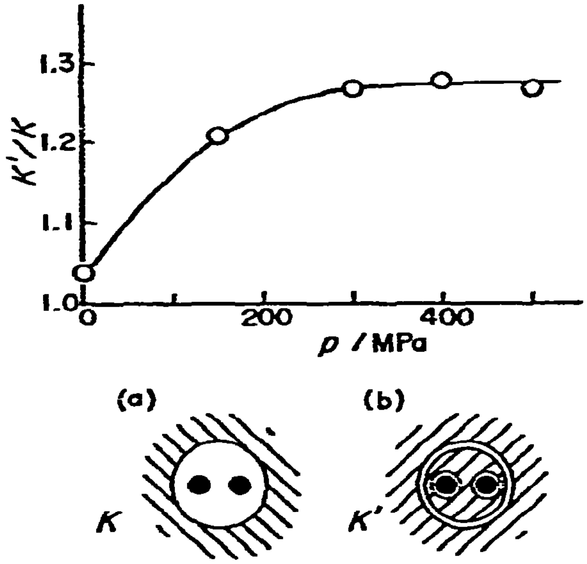


Fig. 7. Effect of the thickness of the thermal barrier on proportionality coefficients. Schematic drawing for arrangement of cells is shown in below (a) Normal cell; (b) cell with a copper heating block. Proportionality coefficients, *K* and *K'*, were obtained on In by using the cells (a) and (b), respectively.

are given in Table 1. As a rough estimate of the pressure dependence of λ at 30°C, we use average values of simple organic liquids given by Bridgman[26]. The ratios on average conductivity, $\bar{\lambda}$, are also given in Table 1. This shows that K under higher pressure is approximately proportional to $\bar{\lambda}$, that is, at least in the high pressure and low temperature region, heat conductively flows within the thermal barrier.

As described in the experimental section, the present cell, being designed mainly from the view point of operation, has a thick thermal barrier. The effect of the thickness on the convection was examined on runs on In. As shown in Fig. 7, a copper block having two holes was placed around the sample containers. The proportionality coefficient, K', obtained by using this cell are compared with K obtained by the normal cell. The ratio of K/K', as shown in Fig. 7, is constant over the higher pressure range, whereas it decreases at low pressure. This also shows that the convection appreciably occurs in the usual cell in the low pressure and high temperature region. It is noted that we could make quantitative, and reproducible measurements despite of the occurrence of the convection. In this connection, the thicker thermal barrier is said to be advantageous from the view points of operation under high pressure and of DTA sensitivity.

CONCLUSION

The simple DTA system described in this paper enabled determinations of heat of transition as well as of transition temperature under high pressure up to 500 MPa. We can obtain basic thermodynamic data on samples limited in size. Stability and sensitivity of the ΔT signal permit investigations on phenomena of minute signal, for example, the determination of glass transition temperature under pressures. It is, in further development, necessary to establish a calibration method by using electrical energy in order to minimize error due to the uncertaintly of ΔH values of standard substances under high pressure.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. T. Ozawa, Electrotechnical Laboratory, for his valuable discussions and Mr. T. Aramaki, Mitsubishi Petrochemical Co., Ltd., for supplying the heat resistant epoxy resin.

REFERENCES

1 T. Davidson and B. Wunderlich, *J. Polym. Sci., Part A-2*, 7 (1969) 377.
2 M. Kuballa and G. M. Schneider, *Ber. Bunsenges. Phys. Chem.*, 75 (1971) 513.
3 M. Yasuniwa, C. Nakafuku and T. Takemura, *Polym. J.*, 4 (1973) 526.
4 B. Turner, *High Temp. High Pressures*, 5 (1973) 273.
5 V. A. Sokol'skii, N. M. Kotov, Yu. A. Zubov, V. I. Selikhova, F. Ya. Frolov and O. S. Veselov, *Vysokomol. Soedin. Ser. A*, 16 (1974) 1420.
6 M. Z. Ugorets, K. M. Akhmetov, K. T. Rustembekov and E. G. Astrakhantsev, *Zh. Fiz. Khim.*, 48 (1974) 1297.
7 A. Würflinger and G. M. Schneider, *Ber. Bunsenges. Phys. Chem.*, 77 (1973) 121.

8 D. C. Bassett and B. Turner, *Philos. Mag.*, 29 (1974) 925.
9 K. Takamizawa, A. Ohno and Y. Urabe, *Polym. J.*, 7 (1975) 342.
10 K. Takamizawa, Y. Sasaki, K. Kono, Y. Urabe and Y. Ogawa, *Polym. Prepr., Jpn.*, 25 (1976) 913.
11 M. Kamphausen, *Rev. Sci. Instrum.*, 46 (1975) 668.
12 K. Takamizawa, T. Takemura, T. Oyama, H. Uchida, K. Toshima and N. Miyamoto, *The 11th Japanese Calorimetry Conference*, Fukuoka, 1975, Abstract Paper, p. 15.
13 T. Ozawa, *Bull. Chem. Soc. Jpn.*, 39 (1966) 2071.
14 T. Ozawa, M. Momota and H. Isozaki, *Bull. Chem. Soc. Jpn.*, 50 (1967) 1583.
15 T. Ozawa, *Nippon Kagaku Zasshi*, 88 (1967) 532.
16 T. Ozawa, H. Isozaki and A. Negishi, *Thermochim. Acta*, 1 (1970) 545.
17 R. M. McIntosh, A. Turnock and F. W. Wilburn, *J. Br. Ceramic Soc.*, 73 (1974) 117.
18 C. Nakafuku, K. Takamizawa and T. Takemura, *Rev. Sci. Instrum.*, 47 (1976) 232.
19 P. W. Bridgman, *Phys. Rev.*, 6 (1915) 1; 48 (1935) 893.
20 R. R. Nelson, W. Webb and J. A. Dixon, *J. Chem. Phys.*, 33 (1960) 1756.
21 S. E. Babb, Jr., *Rev. Mod. Phys.*, 35 (1963) 400.
22 S. E. Babb, Jr., in H. L. D. Pugh (Ed.), *The Mechanical Behavior of Materials under High Pressure*, Elsevier, Amsterdam, 1970, p. 127.
23 Chem. Soc. Japan (Ed.), *Kagaku Binran*, Maruzen, Tokyo, Revised 2nd edn., 1975, p. 915.
24 A. A. Schaerer, C. J. Busso, A. E. Smith and L. B. Skinner, *J. Am. Chem. Soc.*, 77 (1955) 2017.
25 I. M. Kutasov, *Izv. Acad. Sci. USSR, Phys. Solid Earth*, (1974) 4.
26 P. W. Bridgman, *The Physics of High Pressure*, G. Bell and Sons, London, 1958, p. 314.
27 N. M. Bikales (Ed.), *Encyclopedia of Polymer Science and Technology*, Vol. 12, Interscience, New York, 1970, p. 516.