Construction of an Adiabatic Calorimeter Workable under Constant High-pressure[†]

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An adiabatic high-pressure calorimeter was constructed. The calorimeter cell was devised for minimization of the cell mass relative to the volume of the sample chamber. The pressure in the cell was controlled by joining the cell with a transmitting tube to a stabilized high-pressure system. The adiabatic conditions were achieved by temperature control of the transmitting tube as well as of adiabatic shields inside the cryostat. Procedures for the precise pressure control and for the determination of the molar volume and heat capacity with the correction for the mass transfer of pressure-transmitting liquid in a series of measurement were discussed. The apparatus is capable of measurement under constant pressure up to 110 MPa and over the temperature range from 100 to 370 K. The results on liquid 3-methylpentane which was used as the pressure medium proved satisfactory performance of this new-type calorimeter.

Temperature and pressure are among the most fundamental parameters in specifying the thermodynamic state of substances. Various physicochemical phenomena are most profitably studied by detailed and accurate measurement of the heat capacity, volume expansivity, and compressibility as functions of both temperature and pressure. These properties under ordinary pressure have hitherto been measured with high precision and accuracy in a wide temperature range. Although volume measurements for liquids have been extended to high pressures,[1–3] few quantitative measurements of heat capacity under pressure have been reported so far. Development of such measurements is naturally expected to contribute, to a great extent, to further understanding of the behaviors of substances at ordinary pressure as well as under pressure. Among these interesting behaviors are the pressure dependences of characters of phase transitions and the details around multiple points.

The heat capacity of a condensed matter is usually measured under constant pressure because of the difficulty in keeping the volume of the specimen constant. An adiabatic calorimeter is known to give the most reliable data at the atmospheric pressure. High pressure makes it difficult to satisfy some of the conditions favorable for the adiabatic calorimetry through the requisite of placing the specimen under pressure. A fundamental problem originates from increase of the mass of the calorimeter cell. The increase of the mass of the cell necessarily results in decrease in the ratio of the sample heat capacity to the total observed heat capacity vitiating certainty of the measurement. This situation leads to two calorimetric principles applied for construction of the calorimeter, a non-adiabatic or adiabatic method, depending on the pressure range to be covered.

Non-adiabatic methods, d.c. pulse or a.c. calorimeters, are applied to the measurements in the higher pressure than about 1 GPa.[4–7] The adiabatic method, employed in the relatively low pressure range up to ≈ 1 GPa, follows the principle of the adiabatic calorimetry under the ordinary pressure. Two types of apparatuses can be devised depending upon the choice whether the pressurized specimen is isolated from the surroundings or it communicates with an external pressure reservoir. The former condition is realized in a clamp-bomb calorimeter; the high pressure is generated and clamped outside the cryostat beforehand using a screw, and then the measurement is performed with the conventional adiabatic calorimeter as is done just at ordinary pressure.[8–11] Amitin *et al.* adopted this type of apparatus for the measurements on NH_4Cl crystal.[9] The pressure applied to the sample in such a calorimeter changes with the temperature. Especially when the sample undergoes a phase transition, the change should be drastic around that temperature, resulting in quite a complicated thermodynamic path in the p-T plane followed by the specimen in a series of measurement. The latter alternative is achieved by joining the calorimeter cell to the outside pressure-control system with a pressure-transmitting tube. In such a calorimeter, transfer of a part of the pressure medium out of or into the cell is inevitable as the temperature of the cell changes. Mil'ner reported the result on NH_4Br at 35 MPa with an apparatus of this type.[12] He employed argon gas as the pressure medium, which restricted the practical pressure range to the low region in view of the danger associated.

In this paper, we report the detail of a high-pressure adiabatic calorimeter and the results on liquid 3-methylpentane obtained with it. Features of the present calorimeter are as follows; (1) it is capable of heat capacity measurement in the temperature region from 100 to 370 K and the pressure range up to 110 MPa, (2) operates under adiabatic condition, (3) operates under stabilized hydrostatic pressure, and (4) enables to measure the volume (and therefore expansivity and compressibility) simultaneously. Heat of compression can also be derived by taking an extra procedure.

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Construction of Apparatus

Method of Calorimetry. Any high-pressure calorimetry is carried out at the sacrifice of some favorable conditions which are met in adiabatic calorimetry under ordinary pressure. The present calorimeter permits pressure medium to flow into or out of the cell so as to keep the pressure constant. The effect of transfer of a mass of the medium is to be corrected for later using dilatometric data. Heat capacity value obtained experimentally corresponds exactly to C_p on account of self-evident thermodynamic path in a series of measurement.

The whole apparatus consists of a calorimeter cell, a circuit for energy supply and its measurement, a temperature-measuring system, an adiabatic-control system, and a high-pressure system. Most of the parts excepting the temperature- and energy-measuring systems were installed in a room, the temperature of which was kept constant at (30.0±0.1) °C.

The calorimeter cell is equipped with a platinum resistance thermometer and a heating element. The temperature measurement of the cell was performed with a precision a.c. double bridge (AΣΔ Inc. Model H8). The electric energy supplied to the cell was measured by using a digital voltmeter and a digital clock. An adiabatic condition of the calorimeter cell was realized by evacuating space inside the cryostat and by temperature-controlling the shields and high-pressure tube within the cryostat. The pressure in the cell was controlled by connecting the cell with the transmitting tube to the high-pressure system which consists of pressure generation, pressure transmission, pressure gauge, pressure control and dilatometry subsystems. Liquid 3-methylpentane was used as the pressure medium, because it was known to undergo neither crystallization nor glass transition down to liquid nitrogen temperature.

Calorimeter Cell. A calorimeter cell must have the strength enough to withstand the applied pressure. The requirement causes the mass of, and therefore the heat capacity of, the high-pressure cell to increase with increase of the maximum pressure to which the measurement is intended. For this reason, inaccuracy of an adiabatic calorimetry originates primarily from smallness of the heat capacity of the sample compared with that of the empty cell.

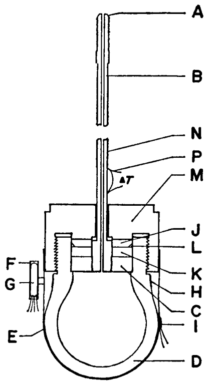

Fig. 1. Sectional drawing of the calorimeter cell.
(A): Cone-shaped connection part, (B): pressure-transmitting tube, (C): high-pressure plug, (D): sample vessel, (E): vessel cover, (F): copper sheath, (G): platinum resistance thermometer, (H): cell heater, (I): thermocouple for temperature control of inner shield, (J): copper-beryllium packing washer, (K): Teflon and indium packings, (L): copper extrusion ring, (M): vessel gland, (N): tube heater, (P): thermocouple for temperature control of tube B.

The present calorimeter cell was so designed as to maximize the volume of the sample space for the given mass of the cell material. Figure 1 shows the sectional drawing of the calorimeter cell and the annexed pressure-transmitting tube made of stainless steel. The sample vessel (D), vessel gland (M), and a packing washer (J) were made of a copper-beryllium alloy which had reasonably high thermal conductance and good mechanical properties necessary for the calorimeter cell. They were machined out from the material annealed at 315 °C for 2.5 h for the purpose of increasing the mechanical strength. A spherical shape of the vessel is one of particular devices for minimization of the mass of the empty cell and maximization of the space of the sample chamber. A sawtooth type of screw between the vessel and the gland was devised to minimize the thickness of the cylindrical part of the gland to the limit compatible with the mechanical strength required. Sealing of the cell was based on Bridgman's principle that the pressure exerting on the indium and teflon packing is larger than the medium pressure. A pressure transmitting tube (B), whose bottom area is unsupported, was screwed into a plug (C) made of stainless steel. An annealed-copper extrusion ring (L) served to prevent the teflon and indium from flowing outside. Heater wire (H) was wound outside the sample vessel. A thin vessel cover (E), made of copper, was installed to intercept heat leak by radiation from the heater as well as to fix thermocouple (I) and a copper sheath which held the platinum thermometer. This cover was gold-plated for reduction of radiative heat leak between the cell and its surroundings. The volume of the sample chamber was 24.522 cm^3 at 19 °C and the mass of the empty cell *ca.* 550 g. The whole cell was attached to or detached from the high-pressure system through a cone connector (A).

Cryostat and Adiabatic-control System. Adiabatic control requires minimization of the heat leak between the calorimeter cell and its surroundings. The minimization was achieved by evacuation of the space inside the cryostat (10^{-4} Pa) and by temperature regulation of the shields and the pressure tube. Figure 2 is a sectional illustration of the cryostat. The shields referred to as inner (B and D) and outer (F), and block (H) were made of copper for its high thermal conductivity. The high-pressure tube and the block were soldered to each other so as to aid their thermal contact. The electrical wires were twisted pair-wise to reduce inductive interference among them. The temperature control system utilizes the temperature difference signals ΔT_1 from the chromel-constantan thermocouples to regulate the current passing through

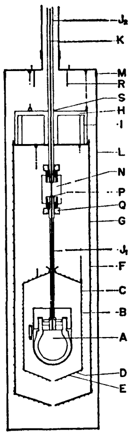

Fig. 2. Schematic diagram of the cryostat.
(A): Calorimeter cell, (B): inner-side shield, (C): side heater, (D): inner-bottom shield, (E): bottom heater, (F): outer shield, (G): outer heater, (H): block, (I): block heater, (J): tube heater, (K): pressure transmitting tube, (L): brass jacket, (M): Wood's alloy joint, (N): coupling, (P): cone connector, (Q): coupling gland, (R): thermal anchor for leads, (S): high-melting solder.

the corresponding heater. Heat leak between the cell and the inner shield (B) and through the high-pressure tube (J_1) affected most severely the experimental results. Five pairs of thermocouple were installed between the cell and the shield. The stainless-steel pressure tube was made as slender as is compatible with the required strength, and temperature-regulated by use of PID control circuit. The bottom and the other part of the inner shield were temperature controlled separately for better temperature-homogeneity within the inner shield. The temperature of the outer shield, block, and upper pressure tube (J_2) were held at several Kelvin below that of the cell. The whole cryostat was immersed into liquid nitrogen.

High-pressure System. The high-pressure system consisted of subsystems for generation, transmission, measurement and control of the pressure, including a dilatometer in it. The whole system is schematically depicted in Fig. 3. Two liquids separated by at the dilatometer were employed as pressure media in the lines; the lines on the pressure generation side (right-hand side in the figure) of the dilatometer (L) were filled with liquid kerosene through pumping at the pressure generator (A), while the lines on the cryostat side (left-hand side) with liquid 3-methylpentane. The pressure was read from the scale of Heise gauge (G). The whole system was installed in a room controlled at (30.0±0.1) °C.

The pressure control subsystem keeps the pressure constant by cancelling pressure change which is induced by the change of the cell temperature during the heat capacity measurement. Detail of the subsystem is illustrated in Fig. 4. The pressure was controlled by adjusting the temperature of the kerosene reservoir. Change of the pressure was monitored as a change in the manganin coil resistance which constituted one arm of a Wheatstone bridge, and this electrical signal was used to regulate the current passing through the heater (B) in the reservoir. The pressure to be set up was selected by changing the variable resistance of the Wheatstone bridge. Adoption of this method enabled to control the pressure automatically within 0.1 MPa in the whole temperature range measured. The coiled manganin wire was left strain-free in a vessel (J). The resistance was measured with the method of three terminals in order to allow for the lead resistance. The whole vessel was immersed in an oil bath (C) controlled at constant temperature of (35.0±0.1) °C.

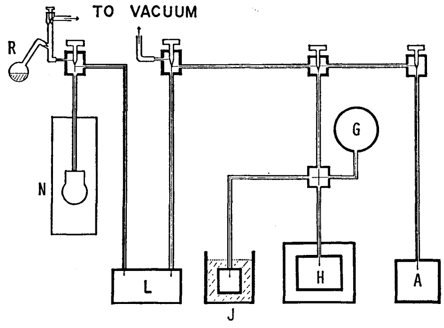

Fig. 3. Schematic drawing of the high-pressure system.
(A): Pressure generator, (G): Heise pressure-gauge, (H): oil reservoir, (J): manganin pressure-gauge, (L): dilatometer, (N): calorimeter cell, (R): glass bulb.

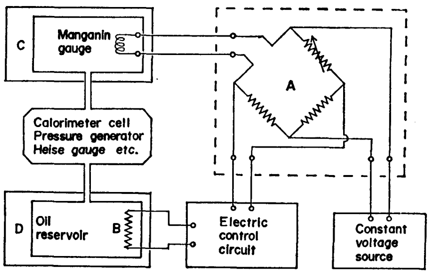

Fig. 4. Block diagram of the pressure control system.
(A): Wheatstone bridge, (B): oil heater, (C): water bath, (D): air bath.

The sectional drawing of the kerosene reservoir is shown in Fig. 5. The method of unsupported area was made use of for sealing. The electrode was fixed and insulated in the same way as in the manganin gauge by using Teflon as the packing material. A high-pressure tube (P) was fixed by screwing into the plug (C) and by tightly sealing with the Araldite resin. Heater wire (D) was glued on vanes (E) with Araldite. The volume of the kerosene chamber is $\approx 250\ \mathrm{cm}^3$ which was *ca.* 10 times larger than that of the sample chamber of the calorimeter cell. The whole vessel was installed in an air bath, the temperature of which was always kept lower by *ca.* 10 °C than that of the kerosene chamber.

Charge of liquid 3-methylpentane into the high-pressure lines was carried out by using a vacuum line as shown in Fig. 3. The liquid was first poured into the glass bulb (R) and then the bulb was connected with a joint to the vacuum line. After repeated degassing of the liquid and evacuation of the calorim-

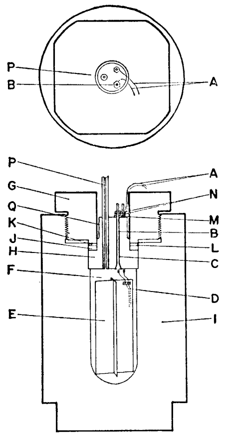

Fig. 5. Schematic diagram of the kerosene reservoir. (A): Heater lead, (B): electrode, (C): Teflon insulator and packing, (D): heater, (E): vane, (F): oil chamber, (G): gland bolt, (H): high-pressure plug, (I): body, (J): Teflon packing, (K): stainless packing washer, (L): copper extruding ring, (M): insulator, (N): nut, (P): high-pressure tube, (Q): self-extractor bolt.

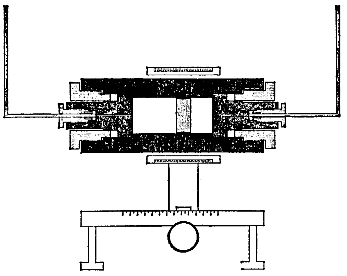

Fig. 6. Sectional drawing of the dilatometer.

eter cell and the dilatometer, the liquid was transferred into the high-pressure system by vacuum distillation at ≈50 °C.

Dilatometer. The present calorimeter permits the pressure medium to flow into or out of the cell for keeping the pressure constant. Calculation of the sample heat capacity from the apparent one requires the mass of the medium contained in the cell to be determined as a function of temperature. The dilatometer gives such data as well as essential information on the temperature dependence of the sample volume. A stainless-steel cylinder and Permalloy core constituted the dilatometer as shown in Fig. 6. The inner diameter of the cylinder was (2.000±0.010) cm. The core with very high magnetic susceptibility moved by pressure difference less than 0.1 MPa. The two pressure media (kerosene and 3-methylpentane) were separated by the core and an O-ring fitted up around it.

Expansion or contraction of the sample associated with the change of the temperature at the cell induced movement of the position of the core inside the cylinder. The position was detected by a combined apparatus of a cathetometer equipped with a differential transformer and a lock-in amplifier. The position of the transformer was read to 0.001 cm corresponding to 0.003 cm^3 in the error of volume measurement. The certainty was good enough for the temperature dependence of the mass of 3-methylpentane in the cell to be used in computing the heat capacity values.

Energy Supply and Temperature Measurement. Energy supply and temperature measurement were carried out by use of the apparatus already constructed.[13] A Minco thermometer of 469.740 Ω at 273.15 K was used as the temperature sensor of the calorimeter cell. The detailed procedure for determination of the temperature and the total input energy was given in the article reported before.[13]

Determination of the Volume and the Heat Capacity. Total heat capacity C consists of contributions from the pressure medium in the cell, mC_{l}, the empty cell, C_{b}, and the sample, C_{s};

$$C = mC_{\mathrm{l}} + C_{\mathrm{b}} + C_{\mathrm{s}}. \tag{1}$$

One analyses the change of state induced by a heating experiment as follows. Let $T-\Delta T$ and $m+\Delta m$ designate the temperature and the mass of the pressure medium in the initial state, and $T+\Delta T$ and $m-\Delta m$ those in the final state. Here T and m are those in the intermediate of the initial and final states. The specific heat capacity of the medium is then approximated as $C_{\mathrm{l}}+at$, where C_{l} is the specific heat capacity at T, t the temperature difference from T, and a the differential coefficient of the heat capacity by temperature. Since the input energy causes the temperature increase of the materials constituting the calorimeter cell, the total input energy ΔH is written as follows;

$$\begin{aligned}\Delta H &= 2\Delta T(C_{\mathrm{s}}+C_{\mathrm{b}}) + \int_{-\Delta T}^{\Delta T}\left(m-\frac{t}{\Delta T}\Delta m\right)(C_{\mathrm{l}}+at)\mathrm{d}t \\ &= 2\Delta T(C_{\mathrm{s}}+C_{\mathrm{b}}) + 2\Delta T mC_{\mathrm{l}} - \frac{2}{3}(\Delta T)^2 a\Delta m. \end{aligned} \tag{2}$$

The apparent heat capacity C_{e} is expressed from this as follows;

$$C_{\mathrm{e}} = \frac{\Delta H}{2\Delta T} = C_{\mathrm{s}} + C_{\mathrm{b}} + mC_{\mathrm{l}} - \frac{a\Delta T\Delta m}{3}. \tag{3}$$

The total heat capacity under constant pressure with the liquid medium of m is given by

$$C_p = C_{\mathrm{s}} + C_{\mathrm{b}} + mC_{\mathrm{l}}, \tag{4}$$

and consequently

$$C_p = C_{\mathrm{e}} + \frac{a\Delta T\Delta m}{3}. \tag{5}$$

The correction given by the second term of the right-hand side is estimated in order of magnitude in the case where the cell contains only the pressure medium 3-methylpentane. The following relations then hold for a typical measurement in which $2\Delta T \approx 2$ K and $T > 100$ K;

$$a\Delta T \lesssim 10^{-2}\, C_{\mathrm{l}}, \tag{6}$$

$$\Delta m \lesssim 10^{-2}\, m, \tag{7}$$

because the volume expansivity is $\approx 10^{-3}$. It follows that the correction is smaller than $10^{-4}\, mC_{\mathrm{l}}$ to be neglected to a good approximation in the determination of C_p. Thus the heat capacity under constant pressure is given by

$$C_p = C_{\mathrm{e}}. \tag{8}$$

But the amount of the pressure-transmitting liquid,

m, at the midpoint of the initial and the final temperatures changes with temperature and pressure and is to be determined from dilatometric data.

The heat capacity of the evacuated cell $C_b(T)$ was measured and assumed to depend only on the temperature. This assumption was tested as follows. The effect of pressure on the heat capacity of the copper-beryllium alloy could be assessed from the equation

$$\left(\frac{\partial C}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p. \qquad (9)$$

With the volume expansivity *vs.* temperature data around 200 K of copper similar to the copper-beryllium alloy, the estimate shows $(\partial C_b/\partial p)_T/C_b \simeq 10^{-5}$ MPa^{-1} for the cell, indicating that the influence is negligible within the error of measurement in the low pressure range ($\approx 10^2$ MPa).

The amount of pressure medium in the cell, m, naturally depends upon the volume of the cell. The volume $V_c(T,\ p)$ was given by

$$\begin{aligned} V_c(T,p)/\mathrm{cm}^3 = \{&0.987740+3.5\times10^{-5}(T/\mathrm{K}) \\ &+2.5\times10^{-8}(T/\mathrm{K})^2\} \\ &\times\{24.520+2.3\times10^{-4}(p/\mathrm{MPa})\}. \end{aligned} \qquad (10)$$

The volume was first calibrated, using water, to be 24.522 cm^3 at 19.0 °C and an atmospheric pressure. The temperature dependence, the former factor in Eq. 10, was determined assuming that the expansion coefficient α was given by a linear function of temperature, $\alpha = 4\times10^{-5}+5\times10^{-6}\{(T/\mathrm{K})-100.0\}$, with the values 4×10^{-5} K^{-1} at 100 K and 5×10^{-5} K^{-1} at 300 K. The pressure coefficient in the latter factor, on the other hand, was estimated at 30 °C by measuring first the pressure dependence of the molar volume of 3-methylpentane, and then the pressure dependence of the volume of 3-methylpentane inside the cell.

The molar volume and the molar heat capacity of 3-methylpentane are derived from calorimetric and dilatometric data as follows. Let $\rho_0(p)$ and $m_0(p)$ be the density and mass of the liquid contained in the cell, respectively, at 30 °C (=303 K) and some constant pressure p. Decreasing the temperature of the cell from 303 K to T displaces the core in the dilatometer toward the cell by l. The mass of the pressure medium in the cell is then given by the expression

$$m(T,p) = m_0(p) + \pi r^2 l \rho_0(p), \qquad (11)$$

where r is the inner radius of the dilatometer. The density is accordingly

$$\rho(T,p) = \{m_0(p)+\pi r^2 l \rho_0(p)\}/V_c(T,p). \qquad (12)$$

From this, the molar volume is given by the expression

$$V_e(T,p) = M/\rho(T,p), \qquad (13)$$

and the molar heat capacity

$$C_l'(T,p) = M\{Q/\Delta T - C_b(T)\}/m(T,p). \qquad (14)$$

Here M represents molar mass of 3-methylpentane, and $Q/\Delta T$ the apparent experimental heat capacity at T. Volume expansivity and compressibility can be calculated through thermodynamic relations.

The similar procedure in the case where the sample replaces greater part of the medium in the cell is shown in the following. Using the same notations of $\rho_0(p)$, $m_0(p)$, $m(T,p)$, and l as described above, one obtains the same relation as Eq. (11). Therefore the molar volume of the sample is expressed by

$$V_s(T,p) = \frac{M_s}{m_s}\left[V_c(T,p) - \frac{m_0(p)+\pi r^2 l \rho_0(p)}{\rho(T,p)}\right], \qquad (15)$$

where $\rho(T,p)$ is the density of pressure medium derived in Eq. 12. The molar heat capacity has the expression

$$C_s(T,p) = \frac{M_s}{m_s}\left[\frac{Q}{\Delta T} - C_b(T) - \frac{m(T,p)}{M} C_l'(T,p)\right], \qquad (16)$$

where m_s is the mass of the sample and M_s its molar mass. Here $m(T,p)$ is not equal to that given by Eq. 11, but is to be derived from dilatometric data using the values of the sample density and $V_c(T,p)$ at a certain temperature and pressure.

In fact, the temperature of the tube immediately above the cell (*i.e.*, the part between a coupling and the cell) changes with the same time-dependence as that of the temperature of the cell for the adiabatic temperature control of the cell. The effect of this temperature change at the tube on the displacement of the core position should be corrected for in the processing of dilatometric data. Let $Y_0(p)$ and $Y(p)$ denote the readings of the core position at 30 °C and T, respectively. The volume inside of the tube the temperature of which changes according to the change in the temperature of the cell being taken 0.1 π cm^3, the reading after above correction, $Y_1(p)$, is derived from the equation

$$Y_1(p)/\mathrm{cm} = Y(p)/\mathrm{cm} + 0.1\left[\frac{\rho(T,p)-\rho_0(p)}{\rho_0(p)}\right]. \qquad (17)$$

The amount of the pressure medium in the cell at T is therefore given by

$$n(T,p) = n_0(p) + \frac{[Y_1(p)-Y_0(p)]\pi\rho_0(p)}{M}, \qquad (18)$$

assuming the amount at 30 °C is $n_0(p)$. This correction was applied to the processing of data in both the cases with and without the sample in addition to the pressure medium in the cell. In the former case, the application for the molar volume of the sample material gives,

$$V_s(T,p) = \frac{M_s}{m_s}\left\{V_c(T,p) - \frac{[n_0 M + (Y_1(p)-Y_0(p)\pi\rho_0(p)]}{\rho(T,p)}\right\}. \qquad (19)$$

Results on 3-Methylpentane

Experimental. All the space inside and outside of the cell was evacuated after connection of the cell into the high-pressure system. Heat capacity of the empty cell was measured under that vacuum condition in the temperature range from 80 to 370 K.

The molar volume and heat capacity of liquid 3-methylpentane were measured in the following procedure. The reagent, purchased from Nakarai Chemical Co., was first introduced into a glass bulb (R in Fig. 3) and degassed carefully. The sample was then transferred into the high-pressure system and

Table 1. Pressure dependence of relative volume of 3-methylpentane at 30 °C

P / MPa	$V(P)$ / V(101 kPa)	P / MPa	$V(P)$ / V(101 kPa)
0.101	1.0000	66	0.9305
3	0.9954	69	0.9282
6	0.9910	72	0.9258
9	0.9869	75	0.9235
12	0.9831	78	0.9213
15	0.9795	81	0.9190
18	0.9760	84	0.9169
21	0.9726	87	0.9147
24	0.9693	90	0.9126
27	0.9661	93	0.9106
30	0.9630	96	0.9086
33	0.9600	99	0.9066
36	0.9571	102	0.9047
39	0.9541	105	0.9027
42	0.9513	108	0.9009
45	0.9485	111	0.8990
48	0.9458	114	0.8972
51	0.9431	117	0.8954
54	0.9405	120	0.8937
57	0.9380	123	0.8920
60	0.9354	126	0.8903
63	0.9330	129	0.8886
		132	0.8870

Table 2. Molar volume of 3-methylpentane

T / K	V(101 kPa) / cm^3 mol^{-1}	V(108.0 MPa) / cm^3 mol^{-1}
100	104.4	
110	105.5	
120	106.6	102.6
130	107.8	103.4
140	108.9	104.2
150	110.1	105.1
160	111.2	105.9
170	112.4	106.8
180	113.6	107.6
190	114.9	108.5
200	116.1	109.3
210	117.4	110.2
220	118.7	111.0
230	120.1	111.8
240	121.5	112.7
250	122.9	113.6
260	124.4	114.5
270	126.0	115.4
280	127.5	116.3
290	129.1	117.2
300	130.9	118.2

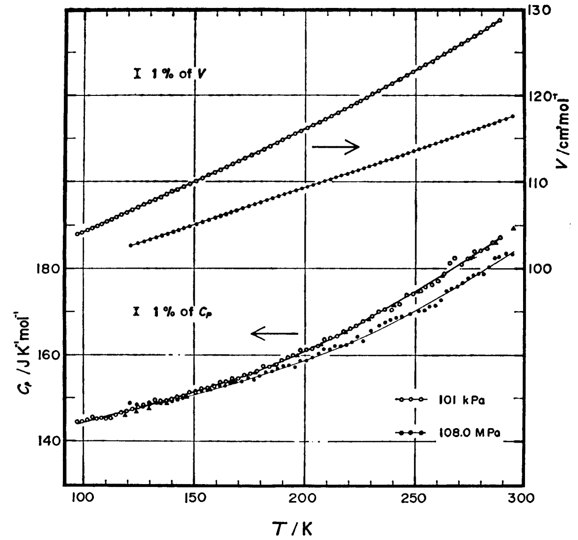

Fig. 7. Molar volume and molar heat capacity of 3-methylpentane.
○: 0.101 MPa, ●: 108.0 MPa.

the cell by vacuum distillation. The core of the dilatometer was brought toward the pressure generator at the room temperature to allow for the contraction of the liquid by pressure increase and/or temperature decrease. The value of molar volume at 20 °C and an atmospheric pressure was taken from a reference.14) The ratio of the molar volume at each pressure to that at 0.101 MPa was first measured at 30 °C and is collected in Table 1. The heat capacity was measured at 0.101 MPa and at 108.0 MPa in the heating direction from 100 to 300 K.

Results. The results of molar volume and heat capacity of liquid 3-methylpentane at the atmospheric pressure (0.101 MPa) and 108.0 MPa are shown in Fig. 7 and collected in Tables 2 and 3. The heat capacity at 0.101 MPa was previously measured by Finke and Messerly using a conventional adiabatic calorimeter (Δ in the figure).16) The present value above 160 K was in good agreement with that and larger by 0.5—1 J K^{-1} mol^{-1} between 120 K and 160 K. The discrepancy in the low temperature region is approximately 0.5%. The relatively large scattering of the heat capacity data is due to the adverse situation that the sample accounted for about one tenth of the total observed heat capacity.

Comparison between the molar heat capacities at 0.101 MPa and at 108.0 MPa shows that the former values is larger by *ca.* 6 J K^{-1} mol^{-1} than the latter one around room temperature, while it is almost the same as the latter below 130 K. Self-consistency between this pressure dependence of the heat capacity and temperature dependence of the molar volume in the present experiment is checked using a thermodynamic relation (9). The second order differential coefficient of the volume with the temperature was derived from the volume data smoothed against temperature, and the average value between those at two pressures was employed in the calculation. At 280 K, the difference between the heat capacities at 0.101 MPa and at 108.0 MPa was calculated with the relation to be -7.2 J K^{-1} mol^{-1}, which should be compared with -6 J K^{-1} mol^{-1}. At 130 K, it was -1.3 J K^{-1} mol^{-1} to be compared with ≈ 0 J K^{-1} mol^{-1}. The consideration on the error included in the derivation of second-order differential coefficients of volume would make such a discrepancy as *ca.* 1 J K^{-1} mol^{-1} insignificant,

TABLE 3. MOLAR HEAT CAPACITY OF 3-METHYLPENTANE

T / K	C_p / J K^{-1} mol^{-1}	T / K	C_p / J K^{-1} mol^{-1}	T / K	C_p / J K^{-1} mol^{-1}	T / K	C_p / J K^{-1} mol^{-1}
		184.11	157.2	282.39	184.6	203.43	159.4
$p=101$ kPa		186.92	157.6	285.30	185.8	206.06	160.4
97.16	144.4	189.70	158.8	288.19	187.1	208.62	161.4
99.43	144.4	192.48	159.5			211.17	161.4
101.87	144.6	195.24	160.0	$p=108.0$ MPa		213.71	162.2
103.67	145.5	197.98	161.2	121.21	148.8	216.24	162.1
106.05	145.1	200.72	161.3	124.42	148.4	218.76	162.4
108.19	145.4	203.43	161.5	127.28	148.1	221.28	163.0
110.31	145.1	206.15	162.1	129.99	148.5	223.78	164.3
112.53	145.3	208.88	163.6	132.67	148.8	226.28	163.3
114.82	146.0	211.65	163.9	135.22	148.7	228.77	164.0
117.09	146.2	214.60	164.3	137.75	149.4	231.31	167.3
117.15	146.6	217.53	165.4	140.26	149.2	233.82	166.8
119.46	146.9	220.37	166.0	142.74	149.5	236.36	167.5
122.07	147.4	223.20	166.7	145.20	149.9	238.89	168.1
124.68	147.9	224.79	166.0	147.87	151.2	241.41	168.6
127.29	148.4	227.59	169.3	150.70	151.6	243.93	168.9
129.87	148.7	230.42	168.9	153.50	151.6	246.45	168.5
132.42	149.4	233.30	170.0	156.29	151.8	248.96	170.3
134.95	149.2	236.17	170.1	159.05	152.8	251.45	170.1
137.45	149.3	239.19	170.4	161.80	151.7	253.95	170.3
139.94	149.6	242.29	171.6	161.57	152.9	256.43	171.2
142.41	150.1	243.09	170.6	163.96	152.8	259.05	171.5
145.07	150.3	245.94	173.9	166.33	153.4	261.51	172.7
147.92	151.1	248.77	174.1	168.89	153.6	263.97	174.9
150.74	151.2	251.61	174.5	171.63	153.8	266.42	175.4
153.54	152.2	254.43	175.7	174.35	154.6	268.88	175.9
156.32	152.2	257.25	176.1	177.06	154.2	271.32	176.7
159.08	152.6	260.05	177.1	179.75	155.1	273.75	177.8
161.82	153.6	262.85	178.7	182.43	156.0	276.18	178.5
164.54	153.7	265.64	181.2	185.10	156.2	278.60	178.8
167.25	154.5	268.42	180.8	187.75	156.9	281.01	178.8
169.96	154.4	267.77	182.3	190.41	157.5	283.42	180.3
172.75	155.2	270.72	180.9	193.04	157.7	285.87	182.5
175.61	155.6	273.66	182.2	195.65	157.3	288.22	182.7
178.46	156.1	276.59	183.9	198.25	158.7	291.06	183.6
181.30	157.3	279.50	184.1	200.85	158.8		

Accordingly, the results of volume and heat capacity would be concluded to be consistent each other.

These facts indicate that the present calorimeter has an excellent ability to give information of volume and heat capacity at constant pressure simultaneously in the temperature region at least from 100 to 300 K and up to 110 MPa. The imprecision and inaccuracy of heat capacity datum are estimated to be 0.5% and 1%, respectively, in comparison with the previous data which were claimed to have 0.2% inaccuracy at an atmospheric pressure.[16)]

Concluding Remarks

A new type of high-pressure calorimeter was constructed in the present work which operated under constant pressure up to 110 MPa.[15)] The results of heat capacities on liquid 3-methylpentane proved that this calorimeter has a satisfactory accuracy. This apparatus also enabled us to measure the temperature and pressure dependences of volume at the same time. This feature should be stressed in view of the facts that any physicochemical phenomenon could be understood through the observation of several kinds of properties.

Many kinds of interesting problems in phase transitions will be studied in relation to two thermodynamic parameters, pressure and temperature. One of the examples will be described in the subsequent paper on NH_4Br and ND_4Br crystals. Another interesting use of this calorimeter will be the application to studies on glass transition phenomena. Detailed enthalpy relaxation can be followed only under adiabatic condition and volume relaxation under constant pressure.

The work to extend the pressure range up to 250 MPa is under way.

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