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Construction of an Adiabatic High-Pressure Calorimeter Using Helium Gas for Pressurization†

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A novel adiabatic high-pressure calorimeter was constructed with using helium gas as a pressure transmitting medium. It works under a constant pressure up to 250 MPa in the temperature range from 12 to 370 K. Sample cell is made of Be-Cu alloy and has internal volume of 26 cm^3. The pressure transmitting tube is connected to an external pressure-control system, which enables to keep automatically the inner pressure constant within ±1 kPa over the whole pressure and temperature ranges. Thus the thermodynamic path that any specimen follows during the heat capacity measurement can be described unambiguously. Heat capacities of the sample cells loaded without and with 158.9 MPa He gas were measured in the temperature range from 25 to 370 K. The imprecision of heat capacity data of the compressed He gas was within 0.3%. Thus the present calorimeter enables us to extend the low-temperature thermodynamic study on various kinds of materials to high pressures without a significant loss of the claimed precision.

Stability of states and thermodynamic properties of a substance can be determined from its Gibbs energy as functions of some parameters, temperature and pressure being two of the most important external parameters. The surface of the energy is experimentally obtained by the accurate measurements of heat capacity vs. temperature and volume vs. pressure. Hence calorimetry over wide temperature and pressure ranges is quite important in such studies.

The most accurate calorimetry has been done under adiabatic condition at the normal pressure. There the adiabatic condition is established as closely as possible between a calorimeter cell and its surroundings, and a path of the measurement is unambiguously specified on the p-T surface so that the obtained heat capacity data can be converted correctly to a thermodynamic quantity at constant pressure. However, the extension of this method to the calorimetry under high pressure is not straightforward, owing to many experimental difficulties. Either direct or indirect contact of a pressure transmitting medium with the sample is required for the application of pressure. Since the volume of the pressure transmitting medium as well as that of the sample changes with temperature and pressure, the unambiguous specification of the path of measurement can only be achieved by taking the following two procedures. One is to follow always the pressure change of the calorimeter cell during a series of measurements and then correct the effect of pressure change by using appropriate thermodynamic data as precisely as possible. Such calorimeters, often described as the clamp-bomb type, have been reported by a number of research groups,[1-4] on account of the convenience that an ordinary adiabatic calorimeter can be used without any drastic modification of the apparatus.

The other is to keep the pressure constant by connecting the cell to a pressure control system external to the cryostat through a pressure transmitting tube and permitting the pressure transmitting medium to flow into or out of the cell. The tube must be temperature-regulated to maintain adiabaticity of the calorimeter. Only two groups[5,6] have constructed this type of apparatus with using a liquid as the pressure transmitting medium. The above two methods are both usable only under relatively low pressures, below 1 GPa. This is because, higher the pressure, the cell must be more massive to withstand the pressure, resulting in the decrease in the ratio of the sample heat capacity to the total.

The adiabatic high-pressure calorimeter on which we reported before used liquid 3-methylpentane as the pressure transmitting medium.[5] While being quite effective in that the hydrostatic pressure is easily generated and transmitted to the system, it restricts the substances to be studied to inorganic compounds which are insoluble in the medium and the measurements in the temperature range above 100 K because of the solidification of the pressure transmitting medium itself below 100 K. The former restriction precludes molecular crystals and liquid crystals from the measurements and the latter limits the consideration based on the third law entropy.

The purpose of the present work is to construct a new high-pressure calorimeter which removes these restrictions. The apparatus uses, as a pressure transmitting medium, helium gas which is chemically inert and exists in the gaseous state down to very low temperatures. The use of this apparatus enables calorimetry with high precision up to 250 MPa. The precision of the calorimetry was estimated by measuring the heat capacities of helium gas at 158.9 MPa.

Construction of Apparatus

Principle. The present apparatus employs helium gas as a pressure transmitting medium to pressurize the sample in the cell. The pressure is maintained at a fixed value by permitting the helium gas to flow into

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or out of the cell through the pressure transmitting tube connected to the high-pressure control system. Heat capacity measurement is performed by the conventional adiabatic method, i.e., by following the temperature increment due to a known quantity of supplied energy under adiabatic condition. Heat flow through helium gas is negligible because the pressure transmitting tube above the cell together with the helium gas contained was maintained the same temperature as the cell. The heat capacity of the sample is obtained by subtracting from the total the contribution of the helium gas in the cell at the average temperature, as described in detail previously.[5] The contribution can be estimated only if the volume of the space occupied by the helium gas and its heat capacity at the confining pressure per unit volume are known.

The total heat capacity C_t obtained experimentally is expressed as

$$C_t(p,T) = nC_s(p,T) + C_e(p,T) + \{V_e(p,T) - nV_s(p,T)\}C_H(p,T). \quad (1)$$

Here, C_s, C_e, and C_H denote the heat capacities at constant pressure of a mole of the sample, empty cell, and helium gas per unit volume, respectively. V_s and V_e are the molar volume of the sample and the volume of the empty cell, respectively, and n the amount of sample. The symbols in the parentheses represent variables; p is the pressure inside the cell and T is the average temperature. Pressure dependence of heat capacity of the empty cell is given by $(\partial C_e/\partial p)_T/C_e \simeq 10^{-5}$ MPa^{-1}. This indicates that the dependence is negligible within the error of measurement in the present pressure range $\approx 10^2$ MPa; i.e.,

$$C_e(p,T) \simeq C_e(T). \quad (2)$$

$C_H(p,T)$ is rewritten as

$$C_H(p,T) = C_H^*(p,T)/V_e(p,T), \quad (3)$$

where $C_H^*(p,T)$ is the heat capacity of the helium gas that occupies the whole space of the cell, and can be determined experimentally. Substituting these two relations into Eq. 1 and rearranging, the molar heat capacity of the sample $C_s(p,T)$ is expressed by

$$C_s(p,T) = [C_t(p,T) - C_e(T) - \{1 - nV_s(p,T)/V_e(p,T)\}C_H^*(p,T)]/n. \quad (4)$$

Here $V_e(p,T)$ is obtained by measuring the total heat capacity $C_t'(p,T)$ containing a standard substance whose heat capacity $C_{st}(p,T)$ and volume $V_{st}(p,T)$ at high pressure are known; *i.e.*,

$$V_e(p,T) = \frac{V_{st}(p,T)\{C_H^*(p,T) - C_e(T)\}}{C_H^*(p,T) + C_{st}(p,T) - C_t'(p,T)} \quad (5)$$

Consequently, the determination of $C_s(p,T)$ requires only the data of $C_t(p,T)$ and $V_s(p,T)$ in Eq. 4. $V_s(p,T)$ must be obtained from other measurements (X-ray diffraction etc.) or by using some reliable equations of state, since it cannot be measured directly with the present calorimeter. When the interest is getting only the anomalous part of the heat capacity, it is not always necessary to know $V_s(p,T)$.

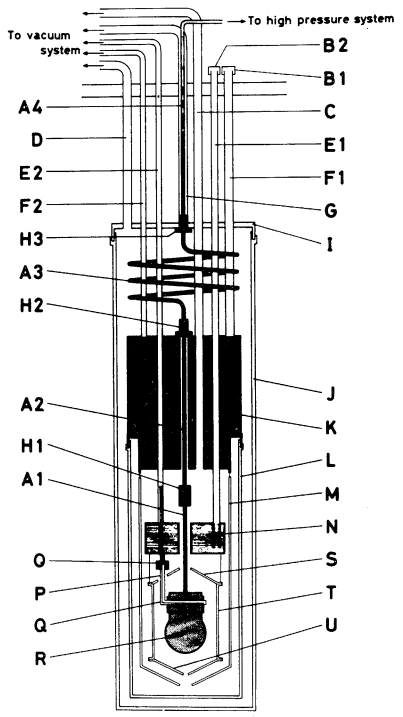

Fig. 1. Schematic drawing of the cryostat.
(A): High pressure transmitting tubes, (B): caps, (C),(D),(G): pumping tubes, (E): liquid nitrogen inlet and outlet, (F): liquid hydrogen inlet and outlet, (H): couplings, (I),(J): outer vacuum jacket, (K): liquid hydrogen tank, (L): inner vacuum jacket, (M): outer adiabatic shield, (N): liquid nitrogen tank, (O): joint,(P): transfer tube, (Q): cooling ring, (R): cell, (S),(T),(U): inner adiabatic shields.

Cryostat and Adiabatic Control. Figure 1 shows a schematic drawing of the cryostat. The pressure transmitting tube, shown in sections by A1, A2, A3, and A4, enters the cell R from the high pressure system through the center of the cryostat. They are made of stainless steel tubes of 0.6 mm I.D. and 3.1 mm O.D. They are connected in series with the couplings H1, H2, and H3. The cell R is dismountable at H1.

Temperatures as low as 12 K can be obtained by the standard cryogenic technique. Normally the cell is cooled from room temperature with the help of He gas of about 10 kPa introduced into the vacuum jackets J and L. However if the sample is volatile, it is possible to cool the cell by introducing liquid nitrogen directly into the cooling ring Q through E1, N, and P without any heat-conduction gas in the jackets. This process of cooling keeps the tubes A1-A4 at higher temperatures than the cell, preventing any volatile sample from condensing on the inner walls of the tubes.

Adiabatic condition between the cell and its envi-

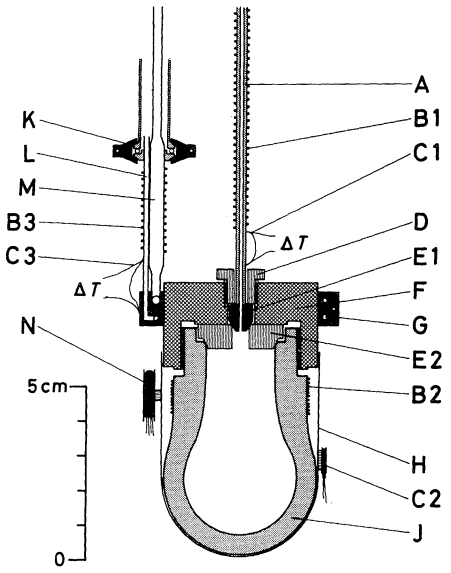

Fig. 2. Sectional drawing of the calorimeter cell. (A): High pressure transmitting tube, (B): heater wire, (C): thermocouples, (D): gland nut, (E): plugs, (F): gland lid, (G): cooling ring, (H): cell cover, (J): body, (K): joint, (L): liquid nitrogen inlet, (M): nitrogen gas outlet.

ronment is achieved during heat capacity measurements by evacuation of the space inside the jacket J and L to 10^{-4} Pa and by temperature-control of the following ten parts surrounding the cell. The inner adiabatic shields S, T, and U, the transmitting tube A1 just above the cell, and the liquid nitrogen transfer tube P are controlled at the same temperature as the cell. The outer shield M and the liquid nitrogen tank N (whose inside space is evacuated) are held a few Kelvins lower than the cell in order to control the inner shields. Furthermore, the tubes A2, A3, and A4 are kept a few Kelvins higher than the cell to prevent the condensation of sample on their inner walls. The temperature control system utilizes the temperature difference signals from the Chromel-P-constantan thermocouples (which are attached to appropriate locations of those parts to be controlled and the respective reference points) and regulates the current passing through the corresponding heaters. The upper temperature limit of the measurement is about 400 K because a low-temperature solder was used in several parts.

Calorimeter Cell. Figure 2 shows the calorimeter cell whose inside volume is 26.271 cm^3 at 30 °C and mass is 622.30 g. The main parts of the cell (J, F, D, E1, and E2) were made of copper-beryllium alloy which has high thermal conductivity and sufficient mechanical strength to withstand the applied pressure. The surface of the cell was gold-plated for reduction of radiative heat transfer and for protection against corrosion. A nearly spherical shape of the body J was devised for the purpose of minimization of the mass of the empty cell and maximization of the inside space. This increased the ratio of the sample heat capacity to the total and contributed to the improvement in the precision of the measurement.

The pressure inside the cell is sealed by two-stage metallic cone connection instead of the traditional Bridgman method. The first plug E2 is pressed down against the tapered top of the inner wall of the body J by driving the screw of the gland lid F and the second plug E1 is pressed against the top of the inside wall of E2 by the gland nut D. The diameter of the contact circle is about 20 mm for the first plug and 5 mm for the second plug, respectively. The sample is introduced through the apertures of E2 and F, after removing plug E1. This sealing method does not require any packing (e.g., tetrafluoroethylene or indium). The packing used in the previous experiments made the pressure and temperature dependence of the cell volume complicated and ambiguous. At present, the maximum pressure that can be applied to the cell without any leak is about 250 MPa.

The cooling ring G, made of copper, serves to cool the cell while the high-pressure tubes are being kept at higher temperatures. Liquid nitrogen is introduced through the inlet L and allowed to vaporize outward through the outlet M. The L and M are controlled during the heat capacity measurement at the same temperature as the cell with the Chromel-P-constantan thermocouple C3 and manganin heater B3. The ring can be removed at the joint K for measurement with nonvolatile samples.

B2 is the manganin heater for supplying electric energy to the cell. The thin cell-cover H made of copper was installed to minimize heat leak by radiation from the heater B2 as well as to fix the thermocouple C2 for the temperature regulation of the inner shields and the copper sheath as a holder for the platinum thermometer N (470 Ω at 273 K, Minco Products, USA).

Calorimetric Measurement. Calorimetric measurement consists of the usual three steps as generally performed: initial temperature measurement, supply of electric energy, and final temperature measurement. The temperature is determined by measuring the resistance of the platinum thermometer with the automatic a.c. resistance bridge (ASL F17, U.K.). The bridge gives a ratio of the thermometer to the standard resistance as a digital output with seven digits and an additional analog output of any umbalance signal. The analog signal is digitalized by the multimeter (Keithley 195, USA), and the resultant resistance readout with eight degits in total is converted to temperature, whose resolution corresponds roughly to 10 μK at temperatures above 50 K. The supplied energy is determined using the digital multimeter (Keithley 195, USA) and the digital clock in the computer.

All operations of the measurement, data processing, and their storage are carried out with the microcomputer (Sharp MZ 2200). The use of the computer contrib-

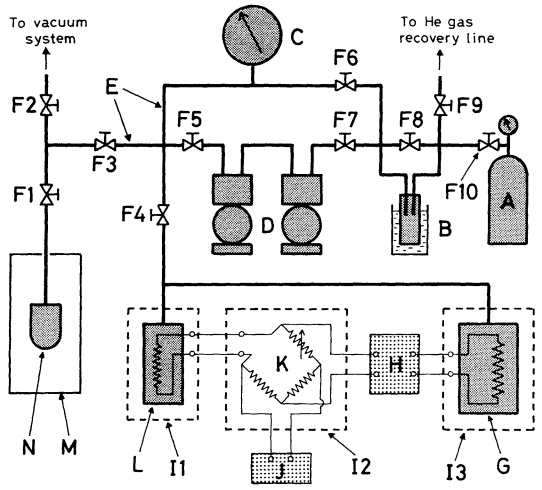

Fig. 3. Block diagram of the high pressure system. (A): Helium tank, (B): trap, (C): Heise gauge, (D): diaphragm compressor, (E): high pressure transmitting tube, (F): valves, (G): helium gas reservoir, (H): PID regulator, (I): thermostats, (J): battery, (K): Wheatstone bridge, (L): manganin wire resistance gauge vessel, (M): cryostat, (N): cell.

utes not only to saving labor but also to improving precision of the thermometry. Usually temperature is read out once in 60 s as the average of 12 readings taken at an interval of 5 s. This procedure of averaging reduces a scattering of data to a large extent, and consequently the precision of the thermometry is estimated to be within 50 μK at temperatures above 50 K. Detailed descriptions of the determination of temperature and input energy were given in the previous articles.[7] The thermometer was calibrated in advance on the IPTS-68.

High-Pressure System. Figure 3 shows the block diagram of the high-pressure system. The system can be divided into three parts; the cryostat in the left portion of the figure, the pressure generation system in the upper right, and the pressure control system in the lower right. Blocks shaded heavily and lightly represent high-pressure parts (A, B, C, D, G, L, and N) and electrical parts (H and J), respectively. Thick and thin solid lines represent high-pressure transmitting tubes and electric wires, respectively. All high-pressure vessels were connected by the transmitting tubes E. Broken lines represent thermostats.

Pressure is generated in the following way. The inner space of the pressure system is first evacuated after opening all valves, except F9 and F10. After closing F2, F6, and F8 and opening F10, helium gas is introduced from tank A into the system to a pressure of about 5 MPa (the specified value for the low pressure side of the compressor). The pressure of the system on the left side of F6 and F7 is increased up to desired value with the double-head model of diaphragm-type compressor D (NOVA SWISS 554.3330-2). While pressurizing, the compressor is supplied with helium gas continuously through the trap B immersed in liquid nitrogen to remove impurities (water etc.). It takes approximately 20 min to pressurize to 200 MPa. After pressurization, pressure generation system is isolated from other parts of the system by closing valve F5. The pressure is read from the Heise gauge C, whose accuracy is within ±0.1 MPa.

The pressure in the cell N is controlled by adjusting the temperature of the helium gas reservoir G, which has about 8 times larger volume than the cell. Pressure change in the cell is detected as the change in resistance of a manganin wire placed in the stainless steel vessel L. This resistance constitutes one arm of the Wheatstone bridge K, and its deviation from the value (corresponding to desired pressure preset with the variable resistance of K) is detected as an electric signal. The signal is amplified with the PID circuit H and utilized to regulate the temperature of the vessel G. Temperatures of the vessel L and of the bridge K are kept constant with air baths thermostatted at 32 °C for I1 and at 35 °C for I2, respectively. This method of pressure control is basically the same as that of the high pressure calorimeter with liquid pressure transmitting medium reported before.[5] The precision of the pressure and the temperature controls of the helium gas reservoir were, however, improved for use of helium gas which has much larger thermal expansivity than the liquid. The detailed description will be given below in separate sections.

Helium Gas Reservoir. Heat capacity measurement is performed at successively increasing temperatures. Consider the process in which the temperature of the cell loaded only with helium gas is increased by ΔT_c from T_c. Correspondingly, the temperature of the reservoir must be decreased from T_r to $T_r-\Delta T_r$ in order to keep the pressure of the system constant. Assuming that the helium behaves as an ideal gas,

$$\Delta T_r = \frac{T_r^2 \Delta T_c}{(V_r/V_c)(T_c+\Delta T_c)T_c + T_r \Delta T_c} \simeq \left(\frac{V_c}{V_r}\right)\left(\frac{T_r}{T_c}\right)^2 \Delta T_c, \quad (6)$$

where V_c and V_r are the volumes of the cell and of the reservoir, respectively. (V_c/V_r) is practically about 1/8. T_r is around room temperature (≈300 K) so that ΔT_r is estimated to be 1/8 K for ΔT_c of ≈1 K, when T_c=300 K; and 4.5 K when T_c=50 K. Since the temperature dependence of thermal expansivity of real high-pressure gas is smaller than that of the ideal gas, the latter value of ΔT_r would have been overestimated. Whatever the real ΔT_r may be, the temperature of the reservoir must be reduced by the same order of magnitude as a rise in temperature of the cell.

The helium gas reservoir and its temperature control system is shown in Fig. 4. The reservoir is made of stainless steel and has the volume of about 200 cm^3. Pressure seal of the upper part was achieved in two stages; at first the plug D2 was Ar-welded to the body J at F and supported by the nut A2, and secondly the

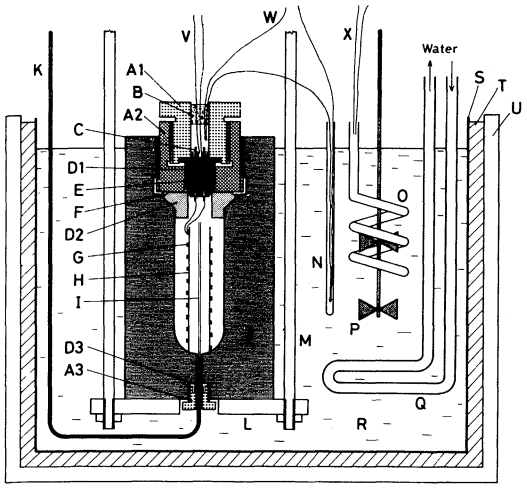

Fig. 4. Schematic drawing of the helium gas reservoir and its temperature control system.
(A): Gland nuts, (B): electric insulator, (C): electrodes, (D): plugs, (E): nylon packing, (F): Ar-welded circle, (G): manganin heater wire, (H): core copper tube, (I): copper capillary, (J): body, (K): high pressure transmitting tube, (L): holder, (M): hanging rods, (N): glass tube, (O): copper tube for heater wire, (P): stirrer, (Q): copper tube for flowing water, (R): silicone oil, (S): stainless steel box, (T): thermal insulator, (U): wooden box, (V): lead wire from PID regulator, (W): Chromel-P-constantan thermocouple, (X): lead wire for heater of oil bath from regulator.

plug D1 was pressed down against the top portion of the inside wall of plug D2 with the nut A1. Pressure seal of the lower part was achieved by the usual metallic cone connection between the plug D3 and the body J. The high pressure transmitting tube K was fixed to plug D3 with silver solder. The helium gas enters or leaves the reservoir through the copper tube I which was also soldered to plug D3. The heater wire G, used to closely control the temperature of the gas in the reservoir, was wound around the copper tube H and connected to the PID circuit through electrodes J and lead wire V. Electric insulation between C and D1 was attained with Nylon packing E.

The reservoir is placed in a variable-temperature thermostatted bath. A Chromel-P-constantan thermocouple W detects the difference in temperature between the space within A1, which reflects the temperature of helium gas in J, and the silicone oil R surrounding the body. Through this signal, the temperature difference is always kept constant by regulating the current passing through the heater installed in the copper tube O. Q is another copper tube in which cold water flows. The temperature of the oil is usually adjusted to be a few Kelvins lower than that of the inside of A1, and should decrease as the temperature of helium gas in the reservoir decreases. The usable temperature of the silicone oil bath is in the range of about 100 to 10 °C. This is broad enough to cover the entire temperature range of the measurement (30—370 K) at 200 MPa, even in the case where the cell is completely filled with helium gas.

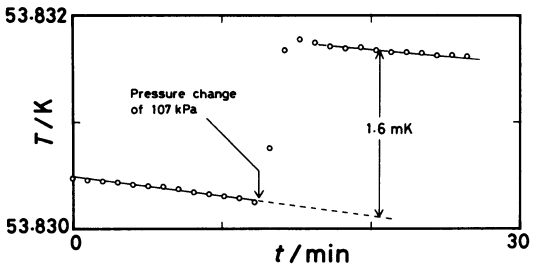

Fig. 5. Temperature response of the calorimeter cell loaded ice specimen to the helium gas pressure change of 107 kPa at 158.9 MPa and 53.83 K.

Precision of Pressure Control. Accurate pressure control is quite important, not only for obtaining the heat capacity of a definite amount of helium gas in the cell at any specified temperature and pressure, but also for attaining adiabataic condition of the cell because the heat of compression of helium gas is considerable. Let us start by deriving the relation according to which the temperature of the cell filled with helium gas is influenced by the change in the pressure within the cell under adiabatic condition. The relation may be regarded as the resultant of two processes through which the temperature of helium gas T_H changes, first by adiabatic compression and next when the gas reaches thermal equilibrium with the cell. Then the following equation is obtained;

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{C_H}{C_H + C_e}\right)\left(\frac{\partial T_H}{\partial p}\right)_S, \tag{7}$$

where C_e and C_H are the heat capacities at constant pressure of the cell and the helium gas within the cell, respectively. $(\partial T_H/\partial p)_S$, which describes the first process, is given by

$$\left(\frac{\partial T_H}{\partial p}\right)_S = \frac{T_H \alpha_H V_H}{C_H}, \tag{8}$$

so that

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{T_H \alpha_H V_H}{C_H + C_e}, \tag{9}$$

where α_H and V_H are the thermal expansivity and the volume of the helium gas. If the pressure transmitting medium is liquid (*e.g.*, 3-methylpentane), α_H is of the order of 10^{-4} K^{-1} and changes little with temperature.[5] For helium gas, however, α_H is of the order of 10^{-3} K^{-1} and increases with decreasing temperature.[8] (By way of an example, the assumption of ideal gas results in α_H being proportional to $1/T$. Therefore, $(\partial T_H/\partial p)_S$ becomes large, especially at low temperatures, because both α_H and $1/(C_H+C_e)$ increase more rapidly compared with the decrease in T_H).

Figure 5 shows the observed response of the cell to pressure change of 107 kPa at 53.8 K and 158.9 MPa. The cell contained 18.2 cm^3 of ice sample so that the

volume remaining for the helium gas was about 8.1 cm^3. The temperature of the cell rose by 1.6 mK just after the compression. Substituting T_H=54 K, V_H=8.1 cm^3, C_H+C_c=81 J K^{-1} (experimental value), and α_H= 3.0×10^{-5} K^{-1} (value extrapolated from the data below 100 MPa[8]) into Eq. 9, the temperature change due to the change in pressure of 107 kPa is calculated to be 1.7 mK, which almost agrees with the observed value.

Figure 6 shows the electric signal which corresponds to the fluctuation of pressure from the preset value of 158.9 MPa at 60 K. Half an hour is normally required for one cycle of heat capacity measurement. Stability of the voltage during the measurement cycle is within 20 nV, which corresponds to about 1 kPa on the basis of the calibration in which a pressure change of 4.2 kPa gave rise to the signal of 100 nV. The fluctuation of 1 kPa corresponds roughly to a fluctuation of 15 μK in temperature from the relation shown in Fig. 5. This is small enough since the actual precision of temperature measurements is 50 μK.

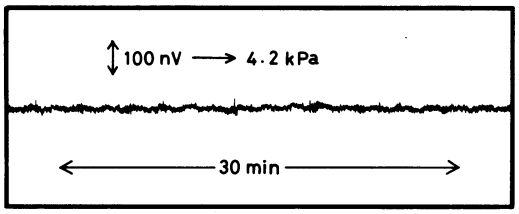

Fig. 6. Electric signal response to the fluctuations of the pressure control system at 158.9 MPa.

Heat Capacity of Helium Gas at 158.9 MPa, and Precision of the Calorimeter

The precision of the present calorimeter was examined by measuring the heat capacity of helium gas at 158.9 MPa in the temperature range between 25 and 370 K. The experimental data are given in Table 1. The starting temperature 25 K is the one below which condensation of the gas is supposed to occur. Plotted in Fig. 7 are the experimental values of the empty cell (○) and the cell fully loaded with helium gas at the constant pressure of 158.9 MPa (●), where the former was measured above 12 K. Reduction of the data to the molar heat capacities of He gas at the high pressure requires the information of equation of state of the gas and volume of the cell as functions of temperature and pressure.

Figure 8 shows the deviations of the experimental

Table 1. Heat Capacities of He Gas in the Sample Cell at 158.9 MPa

T_{av}	C_p	T_{av}	C_p	T_{av}	C_p	T_{av}	C_p	T_{av}	C_p
K	J K^{-1}	K	J K^{-1}	K	J K^{-1}	K	J K^{-1}	K	J K^{-1}
26.52	34.09	70.87	38.61	125.20	33.01	194.96	27.05	275.67	22.33
27.64	34.61	72.30	38.51	127.17	32.76	197.04	26.89	278.52	22.16
28.84	35.10	73.74	38.39	129.15	32.64	199.13	26.62	281.38	21.96
30.11	35.64	75.18	38.28	131.15	32.39	201.25	26.43	284.27	21.89
31.36	36.14	76.63	38.13	133.17	32.15	203.39	26.38	287.18	21.78
32.58	36.60	78.09	37.98	135.22	32.02	205.55	26.26	290.11	21.65
33.83	36.98	79.55	37.78	137.28	31.79	207.74	26.04	293.07	21.56
35.13	37.34	81.02	37.69	139.36	31.65	209.95	25.98	296.05	21.36
36.47	37.69	82.50	37.56	141.47	31.39	212.19	25.83	299.05	21.17
37.82	37.99	83.99	37.35	143.59	31.19	214.45	25.67	302.07	21.10
39.17	38.25	85.49	37.20	145.73	30.93	216.73	25.48	305.12	21.00
40.53	38.47	87.00	37.08	147.90	30.76	219.04	25.27	308.19	20.84
41.88	38.64	88.52	36.89	150.08	30.67	221.37	25.25	311.28	20.65
43.24	38.77	90.07	36.72	152.29	30.47	223.72	25.06	314.40	20.55
44.60	38.99	91.64	36.58	154.51	30.24	226.09	24.93	317.54	20.48
45.96	39.08	93.23	36.42	156.76	29.98	228.50	24.78	320.70	20.38
47.32	39.20	94.84	36.28	159.02	29.76	230.92	24.64	323.88	20.19
48.68	39.28	96.47	36.12	161.31	29.60	233.37	24.48	327.09	20.02
50.05	39.34	98.11	35.89	163.62	29.35	235.84	24.35	330.32	19.95
51.41	39.37	99.78	35.70	165.95	29.19	238.33	24.27	333.57	19.84
52.78	39.47	101.47	35.54	168.30	29.07	240.85	24.15	336.85	19.79
54.15	39.42	103.18	35.34	170.67	28.82	243.39	23.98	340.15	19.73
55.52	39.42	104.91	35.19	173.06	28.62	245.95	23.76	343.47	19.47
56.89	39.50	106.65	35.00	175.22	28.45	248.54	23.74	346.81	19.34
58.27	39.41	108.42	34.71	177.13	28.25	251.15	23.69	350.16	19.25
59.65	39.31	110.21	34.56	179.06	28.10	253.78	23.41	353.54	19.06
61.04	39.23	112.01	34.38	181.00	27.89	256.44	23.16	356.93	18.89
62.43	39.20	113.84	34.22	182.95	27.92	259.11	23.09	360.33	18.76
63.82	39.18	115.68	33.97	184.92	27.74	261.82	23.03	363.75	18.73
65.22	39.02	117.55	33.78	186.91	27.46	264.54	22.77	367.19	18.58
66.63	38.93	119.43	33.66	188.90	27.42	267.29	22.58	370.64	18.44
68.04	38.79	121.33	33.41	190.90	27.28	270.06	22.45		
69.45	38.76	123.26	33.20	192.92	27.04	272.86	22.38		

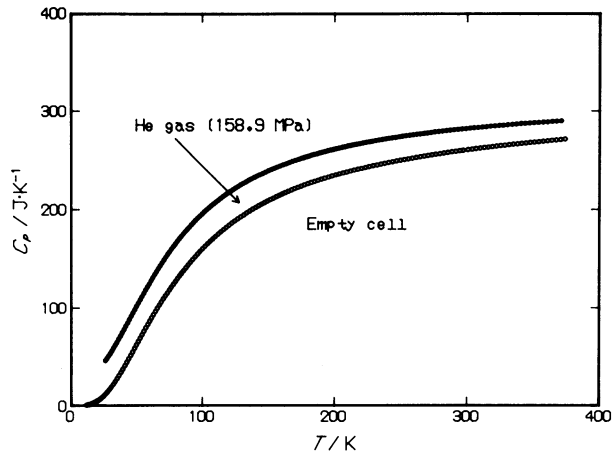

Fig. 7. Heat capacities of the empty cell (○) and of the cell with helium gas at 158.9 MPa (●). The difference between the two curves is equivalent to the heat capacity of the helium gas at 158.9 MPa.

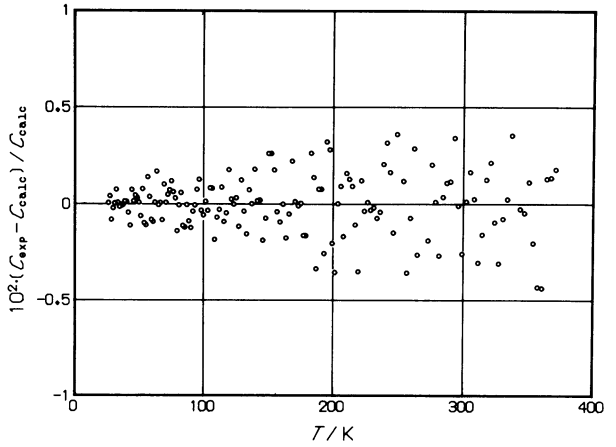

Fig. 8. Deviation plot of the observed heat capacities of helium gas at 158.9 MPa.

values from their smoothed curve. The deviation is within 0.3% over the measured temperature range; remarkably small deviation in the low temperature region is due to the special circumstances that the heat capacity of helium gas is still as large as at higher temperatures while that of the cell decreases rapidly with decreasing temperature. Heat capacities of condensed substances would generally amount only to 50—80% of that of helium gas fully loaded in the cell. The precision of the present calorimeter is therefore estimated to be within 0.5% over the experimental temperature range.

The obtained precision in this instrument is considerably poorer than that of ordinary type of calorimeters, 0.1—0.2%,[7] in the above temperature range at atmospheric pressure. This is attributed to the following two disadvantageous aspects of the present calorimeter. The heat capacity of the empty cell, reaching 270 JK^{-1} at room temperature, is almost ten times larger than that of the ordinary calorimeter. Such a large heat capacity additionally requires a longer period of energy supply for increasing the temperature, yielding the increased ambiguity of the correction for heat leakage. These aspects might have given rise to over ten times larger imprecision than that of the ordinary one unless the thermometry had been improved as described in the previous section. The decreased precision, however, is acceptable as the price for the increased information. Experimental results on some hydrogen bonded crystals will be published in due time.

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