An Adiabatic Calorimeter for Heat Capacity Measurements in the Temperature Range from 80 to 550 K. Heat Capacities of α-Alumina (Sapphire) and Anhydrous Magnesium Acetate

Natsuo Onodera,* Arata Kimoto,** Minoru Sakiyama, and Syûzô Seki
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka
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An adiabatic calorimeter for the measurements of heat capacities of solid and liquid in the temperature range 80—550 K and the automatic temperature control system are described. The working platinum resistance thermometer is calibrated against a standard thermometer. The measurements of heat capacity of α-Al_2O_3 prove the precision to be $\pm 0.3\%$ and give an accuracy of $\pm 0.6\%$. By means of this calorimeter, heat capacities of anhydrous magnesium acetate have been measured for its glassy and crystalline states around the glass transition point.

Adiabatic calorimetry of the intermittent-heating type[1] determines most accurately heat capacities of solid and liquid below room temperature. If this method is carried out ideally, the adiabatic shield is always maintained at the same temperature as that of the sample container it surrounds so that there is no heat exchange between them. Hence the heat capacity of sample (including the container) is calculated from the electrical energy supplied to the sample and the consequent temperature rise. At elevated temperatures, however, heat transfer due to radiation becomes more significant with temperature rise and this makes it difficult to maintain adiabatic conditions during the measurement. Mainly for this reason, isothermal calorimetry (drop method) has been employed above room temperature. In this method, enthalpies at various temperatures relative to a reference temperature, $H(T)-H(T_0)$, are measured in high precision and heat capacity is calculated by differentiating the enthalpy function. Nevertheless, high temperature adiabatic calorimetry is more suitable for investigations of the anomalous thermal effects taking place in a narrow temperature range such as phase transitions or for the studies on non-equilibrium states, annealing effect, *etc.*

As already mentioned, the problem of heat exchange must be considered for adiabatic calorimetry at high temperatures.[2] Limitation in the choice of construction materials also offers a serious problem. For these reasons, an adiabatic calorimeter has not been used frequently in a high temperature region for heat capacity measurements of substances with poor thermal conductivities, as compared with one used in a low temperature region. However, in recent years, several calorimeters with high accuracy up to 500 K or 1000 K have been reported by West and Ginnings,[3] Trowbridge and Westrum,[4] Karasz and O'Reilly,[5] Grφnvold,[6] and Leadbetter,[7] in which great attention was paid to the establishment of adiabaticity and the selection of construction materials. In our laboratory, two kinds of adiabatic calorimeters for low temperatures, from 1 to 20 K and 11 to 300 K, have been constructed[8,9] and studies carried out with them on various solid and liquid samples have been reported. We intended to extend our studies to the more elevated temperature region, since there are many substances indicating interesting thermal behavior above room temperature in view of the changes in state of aggregation or of chemical thermodynamics.

This paper describes an adiabatic calorimeter with an automatic control system which has been used for heat capacity measurements of solids and liquids in the temperature range 80—550 K. Although there was no essential alteration in the structure of this calorimeter in comparison with that[8] for low temperatures, some considerations for high temperature operation were made in the choice of construction materials. Heat capacity measurements of α-Al_2O_3 showed that the precision was within $\pm 0.3\%$ and the accuracy within $\pm 0.6\%$, which were sufficient for our purpose. The apparatus is employed mainly to study phase transitions in polyatomic ionic, ferroelectric, or liquid crystals and thermal behaviors in polymers, amorphous solids, or glasses and also to provide useful chemical thermodynamical data when combined with the measurements with low temperature calorimeters. Heat capacities of anhydrous magnesium acetate have been measured at 300—500 K for the glassy and crystalline states. The glass transition (T_g) of this substance[10] was also studied in detail.

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* Present address: Japan Information Center of Science and Technology, Nagata-cho, Chiyoda-ku, Tokyo.

** Present address: Musashi Works, Hitachi Ltd., Kodaira, Tokyo.

1) For a detailed review and discussion of adiabatic calorimetry, see "Experimental Thermodynamics," Vol. 1, ed. by J. P. McCullough and D. W. Scott, Butterworths, London (1968).

2) E. D. West, *J. Res. Natl. Bur. Stand.*, **67A**, 331 (1963). Also see Chap. 4 by D. C. Ginnings and E. D. West and Chap. 9 by E. D. West and E. F. Westrum, Jr., in Ref. 1.

3) E. D. West and D. C. Ginnings, *J. Res. Natl. Bur. Stand.*, **60**, 309 (1958).

4) J. C. Trowbridge and E. F. Westrum, Jr., *J. Phys. Chem.*, **67**, 2381 (1963); J. C. Trowbridge, Doctoral Dissertation, Univ. of Michigan (1963).

5) F. E. Karasz and J. M. O'Reilly, *Rev. Sci. Instr.*, **37**, 255 (1966).

6) F. Grφnvold, "Thermodynamics," Vol. 1, International Atomic Energy Agency, Vienna (1966).

7) A. J. Leadbetter, *J. Phys. C, Ser.* 2, **1**, 1481 (1968).

8) H. Suga and S. Seki, This Bulletin, **38**, 1000 (1965).

9) M. Sorai, H. Suga, and S. Seki, *ibid.*, **41**, 312 (1968).

10) N. Onodera, H. Suga, and S. Seki, *ibid.*, **41**, 2222 (1968).

Construction of the Calorimeter

The cross sectional view of the calorimeter is shown in Fig. 1. The main body of the calorimeter consists of a sample container A, an adiabatic jacket C which is separated into three parts C_a (side), C_b (top), and C_c (bottom), an upper block D, an outer jacket E, and a vacuum vessel H. The sample container A is suspended by three thin constantan wires from the top portion of the adiabatic jacket. The adiabatic jacket is in turn suspended from the copper upper block D, which serves together with the copper outer jacket E for attenuating the thermal effects from their surroundings and for making favorable adiabatic conditions in the inner system by controlling each heater current.

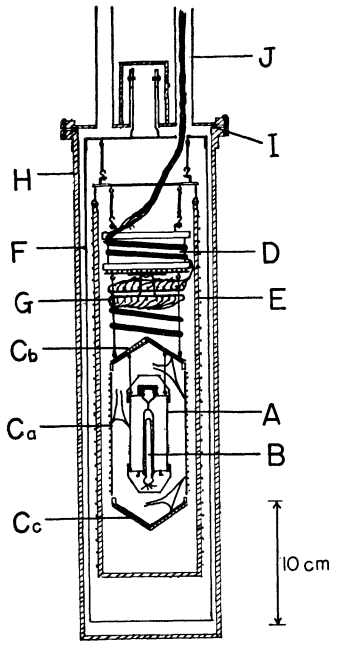

Fig. 1. Cross sectional view of the calorimeter.
A: Sample container B: Thermometer C_a, C_b, and C_c: Adiabatic jackets D: Upper block E: Outer jacket F: Radiation shield G: Terminals H: Vacuum vessel I: Gasket J: Stainless steel pipe

The sample container, whose schematic drawing is shown in Fig. 2, is made of copper, 0.3 mm thick and chromium-plated, with a central reentrant well for setting a combined thermometer-heater. Eight radial fins N silver-soldered to the well and to the inside wall of the container provide good thermal contact of the sample with the container assembly. The size of the main body of the container is 3 cm in diameter and 6 cm long. The total weight of the container is about 70 g and its effective capacity is *ca.* 35 cm^3. A sample entrance at the center of the top of the container is 8 mm in inner diameter. It is crucial to select a suitable seal in order to keep the container gas-tight at all temperatures. A silicone rubber disc-shaped gasket L cut from a sheet 1 mm thick was eventually found to be useful at least up to 550 K. A copper lid is screwed down tightly to the entrance by hand.

The container is equipped with a Leeds & Northrup

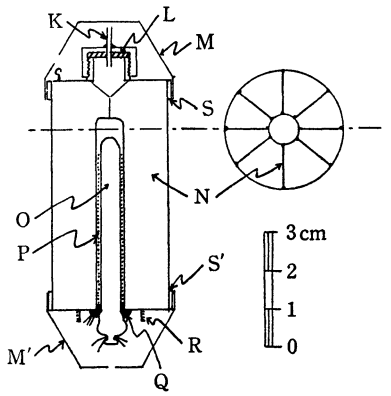

Fig. 2. Cross sectional view of the sample container.
K: Cu tubing L: Gasket M, M': Caps N: Radial fins O: Platinum resistance thermometer P: Heater Q: Beryllia cement R: Spool S, S': Cu bands

capsule type (type 8164) platinum resistance thermometer O, for the temperature measurement of the sample. Around the thermometer, approximately 70 ohms of doubly glass-wound B. & S. #36 constantan wire (Driver-Harris Co.) P is wound non-inductively and as closely as possible, which serves as the calorimeter heater for supplying energy to the sample container. Although the well is machined so as to be well fitted with the combined thermometer-heater, it was necessary to fill the gap with a beryllia cement Q at the entrance portion of the well in order to reduce the temperature gradient in the container assembly. It was confirmed that this device suppressed the temperature distribution to within 0.2 K in the container assembly even in the heating process at 550 K. All the lead wires from the combined thermometer-heater are wound several times around a spool R at the bottom of the container.

Since the outlines of the surface of the top and the bottom of the container are not completely uniform, it is very likely that a significant temperature distribution will arise in these parts particularly during the course of heating. To reduce this, two copper caps M and M' (0.5 mm thick and chromium plated) are closely fitted mechanically to copper bands S and S' soldered to the top and the bottom of the container.

The adiabatic jacket is also of chromium-plated copper and is made as thin as possible (0.5 mm) in order to get quick thermal response. Each part of the jacket, C_a, C_b, and C_c, is equipped with a separate heater: a glass-insulated B. & S. #36 constantan wire wound non-inductively. Adiabatic condition is maintained by adjusting the current in each heater independently. Around C_a are also wound the lead wires from the sample container and those of the thermocouples which detect the temperature differences between A and C_a, C_a and C_b, and C_a and C_c. All the wires are fixed and insulated with silicone varnish or Teflon tapes, aluminum foils being wrapped over them.

Temperature difference between the outer surface of the container and the inner surface of C_a is detected by a six junction (in series) copper-constantan thermocouple. Temperatures of C_b and C_c are also detected differentially against that of C_a by a similar method. The junctions of these thermocouples are insulated with

small, thin pieces of mica, protected with aluminum foils, and inserted tightly into stainless steel bands and pockets set on the sample container and the jacket, respectively. These thermocouples provide an error voltage of about 240 μV per degree of differential at 300 K.

Temperatures of D and E are controlled to an appropriate level lower than that of the adiabatic jacket depending on the operating temperature so that adiabaticity of the interior system may be best maintained.

For measurements in an elevated temperature region (higher than 100°C), another radiation shield F of nickel-plated brass is installed, which remarkably decreases the heat loss due to radiation toward the outside.

All the lead wires employed are Polyflon-coated B. & S. #38 copper wires prepared by immersing the cotton-wound copper wires in Daikin Polyflon dispersion D-1, and then decomposing cotton and sintering the adhered Polyflon at 380°C in a vacuum.[11] All the lead wires are brought to a copper terminal G, wound around the upper block, and then taken out of the calorimeter assembly through one of three stainless pipes J which suspend the assembly, and through a Picein seal. The lead wires are soldered to G by a Kyowa Shôji NEIS 105 silver solder which is composed of silver-cadmium alloy and has a relatively low melting point (*ca.* 380°C).

The interior of the brass vacuum vessel H, which is immersed in a liquid nitrogen or ice temperature Dewar vessel, is kept in high vacuum of 10^{-5} to 10^{-6} Torr by a seal fitted in a rectangular groove (3 mm in width and 1 mm in depth). For the seal a rectangular cross-sectional lead gasket or a neoprene rubber *O*-ring I is found to be suitable in liquid-nitrogen or ice temperatures respectively. It is difficult to attain a vacuum higher than 5×10^{-4} Torr at temperatures higher than 500 K, probably due to some decomposition of silicone varnish used as an insulating adhesive.

Temperature Measurements and Calibration of the Thermometer

Resistance of the platinum resistance thermometer is measured by a Leeds & Northrup type G-2 Mueller Bridge, a Riken high sensitivity galvanometer, and a telescope-scale system in which the distance between the galvanometer and the scale is *ca.* 5 m. This arrangement enables us to measure the temperature to 2×10^{-4} deg in the range 80—550 K.

The working thermometer was calibrated in the conventional manner against a standard thermometer of a similar type calibrated at the National Bureau of Standards (NBS), U.S.A., based on the International Temperature Scale of 1948. The relation between the difference in the resistances of the working and standard thermometers ΔR and the resistance of the standard thermometer R_s can be expressed as follows:

$$\left.\begin{aligned} \Delta R \times 10^5 &= 84.857R_s - 112.5, \\ &\text{for } 4.8 < R_s \leqq 24 \text{ (80—260 K)}, \\ \Delta R \times 10^5 &= 84.857R_s - 112.5 - 0.244(R_s - 24)^2, \\ &\text{for } 24 \leqq R_s < 53 \text{ (260—550 K)}, \end{aligned}\right\} \quad (1)$$

where both R_s and ΔR are in ohm. The accuracy of temperature measurements is estimated to be within ±0.01 deg in absolute value and within ±0.0001 deg in relative value.

Energy Measurements

The circuit for supplying and measuring the electrical energy to the calorimeter heater is nearly the same as the one reported.[8] The calorimeter heater is powered by three 6 V storage batteries in series and the current is adjusted with a six-dial decade resistor (0 to 111, 111.1 ohm). The current and the potential drop across the calorimeter heater are measured in the conventional way with an Otto-Wolff type KDE-3 five-dial potentiometer in conjunction with a Shimadzu galvanometer (type R, class C). Correction is made for the current passing through the by-pass resistors (1 and 100 kΩ) in computing the net current flowing through the calorimeter heater.

To avoid a correction for the small amount of heat generated in the current lead between the sample container and the adiabatic jacket, one of the potential leads terminates just near the container and another just near the jacket, as suggested by Ginnings and West.[12]

The energy input is started and stopped automatically with an electronic timer synchronized with a transistor clock and the heating interval is measured and presented on a digital counter with an accuracy of 0.05% or better.[8]

Adiabatic Control System

Detection of temperature differences for the maintenance of adiabaticity are carried out by use of thermocouples between C_a and A (temperature difference ΔT_1), between C_a and C_b (ΔT_2), between C_a and C_c (ΔT_3), between C_a and D (ΔT_4), and also between C_a and E (ΔT_5). The error signal given as thermal electromotive force of the thermocouples is fed into each servo-circuit, which controls the heater current of each portion of the jacket by on-off control mode.

The error voltage corresponding to ΔT_1 is amplified with an Ohkura AM-1001 microvoltmeter (±10 μV in full scale) by a factor of 2000 and the output voltage is recorded on an Ohkura electronic recorder, while a cum connected with the pen-drive-motor shaft actuates two micro-switch relays and controls the heater current of C_a. The half-span of the recorder is 1 mV, which corresponds to 2×10^{-3} deg at 300 K. The error voltage due to ΔT_2 is amplified with a Tôa type AD-4 DC amplifier and then with a DC difference amplifier which uses a 12AX7. The output voltage is fed into a grid of 6AQ5. which actuates a microswitch for the control of the heater current for C_b. The error signals due to ΔT_3 and ΔT_5 are transformed into deflection of the mirrors of Shimadzu galvano-

11) Polyflon coated wires were inevitably used, as more favorable glass-wound thin copper wires could not be obtained at the time of construction.

12) D. C. Ginnings and E. D. West, *Rev. Sci. Instr.*, **35**, 965 (1964).

meters (type R, class C). Light beams which have passed through optical choppers are reflected by the mirrors and detected with the photoelectric tubes of electronic photo-relays, which actuate microswitches for the control of heater current. The temperature difference ΔT_4 is detected by an Ohkura type AM-101 microvoltmeter ($\pm 25\ \mu$V in full scale) and is controlled manually, since the temperature of the upper block little influences the inner system.

Measurements of Heat Capacity

After the specimen was packed into the sample container, a small amount of helium gas, which facilitates attainment to thermal equilibrium in the container, is introduced through a narrow copper tube K. The tube is then pinched off to keep it gas-tight.

The temperature of the sample is measured at approximately one minute intervals for about ten minutes after adiabaticity and internal equilibrium are nearly established. Temperature drift was found to be within 3×10^{-4} deg·min^{-1} below room temperature, but gradually increases with temperature rise ultimately to 3×10^{-3} deg·min^{-1} at 550 K.

The electric power produced in the calorimeter heater is obtained by measuring the heater current at 0.21 τ and 0.79 τ and the voltage at 0.50 τ according to the Giauque method,[13] where τ is the heating interval (usually 1000 sec in our experiments). The energy supply is adjusted so that the temperature elevation in this heating period can be 4—6 deg in the empty case and 2.5—4 deg in the loaded one. For these heating rates, internal equilibrium in the sample container is attained within 5 min after heating was stopped.

When the automatic adiabatic control works normally, the temperature difference ΔT_1 is kept, in the equilibration period within $\pm7\times10^{-4}$ deg below room temperature and within $\pm3\times10^{-3}$ deg at 550 K, and in the heating period within $\pm4\times10^{-3}$ deg and within $\pm1\times10^{-2}$ deg, respectively. The ΔT_2 and ΔT_3 are controlled at least within 0.15 deg even in the heating period at 550 K.

Calibration of the Calorimeter

The reliability of the present calorimeter was examined by the measurements of heat capacity of the Calorimetry Conference standard sample of α-Al_2O_3 (synthetic sapphire).[14] Approximately 70 g of this sample was used for calibration. The heat capacity of the sample corresponds to about 70% of the total heat capacity above room temperature (including the container), while only about 30% at the lowest temperature employed.

The heat capacity of the sample was given by subtracting the smoothed heat capacity data of the empty cell (r.m.s.: 0.21%) from the total heat capacity. In Table 1 are tabulated the observed and smoothed molar heat capacities of α-Al_2O_3. As shown in Fig. 3 most of the observed points fall within $\pm0.3\%$ in relative deviation from the smoothed curve. The r.m.s. deviation is 0.25%. The difference of our smoothed values from those of Furukawa *et al.*[15] falls almost within $\pm0.6\%$ from 80 to 550 K. This agreement is sufficient for our present purpose.

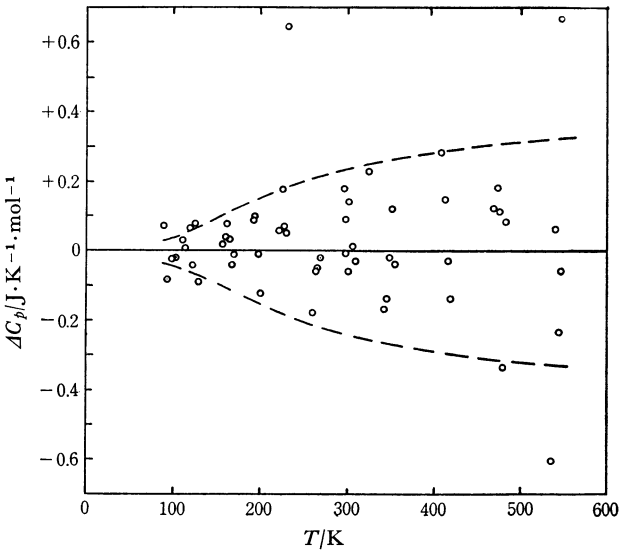

Fig. 3. Deviations of experimental heat capacities ΔC_p of α-Al_2O_3 from a smooth curve. Dashed curves show $\pm0.3\%$ of C_p.

Analysis of Errors

In order to account for the scattering of the experimental points as well as the possible occurrence of some systematic errors, the order of magnitude of errors due to the following instrumental and operational sources was estimated.

(1) Temperature Measurements. Errors in reading the resistance values do not exceed 0.5×10^{-3} deg in terms of temperature even at elevated temperatures where increase in the resistance with temperature reduces the sensitivity of the galvanometer. Therefore, this error source is not of primary importance. However, arbitrariness in drawing the drift straight line to the midpoint of the heating period, on a resistance *vs.* time curve, permits $\pm0.15\%$ error at the highest temperature.

(2) Energy Measurements. Total contribution to the error from instruments such as the potentiometer, the timer, and the standard resistances is estimated to be within $\pm0.05\%$.

(3) Heat Transfer due to Non-adiabaticity. Erroneous heat transfer may arise from or to the sample container owing to the transient non-adiabaticity which reveals itself as the error voltage of the thermocouples. This is significant just after the beginning and the end of the heat supply. This error can be estimated by evaluating various heat transfer coefficients between the container and the adiabatic jacket, which are subdivided as follows.

13) W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

14) This sample was synthesized by the NBS and obtained through their courtesy.

Table 1. Experimental and smoothed values of the molar heat capacity of the calorimetry conference standard sample of α-Al_2O_3 (Sapphire)

T (K)	C_p (exptl) ($J \cdot K^{-1} \cdot mol^{-1}$)	C_p (smoothed) ($J \cdot K^{-1} \cdot mol^{-1}$)	T (K)	C_p (exptl) ($J \cdot K^{-1} \cdot mol^{-1}$)	C_p (smoothed) ($J \cdot K^{-1} \cdot mol^{-1}$)
89.43	9.770	9.696	269.29	72.53	72.55
94.31	11.035	11.119	295.00	78.85	78.67
98.86	12.523	12.547	298.20	79.44	79.35
103.12	13.942	13.963	298.49	79.40	79.41
111.33	16.899	16.868	301.88	80.27	80.13
115.07	18.265	18.257	301.95	80.08	80.14
118.64	19.682	19.617	305.53	80.89	80.88
122.08	20.92	20.96	309.15	81.58	81.61
125.38	22.35	22.27	324.64	84.79	84.56
128.57	23.46	23.55	341.81	86.96	87.13
157.34	35.02	35.00	345.19	87.52	87.66
160.08	36.13	36.09	348.55	88.17	88.19
162.76	37.22	37.14	351.88	88.83	88.71
165.39	38.20	38.17	355.20	89.18	89.22
167.97	39.18	39.22	408.21	96.93	96.65
170.50	40.20	40.21	411.96	97.28	97.13
192.72	48.70	48.61	415.69	97.56	97.59
195.42	49.75	49.65	419.41	97.91	98.05
198.08	50.59	50.60	469.44	103.67	103.55
200.69	51.38	51.50	472.26	104.01	103.83
221.60	58.64	58.58	475.07	104.21	104.10
224.59	59.74	59.56	477.86	104.02	104.36
227.54	60.60	60.53	480.63	104.70	104.62
230.46	61.53	61.48	534.99	108.33	108.94
233.33	63.05	62.40	538.97	109.26	109.20
259.23	69.73	69.91	542.94	109.21	109.45
262.62	70.74	70.80	546.85	109.63	109.69
265.97	71.61	71.66	550.77	110.60	109.93

a) Heat Transfer by Lead-Wire Conduction: This includes the conduction through the lead wires of the combined thermometer-heater, the thermocouples brought to the container, and the constantan wires suspending the container. These are found to contribute below 2×10^{-3} W·deg^{-1} to heat transfer coefficient.

b) Heat Transfer by Gas Conduction: Thermal conductivity of gas is independent of the pressure if the mean free path of the gas λ is much smaller than the size of space in consideration L, and is proportional to the pressure if $\lambda \gg L$, where L is $\sim$1 cm in the present case. Below 500 K, the latter condition holds so sufficiently that heat transfer coefficient is easily evaluated to give approximately 1×10^{-5} W·deg^{-1}. Above 500 K, however, estimation becomes very difficult because λ gets nearer to L owing to the deterioration of vacuum. However, this value probably does not exceed 5×10^{-3} W·deg^{-1}.

c) Heat Transfer by Radiation: This effect becomes rapidly important with increase in temperature. Although the geometrical shape in the present apparatus is rather complicated, the standard equation for the radiative heat transfer[2] is sufficient for rough calculation. If we assume 0.1 both for the emissivities of two parallel planes with small temperature difference (the value is overestimated for polished metal surfaces), heat transfer coefficient by radiation amounts to 3×10^{-3} W·deg^{-1} at 300 K and 15×10^{-3} at 500 K.

Thus, the summation of all these effects give 5×10^{-3} W·deg^{-1} at 300 K and 2×10^{-2} W·deg^{-1} at 500 K. These values explain that under ordinary experimental conditions errors in measured heat capacity caused by transient non-adiabaticity may become $\pm 0.05\%$ at 300 K and $\pm 0.25\%$ at 500 K in maximum estimate. At higher temperatures, therefore, considerable part of the actual errors can be attributed to this source. In practice, fluctuation in the observed heat capacity is not so strongly dependent on temperature as expected from the preceding estimate (see Fig. 3). This may be due to the overestimate of the values for emmissivity.

(4) Heat Transfer due to Thermal Inhomogeneities. Important systematic errors arise frequently from the thermal inhomogeneities on the outer surface of the container or the inner surface of the adiabatic jacket. In the most probable case, heat exchange is caused by generation of temperature distribution on the surface of the container during the heating period. The greater part of this error is compensated if the temperature gradients in the empty and the loaded measurements are alike. Generally, however, the dif-

ference in thermal conductivity, heat capacity, and density in the container between the two cases prevents this situation.[2]

This error is so difficult to estimate that great care must be taken about the design of the container to avoid the generation of the surface temperature gradient. We confirmed experimentally that the beryllia cement as a thermal conducting adhesive between the body of the container and the combined thermometer-heater as well as the two caps on the top and the bottom parts of the container served this purpose. Indeed, an agreement of our data with those of Furukawa *et al.*[15] and also with those of other workers[3-7] is regarded as an evidence showing that the sources of systematic error are sufficiently eliminated in the construction of the present apparatus.

Heat Capacities of Anhydrous Magnesium Acetate

Anhydrous magnesium acetate was prepared by dehydration of magnesium acetate tetrahydrate in a vacuum (10^{-3} Torr) at *ca.* 50°C for 7 days. Further dehydration was carried out in the sample container in a high vacuum (10^{-5} Torr) at 310 K for 20 hr. The dehydrated salt has been found to be in the glassy state.[10] Heat capacities of the glassy sample are given in Table 2 and Fig. 4. The glass transition temperature is found to be located at *ca.* 470 K. The glassy sample crystallizes abruptly when it is heated above 475 K. The heat capacities of the crystalline sample thus formed are also given in Table 2 and Fig. 4. From the temperature drift curves during the measurements and the temperature elevation due to crystallization, the heat of crystallization was estimated to be *ca.* 11.4 kJ mol.$^{-1}$

Table 2. Heat capacity of glassy and crystalline magnesium acetate (MW=142.397)

T (K)	C_p (J·K^{-1}·mol^{-1})	T (K)	C_p (J·K^{-1}·mol^{-1})
Glassy		463.29	30.349
310.02	20.452	466.56	34.065
315.42	20.671	469.22	36.691
320.78	20.887	471.23	38.533
326.06	21.109	473.47	39.194
331.32	21.235		
336.54	21.457	Crystalline	
341.71	21.641	348.14	21.613
346.83	21.813	354.39	21.909
366.21	22.578	361.35	22.226
371.25	22.700	368.99	22.591
376.25	22.981	376.56	22.858
381.37	23.223	383.92	23.110
386.83	23.359	391.28	23.429
392.23	23.681	398.56	23.746
397.60	23.923	405.75	24.089
402.92	24.007	417.35	24.485
409.12	24.384	424.33	24.773
415.18	24.732	431.24	25.027
421.22	24.963	444.20	25.612
427.27	25.219	450.87	26.097
433.36	25.379	457.46	26.114
439.70	25.974	464.84	26.359
445.55	26.139	472.31	26.685
451.39	27.082	479.72	26.834
452.04	26.633	487.00	27.213
456.54	26.995	494.19	27.421
459.94	28.158	501.28	27.823

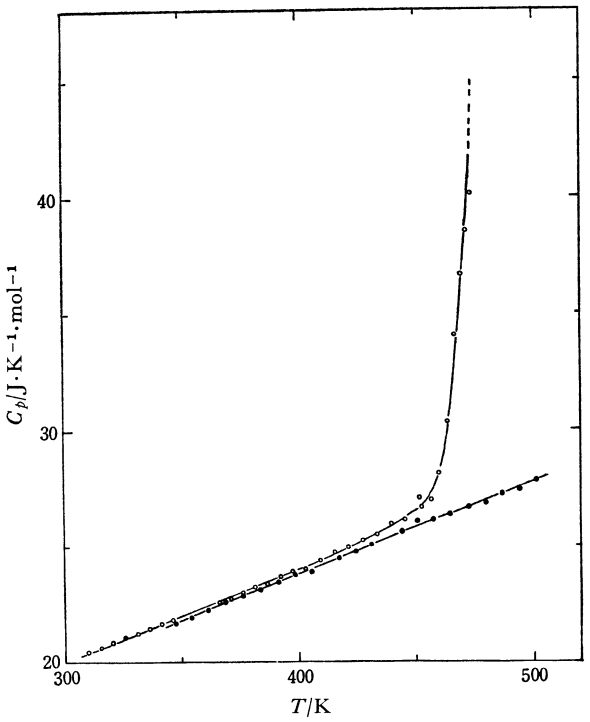

Fig. 4. Molar heat capacities of anhydrous magnesium acetate.
○: glassy state ●: crystalline state

Summary

An adiabatic calorimeter for the heat capacity measurements of solid or liquid sample in the temperature range 80—550 K was constructed with the main purpose of investigating various interesting thermal behaviors of substances demonstrated above room temperature. Most of the temperature control systems to keep an adiabatic condition are semi-automatic and thus need only one operator. The working platinum resistance thermometer was calibrated against a standard one calibrated by the NBS. The reliability of this apparatus was demonstrated through the measurements of heat capacity of the Calorimetry Conference sample of α-Al_2O_3. The results show that the relative errors in heat capacity values are almost within ±0.3% and the smoothed curve values agree with those of Furukawa *et al.* almost within ±0.6% over the whole temperature range available. The non-systematic errors are to some extent explainable in terms of the order of magnitude estimation based on the experiments. Heat capacities of amorphous and crystalline magnesium acetate were measured at 300—500 K. Glass transition phenomenon was observed at *ca.* 470 K. Heat of crystallization was also estimated to be 11.4 kJ·mol^{-1}.

15) G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, *J. Res. Natl. Bur. Stand.*, **57**, 67 (1956); D. C. Ginnings and G. T. Furukawa, *J. Amer. Chem. Soc.* **75**, 522 (1953).