

Specific Heat of Amorphous State. II

True Specific Heat of Glassy State*

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Synopsis

The calorimetric method for the determination of the true specific heat of the amorphous substances in the relaxation process was proposed and applied to glycerol and isobutanol. From the measurements in which the thermal history of the substance and the heating rate were varied, it was shown that the abrupt change in the usual specific heat of glassy substance near T_g was apparent one, being due to the relaxation in the internal configurational change.

I. Introduction

The residual entropy of glassy substance estimated from its specific heat curve including the abrupt decrease near T_g has been attributed to the thermodynamical unstability of the glassy state⁽¹⁾. The abrupt decrease in specific heat curve near T_g has been considered to be due to relaxation effect. For instance, F. Simon⁽²⁾, and W. Kauzmann⁽³⁾ explained the fact by the inability of the structure to reach its equilibrium configuration below T_g (1949). On the other hand some researchers supposed it to be due to a phase transition⁽⁴⁾, because the anomalous change in the specific heats near T_g is very similar to that in the phase transition of the second kind. Such misinterpretations may be due to the scantiness of positive experimental proof and analytical treatment of the specific heat below T_g .

Oblad and Newton⁽⁵⁾ proposed a new calorimetric method of obtaining the equilibrium value of the specific heat of glassy substance below T_g . Their method consists in measuring the difference between the total heat contents at temperature below T_g and room temperature by "mixing method", but it is somewhat tedious and abandons an advantage of "adiabatic calorimetry".

In the preceding paper⁽⁶⁾ the present authors considered the relaxation in the energy interchange between kinetic and configurational degree of freedom in glassy substances and concluded that the apparent specific heat was expressed by

$$c = c_1 / \left\{ \frac{c_1}{c_1 + c_2} - \frac{c_2}{c_1 + c_2} \frac{\tau}{t} (e^{\frac{t}{\tau}} - 1) \right\},$$

* The 804th report of the Research Institute for Iron, Steel and Other Metals.

(1) F. Simon, *Ergeb. Exact. Naturwiss.*, **9** (1930), 243.

(2) F. Simon, *Endeavour*, **8** (1949), No. 32.

(3) W. Kauzmann, *Chem. Rev.*, **43** (1948), 219.

(4) R. Buchdehl and L. E. Nielsen, *J. App. Phys.*, **21** (1950), 482.

(5) A. G. Oblad and R. F. Newton, *J. Am. Chem. Soc.*, **59** (1937), 2495.

(6) T. Haseda, A. Ôtsubo and E. Kanda, *Sci. Rep. RITU*, **A2** (1950), 16.

where c_1 is the kinetic contribution to c , c_2 is the configurational specific heat, t is the duration of heat supply in the specific heat measurement by the Nernst method, and τ is the relaxation time for configurational change in the structure of glassy substance. Thus the temperature range of the characteristic decrease in the specific heat will vary with the heating rate in the measurement. The true specific heat curve, which corresponds to the case $t/\tau \gg 1$ in the preceding formula, can be obtained by the modification of adiabatic calorimetry of ordinary heating rate. The average specific heat between two temperatures below T_g is determined from the difference of heat contents which are necessary to raise the sample from the respective temperature to a temperature at which $t/\tau \gg 1$. This point is several degrees above T_g , and between this point and T_g , the specific heat curve represents a large hump. The hump is due to the absorption of energy for the configurational change which would have taken place at the lower temperature. If the substance could attain the complete thermal equilibrium at every stage during heating in the calorimetry, the energy equal to the area of this hump would be absorbed without lag for the configurational change keeping step with the temperature rise in the course of measurement. Measurements were carried out on glycerol and iso-butanol.

II. Measuring method and experimental results

1. Method

The sample in Nernst type calorimeter was slowly cooled down below the softening point T_g and kept at a constant temperature, say, T_1 (Fig. 2) for many hours (24 to 90 hours). A photoelectric relay method shown in Fig. 1 was used for this purpose, the temperature being kept constant within $\pm 0.05^\circ$. Then the specific heat measurement was performed through a continuous adiabatic process, i.e. the calorimeter can was heated with constant rate and the temperature was measured from T_1 to T_0 continuously. From the rate of heating and the rate of temperature rise, an ordinary specific heat was determined. The results were b_1 or b_1' , b_1'' , b_{1s} in Fig. 2 varying with the duration of stay at T_1 . For the sample which had been cooled down to any point above T_g , the values were as shown in the curve b_0 . The difference between b_0

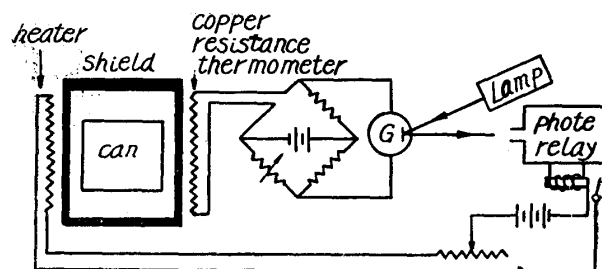


Fig. 1. Arrangement for keeping the sample at constant low temperature for long time.

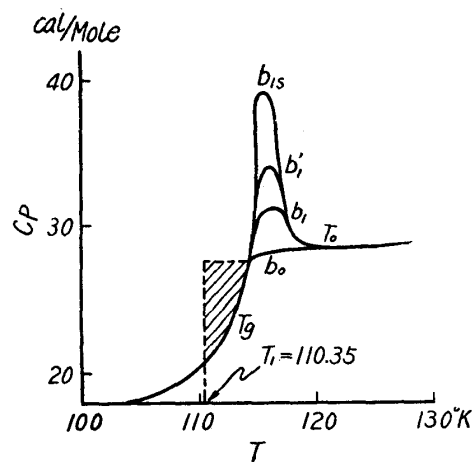


Fig. 2. Apparent specific heats of iso-butanol with different degrees of internal stabilization.

and b_1 or b_1' ,, was considered to be due to the relaxation of the configurational change which could not take place together with the rise of kinetic energy corresponding to the heating rate. Accordingly, the heat energy corresponding to the hump between T_g and T_0 was equal to the difference between the heat contents of configurational part at T_1 and T_g . The area of the hump increased with the duration of stay of the sample at T_1 and reached the saturation amount. The relation is shown in Fig. 3. The mean specific heat of the configurational part between T_1 and T_g is equal to the heat content divided by $(T_g - T_1)$. The peak in the apparent specific heat curve also increased with the fall of temperature at which the sample stayed before the heating for the adiabatic calorimetry.

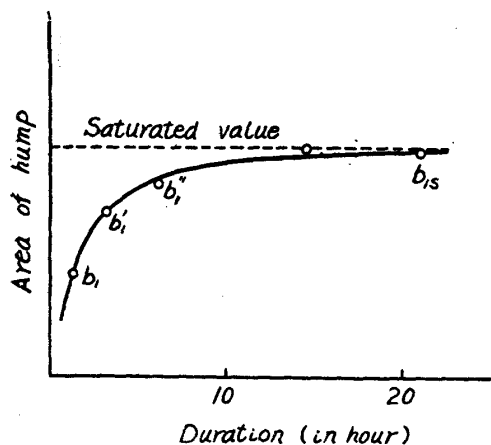


Fig. 3. Variation of the area of hump in the specific heat curve with the duration of stay of the sample below T_g .

In Fig. 4, the peaks b_1 and b_2 correspond to the staying temperature T_1 and T_2 , respectively. The mean specific heat difference between the configurational parts at T_1 and T_2 is determined from the difference in the area of each maximum hump. The difference between a_1 and a_2 , of course, means the difference between the kinetic parts of the specific heat at T_1 and T_2 . The true specific heat C was obtained by adding the configurational part thus determined to the kinetic part or the apparent specific heat as shown in Fig. 4.

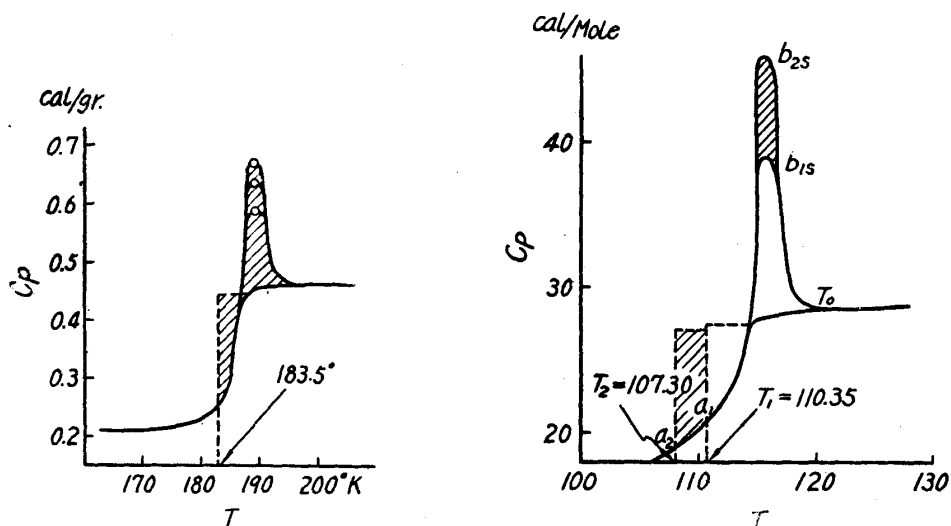


Fig. 4a. Method to obtain the true specific heat, (glycerol) two shaded areas are equal.

Fig. 4b. Method to obtain the true specific heat, (for isobutanol) two shaded areas are equal.

2. Experimental results

The results in glycerol and isobutanol were shown respectively in Fig. 5 and Fig. 6. Thus the true specific heat curves run along the extension of those for

the supercooled liquid.

In Fig. 6 the crystallization of glycerol above T_g is also represented in the specific heat curve. The tendency of crystallization was not observed in this sample, however long the stay in the supercooled state might be, provided that it had never been cooled down below T_g . However, once cooled down below T_g , the sample often crystallized at a certain temperature above T_g . If the specific heat measurement was carried out continuously with the sample in which the crystallization started, the generation of heat of crystallization would cause the decrease in apparent specific heat value. Oblad and Newton⁽⁵⁾

reported that the tendency of crystallization was observed at the temperature below T_g . In our opinion, however, it is difficult to clarify, by the mixing method, whether the crystallization occurs at a temperature above or below T_g .

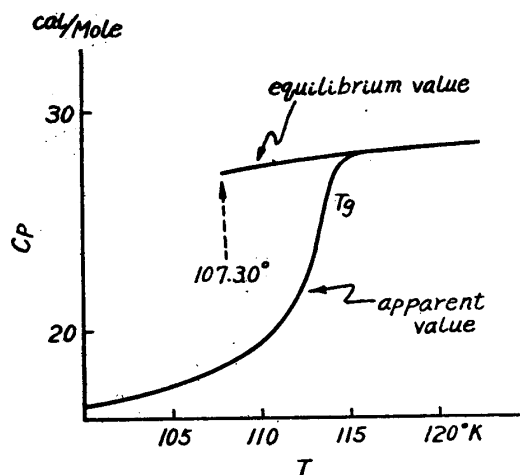


Fig. 5. True specific heat of isobutanol.

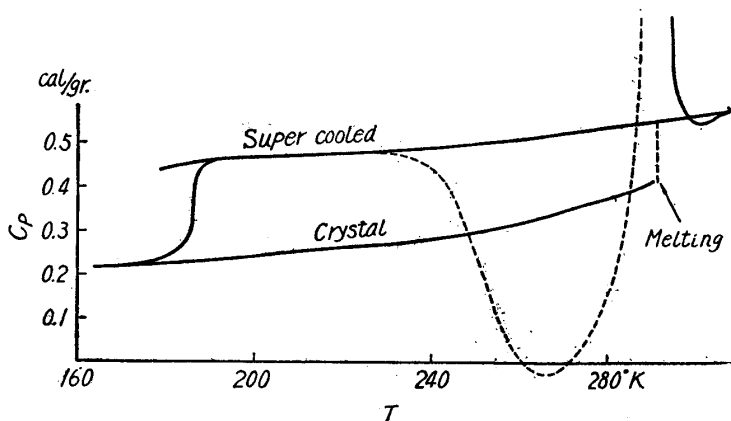


Fig. 6. Specific heat of glycerol.

III. Discussion

In order to show that the lower part of the usual specific heat curve in glassy substance below T_g does not represent the true specific heat of any phase, stable or unstable, the following experimental results will be supplemented.

(i) After switching off the heater in calorimetry the temperature changes of the sample (isobutanol) which was kept at a certain temperature below T_g for a long duration are shown in Fig. 7. The upper most temperature reached by heating is noted in each case. The temperature fall in the first one minute was due to the homogenization of the temperature in the sample. In the case of 115.5°K, a little above T_g , the temperature fell continuously because of the relaxation of the configurational change. In the cases of 107.0°K, far below T_g and 118.5°K, far above T_g , the temperatures were almost constant, because in the former the temperature was too low for relaxation and in the latter the relaxation had already been finished.

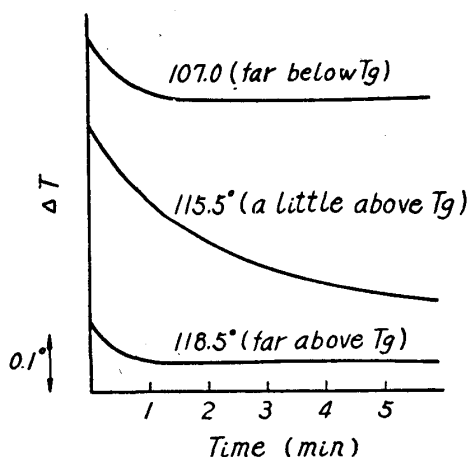


Fig. 7. The change in temperature of the sample in adiabatic calorimeter after cease of heating. The sample was thoroughly stabilized in its internal structure before commencement of heating. The figures added to each curve are the uppermost temperature where the sample was heated.

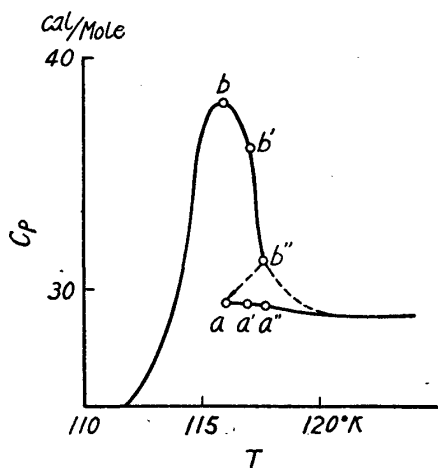


Fig. 8. Decreasing of the specific heat due to stay of the sample above T_g . (isobutanol)

(ii) When the specific heats were measured after the stay of the sample at the temperatures corresponding to the top of the hump or above it, for example, b , b' , or b'' in Fig. 8, the values fall to a , a' or a'' , which shows that the hump in the specific heat curve does not represent any state, stable or metastable, but is only spurious.

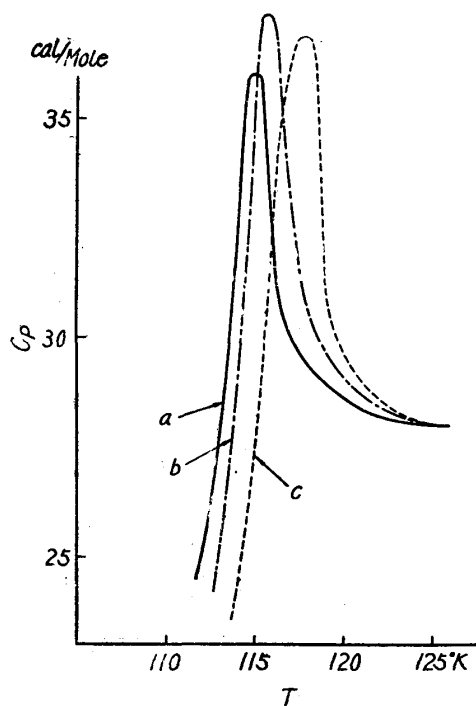


Fig. 9. Apparent specific heats with different heating rates in calorimetry, showing dependency of T_g on heating rates.

	heating current	rate of temperature rise
a :	33 mA,	$0.07^\circ/\text{min}$
b :	77 mA,	$0.4^\circ/\text{min}$
c :	112 mA,	$0.8^\circ/\text{min}$

(iii) It has been proved in the present experiments, that the temperatures of anomaly in the apparent specific heat curves depend on heating rates in the calorimetry as predicted in the preceding paper⁽⁴⁾. The examples for isobutanol are shown in Fig. 9. The apparent specific heat rises abruptly at the lower temperature, the larger the heating rate in the calorimetry is.

It is noted here that these figures do not correspond directly to the preceding formula between c and t/τ , because the formula is derived from the consideration that at the start of each measurement the sample is thoroughly stabilized in its configuration and has no frozen structure. In practice, however, there is always some frozen configurational structure which gives rise to the hump in these figures.

The residual entropy of the glassy substances should be determined from the true specific heat values as stated above*. The true specific heat value, however, cannot be determined even through the present method. The true equilibrium configuration at a too low temperature cannot be obtained even through long stay as much as one can realize in the laboratory**. If we could keep the sample at a certain constant low temperature for a sufficiently long time, the glass would reach true equilibrium configuration at each temperature in the long run. This would increase "order" of structure with falling temperature in its own way similar to that in the temperature region where true specific heat can be determined. Glass would follow down a potential valley of metastable state and gradually approach the internal structure quite similar to the crystal and its specific heat values would be shown, for instance, by a dotted curve in Fig. 10. But it remains uncertain whether the glassy substance retains any disorder in its internal structure and has any finite entropy at absolute zero.

The present method of calorimetry is also suitable for substances showing thermal hysteresis or super-cooling in phase transition, and can reveal the nucleation or growth of a new phase. An instance for glycerol is shown in Fig. 6, and it will be discussed in a succeeding paper.

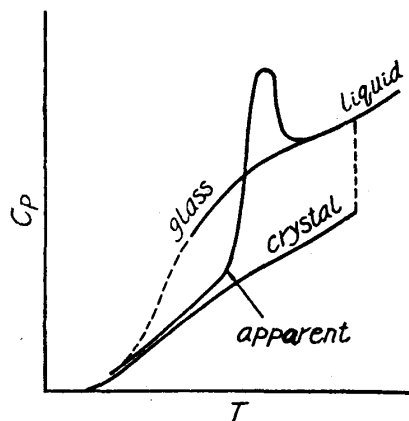


Fig. 10. Trend of specific heat of glassy substance at very low temperature.

* It should be remarked with emphasis that the characteristic figures of usual specific heat curve of glassy substances are frequently represented in some texts on thermodynamics or even in a monograph up to date. (e.g. Fowler and Guggenheim, *Statistical thermodynamics*, 1939, p. 219. A. Winter, *Formation et nature de l'état vitreux: Changements de Phases*, 1952)

** During the long stay at very low temperature, the sample might crystallize as Oblad reported, though it is very doubtful as mentioned before, and in practice the crystallization was not observed below T_g . Even if crystallization does not take place, it would take too much time to reach equilibrium configuration.