Structural Relaxation of Amorphous Solids and the Cybotactic Structure of Super-cooled Liquids

By

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Abstract

A sudden increase of the specific heat of an amorphous solid in its softening temperature range was considered to be caused by the dissolution of molecular aggregates, each composed of a considerable number of molecules, into free liquid molecules, and the temperature dependence of the specific heats of glycerol, ethyl alcohol and *dl*-lactic acid was found to be in good accord with that calculated by applying van't Hoff's reaction isochore to the decomposition of the molecular aggregates into free liquid molecules. As to the specific heats of these substances in their super-cooled liquid state above the softening temperature range, the previous wrong calculation on the decomposition of the cybotactic groups into free liquid molecules is revised. The general tendency of the temperature dependence of the specific heat of an amorphous substance in and above the softening temperature range is thus well understood by the presence of two kinds of molecular aggregates: the one composed of an immense number of molecules and the other the cybotactic group of only a small number of constituent molecules.

Introduction

A cybotactic theory of amorphous solids and supercooled liquids was proposed by the writer in previous papers.[1] In that theory the amorphous solid and the super-cooled liquid of a substance were considered to consist of free molecules of the substance and the cybotactic groups having the size of the order of the unit cell of the crystal. The cybotactic groups have no permanent stability. They are formed and decomposed spontaneously here and there in the liquid. The proportion in equilibrium of the total number of the cybotactic groups in reference to the total number of the free molecules is determined by the temperature, and it increases with decreasing temperature. When the temperature is lowered below the solidifying point of a substance,

1. U. Yoshida: These Memoirs, A, **23**, 207, 233 (1941)

without causing crystallization, it becomes supercooled. On further cooling the substance gets increasingly viscous; and at last it attains the glassy state or the state of amorphous solid, which is supposed to contain a considerable amount of cybotactic groups. The transformation from the amorphous solid to the super-cooled liquid state or *vice versa* takes place in the softening temperature range, and this transformation is accompanied by a remarkable sudden change in various physical properties of the substance, though it is not so sharp as in the case of melting of a crystal. In a paper[1] recently published the writer regarded the softening of an amorphous solid as the relaxation of the cybotactic structure of the substance; and by considering that the proportion between the numbers of the cybotactic groups and the free liquid molecules of a substance is in equilibrium above the softening temperature range, the contribution to the specific heat of the amount of heat required to decompose the cybotactic groups on raising the temperature was calculated with glycerol, ethyl alcohol and *dl*-lactic acid by applying van't Hoff's reaction isochore. However, as was already noticed,[2] the writer made a serious mistake there in calculating the concentration of the cybotactic groups and the free liquid molecules. Hence the calculation is revised and is described in the following, together with a similar calculation in the softening temperature range by considering the softening as due to the decomposition of the molecular aggregates each consisting of such a considerable number of molecules as about 200 into free liquid molecules.

Temperature Dependence of the Proportion of Free Liquid Molecules

Let the numbers of the free liquid molecules and of the cybotactic groups among the total number N of the molecules in a supercooled liquid of a substance be N_f and n_c respectively. If we represent by ν the number of the constituent molecules of a cybotactic group we have:

$$N = N_f + \nu n_c. \qquad \text{(1)}$$

Let us define the ratio x of the number of free molecules and the number of the total discrete particles which is equal to the sum of N_f and n_c as the degree of decomposition of the cybotactic groups. Then we get:

1. U. Yoshida: These Memoirs, A, **24**, 1 (1942)
2. U. Yoshida: These Memoirs, A, (1943)

$$x=\frac{N_f}{N_f+n_c}, \qquad \cdots\cdots(2)$$

and

$$1-x=\frac{n_c}{N_f+n_c}, \qquad \cdots\cdots(3)$$

and the reaction constant K_c becomes:

$$K_c=\frac{\left(\frac{N_f}{N_f+n_c}\right)^\nu}{\frac{n_c}{N_f+n_c}}=\frac{x^\nu}{1-x}. \qquad \cdots\cdots(4)$$

If we represent by T the absolute temperature, by R the gas constant refering to one gram mol, by M the molecular weight of a substance and by L the heat of decomposition of the cybotactic groups per one gram; then the reaction isochore takes the form:

$$\frac{d\log K_c}{dT}=\left(\frac{\nu}{x}+\frac{1}{1-x}\right)\frac{dx}{dT}=\frac{\nu(1-x)+x}{x(1-x)}\frac{dx}{dT}$$
$$=\frac{\nu ML}{RT^2} \qquad \cdots\cdots(5)$$

for a constant value of ν. From equation (5) we have:

$$\frac{dx}{dT}=\frac{\nu x(1-x)}{\nu(1-x)+x}\frac{ML}{RT^2}. \qquad \cdots\cdots(6)$$

The heat of decomposition L of the cybotactic groups changes with temperature. If we represent by L_c the heat of decomposition at the temperature T_c and by $(C_f-C_c)_c$ the difference between the specific heats of the free liquid molecules and the cybotactic groups refering to one gram at the same temperature, then the heat of decomposition L at a temperature T will be given approximately for a temperature range not very much wide by:

$$L=L_c+(C_f-C_c)_c(T-T_c). \qquad \cdots\cdots(7)$$

Thus if we put this value of L into equation (5) we get, on integration:

$$K_c=\frac{x^\nu}{1-x}=Ce^{-\frac{\nu M\{L_c-(C_f-C_c)_cT_c\}}{RT}+\frac{\nu M}{R}(C_f-C_c)_c\log T},$$

or

$$\frac{x}{(1-x)^{\frac{1}{\nu}}}=C^{\frac{1}{\nu}}e^{-\frac{M\{L_c-(C_f-C_c)_cT_c\}}{RT}+\frac{M}{R}(C_f-C_c)_c\log T} \qquad \cdots(8)$$

If we represent the degree of cybotactic decomposition at the temperature T_c by x_c, equation (8) becomes:

$$\frac{x_c}{(1-x_c)^{\frac{1}{\nu}}}=C^{\frac{1}{\nu}}e^{-\frac{M\{L_c-(C_f-C_c)_cT_c\}}{RT_c}+\frac{M}{K}(C_f-C_c)_c\log T_c} \quad \ldots\ldots(9)$$

Hence by combining equations (8) and (9) we obtain:

$$\frac{x}{(1-x)^{\frac{1}{\nu}}}=\frac{x_c}{(1-x_c)^{\frac{1}{\nu}}}e^{-\frac{M}{R}\{L_c-(C_f-C_c)_cT_c\}\left(\frac{1}{T}-\frac{1}{T_c}\right)+\frac{M}{R}(C_f-C_c)_c\log\frac{T}{T_c}}. \quad \ldots\ldots\ldots\ldots(10)$$

Next the relation between x and the proportion of the number N_f of free molecules to the total number N of molecules becomes by eliminating n_c from equations (1) and (2):

$$\frac{N_f}{N}=\frac{x}{\nu(1-x)+x}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

Differentiating equation (11) with respect to T we get:

$$\frac{1}{N}\frac{dN_f}{dT}=\frac{\nu}{\{\nu(1-x)+x\}^2}\frac{dx}{dT},$$

and by using equation (6) this reduces to:

$$\frac{1}{N}\frac{dN_f}{dT}=\frac{\nu^2x(1-x)}{\{\nu(1-x)+x\}^3}\frac{ML}{RT^2}=y'\frac{ML}{RT^2}, \quad \ldots\ldots(12)$$

where y' represents

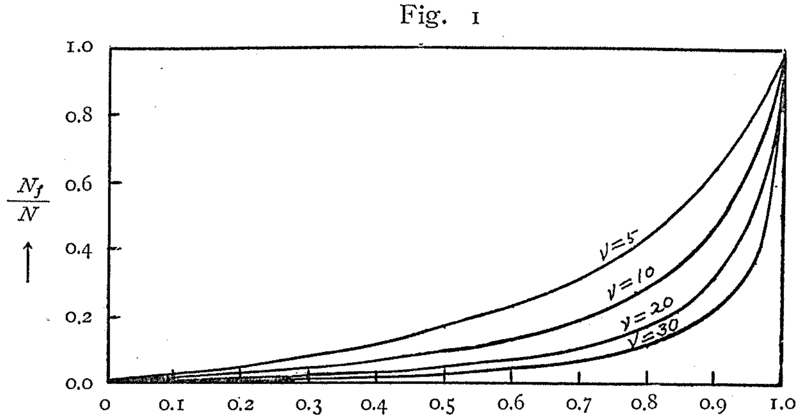
$$y'=\frac{\nu^2x(1-x)}{\{\nu(1-x)+x\}^3}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

Hence the heat quantity C_a required to decompose the cybotactic groups in one gram of the substance in raising the temperature by one degree is given by

$$C_a=L\left(\frac{1}{N}\frac{dN_f}{dT}\right)=y'\frac{ML^2}{RT^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots(14)$$

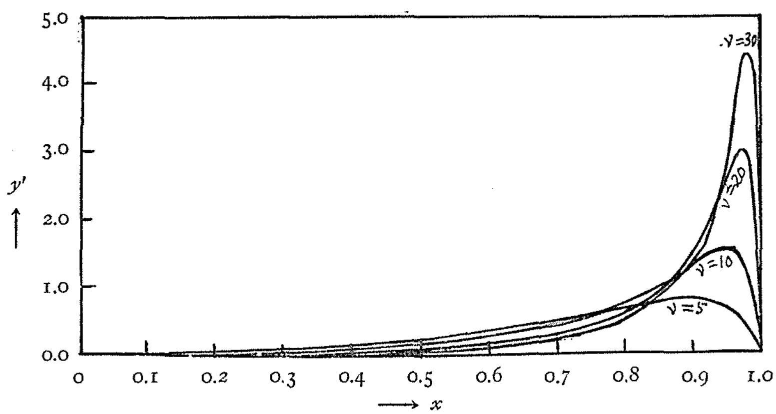
In the following calculations the numerical values of $x/(1-x)^{\frac{1}{\nu}}$,

Fig. 1



N_f/N and y' for various values of ν and x are required, and these relations are represented in graphs. Some of such graphs for comparatively low values of ν are represented as examples in Figs. 1 and 2, to show the general tendency of the dependence of the values of N_f/N and y' upon ν. The variation of the values of N_f/N and y' with x becomes more rapid with increase of the value of ν. When ν tends to infinity in the case of the melting of the adult crystal of a substance the values of y' and N_f/N remain zero at all values of x except at the extreme vicinity of $x=1$, where N_f/N increases abruptly to 1 and y' attains the maximum of infinity and drops suddenly to zero at $x=1$.

Fig. 2



Cybotactic Decomposition in the Super-cooled Liquid State

The substances of which the specific heats were measured at various temperatures both in their crystalline and super-cooled amorphous states are glycerol, ethyl alcohol and *dl*-lactic acid as is stated before. The temperature variation of the specific heats refering to one gram of these substances are shown in Figs. 3, 4, 5 and 6. In these figures the curves drawn in full line refer to the super-cooled liquid and the amorphous solid state, and those drawn in broken line represent the specific heats in the crystalline state. The specific heat curves for the crystalline state run almost linearly with temperature, and those for the super-cooled liquid and the amorphous solid rise very rapidly in the softening temperature range.

The specific heat of a substance in its super-cooled liquid state may be considered to consist of three parts: 1) The specific heat C_c of the cybotactic groups, which we shall consider to be roughly the same as that of the adult crystal at the same temperature. 2) The specific heat C_f of the free molecules which is supposed to be larger than C_c as will be imagined from the value of the specific heat of the liquid at the melting point where almost all the molecules are likely to be in the free state and not in the state of cybotactic configuration. 3) The heat C_d required for the decomposition of the cybotactic groups in raising the temperature. The temperature dependence of C_f is not obvious. However, as almost all the molecules are likely to be in the free state at the melting point of the adult crystal as was stated before, the specific heat observed for the liquid at this temperature may be taken approximately as that of free molecules. Thus, though it may be rough, the writer assumes that the ratio C_f/C_c remains the same for all temperatures below the melting point and is equal to that of the liquid and the adult crystal at the melting point of the latter; and the value C_f at any temperature is calculated from the value of the specific heat of the adult crystal at the same temperature, which is considered to be approximately the same as C_c.

In the softening temperature range of an amorphous solid its structural relaxation takes place as was stated before, and at the temperatures above that range the substance behaves as liquid by being super-cooled below its melting point. Thus by considering that the super-cooled liquid state is in cybotactic equilibrium we shall apply van't Hoff's reaction isochore as was described before to this case.

In carrying out the numerical calculation of the spcific heat we must select to begin with the reference temperature T_c at which the values of x, L, C_f and C_c for a certain value of ν must be determined. The writer took the temperature just above the softening temperature range as such reference temperature; and its value for ethyl alcohol, glycerol and *dl*-lactic acid are given in Tables II and III. In Table I the molecular weight and the melting point of these substances are tabulated together with the latent heat of fusion at the melting point. When the reference temperature T_c is determined as above, the specific heats C_f and C_c of the free liquid molecules and the cybotactic groups and their difference $(C_f - C_c)_c$ at this temperature can be calculated easily from the specific heat in the crystalline state at the same temperature by using the rough assumption described before. Thus once the value of the heat of decomposition L_c of the cybotactic groups at the temperature T_c is known the heat of decomposition L of the cybotactic groups at any temperature T can be approximately obtained by equation (7). In order to know the value of L_c the number ν of the constituent molecules of a cybotactic group and the degree of decomposition x_c of the cybotactic groups at the temperature T_c must be determined. However such determination of the values of ν and x_c can not be made uniquely, and the only way in doing this is, though troublesome, repeated trials. If we assign provisionally a certain value to x_c for a given value of ν, then we can find the values of $x_c/(1-x_c)^{\frac{1}{\nu}}\ y'$ and $(N_f/N)_c$ from the graphs prepared previously. Next from the values of the specific heats C_f and C_c of the free liquid molecules and the cybotactic groups at the temperature T_c as is determined in the way stated before the part C_m of the specific heat of the liquid at the temperature

Table I

	Molecular weight M	Melting point T_m in °K	Heat of fusion at T_m in cal/g
Ethyl alcohol	46	159	25.8
Glycerol	92	292	47.5
dl-Lactic acid	90	290	30.1

Table II

	Structural relaxation				Cybotactic decomposition					
	ν	T_r in °K	x_r	L_r in $\frac{\text{cal}}{\text{g}}$	ν	T_c in °K	x_c	L_c in $\frac{\text{cal}}{\text{g}}$	$(C_f-C_c)_c$ in cal/g	$\left(\frac{N_f}{N}\right)_c$ at T_c
Ethyl alcohol	200	96	0.9975	1.625	5	102	0.93	8.02	0.09	0.726
Glycerol	200	185	0.9975	1.95	5	192	0.97	10.66	0.163	0.865
dl-Lactic acid	200	208	0.9975	2.32	5	215	0.97	12.54	0.172	0.865

Table III

Glycerol

ν	T_c in °K	x_c	L_c in $\frac{\text{cal}}{\text{g}}$	$\left(\frac{N_f}{N}\right)_c$ at T_c	$(C_f-C_c)_c$ in $\frac{\text{cal}}{\text{g}}$
10	190	0.98	7.18	0.83	0.159
5	192	0.97	10.66	0.865	0.163
2	192	0.927	16.4	0.865	0.163

T_c which is required merely to raise the temperature by one degree of the free liquid molecules and the cybotactic groups without causing the cybotactic decomposition will be obtained by

$$C_m = C_f\left(\frac{N_f}{N}\right)_c + C_c\left\{1-\left(\frac{N_f}{N}\right)_c\right\}, \quad \text{.................. (15)}$$

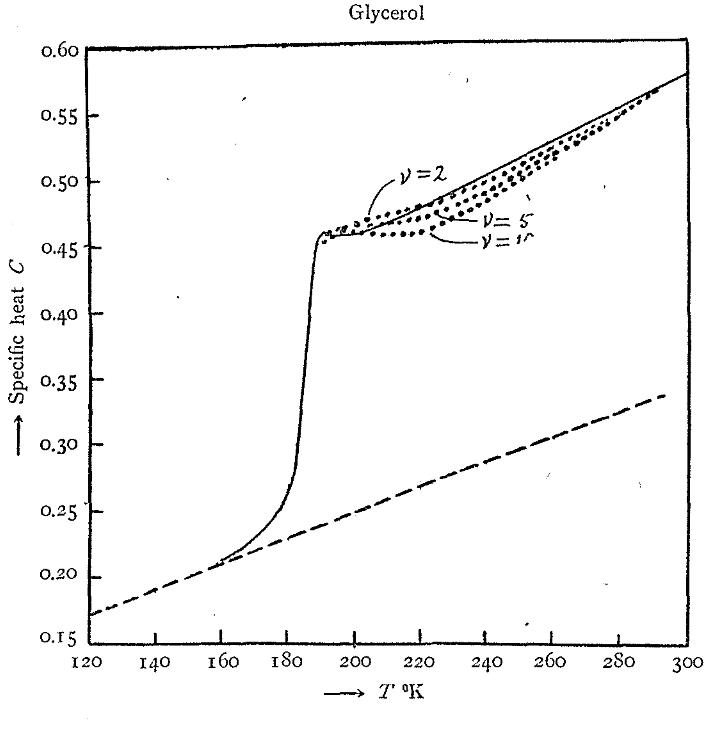
and the other part C_d of the specific heat of the liquid at the same temperature which is caused by the cybotactic decomposition in raising the temperature by one degree is found by subtracting the value of C_m thus obtained from the observed value of the specific heat of the liquid at the temperature T_c. Hence by putting the values of y' and C_d thus found into equation (14) the heat of decomposition L_c of the cybotactic groups per one gram at the temperature T_c is obtained immediately. The values of L_c thus found for some values of ν and x_c are given in Tables II and III. The values of $(N_f/N)_c$ which are calculated with equation (11) for the same values of ν and x_c are also tabulated in the tables. By getting the values of x_c, L_c, $(C_f - C_c)_c$, $(N_f/N)_c$ and y' at the temperature T_c for a given value of ν in the above way, the values of L, x and consequently those of N_f/N, y' and C_d for any temperature T are calculated by means of equation (7), (10), (11), (13) and (14) for the same value of ν. The part C_m of the specific heat of the liquid at any temperature T which is required merely to raise the temperature by one degree of the free liquid molecules and the cybotactic groups without causing the cybotactic decomposition is then obtained by

$$C_m = C_f\left(\frac{N_f}{N}\right) + C_c\left(1-\frac{N_f}{N}\right), \quad \text{...................... (16)}$$

by using the values of N_f/N calculated as above and those of C_f and C_c at the same temperature. From the values of C_d and C_m calculated in the above way for various temperatures the actual values of the specific heat C of the liquid for various temperatures are thus obtained as the sum of C_m and C_d. In short, the essential point in calculating the specific heat of a super-cooled liquid lies in the choice of the values of ν and x_c, and this is done by repeated trials. The necessary data used for a few such trial calculations with glycerol are given in Table III, and the results of calculation for $\nu = 2$, 5 and 10 are shown in Fig. 3 by representing the calculated specific heat with dotted lines. When the values of x_c are smaller respectively than those given in Table III a hump comes about in the calculated specific heat curves at the temperatures just above T_c; and when they are larger the calculated specific heat curves go down more rapidly with the rise of temperature than those shown in Figs. 3, 4, 5 and 6 respectively; and the values of x_c given in Tables II and III are so chosen that any noticeable hump does not appear in the calculated specific heat curve and that at the same time the shortage of the theoretical curve from the experimental one is smallest. The theoretical specific heat curves shown in Fig. 3, which are obtained for the case of $\nu=2$, 5 and 10 by using the values of x_c determined as above, indicate that the departure from the experimental curve decreases with the decrease of the value of ν, and that the agreement with the experimental curve becomes almost satisfactory with $\nu=2$. Thus, at the first sight, it seems to be reasonable to take 2 as an appropriate number of the constituent molecules of a cybotactic group. However, the specific heats of the free liquid molecules and of the cybotactic groups and the heat of decomposition of the cybotactic groups are determined approximately in a very rough manner. Moreover it is conceivable that many different kinds of cybotactic groups consisting of different numbers of molecules are present in a

Fig. 3

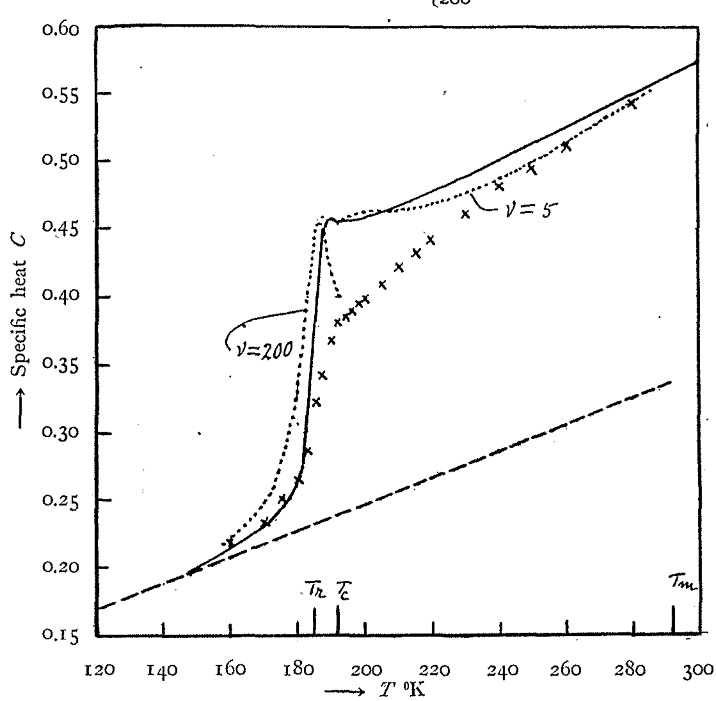
Glycerol



super-cooled liquid. If we take these circumstances into consideration it seems appropriate to conclude, by leaving untouched on the definite number of the constituent molecules, that the general tendency of the specific heat of a super-cooled liquid can be explained by the presence in equilibrium of the free liquid molecules and the cybotactic groups each consisting of several molecules. Thus the writer provisionally took 5 as the number of constituent molecules of a cybotactic group in the case of the super-cooled state of glycerol, *dl*-lactic acid and ethyl alcohol; and the theoretical curves calculated with the data given in Table II are represented by dotted lines in Figs. 4, 5 and 6. General tendency of the theoretical curves is seen to be in accord with the experimental curves. In these figures the crosses represent the part C_m of the specific heat which is required merely to raise the temperature by one degree of the free liquid molecules and the cybotactic groups without causing the cybotactic decomposition; and the sum of C_m and C_a is taken as the theoretical specific heat C and is indicated by the dotted lines.

Fig. 4

Glycerol, $\nu=\begin{cases}5\\200\end{cases}$

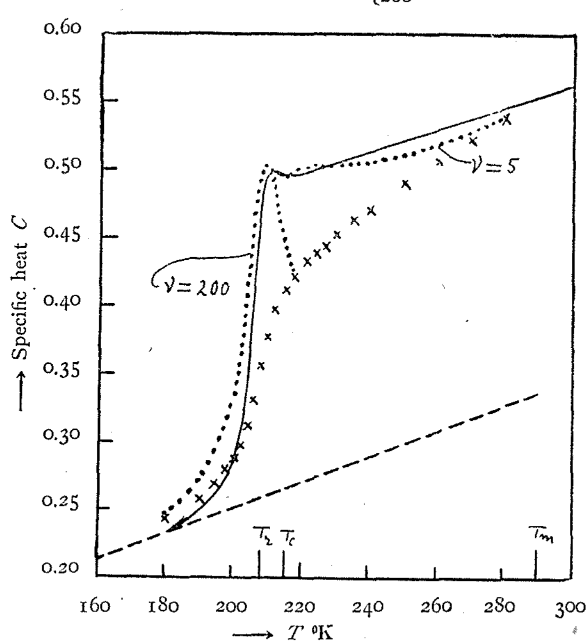


Structural Relaxation in the Softening Temperature Range

The writer considers the softening of an amorphous solid in its softening temperature range as the relaxation of the cybotactic structure, and the solidification of the super-cooled liquid into amorphous solid as the fixing of the cybotactic structure. Thus the solidification of the supercooled liquid can be considered as the fixing of the position of the free liquid molecules by means of the inter-molecular attraction whose effect becomes at low temperatures superior to that of the average kinetic energy of thermal motion of free molecules. Since the fixing of the position of the free molecules by intermolecular attraction signifies the formation of huge molecular aggregates composed of an immense number of molecules, entirely the same reasoning as in the case of the cybotactic equilibrium can be applied to this case. The increase of the specific heat in the softening temperature range is very sudden and this peculiarity seems to be accounted for by taking the number of constituent molecules of a huge molecular aggregate sufficiently great, as will be imagined from the shape of the y'-curve

Fig. 5

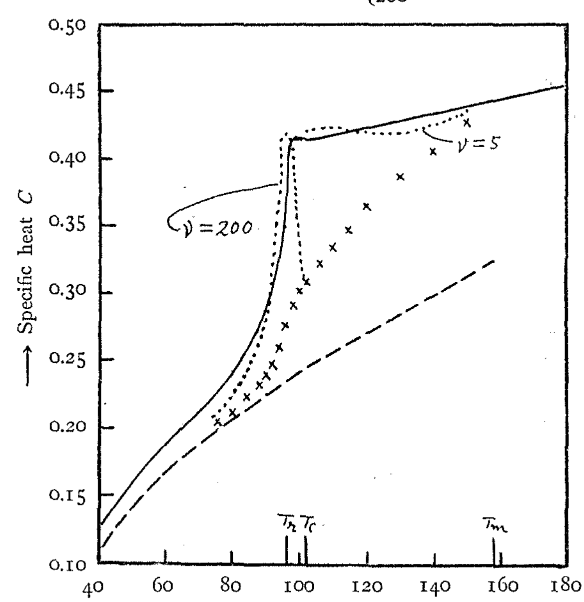
dl-Lactic acid, $\nu=\begin{cases}5\\200\end{cases}$



for a large number of ν as is shown in Fig. 2. Thus the writer provisionally took 200 as the number of constituent molecules of a huge molecular aggregate and an entirely similar calculation of the specific heat as in the super-cooled liquid state was made with glycerol, *dl*-lactic acid and ethyl alcohol. In carrying out the calculation, the writer assumed, for the sake of simplicity, that the amount of the cybotactic groups remained the same as at the temperature T_c, and that the huge molecular aggregates having 200 constituent molecules are formed only among the remaining free molecules so that only the relative proportion between the numbers of free molecules and of the huge molecular aggregates changes with temperature in equilibrium by keeping the amount of the cybotactic groups unaltered. As to the specific heats of the cybotactic groups and the huge molecular aggregates, the writer regarded them roughly to be the same as that of the adult crystal at the same temperature, and the specific heat of the still remaining free molecules was calculated by entirely the same assumption as in the case of the cybotactic equilibrium. As it is usual with an amorphous solid to be accompanied by some hysteresis in various physical pro-

Fig. 6

Ethyl alcohol, $\nu=\begin{cases}5\\200\end{cases}$



perties of it by changing the temperature in its softening range, it is meaningless to go into details in the present case where the equilibrium state is considered. Thus, in order to know only the general tendency of the temperature dependence of the specific heat, the writer disregarded the temperature variation of the heat of decomposition of the huge molecular aggregates and assumed it to be constant. In carrying out the actual calculation we must first select the reference temperature. The writer took the temperature at which the maximum of y' for $\nu=200$ occurs as such reference temperature and designated it to be very close to the temperature at which the sudden increase of the specific heat in the softening temperature range just ended. Such reference temperature is represented by T_r and its values for glycerol, *dl*-lactic acid and ethyl alcohol are tabulated in Table II together with the value of the degree of decomposition x_r of the huge molecular aggregates at these temperatures, which is so determined as to give the maximum value to y' for $\nu=200$. When the value of x_r is thus determined the corresponding value of N_f/N is obtained by equation (11), and the proportion of the number of the free molecules to the total number of molecules at the temperature T_r is found by multiplying this value of N_f/N with $(N_f/N)_c$ which is the proportion of the free molecules at the temperature T_c where the huge molecular aggregates decompose almost perfectly into the free molecules. Consequently the part C_m of the specific heat at T_r which is required to raise the temperature of the free molecules, the cybotactic groups and the huge molecular aggregates without causing the decomposition of the molecular aggregates is obtained from the values of the specific heats of the free molecules, of the cybotactic groups and of the huge molecular aggregates at the same temperature. Thus by knowing the value of C_m at T_r the other part of the specific heat C_d at the same temperature which is due to the decomposition of the huge molecular aggregates in raising the temperature is found immediately by subtracting the value of C_m from the observed specific heat at the temperature where the sudden increase of the specific heat in the softening range just ended. As the proportion of the total number of free molecules which can be transformed into the huge molecular aggregates is $(N_f/N)_c$, the value of C_d is obtained in the present case by multiplying with $(N_f/N)_c$ the equation (14), i. e.

$$C_d=\left(\frac{N_f}{N}\right)_c y' \frac{ML^2}{RT^2}, \quad \text{(17)}$$

The value L of the heat quantity which is necessary to decompose one gram of huge molecular aggregates is obtained by this equation, and the values thus found for glycerol, *dl*-lactic acid and ethyl alcohol are tabulated in Table II by being denoted by L_r. In this manner, essentially similar calculations of C_m, C_d and consequently C as in the case of cybotactic decomposition are performed for the case of decomposition of huge molecular aggregates, and the results are shown in Figs. 4, 5 and 6. In these figures the dotted lines represent the values of the specific heat C and the crosses represent the values of C_m which is required to raise the temperature merely by one degree of the free molecules, the cybotactic groups and the huge molecular aggregates without causing any decomposition. As is seen in the figures the value of C_d rises very rapidly with temperature to its maximum at T_r and then falls very rapidly almost to zero at T_c. The rapidity of the change of C_d with temperature can be still further improved by taking the number of constituent molecules of a molecular aggregate greater than 200. However, for the sake of understanding the general tendency of the change of specific heat with temperature it suffices with 200, and the results calculated for this case are plotted in the figures.

In calculating the specific heat by the structural relaxation the writer assumed, for the sake of simplicity, that the amount of the cybotactic groups remains unchanged at the temperatures below T_c. However, it will be somewhat different in actual case, and we can expect that the molecular exchange between the cybotactic groups and the free molecules still takes place to some degree in the temperature range from T_c to about T_r. Hence, if we assume that the gap found in the theoretical specific heat curve between T_c and T_r is filled in by this cause, the general tendency of the specific heat curve of an amorphous substance at the temperatures in and above its softening range is thus clearly understood.

The cost of this research has been defrayed from the Scientific Research Appropriation of the Department of Education.