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# The Relaxation of the Cybotactic Structure of Amorphous Solids and the Mechanism of Formation of Crystal Nuclei

by Usaburo Yoshida

(Received May 18, 1941)

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## Abstract

The softening range of amorphous solids is considered to be the temperature range in which the relaxation of the cybotactic structure of the substances takes place. By applying van't Hoff's reaction-isochore to the cybotactic equilibrium in the super-cooled liquid state of glycerol, ethyl alcohol and *DL*-lactic acid, the general tendency of the contribution of the effect of cybotactic decomposition to the temperature dependence of the specific heats of these substances in this state was examined. When the number of constituent molecules of a cybotactic crystal becomes infinite, a sharp and well defined temperature is found, below which some cybotactic crystals, but above which none can exist as such. This well defined temperature is the highest at which the crystal nuclei can be formed in equilibrium; and it is designated as the melting point of the substance. Lastly, regarding the relation between the latent heats of fusion of the monoatomic elements and their melting points, a rather satisfactory explanation is proposed.

## Introduction

In previous papers<sup>1</sup> published recently a cybotactic theory of amorphous solids and super-cooled liquids was proposed by the writer. In that theory an amorphous solid of a substance is considered to consist of free molecules of the substance and the cybotactic crystals having the size of the order of the unit cell of the crystal. The cybotactic crystals have no permanent stability. They are formed and decomposed spontaneously here and there in the liquid. The proportion in equilibrium of the total amount of the cybotactic crystals in reference to the total number of the free molecules is determined by the temperature, and it increases with decreasing temperature. When the temperature of a substance is lowered below the melting point of its crystal, without causing crystallization, it becomes super-cooled. On further cooling the substance gets increasingly viscous; and at last it attains the state of amorphous solid, which is supposed to contain a considerable amount of cybotactic crystals. The trans-

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

formation 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 and sudden as in the case of melting of a crystal. In the previous papers, such sudden change in various physical properties in the transformation temperature range was ascribed mostly to the decomposition of the cybotactic crystals of considerable amount by the rise of the temperature. More especially the remarkable increase in the specific heat at this temperature range was regarded as due to the heat absorbed by such decomposition of the cybotactic crystals. A sudden increase in the specific heat on heating in the softening temperature range, as is seen with boric oxide glass, has been found for many substances; and this seems to be a general property of amorphous substances. Among many amorphous substances, whose specific heats in the softening temperature range and in the super-cooled state have been measured, ethyl alcohol, glycerol and *DL*-lactic acid are worthy of mentioning; because the specific heats in their crystalline state have also been measured in the same temperature range. In the following, the contribution to the specific heat of the effect of decomposition of the cybotactic crystals on heating in the super-cooled liquid state was estimated with these three amorphous substances.

#### **Relaxation of the Cybotactic Structure and the Specific Heat due to the Decomposition of the Cybotactic Crystals**

The amorphous substance behaves almost as a solid at the temperatures below the softening range, and it acts as a liquid at the temperatures above that range. As is seen from the specific heat curves of ethyl alcohol, glycerol and *DL*-lactic acid, their specific heats in the state of amorphous solid are almost the same as those in their crystalline state. This seems to indicate that the constituent molecules in the amorphous solid are fixed in their positions just as in the crystalline state; and this is in good contrast with the liquid state, where the constituent molecules are free to change their positions. Thus the cybotactic exchange from the cybotactic crystals to the free molecules and *vice versa* must be considered to be almost, though not entirely, stopped in the amorphous solid. At the temperatures above the softening range the substance behaves as a liquid as is stated above, and noticeable time lag or hysteresis in the change of its physical properties following any temperature change takes place

only in, and extremely remarkably below, the softening range. Consequently the softening range can be regarded reasonably as the temperature range in which occurs the relaxation of the cybotactic structure of the substance, and the substance is transformed from the state of amorphous solid to that of super-cooled liquid on heating in this range. The amount of the cybotactic crystals in an amorphous substance at a temperature higher than the softening range can thus be taken nearly as the equilibrium value corresponding to that temperature; and the thermodynamic relation can be applied to it.

As to the cybotactic groups, several kinds consisting of different numbers of constituent molecules may be imagined<sup>1</sup>. Among these, those composed of smaller number of molecules will require smaller amount of heat of decomposition, and their contribution to the specific heat variation accompanying temperature change will be of much minor degree when compared with that due to the cybotactic crystal, which is supposed to be the same as or larger than the unit cell of the crystal of the substance. Thus the effect of decomposition of cybotactic crystals only is taken into account in the following in approximately calculating the specific heat.

The spontaneous formation and decomposition of a cybotactic crystal in liquid can be considered as a sort of molecular aggregation and dissociation in liquid, and we shall apply van't Hoff's reaction-isochores to this case. Let us suppose that the number of constituent molecules in a cybotactic crystal is definite and to be denoted by  $\nu$ . Then, by the decomposition of one cybotactic crystal  $\nu$  free molecules are formed in the liquid. Next let  $x$  be the degree of decomposition of the cybotactic crystals, then the molecular and cybotactic concentrations in unit volume are proportional to  $\nu x$  and  $1-x$  respectively. As to the heat of decomposition of one cybotactic crystal, which is denoted by  $L$  for 1 gram mol. of the cybotactic crystal, we shall consider it, for the present, to be approximately constant for the temperature intervals we are concerned. Thus, when the volume change accompanying the temperature variation is neglected, the cybotactic equilibrium corresponding to the temperature  $T$  expressed in absolute scale will be given by

$$\frac{(\nu x)^\nu}{1-x} = C e^{-\frac{L}{RT}} \dots\dots\dots(1)$$

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

where  $R$  is the gas constant (1.985 cal per degree), and  $C$  is also a constant independent of  $T$ . If we represent by  $L_0$  the heat of decomposition per 1 gram of the cybotactic crystal, and by  $M$  the molecular weight of the substance; then, by putting  $L = \nu ML_0$ , the equation (1) becomes

$$\frac{x}{(1-x)^{\frac{1}{\nu}}} = \frac{C^{\frac{1}{\nu}}}{\nu} e^{-\frac{ML_0}{RT}} \dots\dots\dots(2)$$

By differentiating equation (1) with  $T$ , we get

$$\frac{dx}{dT} = y \frac{ML_0}{RT^2} \dots\dots\dots(3)$$

where  $y$  is

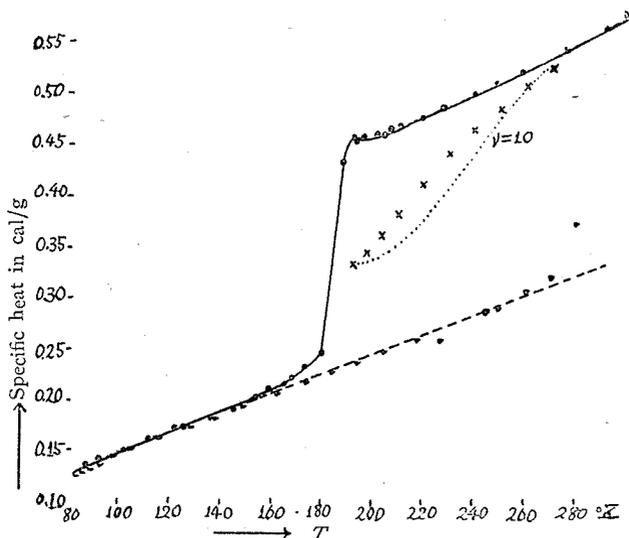
$$y = \frac{\nu x(1-x)}{\nu(1-x) + x} \dots\dots\dots(4)$$

The contribution  $C_d$  of decomposing the cybotactic crystals on heating, to the specific heat per 1 gram of the substance is thus

$$C_d = L_0 \frac{dx}{dT} = y \frac{ML_0^2}{RT^2} \dots\dots\dots(5)$$

Now let us consider the case of glycerol as an example. The

Fig. 1  
Glycerol



specific heats in amorphous and crystalline states of this substance are measured by Gibson and Giaque<sup>1</sup>, and are shown by the curves in Fig. 1. In this figure the curve drawn in full line refers to the amorphous state and that drawn in broken line represents the value of the

specific heat in the crystalline state. The specific heat curve for the

1. G. E. Gibson and W. F. Giaque: J. Amer. Chem. Soc., 45, 93 (1923).

crystalline state runs almost linearly with temperature, except at the temperatures just below the melting point. As this minor departure from linearity seems to be due to some experimental errors, such as caused by the presence of some impurity or in some other way, the broken line is extended straight, in the figure, up to the melting point, by considering it to represent the true value. The values of the specific heat given in Fig. 1 refer to 1 gram of the substance.

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 crystals, which may be taken to be approximately the same as that of the adult crystals 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 at the melting point of the adult crystals, where almost all the molecules are likely to be in free state and not in the state of cybotactic configuration. 3) The heat  $C_d$  required for decomposition of the cybotactic crystals 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 crystals as is stated above, the specific heat observed for the liquid at this temperature may be taken to be approximately 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 above the softening range, and is equal to that of the liquid and the adult crystals at the melting point of the latter; and the value of  $C_f$  at any temperature was calculated from the value of the specific heat of the adult crystals at the same temperature, which is considered to be approximately the same as  $C_c$ .

As to the sudden increase of the specific heat in the softening range, the writer regards it as the cybotactic relaxation. As such cybotactic relaxation is primarily caused by the increased kinetic energy of the molecules due to thermal agitation, the cybotactic exchange between free molecules and the cybotactic crystals should be noticeable in the softening range; and consequently the temperature  $T_2$  at which the rate of the cybotactic decomposition on heating is maximum should be located somewhere about the softening range. Under such a consideration the writer designates the temperature just above the softening range as  $T_2$  at which the maximum rate of the cybotactic decomposition takes place on heating; and in the case of glycerol  $T_2$  is found to be at 192°K. The temperature  $T_2$  obtained by

differentiating  $C_a$  given by equation (5) with temperature and by putting it equal to zero, is

$$T_2 = \frac{\nu^2(1-x)^2 - \nu x^2}{\{x + \nu(1-x)\}^2} \frac{ML_0}{2R} = Y \frac{ML_0}{2R} \dots\dots\dots(6)$$

where

$$Y \equiv \frac{\nu^2(1-x)^2 - \nu x^2}{\{x + \nu(1-x)\}^2} \dots\dots\dots(7)$$

The value of  $x$  in (6) is not independent, and if we put  $T = T_2$  in the equation (2) and eliminate  $x$  from equations (2) and (6), we get the relation between  $T_2$  and  $ML_0$ . Consequently the equation (6) must be regarded as the equation showing the relation between  $T_2$  and  $ML_0$ . The degree of decomposition  $x_2$  at the temperature  $T_2$  is obtained by putting  $T = T_2$  in equation (2), as follows:

$$\frac{x_2}{(1-x_2)^{\frac{1}{\nu}}} = \frac{C^{\frac{1}{\nu}}}{\nu} e^{-\frac{ML_0}{RT_2}} \dots\dots\dots(8)$$

From equations (2) and (8), the relation between the degree of cybotactic decomposition  $x$  and the temperature  $T$  thus becomes

$$\frac{x}{(1-x)^{\frac{1}{\nu}}} = \frac{x_2}{(1-x_2)^{\frac{1}{\nu}}} e^{-\frac{ML_0}{R} \left( \frac{1}{T} - \frac{1}{T_2} \right)} \dots\dots\dots(9)$$

By denoting the values of  $C_a$ ,  $y$  and  $Y$  at the temperature  $T_2$  by  $C_{a,2}$ ,  $y_2$  and  $Y_2$  respectively, we obtain from equations (5) and (6)

$$C_{a,2} = y_2 \frac{ML_0^2}{RT_2^2} \dots\dots\dots(10)$$

and

$$T_2 = Y_2 \frac{ML_0}{2R} \dots\dots\dots(11)$$

By eliminating  $L_0$  from equations (10) and (11), we get

$$\frac{Y_2^2}{y_2} = \frac{4R}{C_{a,2}M} \dots\dots\dots(12)$$

Thus if we know the value of  $C_{a,2}$ , the value of  $\frac{Y_2^2}{y_2}$  is obtained; and consequently the value of  $x_2$  can be obtained for a given number of  $\nu$ . As to the value of  $\nu$ , the number of the constituent molecules for one cybotactic crystal, we do not know any thing definitely. But if we consider the cybotactic crystal to be the same as or greater than the unit cell of the crystal of the substance, then  $\nu$  must be the same as or greater than the number of constituent molecules of the unit cell of the crystal. Thus the writer have assigned the values of

5, 10, 15, 20, 30,  $\frac{x}{(1-x)^{\frac{1}{\nu}}}$   
 50, 100 etc. to  $\frac{1}{\nu}$   
 $\nu$ ; and investigated the temperature dependence of  $C_a$ , to understand rather qualitatively the temperature change of the specific heat of the super-cooled liquid at the temperatures higher than the softening range. For numerical calculation the writer has plotted the curves showing the values of  $\frac{x}{(1-x)^{\frac{1}{\nu}}}$ ,  $y$ ,  $Y$  and  $\frac{Y^2}{y}$  for

Fig. 2.

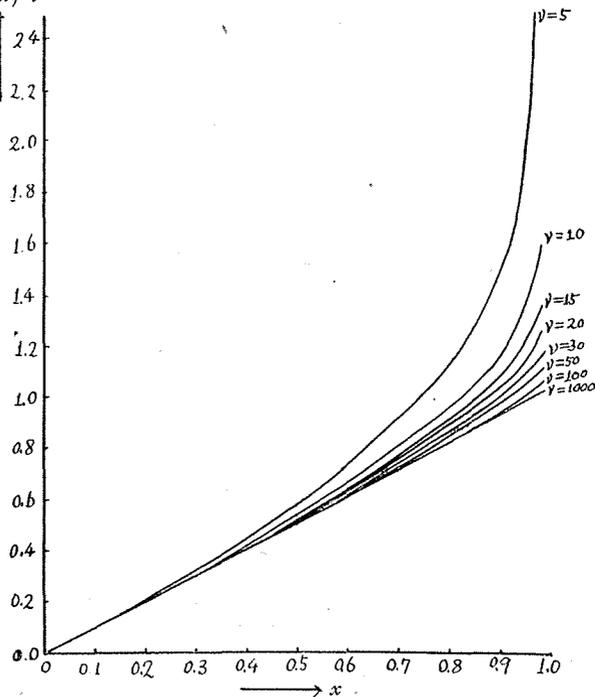
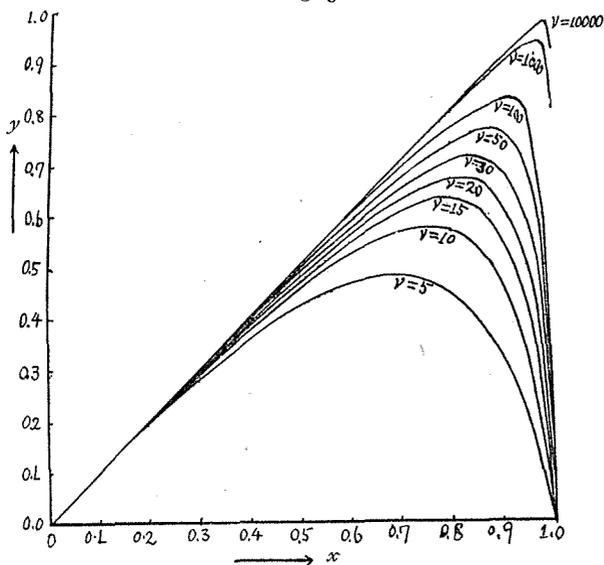
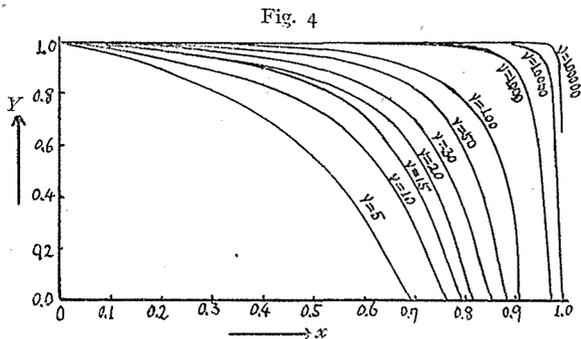


Fig. 3



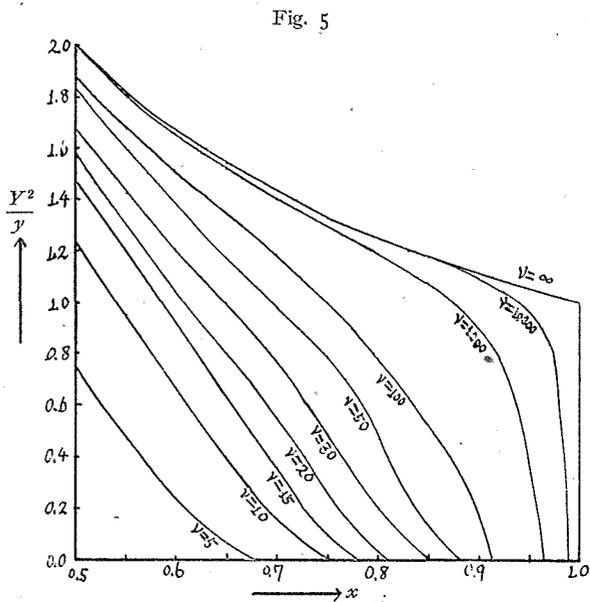
various values of  $x$  by assigning the numbers stated above to  $\nu$ . These curves are shown in Figs. 2, 3, 4, and 5.

As stated above the writer assumes that the ratio  $C_f/C_c$  of the specific heats of the free molecules and that of the cybotactic crystals in the state of super-cooled liquid is the same for dif-



ferent temperatures, and takes the value of the ratio of the specific heat of the liquid and that of the adult crystal of the same substance at the melting point of the latter; and he also assumes that the spe-

cific heat of the cybotactic crystals at any temperature is the same as that of the adult crystal at the same temperature. By this assumption the values of  $C_r$  and  $C_c$  at the temperature  $T_2$ , where the rate of decomposition of the cybotactic crystals is supposed to be maximum, and at the temperatures higher than  $T_2$ , are obtained immediately. Next



we must know the values of  $L_0$  and  $x_2$ . The specific heat of the amorphous substance at the temperature  $T_2$  consists of  $x_2 C_f$ ,  $(1-x_2)C_c$  and  $C_{a,2}$ . Thus if we give a certain value arbitrarily to  $x_2$ , we obtain  $x_2 C_f + (1-x_2)C_c$ ; and consequently the value of  $C_{a,2}$  is obtained immediately by subtracting the value of  $x_2 C_f + (1-x_2)C_c$  from the observed value of the specific heat of the amorphous substance at the temperature  $T_2$ . By putting this value of  $C_{a,2}$  into the equation (12) we get graphically again the value of  $x_2$  for a given value of  $\nu$ . As this value of  $x_2$  must be the same as that initially taken arbitrarily, the method of successive approximation was adopted to get the coincidence. Coincident value of  $x_2$  having been obtained in such a way,

we can find the value of  $L_0$  from either one of the equations (10) and (11) for the same value of  $\nu$  as before. As for a given value of  $Y_2^2/y_2$  the value of  $x_2$  is different for different values of  $\nu$ ; consistent values  $C_{d,2}$ ,  $x_2$  and  $L_0$  are also different for various values of  $\nu$  as is shown in Table I for glycerol. The values of  $ML_0Y_2/T_2$  given in the last column of the table are calculated with the values of  $L_0$  and  $Y_2$

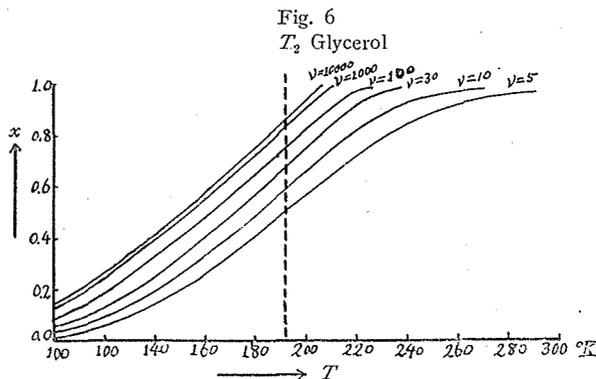
Table I  
Glycerol  
 $M=92$ ,  $T_2=192^\circ K$ ,  $T_m(\text{melting point})=292^\circ K$ , heat of fusion 47.5 cal/g

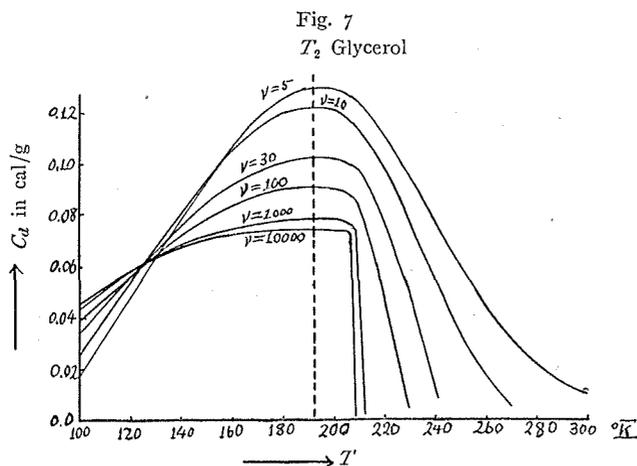
$\nu$	$x_2$	$L_0$	$ML_0$	$Y_2$	$C_{d,2}$	$\frac{ML_0}{T_2}$	$\frac{ML_0}{T_2} Y_2$
5	0.514	15.6	1437	0.525	0.130	7.47	3.92
10	0.59	13.7	1260	0.610	0.121	6.56	4.00
20	0.657	12.4	1140	0.670	0.114	5.94	3.98
30	0.685	11.3	1043	0.730	0.103	5.44	3.97
50	0.72	10.5	966	0.785	0.097	5.03	3.95
100	0.76	9.86	907	0.840	0.090	4.73	3.97
1000	0.84	8.63	794	0.960	0.078	4.13	3.97
10000	0.86	8.30	764	0.998	0.074	3.98	3.97

which are tabulated in the table. As is seen with equation (11), the value of  $ML_0Y_2/T_2$  should be equal to  $2R=3.97$ , irrespective of the value of  $\nu$ ; and this requirement is seen to be satisfied from the table.

With the values of  $x_2$  and  $L_0$  as are given in Table I, the degree  $x$  of decomposition for various values of  $T$  is calculated with equation (9) for several assigned values of  $\nu$ ; and the specific heat  $C_d$  due to the decomposition of the cybotactic crystals by the rise of temperature is obtained with equation (5). The temperature dependence of  $x$  and  $C_d$  thus obtained for various values of  $\nu$  are shown by the curves in

Figs. 6 and 7. In these figures the curves for very large numbers of  $\nu$  are plotted together for the convenience's sake. For very large numbers of  $\nu$  such as 1000 or 10000,





the curves have very sharp break at the last stage of the cybotactic decomposition. This seems to correspond to the upper limit of the temperature for the existence of the crystal nuclei; and this point

will be considered later.

As to the number of the constituent molecules of a cybotactic crystal, the writer considers it to be roughly of the order of those contained in a unit cell of the crystal of the substance; but no definite value is known. However, in order to understand the general tendency of the contribution of the cybotactic decomposition to the specific heat of the super-cooled liquid, the calculation was carried out for several different values of  $\nu$  taken arbitrarily, so as to be consistent with the observed value of the specific heat at the  $T_2$  point. The results are given in Table I and in Figs. 6 and 7. At the  $T_2$  point, which was taken as  $192^\circ\text{K}$  for glycerol, the value of  $C_{a,2} + x_2 C_f + (1-x_2)C_c$  was taken as the same with the observed value of the specific heat in the amorphous or super-cooled liquid state at that temperature. The fact that the values of  $x_2$ ,  $C_{a,2}$  and  $L_0$  differ with  $\nu$ , as is seen in Table I, is due to these circumstances; and it does not signify that these values change in such a manner as is shown in the table by the actual increase of the number of the constituent molecules of a cybotactic crystal accompanying to its growth.

In Figs. 6 and 7 the values of  $x$  and  $C_a$  calculated even at the temperatures below the  $T_2$  point are plotted. But the curves below this point have no significance other than the theoretical one. In the softening temperature range just below the  $T_2$  point the cybotactic structure of the substance tightens or relaxes almost exactly as it is according as it is cooled or heated. At the temperatures below this range any noticeable cybotactic exchange in approaching to the idealised equilibrium state is considered to be almost arrested. However,

by passing the  $T_2$  point on heating the cybotactic exchange begins to be very active, and the equilibrium is likely to be almost attained at the temperatures higher than this point. Under this consideration, the calculated values of  $C_a$  only for the temperatures higher than  $T_2$  are represented in Fig. 1, by the curve drawn in dotted line, for  $\nu=10$ , by subtracting the value of  $C_a$  respectively from those of the specific heat observed in the super-cooled state. As to the definite number of the constituent molecules of a cybotactic crystal we are entirely ignorant as is stated above, but the number 10 was chosen in Fig. 1 as of a reasonable order, so that we may understand the general tendency of the contribution of the cybotactic decomposition to the specific heat of the super-cooled liquid.

The contribution of the presence of the cybotactic crystals and the free liquid molecules to the specific heat of the super-cooled glycerol, i. e.  $x C_f + (1-x) C_e$ , was calculated. As is stated above the writer assumes that the specific heat  $C_e$  of the cybotactic crystals is the same as that of the adult crystal at the same temperature, and that the ratio  $C_f/c_e$  remains the same for all temperatures, and he takes the value of the ratio of the specific heats of the liquid and of the adult crystal at the melting point of the latter. Under this assumption the values of  $x C_f + (1-x) C_e$  are readily obtained for all temperatures from the values of  $x$  already calculated, and they are represented by the crosses in Fig. 1. The position of the crosses does not coincide exactly with the curve drawn in dotted line in Fig. 1. But if we consider that the calculation is made on very rough approximation by assuming the proportionality of  $C_f/C_e$  and by disregarding the temperature variation of the latent heat of fusion of the cybotactic crystals, a small discrepancy such as seen in Fig. 1 may be overlooked.

Specific heat measurement both in amorphous and crystalline states of the same substance was also made with ethyl alcohol<sup>1</sup> and *dl*-lactic acid<sup>2</sup>. With these two substances the writer carried out the same calculation as with glycerol, and obtained entirely similar results as with it. Important numerical data for the case of  $\nu=10$  are given in Table II, and the results of calculation are shown in Figs. 8 and 9 entirely in the same manner as with glycerol. After all, an enor-

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1. G. S. Parks: J. Amer. Chem. Soc., 47, 338 (1925); K. K. Kelley: J. Amer. Chem. Soc., 51, 779 (1929).

2. S. Parks, S. B. Thomas and D. W. Light: J. Chem. Phys. 4, 64 (1936).

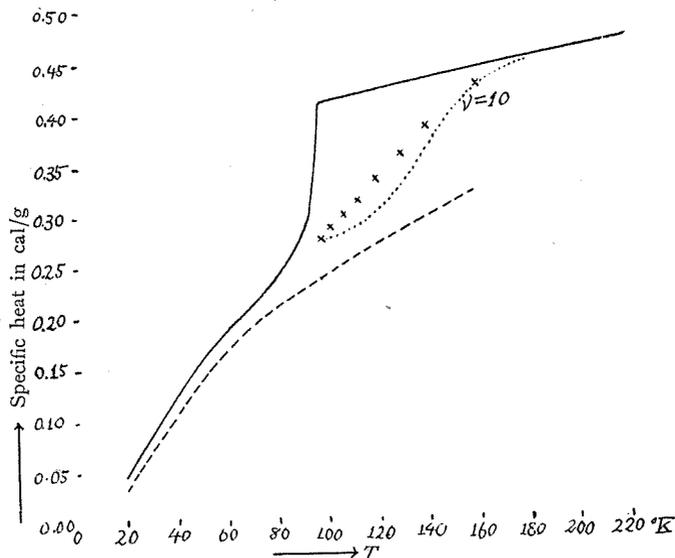
Table II

	$M$	$T_m$ in $^{\circ}K$ (melting point)	$T_2$ in $^{\circ}K$	$\nu$	$x_2$	$L_0$ cal/g
Ethyl alcohol	46	159	98	10	0.495	11.25
<i>d</i> <i>L</i> -lactic acid	90	290	211	10	0.60	15.7
Glycerol	92	292	192	10	0.59	13.7

cybotactic crystals, and thus a part of the sudden increase in the specific heat at the  $T_2$  point is accounted for by this fact. As to the remaining part of this sudden increase the writer considers it, as is stated above, to be due to the relaxation of the cybotactic structure

mous increase of the specific heat of an amorphous substance above the softening temperature range is partly ascribed to the decomposition of the

Fig. 8  
Ethyl alcohol

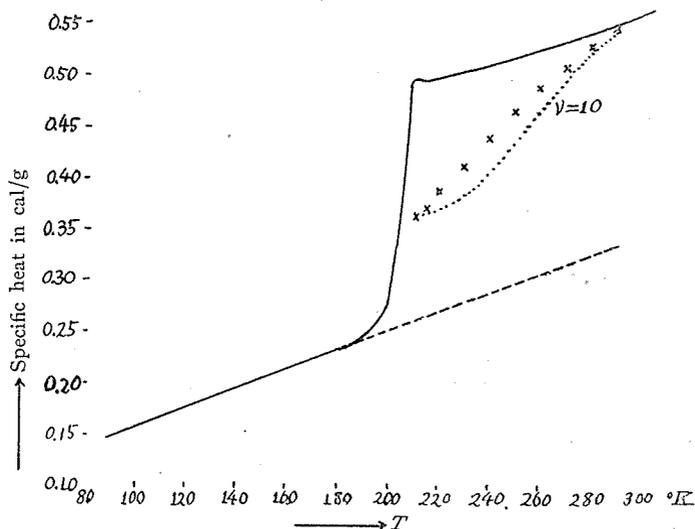


in the softening range, by making the free molecules and the cybotactic crystals behave freely just as in ordinary liquid.

Among many physical properties of amorphous substances which change abruptly in the softening range, the viscosity seems to be especially worthy of mentioning. With many substances their viscosity in the viscous liquid state above the softening range of temperature has been studied<sup>1</sup>. Extrapolation of measurement into the softening

1. Parks, Barton, Spaght and Richardson: *Physics*, 5, 193 (1934); Parks and Gilkey: *J. Phys. Chem.*, 33, 1428 (1929).

Fig. 9  
*dl*-Lactic acid



range shows that, at the middle point of the softening range, the viscosity of the substances is of the same order and takes the value lying between  $10^{13}$  and  $10^{14}$  poises. This rule appears to hold irrespective of the kind of the substance or of the mean temperature at which the softening takes place, as was pointed out by J. D. Ferry and G. S. Parks<sup>1</sup>. According to the writer this is mainly due to the presence of almost the same cybotactic composition in the softening range for different amorphous substances. In the case of ethyl alcohol, *dl*-lactic acid and glycerol the values of  $x_2$  at the  $T_2$  point lie between 0.5 and 0.6; and it seems not unnatural to consider that the degree of cybotactic decomposition in the softening range is of the order of these figures for all amorphous substances.

In previous papers<sup>2</sup> the writer has proposed a cybotactic theory of the amorphous Beilby layer, which is supposed to exist on a polished metal surface and in very narrow interstices between neighbouring crystals of metals; and the phenomenon of recrystallization of metals is ascribed primarily to the melting of the amorphous layer between neighbouring crystals and to the growth of the crystal nuclei formed spontaneously in the melt. If the writer's view of the

1. J. Chem. Phys., 4, 70 (1936).  
 2. U. Yoshida: These Memoirs, A, 23, 207, 233, 325, 351 (1941).

cybotactic structure of the Beilby layer is admitted, the melting of the Beilby layer means the same thing as the relaxation of the cybotactic structure of an amorphous substance in its softening temperature range, and the lowest recrystallization temperature of a metal comes to signify the  $T_2$  point just above the softening temperature range of Beilby's amorphous layer of the metal.

### Formation of the Crystal Nuclei in the Melt, and the Relation between the Latent Heat of Fusion and the Melting Point of Adult Crystals

The melting point of the adult crystal of a substance is entirely fixed, and its two phases as liquid and crystal can coexist only at its melting point. This point was explained, in a former paper, by considering the phenomena of melting and crystallization of a substance as a surface phenomenon taking place at the boundary surface of the crystal and the melt. The same point seems to be also explained from the view point of the cybotactic equilibrium by taking the number of constituent molecules of a cybotactic crystal as infinite. As is stated in the case of the cybotactic equilibrium of glycerol the  $C_d$  curve i. e. the  $\frac{dx}{dT}$  curve for a very great number of  $\nu$  has a very sharp break at the last stage of the cybotactic decomposition. This property of the  $\frac{dx}{dT}$  curve is not confined to any particular kind of substance, but it is universal. We shall apply this property of the  $\frac{dx}{dT}$  curve to the formation of the crystal nuclei in any kind of liquid in general. When the number  $\nu$  of constituent molecules of a cybotactic crystal becomes infinite we can regard it as a crystal nucleus or even as an adult crystal when sufficiently great. Thus the temperature at which the value of  $x$  becomes 1 and that of  $\frac{dx}{dT}$  drops suddenly to zero is the limiting temperature, below which the very small crystals or the crystal nuclei can, and above which can not, exist as such in equilibrium. Below the limiting temperature, if some of the very small crystal nuclei, though small in their number, have grown by chance to a considerable size, they will now become endowed with sufficient stability, and their further growth up to the adult crystals will take place thoroughly by the surface phenomenon as in the case of the growth of the adult crystals. Considered in such a way, the limiting temperature at which the value of  $\frac{dx}{dT}$  falls suddenly to zero at the

final stage of cybotactic decomposition, is nothing but the melting point of the substance. Below this temperature, the degree  $x$  of decomposition of the crystal nuclei should decrease with decreasing temperature according to the present theory: i. e. the number of crystal nuclei should increase with decreasing temperature. This is in good accord with the observations of Tammann and others<sup>1</sup>.

As the value of  $\frac{dx}{dT}$  falls abruptly at the melting point  $T_m$ , this point will be obtained from equation (3) by differentiating it with  $T$ , and by finding the point at which the value of  $\frac{d^2x}{dT^2}$  suddenly becomes  $-\infty$ . So we get from equation (3)

$$\frac{d^2x}{dT^2} = \frac{ML_0}{RT^3} y \left\{ \frac{ML_0}{RT} Y - 2 \right\} \dots\dots\dots (13)$$

where  $y$  and  $Y$  represent

$$y = \frac{\nu x(1-x)}{x + \nu(1-x)}, \quad Y = \frac{\nu^2(1-x)^2 - \nu x^2}{\{x + \nu(1-x)\}^2} \dots\dots\dots (14)$$

When  $\nu$  is sufficiently great, the values of  $y$  and  $Y$  tend to become  $x$  and  $1$  respectively, except at  $x=1$ . Moreover, when  $x$  tends to become  $1$  the value of  $Y$  turns to  $-\infty$  abruptly from its initial value of  $1$  by passing through the zero value. Consequently the point at which the value of  $\frac{d^2x}{dT^2}$  abruptly turns to  $-\infty$  can be designated by putting

$$\nu^2(1-x)^2 - \nu x^2 = 0,$$

i. e.  $1-x = \frac{x}{\nu^{\frac{1}{2}}} \dots\dots\dots (15)$

for very large value of  $\nu$ , and this is the condition to get the melting point definitely. Next the relation between the melting point  $T_m$  and the  $T_2$  point is obtained by putting this condition into equation (9).

As  $\lim_{\nu \rightarrow \infty} \frac{(1-x)^{\frac{1}{\nu}}}{x} = \lim_{\nu \rightarrow \infty} \frac{x^{\frac{1}{\nu}}}{x \nu^{\frac{1}{2\nu}}} = 1,$

and  $\lim_{\nu \rightarrow \infty} (1-x_2)^{\frac{1}{\nu}} = 1,$

we get from equation (9), at  $\nu \rightarrow \infty,$

$$\frac{1}{x_2} = c - \frac{ML_0}{R} \left( \frac{1}{T_m} - \frac{1}{T_2} \right) \dots\dots\dots (16)$$

Thus the temperature difference between the melting point  $T_m$  and

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1. G. Tammann: Kristallisieren u. Schmelzen, p. 151 (1903).

the  $T_2$  point is determined by the degree  $x_2$  of cybotactic decomposition at the  $T_2$  point. When  $x_2$  is nearly equal to 1  $T_m$  approaches to  $T_2$ , and when it becomes less  $T_m$  becomes higher.

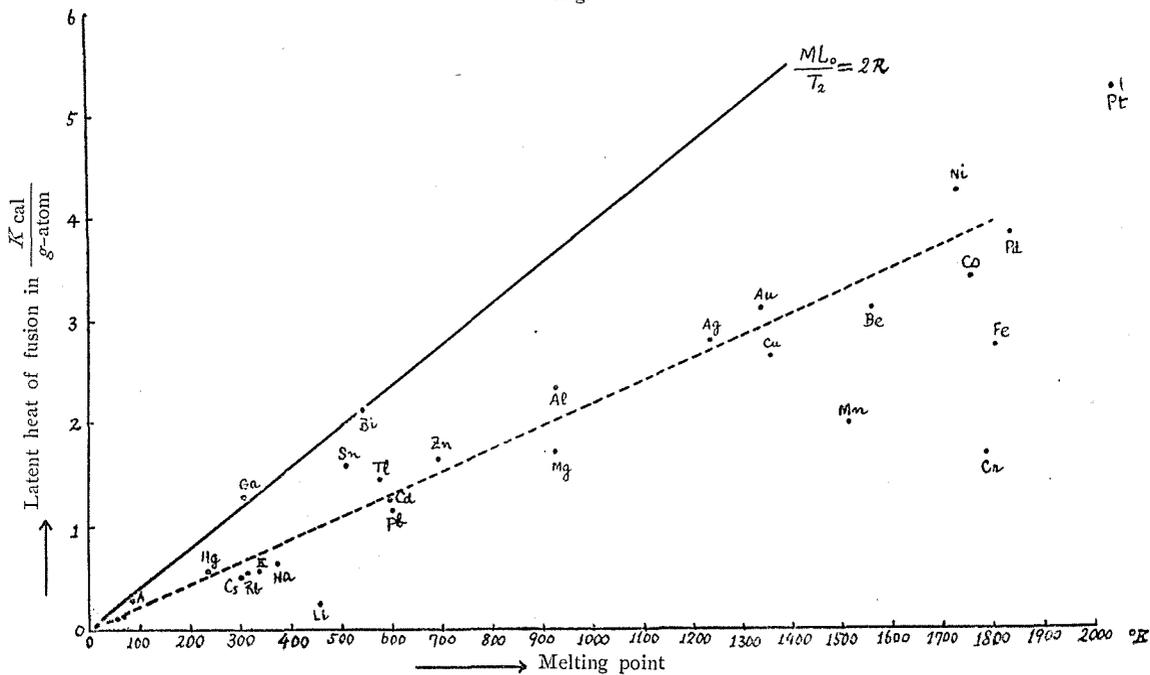
When the  $T_2$  point takes place at a value of  $x_2$  which is definitely smaller than 1, the value of  $\nu$  tends to 1 for very large value of  $\nu$ ; and the  $T_2$  point obtained by equating the right hand side of equation (13) to zero becomes in this case

$$\frac{ML_0}{T_2} = 2R \dots \dots \dots (17)$$

As the value of  $x_2$  is definitely smaller than 1 in this case, the melting point  $T_m$  must be certainly higher than  $T_2$  as is seen from equation (16). As to the value of  $ML_0$  it is considered by the writer that it increases with the value of  $\nu$  and approaches to the value of the adult crystal asymptotically. Thus if we assume that the value of  $ML_0$  of the crystal nuclei is almost the same as that of the adult crystal of the same substance, the relation between  $ML_0$  and  $T_m$  comes to be expressed by

$$\frac{ML_0}{T_m} < 2R \dots \dots \dots (18)$$

Fig. 10



This inequality shown in the relation between the latent heat of fusion and the melting point is satisfied actually by the monoatomic elements except gallium as is shown by Fig. 10. In this figure, the observed values of latent heat of fusion of various monoatomic elements which are expressed in Kilo-calorie per g-atom, are plotted as ordinates against the melting points taken as abscissae. Here most of the observed values of latent heat of fusion are taken from International Critical Table, and a few others from Landolt-Börnstein's *Physikalisch-Chemische Tabellen*. In the figure the relation  $ML_0/T_2 = 2R$  is represented by the straight line drawn in full, and for the monoatomic elements except gallium the values of  $ML_0/T_m$  take the positions beneath this straight line as is expected from the inequality (18). However, when the  $T_2$  point takes place at a value of  $x_2$  which is almost equal to 1 for a very large number of  $\nu$ , the circumstances are different. In this case  $T_m$  approaches very close to  $T_2$ , as will be seen from equation (16); and the value of  $Y$  becomes somewhat smaller than 1 even for a very large number of  $\nu$ , as will be seen from Fig. 4. Thus from the condition to cause the  $T_2$  point, which is obtained by equating the right hand side of equation (13) to zero, we get

$$\frac{ML_0}{RT_2} > 2;$$

and by replacing  $T_2$  by  $T_m$ , by the reason stated above, it becomes

$$\frac{ML_0}{T_m} > 2R \dots\dots\dots(19)$$

This shows that  $ML_0/T_m$  can take the value greater than  $2R$  in some exceptional case, as is actually so with Ga, which occupies the position somewhat greater than  $2R$  in its value of  $ML_0/T_m$  in Fig. 10.

The reason why the degree  $x_2$  of decomposition at the  $T_2$  point is different for different substances is not entirely clear to the writer. But this can be interpreted to some extent in the other way by the difference of the value of  $ML_0/T_2$ . By rewriting equation (11), we get

$$Y_2 = \frac{2R}{\frac{ML_0}{T_2}} \dots\dots\dots(20)$$

As is stated above the value of  $ML_0/T_2$  is equal to  $2R$  for the majority of the monoatomic elements, and  $Y_2$  takes the value of 1 in this case. The value of  $x_2$  corresponding to this value of  $Y_2$  for a very great number of  $\nu$  is, of course, smaller than 1; but, as is seen from

Fig. 4, it is rather indeterminate and may take a much smaller value, as is actually so for the majority of the monoatomic elements. When the value of  $ML_0/T_2$  is greater than  $2R$ ,  $Y_2$  becomes smaller than 1; and this occurs at a value of  $x_2$  very near to 1, as is stated above for gallium.

It is worth while to note that common metals, most of which take the crystal form of face-centred cubic or of hexagonal closed packed, are crowded near the straight line drawn broken in Fig. 10. The writer calculated, by making  $(ML_0)/(RT_2)=2$ , the value of  $x_2$  with equation (16) from the inclination of this straight line, and found it to be  $x_2=0.41$ . This is much smaller than 1, and furnishes the reason for the fact that these metals are situated much lower than the critical position represented by  $ML_0/T_m=2R$ .

In the above consideration the writer has disregarded the variation of the latent heat of fusion with temperature, which arises from the difference of the specific heats in liquid and crystalline phases of the same substance. But, considered from the results of measurements made on several kinds of elements, such difference of the specific heats in the two different phases seems generally to be not noticeable in the case of the elements; and the good agreement between theory and observation as was stated above seems to have arisen from this fact.

With inorganic compounds, and more especially with organic compounds, the values of  $(ML_0)/(T_m)$  are generally much larger than the critical value  $(ML_0)/(T_m)=2R$ . At the same time the specific heats in liquid and in crystalline phases are remarkably different in general, being greater in liquid, as will be seen for example in Figs. 1, 8 and 9 with glycerol, ethyl alcohol and *dl*-lactic acid respectively. In such cases the latent heat of fusion will change considerably with temperature, and the above consideration on the relationship between the latent heat of fusion and the melting point becomes inapplicable. With complex molecules of inorganic compounds, and more especially of organic compounds, some excess energy is required in setting up some more degree of freedom of molecular motion by melting, in addition to that necessary to decompose the constituent molecules from the lattice points of the crystal. If this reasoning is correct, the calculations made before by the cybotactic decomposition of glycerol, ethyl alcohol and *dl*-lactic acid are not perfect; and they must be looked upon as showing rather qualitatively the general tendency of the con-

tribution of the cybotactic decomposition to the temperature dependence of the specific heats of these substances in their super-cooled state.

Lastly it must be noted that the writer found, during the course of the proof reading that the monoatomic elements Ne, Kr, Xe and Rn take the positions in Fig. 10 just beneath the straight line  $ML_0/T_2 = 2R$ , in good accord with the present theory.

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