

A Thermodynamical Research on the Phenomena of Melting and Crystallization

By

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Abstract

As a continuation of the former papers the equilibrium between the free liquid molecules and the crystal nuclei, each composed of an immense number of the molecules, was investigated with various substances by applying van't Hoff's reaction isochore; and it was found that the melting point is well designated at the last stage of the nuclei decomposition, and that the relation between the melting point, the latent heat of fusion and its change with temperature was in good accord with the theory for various elements and compounds.

Introduction

In the former papers¹ the equilibrium between the free liquid molecules and the crystal nuclei, each composed of an infinite number of the molecules, was studied with monoatomic elements by applying van't Hoff's reaction isochore. In that case the change of the latent heat of fusion with temperature, which is mainly due to the difference of the specific heats of the melt and the crystal at the melting point, was neglected approximately; and the latent heat of fusion was taken to be constant and independent from the temperature for monoatomic elements. However, this is not correct in strict sense, the specific heats of the melt and the crystal are different in general at the melting point, slightly with monoatomic elements and remarkably with most of the chemical compounds. In the following such difference of two specific heats was taken into consideration, and its bearing on the ratio between the latent heat of fusion and the melting temperature was examined for various elements and compounds, which are provided with necessary data, by the aid of van't Hoff's reaction isochore.

1. U. Yoshida: These Memoirs, 24, 1, 37 (1942).

**Van't Hoff's Reaction Isochore for the Equilibrium between
the Crystal Nuclei and the Free Liquid Molecules
of a Substance**

Let the number of the free molecules and of the crystal nuclei among the total number N of the molecules in a super-cooled liquid state of a substance be N_f and n_c respectively. If we represent by ν the number of the constituent molecules of a crystal nucleus, we have

$$N = N_f + \nu n_c \dots \dots \dots (1)$$

Let us define the ratio x of the number of free molecules and the number N_d of the total discrete particles which is the sum of N_f and n_c as the degree of decomposition of the crystal nuclei. Then we get

$$x = \frac{N_f}{N_d} = \frac{N_f}{N_f + n_c} \dots \dots \dots (2)$$

$$1 - x = \frac{n_c}{N_d} = \frac{n_c}{N_f + n_c} \dots \dots \dots (3)$$

and the reaction constant K_c becomes

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

If we represent by T the absolute temperature, by R the gas constant referring to one gram mol and by L the latent heat of fusion of the crystal nucleus per one gram mol; then the reaction isochore takes the form

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

for a constant value of ν . By rewriting this equation we get

$$\frac{dx}{dT} = y \frac{L}{RT^2}, \dots \dots \dots (6)$$

where y represents

$$y = \frac{\nu x(1 - x)}{\nu(1 - x) + x} \dots \dots \dots (7)$$

Next by differentiating (6) with T ,

$$\begin{aligned} \frac{d^2 x}{dT^2} &= \frac{dy}{dx} \frac{dx}{dT} \frac{L}{RT^2} - \frac{2yL}{RT^3} + \frac{y}{RT^2} \frac{dL}{dT} \\ &= \frac{yL}{RT^3} \left\{ \frac{dy}{dx} \frac{L}{RT} - 2 + \frac{T}{L} \frac{dL}{dT} \right\} \dots \dots \dots (8) \end{aligned}$$

The value of $\frac{dy}{dx}$ in this equation which will be represented by Y is obtained by differentiating (7) with x as below :

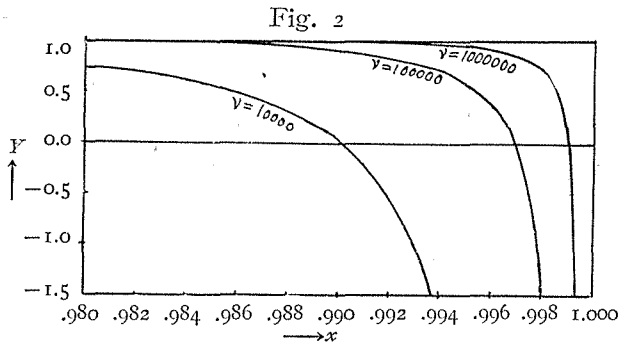
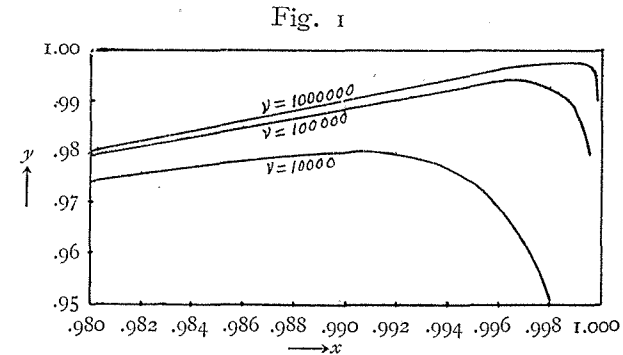
$$\frac{dy}{dx} = Y = \frac{\nu^2(1-x)^2 - \nu x^2}{\{\nu(1-x) + x\}^2} \dots\dots\dots(9)$$

Thus the equation (8) can be expressed as :

$$\frac{d^2x}{dT^2} = \frac{yL}{RT^3} \left\{ Y \frac{L}{RT} - 2 + \frac{T}{L} \frac{dL}{dT} \right\} \dots\dots\dots(10)$$

The condition for the maximum of $\frac{dx}{dT}$ with temperature variation can be obtained by putting the right hand side of the above equation to zero,

and this condition will be employed in the following in discussing the phenomenon of fusion of various substances. As to the values of y and Y corresponding to various values of x for comparatively small values of ν they are already shown in a previous paper¹, and for comparatively high values of 10000, 100000 and 1000000 they are plotted in enlarged



scale in curves in Figs. 1 and 2. For very large values of ν y increases almost proportionally with x and Y remains almost constant by taking the value of 1 except the value of x which is very close to 1. When x approximates extremely to 1 y attains a maximum, which corresponds to $Y=0$ in Fig. 2, and then decreases abruptly to

1. U. Yoshida: *loc. cit.*

zero at $x=1$. The maximum point of y obtained by putting $Y=0$ in equation (9) is

$$1-x = \frac{x}{\nu^{\frac{1}{2}}}, \dots \dots \dots (11)$$

and from this equation we get for a very large value of ν

$$x = 1 - \frac{1}{\nu^{\frac{1}{2}}}, \dots \dots \dots (12)$$

This shows that the maximum point of y approaches asymptotically to $x=1$ as the value of ν is increased indefinitely. If we take the temperature at which the value of x gives the maximum to y for a very large number of ν as the melting point of the crystal nuclei, then the melting of a crystal composed of an infinite number of constituent molecules comes to occur at $x=1$ corresponding to the perfect decomposition of the crystal into free liquid molecules.

In the previous paper¹ an essentially similar expression of K_c as (4) was used for the equilibrium between the cybotactic crystals and the free liquid molecules, and also between the crystal nuclei and the free liquid molecules. However, the writer made a serious mistake there in calculating the concentration of the cybotactic crystals and the free liquid molecules; and consequently he gave erroneous results to the specific heats of the super-cooled liquids. A correct calculation on this problem will be published in near future. As to the result obtained for the relation between the latent heat of fusion and the melting point of monoatomic elements no correction in essential points seems to be needed, because essentially the same expression of K_c as (4) was employed.

Designation of the Melting Point

The curves drawn in Fig. 3 show the manner of variation of the value of $\frac{dx}{dT}$ of ethyl alcohol with temperature for the values of ν of 100000 and 1000000. In this figure T_2 represents the temperature at which $\frac{dx}{dT}$ is maximum, and ΔT denotes the difference $T_2 - T$ for any temperature T . Though the manner of calculation in getting such curves will be explained later, this figure is shown here as an example to show the important behavior of the temperature dependence of

1. *loc. cit.*

$\frac{dx}{dT}$: i. e. the sudden decrease of the value of $\frac{dx}{dT}$ from a cer-

tain positive value to zero at a certain temperature for a very large number of ν . The sudden break of the $\frac{dx}{dT}$ curve is due

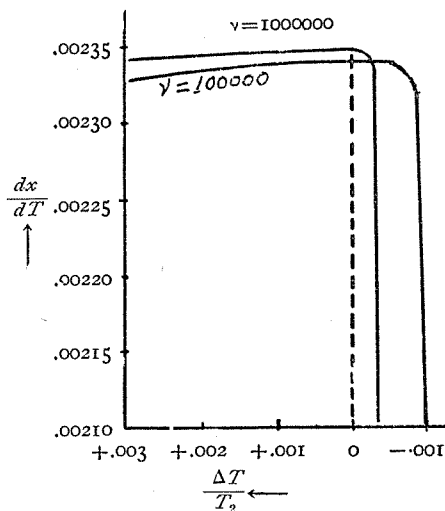
to the presence of the factor y in equation (6), which decreases suddenly to zero from its maximum value at the extreme vicinity of $x=1$ for a very high value of ν . As the occurrence of the nuclear decomposition is due to the presence of the nuclei to be decomposed, such

sudden decrease of the value of $\frac{dx}{dT}$ from a certain positive value to zero at a certain temperature signifies that the crystal nuclei can exist only below that temperature and can not exist above it in stable equilibrium. Consequently the melting point of the crystal of a substance can be well designated sharply to take place at a definite temperature where the sudden decrease to zero of the value of $\frac{dx}{dT}$ happens.

The maximum point of y , at which arises the sudden decrease of $\frac{dx}{dT}$ for a very high value of ν , can be located to $x=1 - \frac{1}{\nu^{\frac{1}{2}}}$ by putting $Y=0$ as is stated before.

From the relation between the melting point T_m and the T_2 point, at which happens the maximum of $\frac{dx}{dT}$ for a very great number of ν , various substances can be classified into two kinds: the one having these two temperatures coincident, and the other with which these two temperatures are separated distinctly. As was found in the previous papers almost all of the monoatomic elements except bismuth and gallium belong to the latter kind. Ethyl alcohol of which the temperature dependence of $\frac{dx}{dT}$ is shown in Fig. 3 belongs to the first kind. As is evident in Fig. 3 the T_2 point which is represented by a broken line in the figure is situated very close to the breaking

Fig. 3
Ethyl alcohol



point of the $\frac{dx}{dT}$ -curve. Moreover the breaking point approaches to the T_2 point with increase of the value of ν , and the final coincidence of these two points for $\nu=\infty$ can be imagined from the curves in the figure.

The Freezing Points of the Solvent and the Solute in a Dilute Solution

Let us apply the above way of reasoning to the crystallization of the solute and the solvent in a dilute solution, and test whether it is consistent or not. Now consider a dilute solution which contains s molecules of a solute in N molecules of a solvent whose freezing point is very low. If we represent respectively by s_f and s_c the numbers of the free molecules and the crystal nuclei of the solute, each one of which is composed of ν molecules, then we have

$$s = s_f + \nu s_c \dots\dots\dots (13)$$

If we define the ratio $\frac{s_f}{s}$ as the degree x of decomposition of the crystal nuclei, then we get

$$x = \frac{s_f}{s} = \frac{s_f}{s_f + \nu s_c} \dots\dots\dots (14)$$

and $1 - x = \frac{\nu s_c}{s_f + \nu s_c} \dots\dots\dots (15)$

The molecular concentrations of the free molecules and the crystal nuclei of the solute are respectively

$$\frac{s_f}{N + s_f + s_c} = \frac{s x}{N + s_f + s_c} \text{ and } \frac{s_c}{N + s_f + s_c} = \frac{\frac{s}{\nu}(1-x)}{N + s_f + s_c}, \dots (16)$$

and consequently the reaction constant K_c for the equilibrium between the free molecules and the crystal nuclei composed of ν molecules becomes

$$K_c = \frac{\left(\frac{s x}{N + s_f + s_c} \right)^\nu}{\frac{\frac{s}{\nu}(1-x)}{N + s_f + s_c}}$$

If we take $N + s_f + s_c \doteq N$ for the case of dilute solution the above equation can be written as

$$K_c = \nu \frac{\left(\frac{s}{N}\right)^\nu}{\frac{s}{N}} \frac{x^\nu}{1-x}, \dots\dots\dots(17)$$

Next let L be the heat of solution per 1 g-mol of the solute in the solvent, and let us suppose that L is approximately independent from temperature, then the integrated form of the reaction isochore becomes

$$\nu \frac{\left(\frac{s}{N}\right)^\nu}{\frac{s}{N}} \frac{x^\nu}{1-x} = C e^{-\frac{\nu L}{RT}}, \dots\dots\dots(18)$$

where C is a constant. This is entirely the same form as the equations (4) and (5) for the case of the freezing of a pure solvent, and the same condition for the freezing point, i. e. $1-x = \frac{x}{\nu^{\frac{1}{2}}}$ can be applied to the present case. From (18) we get

$$\frac{\nu^{\frac{1}{\nu}} \frac{s}{N}}{\left(\frac{s}{N}\right)^{\frac{1}{\nu}}} \frac{x}{(1-x)^{\frac{1}{\nu}}} = C^{\frac{1}{\nu}} e^{-\frac{L}{RT}}, \dots\dots\dots(19)$$

By taking $\nu^{\frac{1}{\nu}} = \left(\frac{s}{N}\right)^{\frac{1}{\nu}} = 1$ for a very large number of ν , and

$$\frac{x}{(1-x)^{\frac{1}{\nu}}} = \frac{x \nu^{\frac{1}{2\nu}}}{x^{\frac{1}{\nu}}} = 1$$

by applying the condition of the freezing point for a very large number of ν , the equation (19) becomes

$$\frac{s}{N} = C^{\frac{1}{\nu}} e^{-\frac{L}{RT}}, \dots\dots\dots(20)$$

This equation represents the relation between the molar concentration $c = \frac{s}{N}$ of the solution and the limiting temperature at which the crystallization of the solute commences. Thus this is nothing but the relation between the temperature and the solubility expressed in molar concentration of a solute in a solution. By expressing in logarithmic form we get the expression of the dependence of the solubility upon the temperature :

$$\log c = -\frac{L}{RT} + A, \dots\dots\dots(21)$$

where A is a constant.

Next let us consider the case of the freezing of the solvent in a dilute solution. If we represent by N_f and n_c respectively the number of the free molecules and that of the crystal nuclei among the total number N of the solvent molecules as before, and if we define $\frac{N_f}{N_f+n_c}$ as the degree of decomposition x of the crystal nuclei, then we have

$$\frac{N_f}{N_f+n_c} = x, \quad \frac{n_c}{N_f+n_c} = 1-x,$$

and

$$K_c = \left\{ \frac{(N_f+n_c)x}{N_f+n_c+s} \right\}^\nu \div \frac{(N_f+n_c)(1-x)}{N_f+n_c+s},$$

where s represents the number of the solute molecules. As the crystal nuclei can not exist at the temperatures higher than the freezing point of the solvent, and begin to be formed at the freezing point, we can regard N_f+n_c as constant and equal to the total number of solvent molecules N above the freezing point. Thus if we represent $(N_f+n_c)/(N_f+n_c+s) = N/(N+s)$ by ϕ , and consider it to be constant, then the integrated form of the reaction isochore becomes

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

i. e.
$$\frac{\phi x}{\phi^{\frac{1}{\nu}}(1-x)^{\frac{1}{\nu}}} = C^{\frac{1}{\nu}} e^{-\frac{L}{RT}}, \dots\dots\dots(22)$$

by assuming that L is approximately constant. By taking $1-x = \frac{x}{\nu^{\frac{1}{2}}}$ which is the condition for freezing, and $\phi^{\frac{1}{\nu}} = 1$ for a very large number of ν , we get from (22)

$$\phi = \frac{N}{N+s} = C^{\frac{1}{\nu}} e^{-\frac{L}{RT}}. \dots\dots\dots(23)$$

Next if we put $s=0$ the equation becomes

$$1 = C^{\frac{1}{\nu}} e^{-\frac{L}{RT_m}}, \dots\dots\dots(24)$$

in which T_m represents the freezing point of the pure solvent. From (23) and (24) we get

$$\frac{N}{N+s} = e^{-\frac{L}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right)} \doteq e^{-\frac{L}{RT_m^2} (T_m - T)}.$$

If we represent $T_m - T$ by ΔT , which is the lowering of the freezing point of the solvent in a dilute solution, and $\frac{s}{N}$ by c the molar con-

centration of solute in a dilute solution, then we get

$$1 - \frac{s}{N} = 1 - \frac{L}{RT_m^2} \Delta T,$$

i. e.
$$\Delta T = \frac{s}{N} \frac{RT_m^2}{L} = c \frac{RT_m^2}{L} \dots\dots\dots(25)$$

This is the well known expression for the lowering of the freezing point of the solvent in a dilute solution.

As the concordant results deduced as above by our mode of reasoning can be considered to be a confirmation of its correctness, we shall apply it in the following to the phenomena of crystallization of various substances which are provided with necessary data.

Crystallization of Elements and Compounds

Ordinarily the latent heat of fusion of the crystal of a substance is confined to that at its melting point. However when we want to discuss the thermal equilibrium between the free molecules and the crystal nuclei in the super-cooled state of a substance, we must know the value of the latent heat of fusion of the crystal nuclei at various temperatures. If we take the latent heat of fusion of the crystal nuclei to be the same as that of the adult crystal of the same substance by considering the number of constituent molecules of a crystal nucleus to be sufficiently large, then the latent heat of fusion L at a temperature T will be obtained approximately by the following equation from the values of the latent heat of fusion L_m , the specific heats C_p and c_p of the liquid and the adult crystal at the melting point T_m by neglecting the variation of $(C_p - c_p)$ with temperature.

$$L = L_m + (C_p - c_p)(T - T_m) \dots\dots\dots(26)$$

With this equation we get

$$\frac{dL}{dT} = C_p - c_p \dots\dots\dots(27)$$

By representing $C_p - c_p$ by a , and by putting the values of L and $\frac{dL}{dT}$ given by (26) and (27) in equation (10), the condition of the maximum of $\frac{dx}{dT}$ becomes

$$Y \frac{L_m + a(T_2 - T_m)}{RT_2} - 2 + \frac{T_2}{L_m + a(T_2 - T_m)} a = 0, \dots\dots(28)$$

where T_2 represents the temperature at which the maximum of $\frac{dx}{dT}$

takes place. When the maximum of $\frac{dx}{dT}$ happens at a temperature T_2 which is distinctly lower than T_m , the value of the degree of decomposition x of the crystal nuclei at the temperature T_2 must be definitely smaller than 1, because the perfect decomposition happens at the melting point T_m which is distinctly higher than T_2 . As the value of Y remains 1 for a very large value of ν and for all the values of x except the extreme vicinity of 1 where it decreases abruptly, the value of Y should be taken to be $Y=1$ in the present case where T_2 is distinctly lower than T_m . Thus by putting $Y=1$ the equation (28) becomes

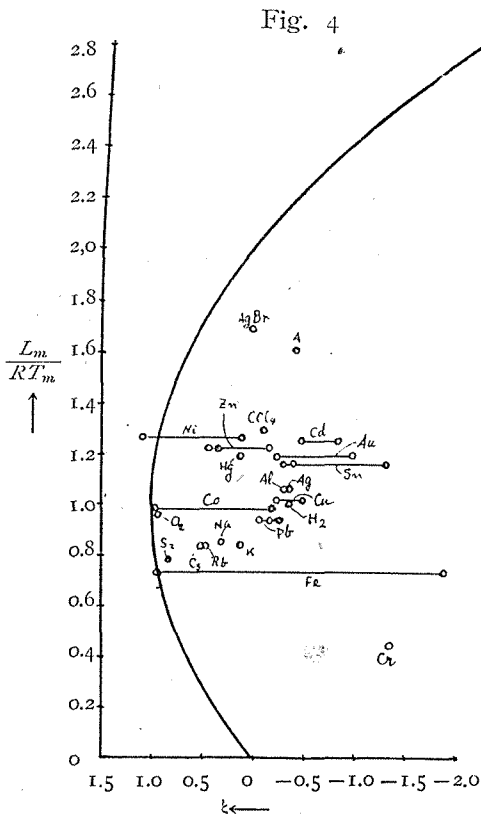
$$\frac{L_m + a(T_2 - T_m)}{RT_2} - 2 + \frac{RT_2}{L_m + a(T_2 - T_m)} \frac{a}{R} = 0$$

By representing $\frac{a}{R}$ by ξ we get from this equation

$$\frac{L_m + R\xi(T_2 - T_m)}{RT_2} = 1 \pm \sqrt{1 - \xi} \dots (29)$$

With this equation the value of T_2 can be calculated when the values of L_m , T_m and a for a substance is known. It is clear from equation (29) that for the value of T_2 to be different distinctly from T_m the value of ξ should be not greater than 1. Another condition which must be satisfied to conform with our way of reasoning is that T_2 must not exceed T_m . Consequently the limiting case for this condition will be found by taking $T_2 = T_m$ in equation (29) as follows:

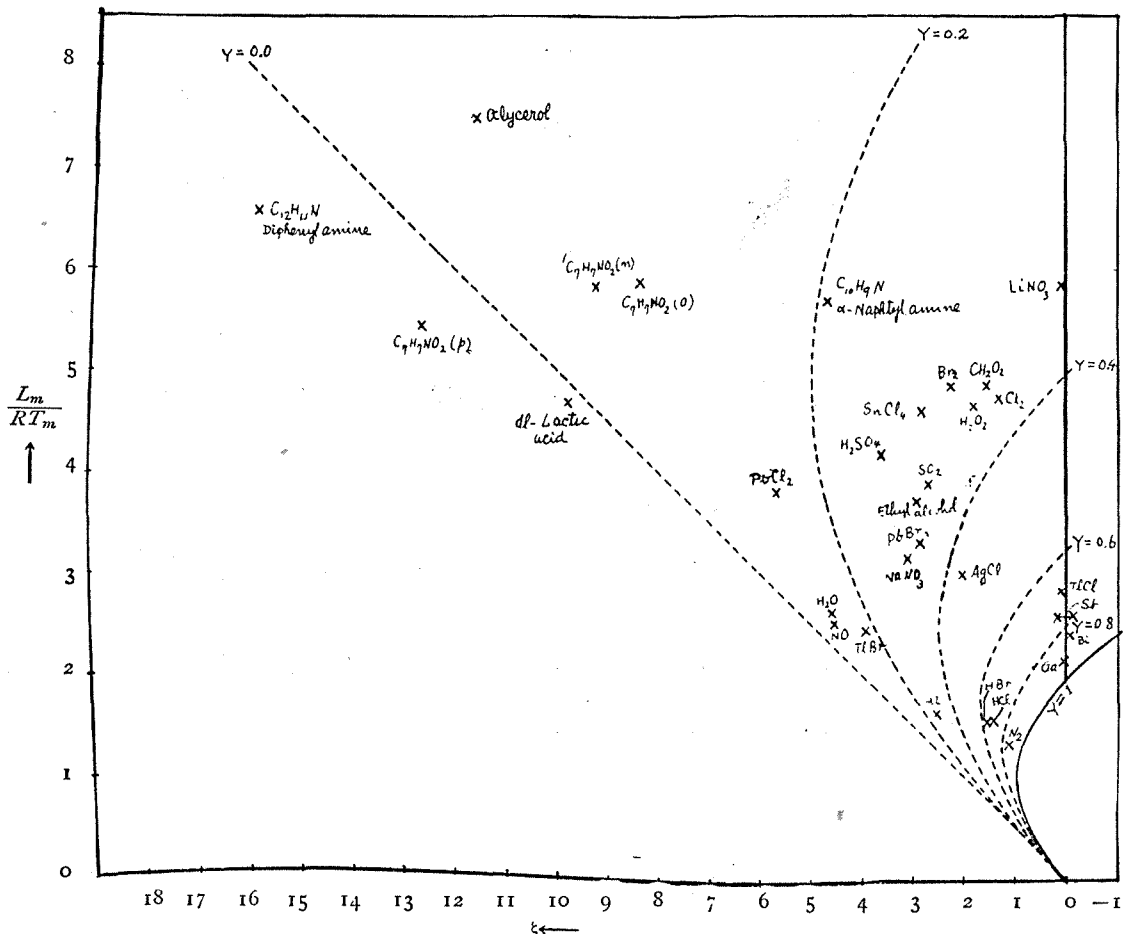
$$\frac{L_m}{RT_m} - 1 = \pm \sqrt{1 - \xi}$$



i. e. $\left(\frac{L_m}{RT_m} - 1\right)^2 = 1 - \xi$(30)

This boundary relation between L_m/RT_m and ξ , within which the situation of a substance referring to its values of L_m/RT_m and ξ must be confined in order to have the value of T_2 smaller than T_m , is represented by the parabola in Figs. 4 and 5. In these figures the situations of various substances as regard to the values of L_m/RT_m and ξ , which are taken as ordinates and abscissae respectively, are shown by small circles and crosses, by being distinguished according as they are confined or not in the parabolic domain.

Fig. 5



Most of the data necessary in our computation are taken from International Critical Table and are compiled in Tables I and II. As to the values of the difference of the specific heats $C_p - c_p$ of the elements, measurements on some substances which are considerably different according to the authors were compiled in International Criti-

Table I

Substance	Melting point T_m in $^{\circ}K$	Heat of fusion L_m in Cal g-mol	$\frac{L_m}{RT_m}$	Specific heat C_p in cal g-mol (liquid)	Specific heat c_p in cal g-mol (solid)	$\frac{C_p - c_p}{R}$
A	84°	268.0	1.61	5.35	6.18	-0.418
Ag*	1234°	2625.	1.07	—	—	-0.34
Al*	933°	1910	1.07	—	—	-0.30
Au*	1336°	3180	1.20	—	—	{-0.22 -0.99
Cd*	594°	1480	1.258	—	—	{-0.48 -0.83
Co*	1753°	3440	0.988	—	—	{+1.0 -0.18
Cr*	1888°	1650	0.441	—	—	-1.33
Cs	299°	501	0.845	7.92	6.92	+0.51
Cu*	1355°	2750	1.021	—	—	{-0.22 -0.50
Fe*	1808°	2680	0.746	—	—	{+0.97 -1.86
Hg	234°	556	1.196	6.95	6.67	+0.14
K	335°	569	0.855	7.16	6.93	+0.115
Na	371°	633	0.860	7.40	6.78	+0.31
Ni*	1725°	4340	1.270	—	—	{+1.1 +0.12
Pb*	601°	1123	0.941	—	—	{-0.055 -0.145 -0.19
Rb	312°	521	0.840	7.76	0.85	+0.46
Sn*	505°	1670	1.665	—	—	{-0.28 -0.37 -1.3
Zn*	693°	1695	1.225	—	—	{+0.46 +0.36 -0.15
H ₂	14°	28.2	1.013	0.466	1.146	-0.343
O ₂	55°	1050	0.961	12.60	10.72	+0.947
S ₂	386°	600	0.783	14.5	12.8	+0.856
AgBr	703°	2365	1.69	14.3	14.3	0.0
CCl ₄	249°	641	1.30	30.8	30.96	-0.078

Table II.

Substance	Melting point T_m in $^{\circ}K$	Heat of fusion L_m in cal g-mol	$\frac{L_m}{RT_m}$	Specific heat C_p in cal g-mol (liquid)	Specific heat c_p in cal g-mol (solid)	$\frac{C_p - c_p}{R}$ in cal g-mol	Y
Bi*	544°	2602	2.41	—	—	{ -0.024 -0.18	{ 0.834 0.861
Ga	303°	1324	2.205	5.49	5.49	0.0	0.907
Sb*	904°	4660	2.60	—	—	{ +0.44 -0.084	{ 0.705 0.782
Br ₂	266°	2580	4.89	17.18	12.8	+2.21	0.317
Cl ₂	171°	1624	4.77	16.0	13.4	+1.31	0.361
I ₂	387°	4000	5.20	13.4(?)	13.3	+0.050(?)	0.383(?)
N ₂	63°	170	1.36	13.28	10.98	+1.16	0.844
HCl	159°	505	1.60	14.86	11.95	+1.47	0.676
HBr	186°	576	1.56	14.5	11.4	+1.56	0.641
HI	220°	726	1.66	16.4	11.35	+2.55	0.28
NO	110°	555	2.54	17.4	8.46	+4.51	0.089
H ₂ O	273°	1433	2.65	18.0	8.85	+4.62	0.098
H ₂ O ₂	271°	2503	4.66	19.6	16.0	+1.84	0.344
SO ₂	243°	1900	3.94	20.0	14.65	+2.71	0.334
H ₂ SO ₄	283.4°	2360	4.20	33.75	26.45	+3.66	0.268
SnCl ₄	240°	2190	4.60	38.6	32.9	+2.89	0.298
PbCl ₂	758°	5800	3.85	33.63	22.22	+5.70	0.125
PbBr ₂	771°	5140	3.36	20.8	15.0	+2.90	0.338
TiCl ₄	700°	3970	2.86	14.15	13.85	+0.145	0.677
TiBr ₄	733°	3610	2.48	22.70	14.93	+3.92	0.169
AgCl	724°	4400	3.06	18.45	14.45	+2.02	0.437
LiNO ₃	523°	6090	5.86	26.90	26.70	+0.104	0.338
NaNO ₃	606°	3850	3.20	36.6	30.4	+3.09	0.324
CH ₂ O ₂ (Formic acid)	281°	2710	4.87	22.8	19.8	+1.53	0.346
C ₂ H ₆ O(Ethyl alcohol)	159°	1188	3.76	20.7	14.93	+2.91	0.327
C ₃ H ₈ O ₃ (Glycerol)	292°	4370	7.49	52.4	31.3	+10.63	0.079
C ₃ H ₆ O ₃ (<i>DL</i> -Lactic acid)	290°	2710	4.71	49.8	30.36	+9.80	-0.016
C ₇ H ₇ NO ₂ (<i>o</i> -Amino benzoic acid)	418°	4870	5.87	71.9	55.3	+8.32	0.101
C ₇ H ₇ NO ₂ (<i>m</i> -Amino benzoic acid)	453°	5220	5.81	71.9	53.5	+9.24	0.071
C ₇ H ₇ NO ₂ (<i>p</i> -Amino benzoic acid)	461°	5000	5.47	73.3	48.2	+12.67	-0.058
C ₁₀ H ₉ N(α -Naphthyl amine)	323°	3660	5.71	87.0	77.8	+4.70	0.206
C ₁₂ H ₁₁ N(Diphenyl amine)	326.4°	4260	6.58	104.5	73.1	+15.84	-0.062
C ₁₆ H ₃₂ O ₂ (Palmitic acid)	328°	10070	15.48	209	137.5	+36.1	-0.022

cal Table. Though these measurements are not reliable they are tabulated in Tables I and II by being marked by * for these substances, and these substances are also plotted in Figs. 4 and 5. When the situation of a substance in the figures is different for different values of $(C_p - c_p)/R$ the different situations are connected by a horizontal line indicating that they belong to a same substance. The substances which are provided with reliable values of C_p and c_p are water, mercury, ethyl alcohol, glycerol and *dl*-lactic acid; and they are also tabulated and plotted in Tables I and II and in Figs. 4 and 5. For the other substances the specific heats C_p and c_p have not been measured just at the melting point. But there are some for which the specific heats C_p and c_p are measured respectively at the temperatures not much far off the melting point; and these substances, though accompanied by considerable errors, are tabulated and plotted in the tables and the figures respectively. In Fig. 4, only the substances whose situations are confined within the parabolic domain are represented, and in Fig. 5, only those situated outside the parabolic domain are shown in reduced scale.

It is especially note-worthy that all substances which are situated within the parabolic domain have the values of L_m/RT_m smaller than 2. For the positive value of ξ which is smaller than 1 this must be satisfied in order that the temperature T_2 be lower than T_m . However, the circumstances are different for the negative values of ξ ; and L_m/RT_m can take the values higher than 2 even within the parabolic domain. In spite of this possibility of L_m/RT_m being greater than 2, it remains always smaller for all the substances in the parabolic domain, which consist mostly of monoatomic elements. According to the writers's view, the main cause for this is probably erroneous measurements or erroneous estimations of the specific heats C_p and c_p at the melting point. As is stated above no reliance on the values of $C_p - c_p$ must be put for all the substances situated in the parabolic domain except Hg. Ordinarily the specific heat of a solid is measured with polycrystalline material. As is imagined in a former paper¹ the crystalline boundaries are cemented by the super-cooled liquid or solid of the same substance, and the width of this boundary liquid layer increases with rise of the temperature. This signifies a partial melting of the crystals at their boundary liquid layer which increases as the tempera-

1. U. Yoshida: These Memoirs, 24 (1943); 學術研究會編物理學講演集 4, (昭 18).

ture approaches to the melting point. This fact will assist in giving a value higher than the ideal one of the specific heat of a solid near the melting point. Thus if we assume, ideally speaking, that the value of the specific heat of a solid can not exceed that of the liquid of the same substance at the melting point at least for the monoatomic elements, then it follows that the value of L_m/RT_m should be smaller than 2 in order to cause the melting of the crystal at a temperature which is definitely higher than the T_2 point. This is nothing but the T_2 -point law deduced by taking approximately $\xi=0$ in previous papers as being valid for most of the monoatomic elements except bismuth and gallium. Besides the monoatomic elements, five substances H_2 , O_2 , S_2 , $AgBr$ and CCl_4 obey also the T_2 -point law as is seen in Fig. 4.

Next let us consider the substances which are situated outside the parabolic domain. For a substance situated in the parabolic domain the maximum of $\frac{dx}{dT}$ occurs with $Y=1$ as is stated above.

The maximum of $\frac{dx}{dT}$ can also take place with the values of Y which are definitely smaller than 1. But for a very great number of ν , Y can take a value which is distinctly smaller than 1 only at the limit when x tends to 1. As the melting point is also designated at the same limit, the T_2 point becomes thus coincident with the melting point T_m in the present case. Consequently by putting $T_2=T_m$ in equation (28), we get

$$Y \frac{L_m}{RT_m} - 2 + \frac{RT_m}{L_m} \xi = 0,$$

or $Y = \left(2 - \frac{RT_m}{L_m} \xi \right) \frac{RT_m}{L_m} \dots \dots \dots (31)$

The value of Y calculated by this equation for various substances are tabulated in the last column of Table II. The curves drawn in broken line in Fig. 5 show the relation between L_m/RT_m and ξ for various constant values of Y , i. e. for $Y=0, .2, .4, .6$ and $.8$; and they represent the situation of the substances as regard to the value of Y . As the peculiarity of the substances situated outside the parabolic domain is that they have the T_2 points which are coincident respectively with their melting points T_m , this will be called "the coincident T_2-T_m points law."

Considering in the above way, all substances including elements and compounds can be divided with respect to their crystallizing or melting property into two kinds: the one those obeying the T_2 point

law, and the other those governed by the coincident $T_2 - T_m$ points law. Most of the monoatomic elements, of which L_m/RT_m is smaller than 2, obey the former law; and most of the compounds including inorganic and organic ones obey the latter law. As is seen from Fig. 5 the value of ξ is positive for all the compounds, indicating that the specific heat in the liquid state is greater than that in the crystalline state at the melting point. This seems to be caused by the setting up of new degree of freedom of thermal motion by the melting. It is also very interesting to note in Fig. 5 that the situation of all the substances belonging to the coincident $T_2 - T_m$ points law is not only bounded by the straight line $\xi=0$, but is almost bounded also by the other straight line $Y=0$. This indicates that a further approach to the limit $x=1$ than that corresponding to $Y=0$, (i. e. $1-x=\frac{x}{\nu^{\frac{1}{2}}}$) for a very large number of ν is not necessary in causing the melting of the crystal of a substance. For the organic compounds having high molecular weight, both the values of L_m/RT_m and ξ become considerable in general; and with palmitic acid having the molecular weight of 256 they are so large as 15.48 and +36.1 respectively that this substance escaped far from the scope of Fig. 5.

Till now we have considered that the temperature T_2 at which the maximum of $\frac{dx}{dT}$ takes place coincides with the melting point T_m of the substance when Y becomes definitely smaller than 1 for a very great number of ν . This is of course an approximation for a finite number of ν , however great it may be, as we have defined the melting to take place at $Y=0$ ($1-x=\frac{x}{\nu^{\frac{1}{2}}}$). However, this approximation is well allowable if we take the value of ν sufficiently great, as is shown in the following by taking the case of ethyl alcohol as an example.

From the necessary data given in Table II for ethyl alcohol we get the value of Y as $Y=0.327$ with equation (31); and for this value of Y , the values of x becomes 0.9962 and 0.9988 respectively for $\nu=100,000$ and $\nu=1,000,000$. If we call the temperature at which Y and x take these values respectively as "the T_2 point," then the latent heat of fusion L can be expressed, by taking T_2 as almost the same as T_m the real melting point at which Y becomes zero, as follows:

$$L=L_m+a(T-T_2)$$

By using this value of L the equation (5) becomes on integration

$$\frac{x}{(1-x)^{\frac{1}{\nu}}} = Ce^{-\frac{L_m - aT_2}{RT} + \frac{a}{R} \log T}, \dots\dots\dots(32)$$

where C is a constant. Next if we represent the value of x at the temperature T_2 by x_2 , then we get from equation (32)

$$\frac{x_2}{(1-x_2)^{\frac{1}{\nu}}} = Ce^{-\frac{L_m - aT_2}{RT_2} + \frac{a}{R} \log T_2} \dots\dots\dots(33)$$

By dividing (32) by (33) we have

$$\frac{x}{(1-x)^{\frac{1}{\nu}}} = \frac{x_2}{(1-x_2)^{\frac{1}{\nu}}} e^{-\frac{L_m - aT_2}{R} \left(\frac{1}{T} - \frac{1}{T_2} \right) + \frac{a}{R} \log \frac{T}{T_2}} \dots\dots(34)$$

If we represent $T_2 - T$ by ΔT , and consider it to be very small when compared with T_2 , then (34) becomes, by expanding into the power series of $\Delta T/T_2$, as follows:

$$\frac{x}{(1-x)^{\frac{1}{\nu}}} = \frac{x_2}{(1-x_2)^{\frac{1}{\nu}}} \left\{ 1 - \frac{L_m}{RT_2} \frac{\Delta T}{T_2} \right\} \dots\dots\dots(35)$$

Similarly we get from equation (6)

$$\frac{dx}{dT} = \frac{\gamma}{T_2} \left\{ \frac{L_m}{RT_2} + \left(2 \frac{L_m}{RT_2} - \xi \right) \frac{\Delta T}{T_2} \right\} \dots\dots\dots(36)$$

By taking, as for the case of ethyl alcohol, $T_2 = T_m = 159^\circ\text{K}$, $L_m/RT_2 = L_m/RT_m = 3.76$, $\xi = +2.91$, $x_2 = 0.9962$ for $\nu = 100,000$ and $x_2 = 0.9988$ for $\nu = 1,000,000$, the values of $\frac{dx}{dT}$ for different values of $\Delta T/T_2$ were calculated with equations (35) and (36). In carrying out the calculation, the values of x corresponding to various values of $\Delta T/T_2$ were first obtained with equation (35), then the values of γ corresponding to the values of x which again correspond to the various values of $\Delta T/T_2$ were found by the aid of Fig.1, and lastly the values $\frac{dx}{dT}$ for different values of $\Delta T/T_2$ were calculated from equation (36) by using the values of γ thus calculated. The results of calculation for $\nu = 100,000$ and $\nu = 1,000,000$ are shown by Fig.3. As is seen in the figure the value of $\frac{dx}{dT}$ drops suddenly to zero at a certain temperature which corresponds to the melting point according to our definition and is slightly different from the T_2 point. However, as T_m approaches very rapidly to T_2 when ν increases from 100,000 to 1,000,000, we can say that T_2 coincides with the melting point T_m at the limit when ν tends to infinity.

Lastly it must be noted that the cost of this research has been defrayed from the Scientific Research Expenditure of the Department of Education.
