The Corresponding Temperature of Liquid Elements and its Bearing on the Melting Points and the T_2 Points

by Usaburo Yoshida

Abstract

From Trouton's rule of the approximate proportionality between the latent heat of vaporization L_v per gram molecule of the elements and the normal boiling point T_b expressed in the absolute temperature scale, the mean value of the ratio L_v/T_b was found to be 27.4 cal per degree. The temperature $T_{c.\,b.\,p.}$ obtained by dividing the observed value of L_v of an element by 27.4 is called the corresponding boiling point of the element, which is somewhat different from the normal boiling point. Relying upon Young's formula for the saturated vapour pressure the ratio of the vapour pressure at the corresponding boiling point of a liquid to that it would have to acquire at the infinitely high temperature becomes the same for all substances. By plotting in a graph the corelation among the corresponding boiling points, the melting points and the T_2 points of monoatomic elements, the correspondency of the state of different elements and the unaccordance of their melting points with any simple energy law were investigated.

Introduction

In a paper[1] published recently the writer applied van't Hoff's reaction isochore to the equilibrium between the cybotactic crystals and the free molecules of a substance in liquid state; and by taking the number of constituent molecules of a cybotactic crystal as infinite the case was transferred to the equilibrium between the crystal nuclei and the free liquid molecules of a substance in its super-cooled state. By denoting the absolute temperature by T and the degree of decomposition of the crystal nuclei by x, the change of $\dfrac{dx}{dT}$ with temperature for monoatomic elements was investigated; and it was found that the temperature T_2 at which $\dfrac{dx}{dT}$ is maximum has a simple and important relation with the latent heat of fusion referred to one gram atom for the majority of elements, excepting bismuth and gallium. When the

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1. U. Yoshida: These Memoirs, A, **24**, 121 (1941).

latent heat of fusion of a monoatomic element referred to one gram atom is represented by L_f calorie, the T_2 point was found to be given by

$$\frac{L_f}{T_2} = 2R, \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

where R is the gas constant, and takes the value of 1.985 calorie per degree. This relation will be called " the T_2 -point-law " hereafter. Next it was found that when the temperature is raised the value of $\frac{dx}{dT}$ falls to zero abruptly at the limit when x approaches to 1 at a certain temperature. This temperature was taken as the melting point T_m of the substance, because the crystal nuclei can exist in equilibrium only in lower temperatures than this but not above it. As the T_2 point occurs at a smaller value of x than 1 for the majority of monoatomic elements excepting bismuth and gallium, this point is usually lower than T_m. The T_2-point-law and this relation between T_2 and T_m for the rare gases in their super-cooled liquid state are

Fig. 1
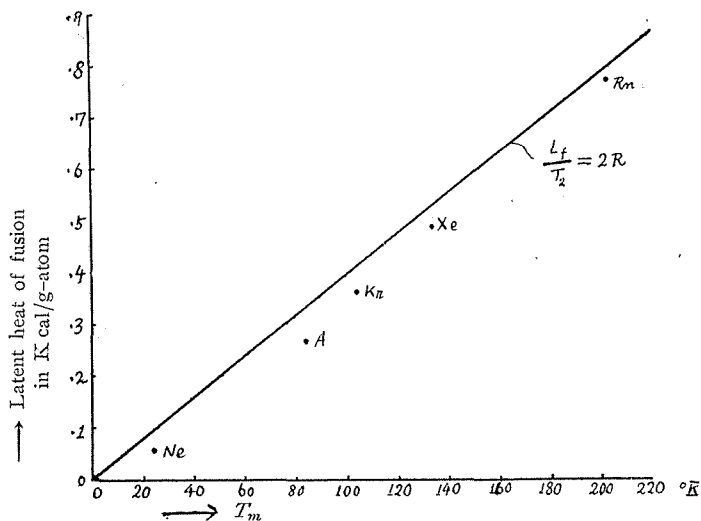
shown by Fig. 1, as a supplement to Fig. 10 of the former paper. In this figure the latent heat of fusion L_f is taken as ordinate and the melting point T_m and the T_2 point as abscissa, and the T_2-point-law is represented by the straight line. As is seen in the figure all the dots which represent the observed values of L_f and T_m occupy the positions just on the right hand side of the straight line. This shows

that T_m is slightly higher than T_2 for every substance as was deduced theoretically.

Trouton's Rule and the Graphical Representation of the Latent Heats of Vaporization, Boiling Points, T_m and T_2 Points of Monoatomic Elements

As is stated above, if we imagine the state of super-cooled-liquid of a substance, we can follow the temperature change of its property even below the melting point without any discontinuity, and a comparison of corresponding states of different substances in wider temperature range becomes thus possible. For the present, only monoatomic elements which are provided with necessary data are investigated; and if not particularly noticed, monoatomic elements will be meant by the substances in the present paper. The observed values for many substances of normal boiling point T_b, latent heat of vaporization L_v at T_b referred to one gram atom, melting point T_m and latent heat of fusion L_f at T_m referred to one gram atom are taken mostly from the International Critical Table, and are tabulated in Table I. The values of T_2, which are given in the 6th column of Table I are calculated by means of the T_2-point-law from the observed values of L_f for the majority of the elements; but for bismuth it was taken to be the same as its melting point. The corelation among the T_2 points, melting points, boiling points and the latent heats of vaporization at the boiling points is shown in Fig. 2 for most of the elements and in Fig. 3 for the rare gases. In these figures the latent heat of vaporization is taken as ordinate and the temperature as abscissa, and the boiling points are represented by the dots. As is seen in Fig. 2 most of the dots take the positions near the straight line passing through the origin of coordinates; showing that the values of L_v/T_b for different substances are approximately the same in accord with Trouton's rule. The straight line OA in Fig. 2 is so drawn that the value of L_v/T_b is the same as the mean for the elements having comparatively high boiling points and takes the value of 27.4. Thus the straight line OA may be called the "mean boiling point line"; but the writer prefers to call it "the corresponding boiling point line" by the reason as will become clear later. Next vertical lines were drawn to pass through every one of the dots, and from their intersections with the straight line OA horizontal lines were drawn. On each of these horizontal lines, the T_2 point and the melting point T_m of the corresponding element were marked by a small circle and a

Table I

Element	Normal boiling point T_b in °K {(S) : Sublimation}	Latent heat of vaporization L_v at T_b in $\dfrac{\text{K cal}}{\text{g-atom}}$	Melting point T_m in °K	Heat of fusion L_f at T_m in $\dfrac{\text{K cal}}{\text{g-atom}}$	T_2 in °K	$T_{c.b.p.}$ in °K
A	87	1.502	84	0.268	67.5	54.9
Ag	2223	59.5	1233	2.63	663	2175
Al	2073	53.7	933	1.91	482	1960
As (metallic)	888(S)	33.2(S)	1087$\left(\begin{smallmatrix}36\\ \text{atms}\end{smallmatrix}\right)$			1210
Au	2873	88.0	1336	3.18	803	3220
Bi	1723	46.1	544	2.60	544	1685
Cd	1040	25.6	594	1.48	374	935
Co	3173	90.8	1753	3.44	868	3120
Cr	2473	76.5	1888	1.65	416	2800
Cs	943	17.45	299	0.501	126	637
Cu	2573	70.6	1356	2.75	693	2580
Fe	3273	90.8	1808	2.68	776	3315
He	4	0.024	< 0.8			
Hg	630	14.2	234	0.556	140	519
K	1033	20.1	335	0.57	144	735
Kr	121	2.24	104	0.36	91	82
Li	1470	40.6	459	0.835	211	1482
Mg	1383	62.6	924	1.7	429	2285
Mn	2173	57.4	1533	2.01	507	2097
Na	1153	25.1	371	0.633	159	915
Ne	27	0.416	24	0.057	14.4	15.2
Ni	3173	90.6	1725	4.33	1090	3310
Pb	1893	46.1	600	1.12	282	1682
Pt	4573	124.0	2028	5.25	1325	4530
Rb	973	17.7	312	0.52	131	646
Rn	211	4.3	202	0.776	196	157
Sn	2533	77.6	505	1.67	421	2835
Xe	164	3.2	133	0.49	124	117
Zn	1180	23.7	692	1.7	429	865

cross respectively. Fig. 3, which is for rare gases, is drawn in a magnified scale entirely in the same manner as Fig. 2. From these figures we note that, while the crosses are distributed widely apart, the small circles rather crowd together near a straight line passing through the origin of coordinates.

With metallic arsenic, the vapour pressure due to sublimation from the solid is very high, and it boils under atmospheric pressure,
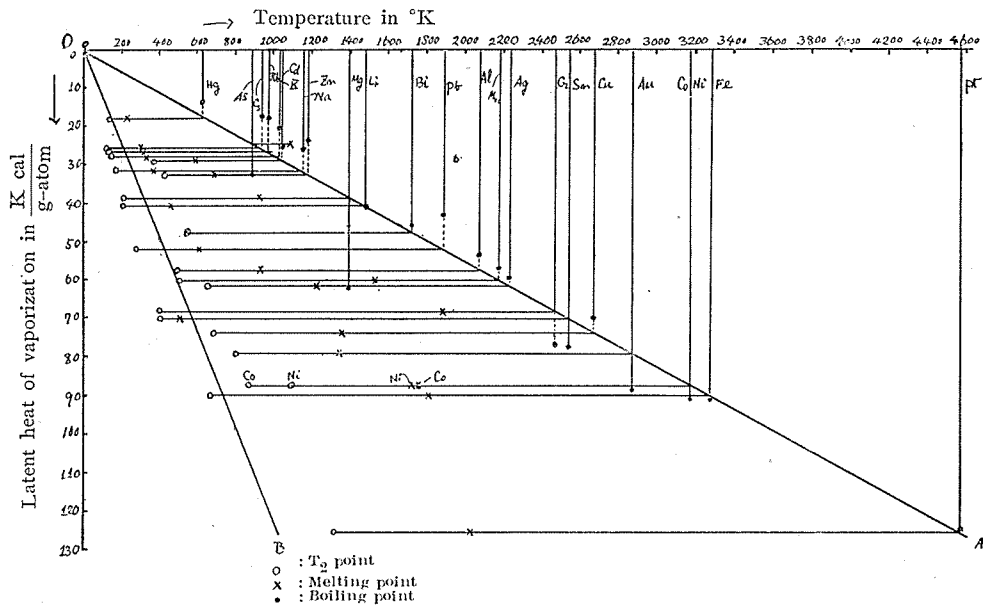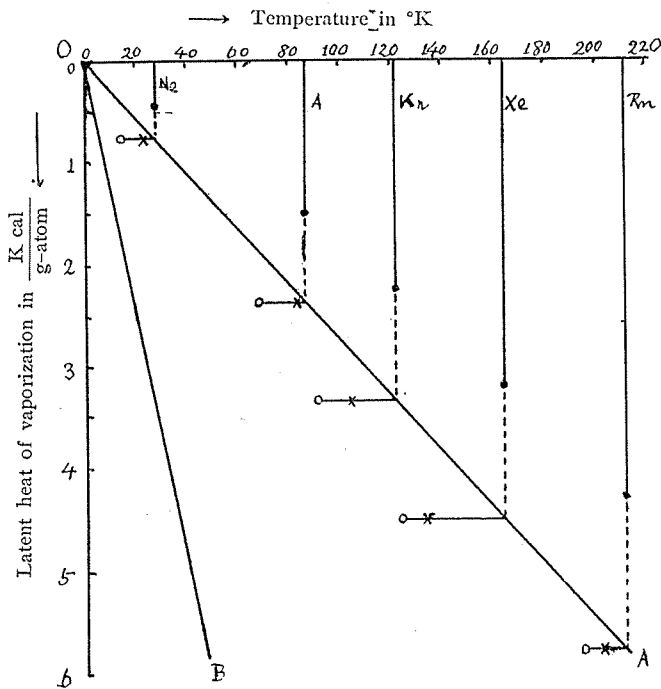
Fig. 2

→ Temperature in °K

o : T_2 point
x : Melting point
• : Boiling point

Fig. 3

→ Temperature in °K

from the solid state instead of from the liquid. This is indicated by
inserting (s) in Table I. Thus the latent heat of vaporization L_v at
T_b as is given in the table is somewhat greater than that in the case
of the vaporization from the liquid. But the writer regards the for-
mer as approximately the same with the latter, and he treats arsenic
entirely in the same manner as the other elements. The vapour pres-
sure at the triple point of arsenic is so high as 36 atmospheres, the
temperature at this point being 1087°K. Consequently if we take the
melting point of this element as 1087°K, it comes to be higher than
the boiling point 888°K, in contrary to the ordinary case. This ap-
parent contradiction is caused by the conventional definition of the
normal boiling point in taking it as the temperature at which the
vapour pressure attains the standard atmospheric pressure. Instead
of it, if we take a sufficiently high vapour pressure as that at the
boiling point, then the boiling point rises correspondingly and comes
to be higher than the melting point, in right order, as the melting
point is only slightly affected by the change of pressure.

Vapour Pressure at the Melting Point

The vapour pressure of a substance at its melting point is con-
siderable when the melting point is very close to its boiling point as
in the case of rare gases. On the contrary when the melting point
of a substance is very much lower than its boiling point, its vapour
pressure at the melting point decreases so remarkably as is impossible
to be measured as in the case of most metals. In the latter case the
vapour pressure at the melting point is only to be estimated by ex-
trapolation from its values measured at much higher temperatures. In
doing so Young's formula representing the vapour pressure as a func-
tion of temperature was used. If we take the latent heat of vapo-
rization L_v as approximately constant irrespectively of temperature,
then Young's formula can be written as

$$p = p_0 e^{-\frac{L_v}{RT}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

where p represents the vapour pressure at the temperature T, and p_0
that which the substance would take at infinitely high temperature if
the value of L_v is supposed to remain constant. By taking logarithm
the equation (2) becomes

$$\log_{10} p = \log_{10} p_0 - \frac{L_v}{RT} \log_{10} e,$$

and can be rewritten as

$$\log_{10} p = B - \frac{A}{T} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3)$$

where A and B are constants.

For many metals their vapour pressures were measured in a range of temperature much higher than their melting points, and the numerical values of A and B were determined. By using these values

Table II

Element	Vapour pressure p_m in mm Hg at T_m	$\log_{10} p_m$	$\dfrac{T_b}{T_m}$	$\dfrac{L_f}{L_v}$	$\dfrac{T_{c.b.p.}}{T_m}$
A	512(Trip.)	+ 2.71	1.035	0.178	0.654
Ag	1.51×10^{-2}	− 1.82	1.80	0.0441	1.76
Al	—	—	2.20	0.0356	2.10
As	2.74×10^4 (Trip.)	+ 4.44	0.818	—	1.11
Au	6.21×10^{-6}	− 5.21	2.15	0.0361	2.41
Bi	5.1×10^{-11}	−10.29	3.17	0.0564	3.10
Cd	1.07×10^{-1}	− 0.971	1.75	0.0578	1.57
Co	2.35×10^{-2}	− 1.63	1.81	0.0379	1.78
Cr	—	—	1.32	0.0216	1.48
Cs	1.4×10^{-6}	− 5.85	3.16	0.0287	2.13
Cu	2×10^{-6}	− 5.69	1.90	0.0389	1.91
Fe	3.47×10^{-2}	− 1.46	1.81	0.0295	1.83
Hg	1.2×10^{-6}	− 5.91	2.69	0.0391	2.22
K	9.12×10^{-7}	− 6.04	3.09	0.0284	2.195
Kr	133(Trip.)	+ 2.124	1.165	0.161	0.789
Li	—	—	3.20	0.0206	3.24
Mg	1.95×10^{-2}	− 1.71	1.50	0.0272	2.47
Mn	1.63	+ 0.21	1.42	0.0350	1.37
Na	1.05×10^{-7}	− 6.98	3.11	0.0252	2.47
Ne	300	+ 2.477	1.13	0.137	0.633
Ni	1.78×10^{-2}	− 1.75	1.84	0.0477	1.92
Pb	2.9×10^{-9}	− 8.53	3.16	0.0243	2.81
Pt	2.1×10^{-5}	− 4.68	2.26	0.0423	2.23
Rb	1.9×10^{-6}	− 5.72	3.12	0.0294	2.07
Rn	500(Trip.)	+ 2.70	1.04	0.180	0.778
Sn	4.7×10^{-26}	−25.33	5.03	0.0215	5.61
Xe	80	+ 1.90	1.23	0.153	0.88
Zn	1.5×10^{-1}	− 0.82	1.71	0.0719	1.25
		Mean value		0.0318	

of A and B, given in the International Critical Table, the writer cal-culated by extrapolation the vapour pressures and their logarithms at the melting points of metals; and they are tabulated in Table II. As the melting points were very much lower than the temperature ranges in which the vapour pressures were measured the values of vapour pres-sures and their logarithms given in Table II are considered to contain considerable errors of course. However, for an investigation upon their orders of magnitude they will still be of use sufficiently. For the vapour pressures of the rare gases and arsenic values directly measured at the melting point or at the triple point are available. As the mel-ting point is very near to the triple point, the writer regards for the present that the vapour pressures at the triple points are the same as those at the melting points, and they are given in Table II by noting them with (Trip.).

It has already been stated that the vapour pressure of a substance at its melting point gets the smaller as the greater apart the melting point is removed from its boiling point. Now let us consider this point quantitatively. As is stated before the vapour pressure of a substance at a temperature T can be expressed approximately by equation (2). At the melting and boiling points it becomes respectively
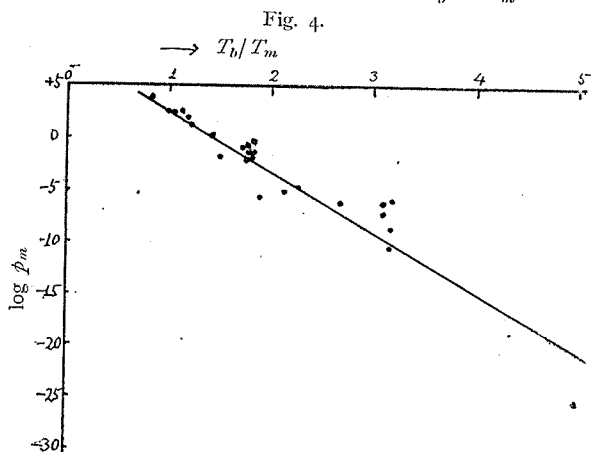
$$p_m = p_0 \, e^{-\frac{L_v}{RT_m}},$$

and

$$p_b = p_0 e^{-\frac{L_v}{RT_b}}$$

where p_m and p_b represent the vapour pressures at the melting and boiling points respectively. Dividing one with the other and then taking the logarithm we get

$$\log_{10} p_m = \log_{10} p_b - \left\{ \frac{L_v}{RT_b} \left(\frac{T_b}{T_m} - 1 \right) \right\} \log_{10} e \quad \ldots\ldots\ldots (4)$$

Fig. 4.

$\longrightarrow T_b / T_m$

If Trouton's rule is valid for different substances, we can see from equation (4) that the values of $\log_{10} p_m$ for different substances must dec-rease linearly with the values of T_b / T_m. This point was exa-mined by represen-ting the values of $\log_{10} p_m$ and T_b / T_m,

given in Table II, by the dots plotted in Fig. 4 ; and an approximately linear relation between $\log_{10} p_m$ and T_b/T_m was obtained. The straight line shown in Fig. 4 is so drawn that it passes through the average position of the dots. The average value of L_v/T_b obtained from the inclination of the straight line is 27.0, and is in good accord with 27.4 which is given above.

The Corresponding Temperature of Different Substances in the Liquid State, and the Situation of their Boiling, Melting and T_2 Points

The values of the vapour pressure, p_0, which a liquid would take at infinitely high temperature is different according to the kind of substances as will be seen from the deviation of the normal boiling points from Trouton's rule. However, at the normal boiling points all substances must possess the same normal atmospheric pressure. Considered from this angle the normal boiling points of different substances can not be accepted as physically corresponding temperatures in their liquid state. It seems more reasonable, from the theoretical point of view, to define the corresponding temperatures of different liquid substances as those at which the ratio p/p_0 is constant. If we take the latent heat of vaporization L_v of a substance as approximately constant independent of the temperature change, then the value p/p_0 is determined, by the aid of Young's formula, only by the value of L_v/T irrespectively of the kind of substances. Hence the writer will define the corresponding temperatures as those at which L_v/T is constant for different substances. It has already been stated that the average value of L_v/T_b for many elements having comparatively high boiling points is 27.4. Accordingly, the temperatures determined by equating L_v/T to 27.4 and by assigning to L_v the observed values will be called " the corresponding boiling points " and they will be represented by $T_{c.b.p.}$. The values of $T_{c.b.p.}$ thus calculated for different elements are given in the last column of Table I. As the values of p_0 are different for different elements the actual values of the vapour pressure at the corresponding boiling points are different with the kind of elements. However, the mean of these different actual values will be very close to the normal atmospheric pressure, because the proportional constant 27.4 of $L_v/T_{c.b.p.}$ was obtained by taking the average of the values of L_v/T_b for the elements having comparatively high boiling points.

Defining the corresponding boiling point as above, the writer re-

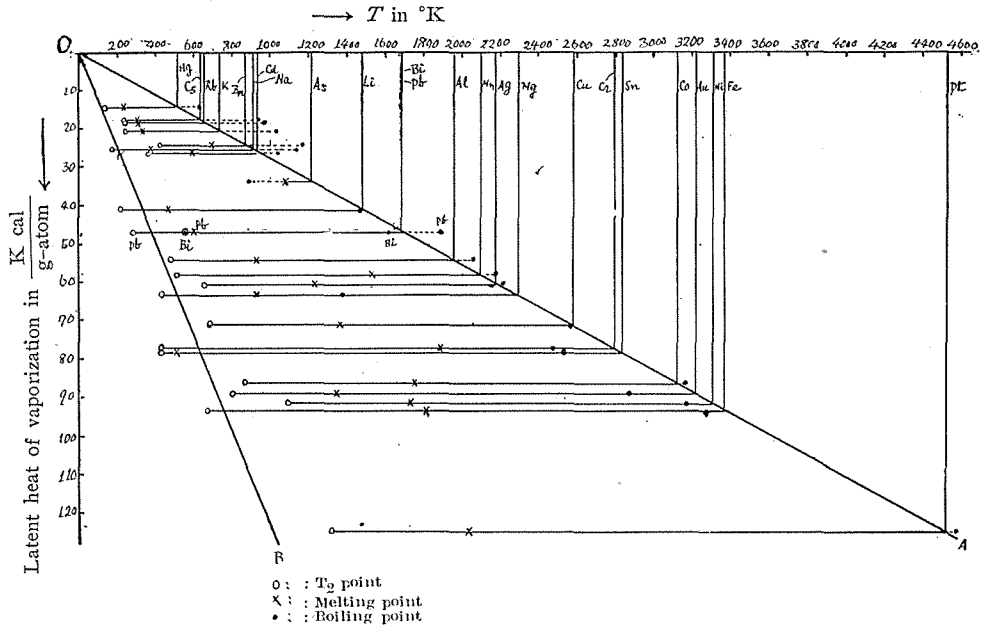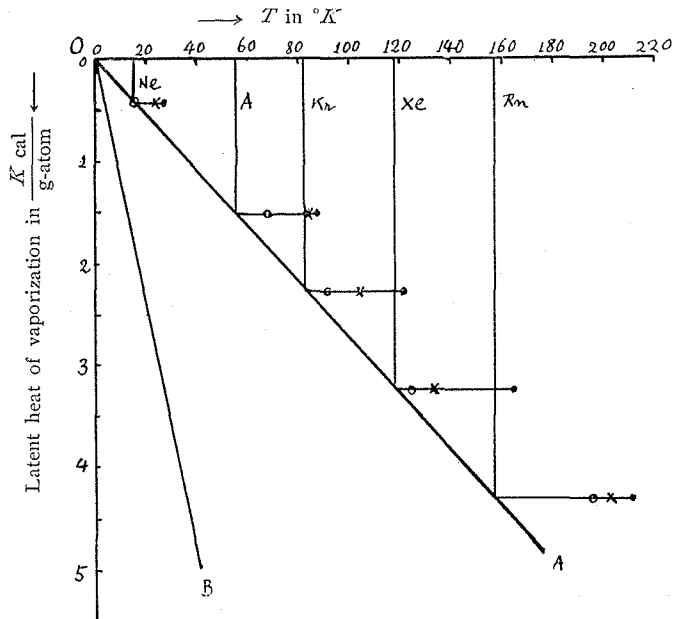plotted the corelation, as seen in Figs. 2 and 3, among the values of

Fig. 5

→ T in °K

o : : T₂ point
x : : Melting point
• : : Boiling point

Fig. 6

→ T in °K

L_v, T_b, T_m and T_2 for many elements, by taking the corresponding boiling points as the reference points and by arranging them on a straight line. In Figs. 5 and 6, the latent heat of vaporization is taken as ordinate and the temperature as abscissa, and the corresponding boiling points occupy the intersections of the line OA with the vertical lines (which we shall call "the lines of heat of vaporization") whose lengths are taken to represent respectively the values of the latent heat of vaporization of the elements. Fig. 6 is drawn in enlarged scale for the rare gases entirely in the same manner as Fig. 5. In these figures the T_2 point, the melting point and the normal boiling point of the element are marked respectively by a small circle, a cross and a dot on the horizontal line passing through the position of the corresponding boiling point of that element on the line OA. Such a horizontal line representing the temperature of a substance will be called "the temperature line" of that element.

If we take the corresponding boiling points of different substances

Fig. 7

as above the correspondency of different elements as regard to their vapour pressures can be seen very clearly with Figs. 5 and 6. If we call p/p_0 "the relative vapour pressure" for the sake of convenience then the relative vapour pressure is constant for all elements at their corresponding boiling points which lie on the straight line OA. Moreover, we can see easily with Figs. 5 and 6 that the relative vapour pressures of different elements at the temperatures determined by the intersections of their temperature lines with a straight line passing through the origin are the same for all substances. In order to illustrate this point, an outline of Figs. 5 and 6 are represented by Fig. 7, where the line OA, vertical and horizontal lines etc. have the same significances as in the case of Figs. 5 and 6. Let the latent heats of vaporization of two different substances be L_v' and L_v'', and their corresponding boiling points be $T'_{c.b.p.}$ and $T''_{c.b.p.}$ respectively. Next let OC be a straight line passing through the origin O, the points P' and P'' be the points of insersection of the line OC with the temperature lines of two different substances
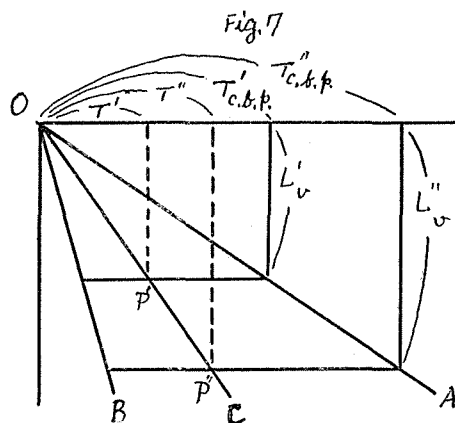
respectively, and T' and T'' be the temperatures corresponding to the points P', and P'' respectively. Then we have

$$\frac{T'}{T''} = \frac{L_v'}{L_v''} = \frac{T'_{c.b.p.}}{T''_{c.b.p.}}, \quad \dots\dots\dots\dots\dots\dots(5)$$

and consequently

$$\frac{L_v'}{T'} = \frac{L_v''}{T''} \quad \dots\dots\dots\dots\dots\dots\dots\dots(6)$$

This makes the relative vapour pressures of two different substances the same at the temperatures T' and T'' respectively. Thus the temperatures determined by the positions on a straight line passing through the origin can be considered to be the corresponding temperatures for different substances; and the liquid state of different substances at their corresponding temperatures can be regarded as the corresponding state, so far as the vapour pressure is concerned. If the straight line OC moves from left to right by keeping the position of O fixed, then the relative vapour pressure, which is the same for different substances at the corresponding temperatures determined by the posititfon of OC, increases. On the contrary, if the line OC moves from right to left the relative vapour pressure decreases.

Next, the T_2 points of different substances must be investigated in connection with the corresponding temperature. For this purpose let us imagine that the substances are in super-cooled state below their melting points. Now we shall consider the case, in which the T_2 points of two different substances lie on a same straight line which passes through the origin. Let the points P' P'' in Fig. 7, whose temperatures are respectively T_2' and T_2'', be such two T_2 points of different substances, then we have from equation (5)

$$\frac{T_2'}{T_2''} = \frac{L'_v}{L''_v} = \frac{T'_{c.b.p.}}{T''_{c.b.p.}} \quad \dots\dots\dots\dots\dots\dots(6)$$

If we represent the latent heats of fusion of the two substances by L_f' and L_f'' respectively, we get from equation (1)

$$T_2' = \frac{L_f'}{2R} \quad \text{and} \quad T_2'' = \frac{L_f''}{2R}$$

for all the monoatomic elements. By using these values of T_2' and T_2'' (6) becomes

$$\frac{L_f'}{L_f''} = \frac{L_v'}{L_v''} ;$$

and consequently we get

$$\frac{L_f'}{L_v'} = \frac{L_f''}{L_v''} \quad \dots\dots\dots\dots\dots\dots\dots\dots(7)$$

This shows that for different substances whose T_2 points lie on a same straight line passing through the origin the ratio of the two latent heats, of fusion and of vaporization, is constant. It is also evident that the T_2 points of different substances whose values of L_f/L_v are different do not lie on a same straight line passing through the origin, As is seen in Fig. 5, the positions of the T_2 points for different substances are scattered to some extent; but, roughly speaking, they may be considered to be crowded near the straight line OB which passes through the origin. This indicates that the value of L_f/L_v does not much differ according to the kind of substances. The values of L_f/L_v for the elements are given in the 5th column of Table II. The values for rare gases are comparatively great, but for the other substances they are not much different from each other. By taking an average for all the elements tabulated in Table II the value of 0.0318 was obtained as the mean, and the straight line OB in Figs. 5 and 6 was drawn with this mean value. From these figures the relative situation of the T_2 points i. e. the values of L_f/L_v for different substances can be seen very clearly. When the T_2 point of a substance is situated to the right of the line OB the value of L_f/L_v is greater than the mean value, and when it is situated to the left the value of L_f/L_v is smaller than the mean value. Thus Figs. 5 and 6 show very clearly the correspondency or uncorrespondency of different elements with regard to their values of L_f/L_v as well as their relative vapour pressures. As is stated above, the T_2 points of the elements are rather crowded in the vicinity of the line OB. This is not the case with their melting points, whose positions in Fig. 5 are much scattered indicating that the correspondency of the melting points of different elements is much worse than that of the T_2 points. This shows that the difference of the relative vapour pressure with the kind of substances is much greater at the melting point than at the T_2 point.

The positions, in Figs. 5 and 6, of the normal boiling point and melting point of arsenic, and of the T_2 points and the melting points of rare gases are different from those of other elements. For the latent heat of vaporization of liquid arsenic the writer assigned approximately the same value as that of its solid. But the abnormality of arsenic as stated above is not due to this approximation. It is entirely caused by an enormously high vapour pressure for the solid state, so that its melting takes place at the temperature higher than the boiling point and under enormously high vapour pressure. With

rare gases all of the T_2 points, the melting points and the normal boiling points appear to the right of the corresponding boiling point line OA. This is due to the facts that their melting points are very close to their normal boiling points and also that their latent heats of vaporization are much smaller than the average thus causing their corresponding boiling points to become much lower. However such abnormality with rare gases will entirely disappear if we turn the corresponding boiling point line OA to the right.

The T_2 points of the elements are proportional in general to their latent heats of fusion. But the melting points have no such direct concern with the latent heats of fusion as is evident from Fig. 10 of the former paper; and the reason for this will be now considered. As is stated above the vapour pressure at the melting point has a direct connection with the value of T_b/T_m or $T_{c.b.p.}/T_m$, and the former increases as the melting point approaches to the normal or corresponding boiling point. Considered from this view point, it will be fruitful to interpret the melting point by means of the magnitude of the vapour pressure at that point. To do this, it is more convenient to consider on the triple point instead of on the melting point, as the latter is practically the same as the former. Let us suppose that the vapour, the liquid and the crystal phases of a substance are in equilibrium in a closed vessel as is shown in Fig. 8, and that the manner of energy levels for a molecule in these three states is as shown in Fig. 9. In this figure L_v and L_f are the latent heats of vaporization and of fusion respectively, and N is Loschmidt's number. Thus L_v/N and L_f/N represent respectively the energies which are necessary to carry one molecule from liquid to vapour and from crystal to liquid. Now let us assume that in

Fig. 8
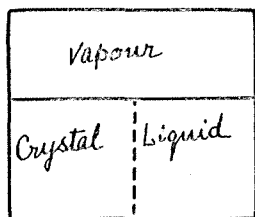
the transition of a molecule from crystal to liquid some more energy P is necessary in excess of L_f/N. This excess potential energy, which will be called " the excess potential barrier ", is represented by a broken line in Fig. 9; and it is to be jumped over by the molecules in their transition from crystal to liquid or vice versa. The presence of such excess
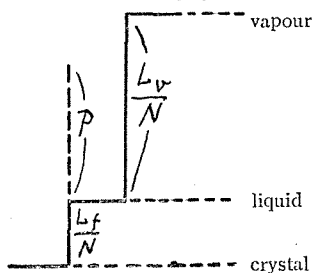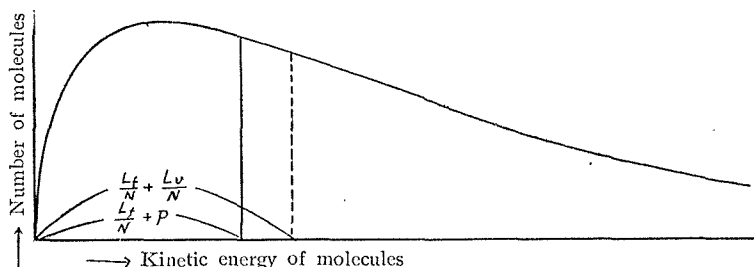
Fig. 9

Fig. 10

potential barrier, which does not appear in the thermodynamical treatment, will hinder the molecules from travelling mutually between the crystal and the liquid phases, and will affect the melting point of the crystal and consequently the vapour pressure at that point. The effect of the presence of the excess potential barrier seems to be understood more clearly by considering the distribution of the kinetic energy among the molecules in the crystal. The curves shown in Figs. 10 and 11 represent diagramatically such distribution of the kinetic energy among molecules by taking the number of molecules as ordinate and the magnitude of the kinetic energy as abscissa, and they correspond to two different temperatures, being much higher in Fig.

Fig. 11
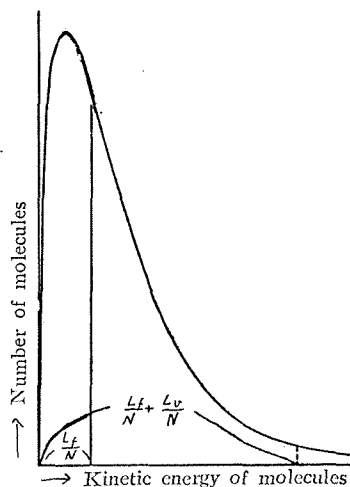
10. Now let us compare two extreme cases: (1) when the excess potential barrier P is very great, and (2) when P is zero. In the first case the height of the potential level $\dfrac{L_f}{N} + P$ which the crystal molecules must jump over in going to the liquid is not much different from the potential height $\dfrac{L_f}{N} + \dfrac{L_v}{N}$ which the crystal molecules must jump over in subliming to the vapour. In Fig. 10 these two potential heights are represented by the full and the broken lines respectively. As these two lines are situated very closely the number of molecules possessing the kinetic energy greater than that just necessary in melting and in subliming will not be much different. Consequently if the temperature about this state is that of the triple point, we can see

that the vapour pressure at the triple point or the melting point is considerable, because the number of subliming molecules is considerable, being the same as that of molecules condensing from the vapour to the crystal in equilibrium. Next, let us consider the second case where P is zero. In this case the height of the potential level $\dfrac{L_f}{N}$ which the crystal molecules must jump over in melting is very much smaller than $\dfrac{L_f}{N}+\dfrac{L_v}{N}$ which the crystal molecules must jump over in subliming to the vapour. Thus is obtained a considerable number of molecules which can transform into the liquid from the crystal, as is seen in Fig. 11, at a temperature much lower than that in the case of Fig. 10. This shows that the melting point is very much lowered when compared with the case of Fig. 10. If we take the potential height for the sublimation in this case as the same as in the case of Fig. 10, the number of molecules which sublime into the vapour is reduced remarkably due to the decrease of temperature of equilibrium, as is seen in Fig. 11. This shows that the vapour pressure at the triple point or at the melting point is reduced remarkably. The two cases considered above are the extreme ones; and the heights of the excess potential barrier for many elements will be within these two extremes. Consequently the degree of the effect of the presence of the excess potential barrier upon the increase of the melting point and of the vapour pressure at the melting point will be different from element to element, being greater with higher excess potential barrier.

The above argument is entirely qualitative. However, the general tendency of the vapour pressure at the melting points of the elements,— that it increases as the melting point approaches to the boiling point and at the same time as the melting point recedes apart from the T_2 point as was seen from Figs. 2, 3, 4, 5 and 6, — will be clearly understood in the above way. Moreover, the above view assuming the presence of the excess potential barrier in the transition from crystal to liquid or vice versa affords a very probable explanation for why the melting point of a substance does not directly depend upon its latent heat of fusion.

As the height of the excess potential barrier diminishes the melting point recedes apart from the boiling point, and approaches to the T_2 point which is determined by the latent heat of fusion. With the rare gases the melting points are very close to their respective T_2 points as is seen in Fig. 1, and the height of the excess potential barriers

is likely to be very small as compared with their latent heat of fusion. However the ratios of L_f/L_v are exceptionally great in these cases, and consequently the values of $\left(\dfrac{L_f}{N}+P\right)\Big/\left(\dfrac{L_f}{N}+\dfrac{L_v}{N}\right)$ which affect the vapour pressure remains remarkably great despite of the small value of P. This acts entirely in the same way as when P is very great, and causes the enormous vapour pressure at the triple point or the melting point by bringing the boiling point also very close to the melting point. With arsenic, whose value of the latent heat of fusion is not known, we can not enter into details in this connection, though an enormous vapour pressure of 36 atmospheres at its triple point seems to be due to its exceptionally large value of

$$\left(\frac{L_f}{N}+P\right)\Big/\left(\frac{L_f}{N}+\frac{L_v}{N}\right).$$