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LATENT HEAT OF FUSION AS THE ENERGY OF MOLECULAR ROTATIONS.

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IN the theory of specific heat of a solid, it is usually assumed that each molecule (or atom) of a substance vibrates about its mean position with three degrees of freedom. Since the motion of each molecule is a vibration, but not a uniform translation, its energy is just twice the mean kinetic energy during a complete period of vibration. Hence the energy belonging to each degree of freedom is given by

$$E_T = \frac{hv}{e^{hv/kT} - 1},$$

if we assume the quantum hypothesis. T is the absolute temperature, k the gas-constant referred to one molecule, h the universal constant and v the frequency of vibration.

We may also with good reason suppose that the above mode of rectilinear vibration is associated with small rotational vibrations of the molecules (or atoms) about their centers of mass, probably with a common period of vibration. At ordinary temperatures, this mode of rotational vibration is very small; but as the temperature becomes higher, it increases at a steady rate. The fact that at very high temperatures, the specific heat experimentally found is in many cases greater than the theoretical value, 5.96, indicates the presence of this rotational vibration. In approaching the melting point of the substance, the amplitude of this vibration attains such a value that the rotational vibration at last becomes a continuous rotation. In the case of a cubic crystal, it is possible that this limiting half-amplitude is a little less than $\pi/4$. As soon as the rotational vibration is changed into a continuous rotation, the regular spacing of the molecules breaks down, disorder beginning to take place, and therefore the rotation becomes independent of the translation. For, since the molecules of a solid may be regarded as sending out their tubes of force in a few definite directions, the regular spacing of the molecules is only possible for their definite orientations. The molecules thus set free have now two or three degrees of freedom for rotation; the angular velocity of each component rotation increases to such an extent that its energy becomes equal to that corresponding to one degree of freedom, that is, $1/2\ E_{T_m}$, T_m being the melting point. If all the molecules undergo the above change, the fusion is completed and the crystal changed to a liquid.

If there are N molecules in one gram-molecule, the total energy of rotation received by the molecules is $Ne_{T_m}(=E_{T_m})$ or $3/2\ Ne_{T_m}$ $(=3/2\ E_{T_m})$ according as the liquid molecules have the shape of a body of revolution or not. Since the molecular distances in solid and liquid states do not differ much, the rectilinear motion of the liquid molecules is also vibratory, its amplitude remaining the same. Hence the translational energy of each liquid molecule corresponding to one degree of freedom must be equal to e_T, that is, the same as that in the solid state. In general, the change of volume during melting is small, so that the energy required for doing the internal and external work is also small; we denote it by Q. If λ be the latent heat of fusion of a substance and w its molecular (or atomic) weight, we have the relation

$$w\lambda = nE_{T_m} + Q,$$

where $n = 1$ or $3/2$. If we neglect Q in this relation, we have simply

$$w\lambda = nE_{T_m} \quad \text{or} \quad \frac{w\lambda}{T_m} = \frac{nE_{T_m}}{T_m};$$

E_{T_m}/T_m has a value a little less than $R = 1.98$, the gas-constant referred to one gram-molecule, the calorie being the unit of heat.

In order to see whether in the case of elements, the above simple relation is actually satisfied or not, we must calculate E_{T_m}. For this purpose, it is necessary to know the frequency v proper to the elements. This value can be calculated by one of the formulæ by Einstein,[1] Lindemann,[2] Alterthun,[3] and Grüneisen.[4] The values of v for the same element as calculated by the different formulæ do not exactly coincide with each other; but at high temperatures, the value of E_T varies very little with a small change in the value of v, and therefore the disagreement among the values of v does not much affect the values of E_{T_m}. In our case, E_{T_m} was calculated from the values of v given by Lindemann's formula

$$v = k\sqrt{\frac{T_m}{wV^{2/3}}}$$

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[1] Ann. der Phys., 34, 1911, 170.

[2] Phy. Zeitschr., 11, 1910, 609.

[3] Deutsch. Phys. Gesell. Verh., 15, 1913, 25, 65.

[4] Ann. der Phys., 39, 1912, 257.

where V is the atomic volume and 3.08×10^{12} taken as the value of k. The following table contains the melting points T_m, the atomic heat of fusion $w\lambda$ and their ratios $w\lambda/T_m$ for different elements, as given in Landolt and Börnstein's table, together with the values of v and nE_{T_m}, the values of n being properly chosen.

Group I.

Elements.	v.	T_m.	$w\lambda$.	$w\lambda/T_m$.	nE_{T_m}/T_m.	n.
Pt	4.75×10^{12}	2028° K	5360 Cal.	2.64	2.67	3/2
Pd	6.15	1818	3860	2.11	1.80	1
Fe	9.09	1773	3348	1.89	1.75	1
Ni	8.87	1724	2710	1.57	1.75	1
Cu	7.39	1356	2650	1.96	1.73	1
Ag	4.29	1234	2270	1.84	1.82	1
Al	8.32	930	2160	2.33	2.37	3/2
Zn	4.78	692	1840	2.66	2.49	3/2
Pb	1.99	600	1118	1.86	1.83	1
Cd	3.01	594	1540	2.59	2.64	3/2
Tl	2.01	560	1470	2.60	2.73	3/2
S_2	4.26	392	660	1.70	1.51	1
Na	4.30	390	730	1.87	1.49	1
K	2.53	331	610	1.84	1.64	1
P_4	3.83	317	584	1.84	1.46	1
Hg	1.38	234	562	2.40	2.58	3/2
Group II.						
Bi	1.79×10^{12}	544° K	2580 Cal.	4.74	2.76	3/2
Sn	2.51	505	1667	3.30	2.64	3/2
I	1.82	389	1488	3.83	2.64	3/2
Ga	2.81	303	1339	4.39	2.34	3/2
Br	1.38	266	1280	4.82	2.61	3/2
Cl	——	170	814	4.79	——	3/2

From the above tables, we see that for the elements in group I., the above relation is well satisfied, though the melting points of these elements vary from 2028° K. to 234° K. Here it is to be remarked that the values of λ are not accurately known and usually admit of an error amounting to 10 per cent. Considering these circumstances, we may conclude that for these elements, the value of Q is negligibly small.

The elements in group II. have a much greater value for the ratio $w\lambda/T_m$ than for the values of nE_{T_m}/T_m. It is however to be noticed that the two elements bismuth and gallium appear to undergo a transformation during melting; because the electric resistance of these two elements diminishes during melting,—an abnormal phenomenon. Hence, the latent heat of fusion is probably increased by the heat of this transformation. A similar remark will also apply to tin, the sign of the magnetic susceptibility of which changes abnormally during melting. It is well known that the halogen elements have a large specific heat; this is probably the main cause of the large deviation of the above ratio from the values of nE_{T_m}/T_m, the value of Q being considerably large.

From the above result, it is to be concluded that unless some transformation takes place in a substance during fusion, or its specific heat is abnormally large, the latent heat of fusion consists of the energy of rotation of the molecules, gained during fusion.

As to the compounds, a similar relation holds good; but here the ratio $w\lambda/T_m$ is generally much greater than that in the case of the elements, the values lying between 2 and 10. Some results of my calculation are given in the following tables:

Group I.

Compounds.	V.	T_m.	$w\lambda$.	$w\lambda/T_m$.	nE_{T_m}/T_m.	n.
KOH	3.26×10^{12}	633° K	1610 Cal.	2.54	2.61	3/2
NaOH	4.87	691	1600	2.33	2.49	3/2
RbOH	2.21	574	1620	2.82	2.73	3/2
CsOH	1.71	545	1610	2.95	2.73	3/2
AgBr	1.92	703	2370	3.38	2.79	3/2

Group II.

KF	4.67×10^{12}	1133° K	6270 Cal.	5.53	4.50	5/2
NaCl	4.50	1077	7220	6.71	4.45	5/2
KCl	3.41	1045	6410	6.13	4.60	5/2
TlBr	2.37	733	3610	5.93	4.55	5/2
AgCl	2.34	728	3050	4.15	4.55	5/2
TlCl	1.62	700	3980	5.69	4.65	5/2
$BaCl_2$	1.66	1232	5800	4.70	4.80	5/2
$CaCl_2$	3.17	1047	6060	5.78	4.60	5/2
$PbCl_2$	1.34	764	5150	6.67	4.75	5/2
$PbBr_2$	1.16	761	3650	4.80	4.75	5/2

For the compounds of group I., if we assume three degrees of freedom for rotation, the values of $w\lambda/T_m$ nearly coincide with those of nE_{T_m}/T_m. For the halogen compound in the same group, the value of $w\lambda/T_m$ is considerably larger. The diatomic compounds may have five degrees of freedom for rotation—3 as a whole molecule and 1 for each atom; the triatomic or multiatomic compounds may have more degrees of freedom than five. For the elements in group II., we have calculated nE_{T_m}/T_m for $n = 5/2$. As in the case of elements, the ratio $w\lambda/T_m$ for halogen compounds is generally much greater than the corresponding values of nE_{T_m}/T_m. For the compounds, there is, however, some ambiguity in choosing the number of degrees of freedom gained during fusion. Hence the case of the compounds cannot be considered as a verification of the above theory.

Next, we shall consider the specific heat of a liquid. If the temperature of a liquid is high, E_T is nearly equal to RT, where R is the gas-constant, and the total content of heat energy possessed by a liquid per gram molecule is

$$3RT + nRT = 4RT \text{ or } \tfrac{9}{2}\,RT$$

for an element. Hence the specific heat at constant volume is

$$C_v' = 4R \text{ or } \tfrac{9}{2}\,R = 7.92 \text{ or } 8.91.$$

According to the first law of thermodynamics, we have, at the melting point of a substance,

$$\frac{d(w\lambda)}{dT_m} = C_p' - C_p,$$

where Cp' and Cp are the specific heats of liquid and solid states at constant pressure, respectively. But, as we have seen above, we have for elements

$$w\lambda = nE_{T_m},\ n = 1 \text{ or } 3/2.$$

$$C_p' = C_p + n\frac{dE_{T_m}}{dT_m}.$$

Since, at melting point, dE_{T_m}/dT_m has a value nearly equal to R, the above relation may be written

$$C_p' = C_p + nR = C_p + 1.98 \text{ or } C_p + 2.97.$$

Generally speaking, these results agree with the observed facts.

As a further confirmation of the above view, we may also add the following facts. It is well known that during gradual melting of an amorphous substance, no appreciable amount of latent heat is absorbed. Since an amorphous substance is to be considered as an extremely viscous fluid, its molecules in a solid state already possess freedom of rotation, so that for liquefaction no latent heat is required.

It is also generally admitted that the molecules of a gas or a liquid exert their action according to the law of central force, that is, the molecular force radiates from its center uniformly in all directions. For explaining a crystalline structure, it is, however, necessary to assume that each molecule sends out its tubes of force only in a few definite directions so as to form a given arrangement of the molecules in the space-lattice. What change will then occur in the molecules during fusion? According to our view, no change generally takes place in the molecules; but during melting, the molecules acquire rotational motion, whose axes are continuously changing from one instant to another, so that the mean action of the molecular force is equivalent to the force equally distributed in all directions.

Lastly it should be noticed that according to our view, even the molecules of a monoatomic element make, in a liquid state, rotational motion with two or three degrees of freedom, the energy of rotation increasing with its temperature. During vaporization, the molecules start with the initial energy of rotation; but this energy does not increase with the rise of temperature, as is the case with diatomic or polyatomic gases. For, in the gaseous state, in which the mutual distances of the molecules are very large as compared with those in a solid or liquid state, the molecules of a monoatomic element are considered to behave with respect to their mutual impacts like small spherical balls and therefore their impact cannot cause any further increase of the energy of rotational motion. Hence, the energy content of a monatomic gas may be given by

$$Q = \tfrac{3}{2} RT + nR\theta,$$

where θ is the temperature of vaporization; its specific heat C_v is therefore

$$C_v = \frac{3R}{2} = 2.97,$$

which agrees with the observed value.