F I Z I K A V O L U M E 10 S U P P L E M E N T 2, 1978
Proceedings of the VI Yugoslav Symposium of the Physics
of Condensed Matter, Kruševac, September, 18-22, 1978

SIMPLE MODEL FOR VOLUME CHANGE AT MELTING OF ELEMENTS. I.

A. Rubčić and J.B.-Rubčić

Institute of Physics, University of Zagreb, Yugoslavia

Abstract: The change of volume of elements at melting at normal pressure is analyzed. The main assumption is that during melting, ions or molecules perform oscillatory jumps equal to the distance of the nearest neighbours. A formula of general validity for volume change, including the coordination number as the only parameter, is introduced. The calculated enthalpy of melting is consistent with the proposed model.

1. Introduction

The purpose of this paper is to introduce a simple model for volume change at melting for metals, noble gases and halogens. The model is based mainly on the geometrical considerations of ionic or molecular motions in solids and liquids. It applies particularly to metals, because there exists the simple Einstein model for solids[1] with a possible modification for liquids. Ions vibrate around equilibrium positions in a solid, with constant frequency ν_o, and also in liquid near the melting point. However, in liquid, ions have an additional low frequency motion with a $\nu < \nu_o$[2]. The volume change in this simple model is merely a geometrical consequence of the solid state perameters, with which the enthalpy of melting may also be estimated, and both are in good agreement with experimental data. Moreover, consistency is achieved because several characteristic quantities as enthalpy of melting, change of volume, specific heat capacity and entropy appear quite naturally.

2. Change of volume

2.1 Metals. One may suppose that at melting all atoms must have sufficient room to move freely to any of the positions of the nearest neighbours. This movement would be possible in a regularly enlarged crystal lattice of the "liquid", if the radii of ions, including their vibrations, could be defined by means of their close packing. Thus, with a as the lattice constant of solid, r will be $a\sqrt{3}/4$ for the bcc structure, according to Fig.1a. A new "liquid" constant a' can then be defined, according to Fig.1b, by

$$(2r)^2 - (a'\sqrt{2}/2)^2 = (a'\sqrt{2}\sqrt{3}/2 - 2r)^2$$

or it may be written as $a'=a(1+\Delta)=1.061a$. The expected increase of solid volume V_s corresponds to the increase of a unit cell volume $V'/V_s = a^3(1+\Delta)^3/a^3 = 1.193$ i.e. 19.3%. In comparison with the experimental values in the Table, which are an order of magnitude smaller, it may be concluded that such an approach is impossible, because only minor interruption of the atomic structure actually occurs at melting[3]. Thus, one may assume that the melting may be effected so, that a central atom, for example O, in the unit cell of Fig.1a, cannot move to any of the positions of its eight nearest neighbours, but only to a definite one O', which is dynamically the most probable at that particular moment. Obviously, now the unit cell will not be regularly enlarged, and the lattice will be deformed with a relatively smaller increase of volume.

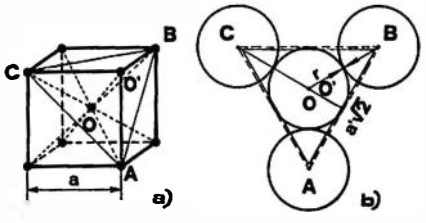

Fig.1 a) Unit cell for metals of bcc structure, b) regularly enlarged cross-section through the sites A, B and C of unit cell.

If one unit cell is considered, only 1/8 of a boundary atom belongs to that cell. Thus, for the supposed movement of the ion from O to O', only 1/4 of the atom cross section in positions A, B and C should move away along O'A, O'B and O'C directions, respectively, with displacement Δa. This results in an irregular actual increase of the unit cell volume $\Delta V_{uc} = \Delta a \cdot 3r^2\pi/4 = 0.027a^3$, while the corresponding relative total volume increase would be $\Delta V/V_s = \Delta V_{uc}/a^3 = 0.027$ or 2.7%. This value closely approaches the experimental values shown in the Table[4].

The restriction of ionic movement from the eight possible directions to only one, suggests a simple phenomenological approach. The increase of the unit cell linear dimension would be smaller by a factor which is equal to the coordination number n, i.e. for the bcc structure n=8. The volume increase would then be $V_1/V_s = (1+\Delta/8)^3 = 1.023$ or 2.3%. Here, $\Delta = (a'-a)/a$ is a relative

change of the idealized overestimated regular increase of the "liquid" lattice constant, and generally

$$V_l/V_s = (1 + \Delta/n)^3 \qquad (1)$$

For fcc metals, in complete analogy with the bcc lattice, a hypothetical regular increase of the lattice constant can also be easily calculated. Geometrically, a central ion should have the way open to whichever boundary ion of the unit cell, i.e. have a channel of ionic diameter, now equal to $2r=a/\sqrt{2}$. (Detailed calculations are to be published elsewhere.) The calculated value of Δ is 0.155. This, with n=12, results in $V_l/V_s=1.039$ or 3.9%, which is in good agreement with experimental data in Table.

TABLE

	n	$\Delta V/V_s$(%) exp.	$\Delta V/V_s$(%) calc.	S_m(e.u.) exp.	ΔH_m(exp) (kcal mole^{-1})	ΔH_m(calc) (kcal mole^{-1})
Li	8	1.7		1.53	0.69	0.69
Na	8	2.5		1.70	0.63	0.62
K	8	2.6	2.3	1.70	0.56	0.54
Rb	8	2.5		1.68	0.53	0.51
Cs	8	2.5		1.65	0.50	0.45
Cu	12	4.5		2.29	3.11	3.28
Ag	12	3.3		2.22	2.73	3.32
Au	12	5.1		2.29	3.06	3.77
Al	12	6.0	3.9	2.70	2.50	2.74
Pb	12	3.5		1.98	1.19	1.57
Co	12	3.5		2.20	4.10	4.37
Ni	12	4.5		2.45	4.23	4.08
Ne	12	15.3		3.26	0.080	0.063
Ar	12	14.4	15.4	3.35	0.284	0.327
Kr	12	15.1		3.36	0.392	0.429
Xe	12	15.1		3.40	0.584	0.611
N_2		7.5		2.7	0.172	-
O_2		3.8	3.9	2.0	0.106	-
F_2		4.6		2.3	1.122	-
Cl_2	4	19.8	19.2	8.9	1.531	-
Br_2	4	-	19.5	9.5	2.527	-
I_2	4	21.4	20.6	9.7	3.740	-

As expected, the volume change is greater for the fcc lattice in correspondence with the enlarged entropy change, compared to bcc lattice for which both quantities are minimal in the case of elements[5].

2.2 Noble gases. In solid state, they have an fcc crystal structure, and the expected volume change at melting would be 3.9%,

as in the case of metals. However, experimental values are around 15%. This is not very surprising, because the entropy change is also increased to about 3.4 e.u. as compared with 2 e.u. for fcc metals. This suggests that the activated motions of atoms of noble gases at melting are qualitatively different from the positional disorder of liquid metals. It is possible that a pair of atoms form a momentary "molecule" which may rotate in liquid[6]. Such a mechanism may justify the increased volume and entropy change. In analogy with previous considerations a certain regular increase of lattice is sought, if the rotational pairs make a rigid spheres with radius $R=2r=a/\sqrt{2}$. The enlarged volume of such a hypothetical fcc structure will be $V'=(N/2)(a')^3/4$ with the starting volume of solid $V_s=Na^3/4$, N being Avogadro's number, and $a'=4R/\sqrt{2}=2a$, resulting in $V'/V_s=4$ and $\Delta=0.587$. Now using eq.(1), and thus taking the coordination number n as a correction to the idealized volume increase, it follows that $V_l/V_s=1.154$ or 15.4%. This shows a nice agreemnet with experiment.

Here it is interesting to note that the melting of noble gases at higher pressure requires a small change of volume[7], which already at a pressure of about 10 kbars approaches a limiting value of nearly 4%. This points to the positional mechanism of melting[8], which is also supported by the decrease of entropy, with increasing pressure, to a value of about 2 e.u., as in the case of metals.

2.3 Halogens. For halogens the entropy of melting is around 9 e.u. the highest for elements, while volume increase is about 20%. This means that the additional motion of molecules in liquid is even more complicated. During melting, energy is absorbed by all the five possible degrees of freedom. Similarly, as for noble gases a free rotation of linear molecule may be supposed, leading to ideal fcc close-packed spheres with radius $r=(\ell+d)/2$; ℓ is the distance between the atoms in a molecule, and d is the nearest neighbour distance between two atoms belonging to different molecules, and both values follow from the experimental determination of the crystal structure[9]. Volume V_s of solids is also known from experiments[10], and using $V'=N(2r\sqrt{2})^3/4$, we can calculate $V'/V_s=(1+\Delta)^3$, giving Δ. Actually, molecules do not rotate freely in liquid not even at the boiling point[10] and the inclusion of the coordination number reduces too large increase of volume V' to a smaller, experimental value. The results for Cl_2, Br_2

and I_2 are given in the Table.
Fluorine F_2 shows quite a different behaviour at melting. It has a solid-solid transition[4], with almost spherical F_2 molecules in the higher temperature phase. Due to this sphericalness the F_2 molecules are in fact equal to ions in metal, and thus the melting process should be the same. Actually, the volume change is 4.6% and the entropy change only 2.3 e.u. (see Table). This also applies to oxygen O_2. In the case of nitrogen N_2 the entropy and volume change are somewhat greater, which indicates that the mechanism is slightly more complicated than in the case of F_2 and O_2. Details are to be discussed in a later work.

3. Latent heat of melting for metals

In our study of volume changes we assumed that ions jump from site to site within the crystal lattice. During the jump, an ion passes the potential barrier caused by the surrounding ions. This motion of ion one can represent by means of one-dimensional oscillator. The amplitude of the oscillator should be equal to the distance of the nearest neighbours $d_o = a/\sqrt{2}$, for the fcc structure, and $a/\sqrt{3}$ for the bcc structure. The latter represents an effective amplitude, because the top of the potential barrier determined by the bcc structure is not in the middle of two neighbouring ions. From considerations in Sect.2 it follows that for melting it is sufficient that one ion is dynamically absent from its n neighbours in a unit cell. Therefore the ion has to perform an average of n vibrations with Einstein's frequency ν_o until it finds the n-th place empty. Thus the frequency of the jump is ν_o/n, where n is again the coordination number. The total energy of the oscillator may be written as

$$E_{diff} = 2\pi^2 m(\nu_o/n)^2 d_o^2 \qquad (2)$$

where m is the ionic mass. E_{diff} is, in fact, a diffusional component of ionic motion in liquid i.e. additional motion as previously described. Thus, the energy of ion E_l in liquid may be expressed by

$$E_l \simeq E_s + E_{diff} \qquad (3)$$

and then, the latent heat of melting in kcal mole^{-1} may be written as

$$\Delta H_m \simeq C\, A\, \nu_o^2\, a^2 \qquad (4)$$

where C is $1.637\ 10^{-12}$ or $2.456\ 10^{-12}$ for the fcc and bcc structures, respectively. A is the atomic mass, frequency ν_o is correlated to the Debye characteristic temperature Θ_D by $\nu_o = 3k\,\Theta_D/4h$, and k and h are the Boltzman and Planck constants, respectively. Our results, which are consistent with experiments, are given in the Table.

4. Conclusion

Although the model grossly oversimplifies the actual complex situation (as presented by MC or MD "computer experiments"), agreement with experimental values appears satisfactory as regards general behaviour, and it justifies an important elements of truth in the assumption of ionic jumps from site to site within the crystal lattice. On the other hand, from the derivative of eq.(3) it follows that near the melting point specific heat capacity is approximately equal for both the solid and the liquid, which has been observed experimentally. This seems to be the consequence of negligible change of ν_o and $\underline{a}$ with temperature. At the same time, the entropy of melting appears naturally to be equal to 2 e.u., because $S_m = \Delta H_m/T_m = NkT_m/T_m = R$. Therefore, it may be stated that the melting of metals or molecular crystals with spherical units is a "quasi one-dimensional" process, as regards the additional motion of ions or molecules in liquid. In the case of linear molecules such as halogens, and non-spherical molecules[12], the multi-dimensional process takes place. Details are to be published elsewhere.

References.

1) P.M.Morse, Thermal Physics, Benjamin, New York, 1069;
2) C.A.Croxton, Introduction to Liquid State Physics, Wiley, 1975;
3) A.F.M.Barton, The Dynamic Liquid State, Longman, 1974;
4) American Institute of Physics Handbook, McGraw Hill, 1972; J.A.Jahnke, J.Chem.Phys., 47,336(1973); J.C.Smithells, Metal Reference Book, Butterworths, London, 1967; B.K.Jindall, Acta Metallurgica, 21,1029(1973); J.de Launay, Solid State Physics, 2, (Eds. F.Seitz and D.Turnbull), Academic Press, New York, 1965;
5) S.-A.Cho, J.Solid State Chem., 16,355(1976);
6) V.Nardy and J.K.Percus, Phys.Rev., 160,No.1,259(1967);
7) S.M.Stishov, Usp.Fiz.Nauk, 96,267(1968);
8) A.R.Ubbelohde, Melting and Crystal Structure, Clarendon Press, Oxford, 1965;
9) R.L.Collin, Acta Cryst., 5,431(1952;
10) T.R.Thomson,H.Eyring and T.Ree, Proc.N.A.S., 46,337(1960);
11) T.H.Jordan,W.E.Streib and W.N.Lipscomb, J.Chem.Phys., 41,760 (1964);
12) A.Rubčić and J.B.-Rubčić, Fizika, 8,(Suppl.),255(1976).