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Abstract

Full Text

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MAXIMUM CONCENTRATIONS OF VACANCIES AND SATURATED VAPOR PRESSURES OF SIMPLE SUBSTANCES AT THE MELTING POINT

(Presented by Academician P. A. Rebinder on 6 VII 1963)

The importance of the vacancy problem for the theory of the solid state is generally recognized. Here we shall consider this question as applied to simple substances, bearing in mind the formation of Schottky vacancies. A number of propositions have been put forward ⁽¹⁾, in particular: a) the energy of formation of 1 g-atom of vacancies \mathcal{E}_f should be approximately equal to the energy of evaporation; b) the number of vacancies inside a crystal should be approximately equal to the number of atoms in an equal volume of vapor of the same substance; c) according to the Boltzmann principle, the vacancy concentration should be determined by the equation $C = n/N = \exp(-\mathcal{E}_f/kT)$, i.e., should increase with temperature (n is the number of vacancies, N is the number of atoms, $n \ll N$); d) near the melting point T_s , the vacancy concentration C_{T_s} may reach 1 at. %. These ideas were cited in ⁽²⁾ without comment. It was further indicated ⁽³⁾ that a pre-exponential factor A , taking into account the expansion of the lattice and the change in the vibration frequency of atoms in the bond neighboring the vacancy, must be introduced into the preceding equation. Thus,

$$C_T = A \exp(-\mathcal{E}_f/kT). \quad (1)$$

In the modern literature ⁽³⁻⁵⁾, data are given for A : $1 < A < 10$, on average 5. In a number of recent works ⁽⁶⁾, equation (1) takes the form:

$$C_T = n/N = g_i \exp(-G_f/kT) = g_i \exp(S_f/k) \exp(-\mathcal{E}_f/kT), \quad (2)$$

where g_i is the statistical weight and G_f is the free energy. The maximum vacancy concentration C_{T_s} , according to (1) and (2), should be reached near T_s .

The most widespread methods for studying C_{T_s} are: 1) from the increase in the resistance $\Delta\rho$ of a specimen ^(7,8), where $\Delta\rho = m$ ($\mu\text{ohm} \cdot \text{cm}$) $\exp(-\mathcal{E}_f/kT)$; 2) dilatometric ^(6,9,10), from the relative increase in the specimen $\Delta l/l$ and the identity period of cubic lattices $\Delta a/a$: $C_T = n/N = 3(\Delta l/l - \Delta a/a)$; 3) calorimetric ^(11,12). In the modern literature, reports on the determination of \mathcal{E}_f and C_{T_s} in metals are very numerous. The most thoroughly studied are Al, Au, Ag, Cu, Pt and, in part, Pb. Some of the recently published data are given in Table 1. The data of ⁽²¹⁾ were obtained by a new method—measurement of thermoelectromotive forces.

In the literature, the small error of the determinations is usually emphasized (for example, for \mathcal{E}_f , ± 0.02 - 0.03 eV), as well as the good agreement of the values of \mathcal{E}_f and C_{T_s} for one and the same metal (Table 1). It should be noted, however, that according to the literature data for the most diverse metals, the concentrations C_T differ hardly at all and vary within the range from 10^{-3} to 10^{-4} . As is noted in ⁽²¹⁾, the values of C_{T_s} for different metals lie between 0.1 and 0.2%.

On deeper consideration, in our view, one cannot avoid comparing \mathcal{E}_f with the values of the atomization energy ⁽¹³⁾ Ω (i.e., the sublimation energy with formation of monatomic vapor). Of course, the conclusions of ^(1,2) are roughly approximate. Thus, the energy of formation of 1 g-atom of vacancies should not be equal to, but less than, the atomization energy Ω . For example, for the escape of atoms from a site in the bulk onto the (111) face of a cubic face-centered lattice, with the underlying vacancy left behind, the rupture of 4 bonds out of 12 is required, i.e., $\mathcal{E}_f = 0.33\Omega$. In the case of crystals with covalent bonds, experi-

Table 1

Element	Source	\mathcal{E}_f , eV	Ω_{T_s} , eV	p_{cp}	C_{T_s} , exp.	C_{T_s} , calc. by (4)	N'	n'
Pb	(10)	0.59	2.0	0.29	$1.5 \cdot 10^{-4}$	$5 \cdot 10^{-6}$	$4.8 \cdot 10^7$	$1.6 \cdot 10^{17}$
Al	(6, 16)	0.75	—	—	$9.4 \cdot 10^{-4}$	—	—	—
	(15)	0.79	3.21	0.24	—	$3.2 \cdot 10^{-5}$	$1.9 \cdot 10^8$	$3.2 \cdot 10^{18}$
	(4, 10)	0.76	—	—	$3.0 \cdot 10^{-4}$	—	—	—
Au	(16)	0.94	—	—	—	—	—	—
	(11, 17)	0.82	—	—	$2.1 \cdot 10^{-3}$	—	—	—
	(9)	0.98	3.7	0.25	$7.2 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$	$1.3 \cdot 10^{11}$	$2.2 \cdot 10^{19}$

Element	Source	\mathcal{E}_f , eV	Ω_{T_s} , eV	p_{cp}	C_{T_s} , exp.	C_{T_s} , calc. by (4)	N'	n'
Pt	(4)	0.95	—	—	—	—	—	—
	(12, 15)	0.97	—	—	$2.7 \cdot 10^{-4}$	—	—	—
	(17)	1.2	—	—	10^{-4}	—	—	—
	(24)	1.23	—	—	10^{-4}	—	—	—
	(4)	1.4	5.1	0.26	$5 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$1.2 \cdot 10^{12}$	$3.1 \cdot 10^{19}$
Cu	(21)	1.39	—	—	—	—	—	—
	(19)	1.0	—	—	—	—	—	—
	(25)	1.05	3.4	0.28	$3.8 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	$2.8 \cdot 10^{12}$	$9.9 \cdot 10^{19}$
Ag	(16, 23)	1.09	—	—	—	—	—	—
	(18, 20)	1.10	2.9	0.38	$1.7 \cdot 10^{-4}$	$2.0 \cdot 10^{-3}$	$1.9 \cdot 10^{13}$	$1.1 \cdot 10^{20}$
	(21)	1.01	—	—	—	—	—	—
Cd	(22)	1.06	—	—	—	—	—	—
	—	—	1.15	—	—	$4.0 \cdot 10^{-3}$	$1.9 \cdot 10^{15}$	$1.7 \cdot 10^{20}$
Zn	—	—	1.33	—	—	$5.0 \cdot 10^{-3}$	$2.1 \cdot 10^{15}$	$2.8 \cdot 10^{20}$
Nb	(29)	2.04	7.28	0.28	$1.2 \cdot 10^{-2}$	$0.5 \cdot 10^{-2}$	—	—
W	(30)	3.14	7.85	0.40	$2.7 \cdot 10^{-2}$	$1.6 \cdot 10^{-2}$	—	—

¹ According to the present work. ² According to the corresponding publications.

³ Recalculated by us from the data of (12).

Experimental determinations of the specific surface energy (14) agree well with the calculated ones (13) based on the equation for an analogous model. For metals, however, a correction is necessary. Independently of this, one may accept that, for metals with close packing (face-centered cubic or hexagonal), \mathcal{E}_f is proportional to Ω_T , i.e. $\mathcal{E}_f = p\Omega_T$, where p is a constant ($p < 1$), the same for all metals of these structures. From this follows an important conclusion. If

$$\lg C_T = -\frac{p\Omega_T}{4.575T} + B', \quad (3)$$

$$\lg P_T = -\frac{\Omega_T}{4.575T} + B'', \quad (3a)$$

where B' and B'' are entropy terms, then, subtracting (3a) from (3), we obtain

$$\lg C_T = \lg P_T + \frac{(1-p)\Omega_T}{4.575T} + \Delta B_T. \quad (4)$$

If one takes $p = 0.33$, $B'_T = 1$ and $B''_T = 6$ (on average), then $\Delta B_T = -5$ and

$$\lg C_{T_s} = \lg P_{T_s} + \frac{0.67\Omega_{T_s}}{4.575T} - 5 = \lg P_{T_s} + Z. \quad (4a)$$

The quantity B'' is determined rigorously for each metal. In a more thorough further study, the quantities B' (taken from experimental works, which in this part we do not consider reliable) and p will have to be refined. However, even in the form (4a), the dependence $\lg C_{T_s} = f(\lg P_{T_s})$ is of great interest. We have calculated $\lg P_{T_s}$ (see Table 2).

The experimental values of $\lg P_{T_s}$ in atmospheres (Table 2) were recalculated by us from data systematically considered in (26). To check these values, we also calculated the values of $\lg P_{T_s}$ from the va-

Table 2

$\lg P_{T_s}$ and $\lg C_{T_s}$ of simple substances

Element	Melting temp., °K	Ω_{298} , kcal/g-at	$-\frac{\Omega_{298}}{4.575T}$	$-\frac{\Delta S_{298}^0}{4.575}$	$\lg P_{T_s}$, calc.	$\lg P_{T_s}$, exp.	Z	$\lg C_{T_s}$, calc.
Ga ¹	303	64.7	-46.7	+6.6	-40.1	-40.0	+21.8	-18.2 (2)
Sn ¹	505	72.2	-31.3	+6.1	-25.2	-25.2	+16.0	-9.2 (?)
In ¹	429	56.7	-28.9	+6.3	-22.6	-21.8	+14.4	-7.4 (?)
Li ¹	454	38.4	-18.6	+5.8	-12.8	-12.8	+7.5	-5.3 (?)
Pb	601	46.9	-17.1	+5.7	-11.4	-11.4	+6.2	-5.2
Al	932	75.0	-17.6	+7.1	-10.5	-10.6	+6.1	-4.5
Hg	234	14.7	-13.7	+5.1	-8.6	-8.7		
Cs	302	18.4	-13.3	+4.8	-8.5	-8.6		
Au	1336	87.7	-14.3	+6.9	-7.4	-7.6	+4.2	-3.4
Pt	2043	132.8	-14.2	+7.8	-6.4	-6.5	+3.2	-3.3
Cu	1356	80.9	-13.0	+6.9	-6.1	-6.3	+3.4	-2.9

Element	Melting temp., °K	Ω_{298} , kcal/g-at	$-\frac{\Omega_{298}}{4.575T}$	$-\frac{\Delta S_{298}^0}{4.575}$	$\lg P_{T_s}$, calc.	$\lg P_{T_s}$, exp.	Z	$\lg C_{T_s}$, calc.
Nb	2770	172.5	-13.6	+7.9	-5.7	-6.1	+3.8	-2.3
Ag	1234	68.1	-12.1	+6.8	-5.7	-5.5	+2.8	-2.7
Ta	3270	186.5	-12.5	+7.5	-5.0	-5.1		
W	3650	201.9	-12.1	+7.3	-4.8	-4.4	+2.6	-1.8
Cd	594	26.8	-9.9	+6.1	-3.8	-3.8	+1.4	-2.4
Zn	693	31.3	-9.9	+6.2	-3.7	-3.7	+1.4	-2.3
Co ²	1768	83.1	-10.2	+7.9	-3.3	-2.7		
						(?)		
Ni ²	1728	81.0	-10.2	+7.9	-3.3	-2.6		
						(?)		
Sr	1043	39.1	-8.2	+5.7	-2.5	-2.6		
Ca	1123	42.1	-8.2	+5.9	-2.3	-2.4	+0.4	-2.0
Mg	2176	93.3	-9.4	+7.8	-1.6	-2.0	+0.4	-1.6
Lu ³	1934	76.4	-8.3	+7.0	-1.3	-1.6		
				(?)		(?)		
Lu ³	1934	94.7	-10.1		-3.1			
Gd ³	1600	51.7	-7.1	+7.0	-0.1	-0.6		
				(?)		(?)		
Gd ³	1600	83.6	-11.4		-4.3			

¹ The calculations of C_{T_s} for Ga, Sn, In, and Li are tentative, since the vapor-elasticity data are unreliable and the structures are not close packings. ² The vapor elasticities of Co and Ni according to ⁽²⁶⁾ are apparently overestimated. This follows both from the fact that the calculated values of $\lg P_T$ are considerably smaller than the experimental ones, and from the fact that the values of $\lg C_{T_s}$ based on $\lg P_{\text{exp}}$ fall out of the series (toward overestimation). ³ Of interest are the high vapor elasticities of Lu and Gd according to ⁽²⁶⁾. However, these data are completely contradicted by the much higher values of Ω_{298} according to ⁽²⁸⁾, which leads to the conclusion that the vapor elasticities of Lu and Gd must be several orders of magnitude smaller. The question remains open.

values of Ω_{298} : for the reactions $M_{\text{vap}} = M_{\text{solid}} + \Omega$ (kcal/g-at), it should have been expected that, in any case up to 1500° K, the algebraic sum of the integrals

$$\int_{298}^T \Delta C_p dT - T \int_{298}^T \Delta C_p d \ln T$$

in the expression for the thermodynamic potential is close to zero. This makes Ulich' s approximation convenient and sufficiently accurate for calculating the equilibrium constant,

$$\lg P_T = -\Omega_{298}/4.575T - \Delta S_{298}^0/4.575. \quad (5)$$

Indeed, in most cases the discrepancy between $\lg P_{T_s}$, calculated and obtained experimentally (Table 2), lies within ± 0.2 , with the exception of In (an obvious experimental error), Nb, Co, Ni, and Mg (experimental errors, especially for Co, Ni, Gd, and Lu; see the notes to Table 2, are evident).

Next, for a series of metals we calculated $\int_{298}^T \Delta C_p dT$ and found Ω_{T_s} . Expressed in electron volts, they are included in Table 1. Comparison with the values $\mathcal{E}_{fs,exp}$ made it possible to find the quantities p (Table 1). It is interesting that for different metals $p = 0.33 \pm 0.9$. This good agreement should not yet be overestimated.

The values Z from equation (4) and $\lg C_T$ (calculated by equation (4)) are given by us in Table 2. Table 1 gives the corresponding concentra-

vacancies—calculated and found experimentally. For Cd and Zn no comparison was made, since we were unable to find reliable experimental data on C_{T_s} . Table 1 also gives a comparison of the number N' of metal atoms in 1 cm^3 of vapor and the number n' of vacancies in 1 cm^3 of solid at the melting point.

It follows from Table 2 that for the metals in its upper and lower parts the values of $\lg P_{T_s}$ differ by 36 orders of magnitude and, consequently, at $p = 0.33$ the vacancy concentrations should differ by 12 orders of magnitude. The largest vacancy concentrations should be observed in Cr, Mg, Ca, Nb, W, Zn, Cd, whereas in the literature metals from the middle and upper parts of the table have been studied, chosen without taking into account the interrelations set forth above.

Contrary to ^(1,2), the quantities N' and n' , as was to be expected, differ very greatly—by approximately 7 orders of magnitude (see Table 1).

It follows from Table 1 that the calculated vacancy concentrations agree with the experimental ones in the case of Pt and Au. But the main point is that the variation of the calculated vacancy concentrations for different metals, as we expected (see also ^(1,2)), is sympathetic with the variation of the vapor pressures (Table 2)—they increase from Al to Ag from $3 \cdot 10^{-5}$ to $2 \cdot 10^{-3}$, i.e., by a factor of 66. The data published in the literature, however, show the opposite trend: from $9 \cdot 10^{-4}$ for Al to $1.7 \cdot 10^{-4}$ for Ag, i.e., a decrease by a factor of 5.

The cause of the inaccuracy of the experimental data is, in our opinion, the failure to take account of the influence of dislocations and cavities on the quantities $\Delta\rho$ or $(\Delta l/l) - \Delta a/a$ and others, the absence of control over the density of the specimens, etc. Meanwhile, drawn (wire) and rolled (foil) specimens, rich in dislocations, are studied. Since, on cooling, vacancies, like Cottrell clouds, can be segregated at dislocations, forming cavities, etc., repeated heating and cooling in order to stabilize the results may also lead to the pumping of cavities into the crystals. In such cases attributing the results only to vacancies may

lead to a scatter of the numbers and to a strong deviation from the sympathetic relation between $\lg C_{T_s}$ and $\lg P_{T_s}$, contrary to equation (4). The drainage of vacancies to dislocations was also noted in ⁽²¹⁾ (see also ⁽²⁷⁾).

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CITED LITERATURE

1. Ya. I. Frenkel, *Statistical Physics*, 1947, p. 465.
2. Ya. I. Frenkel, *Introduction to the Theory of Metals*, 1958, p. 203.
3. N. Mott, G. Gurney, *Electronic Processes in Ionic Crystals*, 1950.
4. F. J. Bradshaw, S. Pearson, *Phil. Mag.*, a) **1**, 812 (1956); b) **2**, 379, 570 (1957).
5. P. Jongenburger, *Phys. Rev.*, **106**, 66 (1957).
6. R. O. Simmons, R. W. Balluffi, *Phys. Rev.*, **117**, 52 (1960).
7. P. Jongenburger, *Phys. Rev.*, **90**, 710 (1953).
8. P. M. Lee, N. H. March, *Phil. Mag.*, **2**, 1226, 1235 (1957).
9. J. E. Bauerle, J. S. Koehler, *Phys. Rev.*, **107**, 1493 (1957).
10. R. Feder, A. S. Nowick, *Phys. Rev.*, **109**, 1959 (1958).
11. V. A. Pervakov, V. I. Khotkevich, *DAN*, **134**, 1328 (1960).
12. W. DeSorbo, *Phys. Rev.*, **117**, 444 (1960).
13. B. F. Ormont, *DAN*, **106**, 687 (1956); **124**, 129 (1959).
14. J. Gilman, *J. Appl. Phys.*, **31**, 2208 (1960).
15. W. DeSorbo, D. Turnbull, *Acta Metall.*, **7**, 83 (1959).
16. R. O. Simmons, R. W. Balluffi, *Phys. Rev.*, **125**, 862 (1962).
17. B. G. Lazarev, O. N. Ovcharenko, *JETP*, **36**, 60 (1959).

18. W. Schüle, A. Seeger, F. Ramsteiner et al., *Zs. Naturforsch.*, **16a**, 323 (1961).
19. G. Airoidi, G. L. Bachella, E. Germagnoli, *Phys. Rev. Letters*, **2**, 145 (1959).
20. M. Doyama, J. S. Köhler, *Phys. Rev.*, **119**, 939 (1960).
21. S. D. Gertsriken, N. N. Novikov, *Physics of Metals and Metallography*, **9**, 224 (1960).
22. Y. Quere, *C. R.*, **251**, 367 (1960).
23. R. O. Simmons, R. W. Balluffi, *Phys. Rev.*, **119**, 600 (1960).
24. A. Ascoli, M. Asdente, E. Germagnoli, A. Manara, *J. Phys. Chem. Solids*, **6**, 59 (1958).
25. A. Granato, A. Hickata, K. Lücke, *Phys. Rev.*, **108**, 1344 (1957).
26. A. N. Nesmeyanov, *Vapor Pressure of the Chemical Elements*, 1961.
27. L. M. Clarebrough, M. E. Hargreaves, G. West, *Phil. Mag.*, **1**, 528 (1956).
28. D. White, P. N. Walsh, H. Goldstein, D. F. Dever, *J. Phys. Chem.*, **65**, 1404 (1961).
29. Ya. A. Kraftmakher, *Physics of the Solid State*, **5**, 950 (1963).
30. Ya. A. Kraftmakher, P. G. Strelkov, *Physics of the Solid State*, **4**, 2271 (1962).

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