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Calculation of Dissociation Energies in Interatomic Pair Potentials and Review of the Relationship between Coefficients of Thermal Expansion and Heat Capacities of Simple Metals

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Dissociation energies for a two-term inverse power type of interatomic pair potential have been calculated for several metals by considering all interatomic interactions in the solid and using the experimental values of the cohesive energies. The results are then employed to calculate the ratio of thermal expansion coefficients and heat capacities of metals. It is found that the calculated values are in much better agreement with the experimental observations compared to an earlier work.

I. Introduction

Various models have been proposed for the interatomic pair potential energy function $\phi(r)$. At the present time one of the most frequently used models for nonpolar atoms is that studied by Mie (*1*), Grüneisen (*2*), and Fürth (*3*), given by

$$\phi(r) = \frac{D_0 nm}{n - m}\left[-\frac{1}{m}\left(\frac{r_0}{r}\right)^m + \frac{1}{n}\left(\frac{r_0}{r}\right)^n\right] \quad (1)$$

where D_0 is the dissociation energy and r_0 is the equilibrium interatomic separation at which $\phi(r)$ is a minimum. m and n are dimensionless constants whose values have been obtained for a variety of elements by Fürth (*3*).

So far the dissociation energies, D_0, of Eq. (1) have not been calculated accurately for metals. It is usually assumed that they can be obtained using the well-known equation (*4*)

$$D_0 = \frac{2\Delta H_s}{NW} \quad (2)$$

where ΔH_s is the heat of sublimation of the metal, N is the number of atoms, and W is the coordination number of atoms in the metal.

Equation (2) considers only the nearest neighbor interactions among the atoms of the solid. In this paper, we have recalculated the values of D_0 by considering not only the nearest neighbor interactions but the interactions between all atoms of the

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solid. The results indicate that significant errors are introduced when interactions beyond the nearest neighbors are neglected. With the complete interatomic potential energy functions obtained in this way, we decided to recalculate the ratio of the linear thermal expansion coefficient, α, and the heat capacity at constant pressure, C_p, for different metals as studied by McLachlan and Foster (*4*). This ratio, α/C_p, is expected to be a constant, independent of temperature, for a given metallic solid. Our results turn out to be in fair agreement with the experimental observations.

During the course of this study, we also discovered a serious error in the results obtained by McLachlan and Foster (*4*). Their values, after correction, are found to be far from the experimental values.

II. Theory

We shall first derive an expression for D_0 of Eq. (1) by considering the interactions of all atoms in the solid.

We rewrite Eq. (1) for a pair of atoms i and j of the solid in terms of the nearest neighbor distance, R, as

$$\phi_{ij}(r) = \frac{D_0 nm}{n-m} \left[-\frac{1}{m}\left(\frac{r_0}{p_{ij}R}\right)^m + \frac{1}{n}\left(\frac{r_0}{p_{ij}R}\right)^n \right]$$

where the distance between atom i and atom j has been expressed as $p_{ij}R$. The total interaction energy of the solid, U, is then given by

$$U = \frac{D_0 nmN_0}{2(n-m)} \left[-\frac{S_m}{m}\left(\frac{r_0}{R}\right)^m + \frac{S_n}{n}\left(\frac{r_0}{R}\right)^n \right] \quad (3)$$

where N_0 is the number of atoms in the solid and is taken to be equal to Avogadro's number as we are considering one mole of the solid. The factor $\frac{1}{2}$ appears to avoid counting each pair of atoms twice. S_m and S_n are the lattice sums given by

$$S_m = \sum_j p_{ij}^{-m} \quad \text{and} \quad S_n = \sum_j p_{ij}^{-n}.$$

At absolute zero temperature, i.e., the minimum of potential energy, we have

$$\left.\frac{\partial U}{\partial R}\right|_{R=R_0} = 0$$

where R_0 is the equilibrium nearest neighbor distance of atoms in the solid. This gives

$$R_0 = r_0 \left(\frac{S_n}{S_m}\right)^{1/(n-m)}. \quad (4)$$

The total potential energy of the solid at 0°K is then given by

$$U_{0°\mathrm{K}} = U\Big|_{R=R_0} = -\frac{D_0 N_0 S_n}{2}\left(\frac{S_m}{S_n}\right)^{n/(n-m)}. \quad (5)$$

The cohesive energy, $\Delta H_0^{(s)}$, the zero-point energy, $\frac{9}{8} N_0 k_B \theta_D$, and the potential energy at absolute zero, $U_{0°\mathrm{K}}$, are related by (*5*)

$$U_{0°\mathrm{K}} + \tfrac{9}{8} N_0 k_B \theta_D = -\Delta H_0^{(s)}$$

where k_B and θ_D are the Boltzmann constant and the Debye temperature of the solid, respectively. Therefore, we obtain

$$D_0 = \frac{2}{N_0 S_n}\left[\Delta H_0^{(s)} + \frac{9}{8} N_0 k_B \theta_D\right] \left(\frac{S_n}{S_m}\right)^{n/(n-m)}. \quad (6)$$

We shall now derive an expression for α/C_p. From Eq. (3) the potential energy of the solid per atom per degree of freedom, u, will be given by

$$u = \frac{U}{3N_0} = \frac{D_0 nm}{6(n-m)} \left[-\frac{S_m}{m}\left(\frac{r_0}{R}\right)^m + \frac{S_n}{n}\left(\frac{r_0}{R}\right)^n \right]. \quad (7)$$

Letting $\Delta R = R - R_0$ and using Eq. (4) we obtain

$$u = \frac{D_0 nmS_n}{6(n-m)} \left(\frac{S_m}{S_n}\right)^{n/(n-m)} \left[-\frac{1}{m}\left(1 + \frac{\Delta R}{R_0}\right)^{-m} + \frac{1}{n}\left(1 + \frac{\Delta R}{R_0}\right)^{-n}\right].$$

Since $\Delta R/R_0 \ll 1$ we may expand $(1 + \Delta R/R_0)^{-m}$ and $(1 + \Delta R/R_0)^{-n}$, neglecting terms higher than the cubic power of $\Delta R/R_0$, to obtain

$$u = -\frac{D_0 S_n}{6}\left(\frac{S_m}{S_n}\right)^{n/(n-m)} + \frac{D_0 nmS_n}{12}\left(\frac{S_m}{S_n}\right)^{n/(n-m)}\left(\frac{\Delta R}{R_0}\right)^2 - \frac{D_0 nmS_n}{36}\left(\frac{S_m}{S_n}\right)^{n/(n-m)}(n + m + 3)\left(\frac{\Delta R}{R_0}\right)^3.$$

The average value of ΔR is calculated using the Boltzmann distribution function

$$\overline{\Delta R} = \frac{\int_{-\infty}^{+\infty} \Delta R \exp(-u/k_B T)\, d(\Delta R)}{\int_{-\infty}^{+\infty} \exp(-u/k_B T)\, d(\Delta R)}$$

to obtain (*4, 6*)

$$\frac{\overline{\Delta R}}{R_0} = \frac{n + m + 3}{D_0 nmN_0 S_n}\left(\frac{S_n}{S_m}\right)^{n/(n-m)} E$$

where E is the total vibrational energy of the solid. Since the difference between E and the enthalpy, H, is very small (*4*), we may replace E by H in this equation. Differentiating the resulting equation with respect to absolute temperature at constant pressure and using the fact that

$$\frac{\partial}{\partial T}\left(\frac{\overline{\Delta R}}{R_0}\right) = \frac{1}{R_0}\left(\frac{\partial \overline{R}}{\partial T}\right) = \alpha$$

we obtain

$$\frac{\alpha}{C_p} = \frac{n + m + 3}{D_0 nmN_0 S_n}\left(\frac{S_n}{S_m}\right)^{n/(n-m)}.$$

Substituting for D_0 from Eq. (6) we get

TABLE I

DISSOCIATION ENERGIES OF THE PAIR POTENTIAL ENERGY FUNCTIONS OF DIFFERENT METALS AND THE RELEVANT QUANTITIES

Metal	$\Delta H_0^{(s)}$ (kcal/mole)	θ_D (°K)	m	n	S_m	S_n	D_0 from Eq. (6) (10^{-21} cal)	D_0 from Eq. (2) (10^{-21} cal)
Al	76.9	428	4	7	25.338	13.359	4.347	21.283
Cr	94.5	630	5	7	14.758	11.054	10.479	39.231
Cu	80.8	343	4	7	25.338	13.359	4.554	22.362
Au	87.6	165	5.5	8	15.711	12.802	11.852	24.244
Fe	99.4	467	4	7	22.639	11.054	5.666	41.265
Mo	157.1	450	5	7	14.758	11.054	17.275	65.219
Ag	68.3	225	4.5	7	21.153	13.359	4.724	18.903
W	199.7	400	5	7	14.758	11.054	21.917	82.904
Pt	134.8	240	5.5	8	15.711	12.802	18.234	37.308
Ca	42.1	230	4	6	25.338	14.454	1.818	11.652
Sr	39.3	147	(4)	(6)	25.338	14.454	1.690	10.877
Ba	42.8	110	(4)	(6)	22.639	12.253	1.850	17.768
Cd	26.8	209	6	7	14.455	13.360	3.906	7.417
Ni	102.3	450	4	7	25.338	13.359	5.767	28.313

$$\frac{\alpha}{C_p} = \frac{n + m + 3}{2nm[\Delta H_0^{(s)} + \frac{9}{8} N_0 k_{\mathrm{B}} \theta_{\mathrm{D}}]}. \tag{8}$$

III. Results and Discussion

Table I shows the cohesive energies (*7*), Debye temperatures (*8*), values of m and n (*3*), and values of S_m and S_n (*5*) for several metals. Values of D_0 calculated from Eqs. (6) and (2) are also listed in this table. As may be observed, there is a significant difference between D_0 obtained when all interactions among atoms of the solid are considered and those obtained when only nearest neighbor interactions are taken into account.

Table II shows the average experimental values of α/C_p (obtained by averaging these quantities over the temperature range 25 to 1000°K) (*4*), our theoretical values from Eq. (8), and the theoretical values of McLachlan and Foster after correcting their final equation.

TABLE II

EXPERIMENTAL AND THEORETICAL VALUES OF α/C_p FOR DIFFERENT METALS (10^{-6} mole/cal).

Metal	$(\alpha/C_p)_{\mathrm{expt}}$ (average)	$(\alpha/C_p)_{\mathrm{theory}}$ (our results)	$(\alpha/C_p)_{\mathrm{theory}}$ (McLachlan and Foster)
Al	4.14	3.21	6.50
Cr	1.36	2.23	3.02
Cu	2.89	3.06	6.19
Au	2.45	2.13	4.28
Fe	1.86	2.49	3.35
Mo	0.97	1.36	1.82
Ag	3.25	3.35	6.74
Tl	4.43	5.10	10.24
W	0.75	1.07	1.43
Pt	1.47	1.39	2.78
Pb	4.43	5.29	10.64
Be	3.01	3.38	7.04
Ca	3.37	6.36	12.87
Cd	5.48	6.99	14.21
Ni	2.02	2.42	4.89
Mg	4.44	7.48	15.34
Zn	5.42	6.75	13.82
Co	2.23	2.43	4.92
Se	7.43	7.42	—
Mn	3.48	3.93	—

As pointed out earlier, the final equation obtained by McLachlan and Foster is in error. When derived correctly, it should read

$$\left(\frac{\alpha}{C_p}\right)_{\mathrm{theory}} = \frac{(m + n + 3)W}{12mn\,\Delta H_{\mathrm{s}}}. \tag{9}$$

This is the equation we have used to calculate the values listed in the last column of Table II. It should be noted that even though Eq. (8) is independent of whether or not interactions beyond nearest neighbors are considered, it does not reduce to Eq. (9) even if the zero-point energy is neglected. This is due to the fact that the energy term, u, used by us in the Boltzmann distribution function is the total interaction energy of an atom per degree of freedom in the solid, while that used by McLachlan and Foster is an interatomic energy between only two atoms. We feel that the former approach is more appropriate.

It may be seen from Table II that our theoretical values for α/C_p are in much better agreement with the experimental results as compared with those obtained by McLachlan and Foster.

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