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The Relationship between Coefficients of Expansion and Heat Capacities of Simple Metals

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The authors of this paper, being intrigued by statements in the literature that the coefficients of expansion of metals are proportional to the heat capacities, have put these statements to the test. This paper shows that the experimental ratios of coefficients of expansion and heat capacities at constant pressure are indeed a constant for each metal over wide temperature ranges and the constants are in fair agreement with the values computed from theory.

Although it is well known that the coefficients of expansion of metals are inclined to be proportional to the heat capacities, there are no published tables of quantitative examples to demonstrate to what extent this is so. The purpose of this paper is to present such a table for 13 metals over a temperature range from 25 to 1000°K and to develop a theoretical equation to correlate with the experimental results.

Regarding the theoretical relationship Grüneisen (*1*) derived the well-known equation

$$\alpha = \gamma C_v / 3V\beta, \tag{1}$$

where α is the coefficient of expansion, C_v is the heat capacity at constant volume, V is volume, β is the compressibility, and γ is the Grüneisen constant. With this equation and other considerations, it can be shown that α is approximately proportional to C_v. Also Fürth (*2*) used the relationships between α, C_v, and β to determine the values of m and n in the equation by Mie (*3*), Grüneisen (*1*), and Fürth (*2*) of the following form:

$$e(r) = e_\infty \left\{ 1 + \frac{1}{m-n} \left[-m \left(\frac{r_0}{r} \right)^n + n \left(\frac{r_0}{r} \right)^m \right] \right\}, \tag{2}$$

where e_∞ is the energy required to separate two atoms an infinite distance from one another, r_0 is the equilibrium distance at which the potential energy is zero, while m and n are constants with m greater than n, the values of which Fürth (*2*) endeavoured to determine and which he tabulated.

We will derive the ratio of α to C_v by starting with a derivation presented in a textbook by Levy (*4*) who expressed the interatomic potential as a function of the displacement, Δr of atoms from their equilibrium positions by a power series,

$$e(\Delta r) = a(\Delta r)^2 + b(\Delta r)^3 + \cdots +, \tag{3}$$

where a and b are, as yet, undetermined constants.

To get the mean displacement $\overline{\Delta r}$, the average is taken as

$$\overline{\Delta r} = \frac{\int_{-\infty}^{\infty} (\Delta r) \exp\left[\frac{-e(\Delta r)}{KT} \right] d\Delta r,}{\int_{-\infty}^{\infty} \exp\left[\frac{-e(\Delta r)}{KT} \right] d\Delta r}, \tag{4}$$

or, using Eq. (3),

$$\overline{\Delta r} = \frac{\int_{\infty}^{\infty} \Delta r \exp\left[-a(\Delta r)^2 - b(\Delta r)^3\right] \frac{d}{KT}(\Delta r)}{\int_{\infty}^{\infty} \exp\left[-a(\Delta r)^2 - b(\Delta r)^3\right] \frac{1}{KT} d(\Delta r)}. \tag{5}$$

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Rather than reproduce the procedures by which the integrations in Eq. (5) are carried out, we take Levy's results (*4*). He gets:

$$\overline{\Delta r} = \frac{3}{4}\frac{b}{a^2}\bar{\varepsilon} \qquad (6)$$

where $\bar{\varepsilon}$ is the average energy of vibration per atom per degree of freedom in a crystalline solid.

Since

$$\bar{\varepsilon} = E/3N,$$

Eq. (6) is

$$\overline{\Delta r} = \left(\frac{3}{4}\right)\frac{b}{a^2}\frac{\mathrm{E}}{3N}, \qquad (7)$$

where E is the energy of vibration per mole. (This is Levy's equation.)

Fortunately the values of a and b needed for Eqs. (3) and (7) can be determined from Eq. (2) as follows, since for small displacements of the atoms from the equilibrium positions,

$$r = r_0 + \Delta r = r_0\left(1 + \frac{\Delta r}{r_0}\right). \qquad (8)$$

Then Eq. (2) becomes

$$e(\Delta r) = e_\infty\left\{1 + \frac{1}{m-n}\left[\frac{-m}{\left(1+\frac{\Delta r}{r}\right)^m} + \frac{n}{\left(1+\frac{\Delta r}{r}\right)^n}\right]\right\}. \qquad (9)$$

Knowing that

$$(1+x)^{-n} = 1 - nx + \frac{n(n+1)x^2}{2!} - \frac{n(n+1)(n+2)x^3}{3!} - \cdots -,$$

Eq. (3) approximates

$$e(\Delta r) = e_\infty\frac{mn}{2}\left(\frac{\Delta r}{r_0}\right)^2 + e_\infty\frac{mn}{6}(m+n-3)\left(\frac{\Delta r}{r_0}\right)^3. \qquad (10)$$

Letting

$$e_\infty\frac{mn}{2r_0^2} = a, \qquad (11a)$$

$$e_\infty\frac{mn}{6r_0^3}(m+n-3) = b, \qquad (11b)$$

and introducing Eqs. (11a) and (11b) into Eq. (7) gives

$$\frac{\overline{\Delta r}}{r_0} = \left(\frac{m+n-3}{6mne_\infty}\right)E. \qquad (12)$$

Replacing E by H for convenience (since the difference between them is less than the combined errors in the assumptions and the data to be used) and replacing e_∞ by the well-known relation

$$e_\infty = \frac{2\Delta H_s}{NW}, \qquad (13)$$

where ΔH_s is the heat of sublimation and W is the coordination number, then Eq. (12) becomes

$$\frac{\overline{\Delta r}}{r_0} = \left(\frac{m+n-3}{12mn\Delta H_s}\right)H, \qquad (14)$$

and

$$\frac{\delta\left(\frac{\Delta r}{r_0}\right)}{\delta T} = \left(\frac{m+n-3}{12mn\Delta H_s}\right)\frac{\delta H}{\delta T}. \qquad (15)$$

Since the linear coefficient of expansion is

$$\alpha = \frac{1dr}{r_0 dT} = \frac{d(r_0+\Delta r)}{r_0 dT} = \frac{d}{dT}\left(\frac{\Delta r}{r_0}\right),$$

and the heat capacity at constant pressure is

$$C_p = \frac{\delta H_s}{\delta T},$$

then Eq. (15) predicts that

$$\alpha = \frac{(m+n-3)WC_p}{12mn\Delta H_s} \equiv B_{\mathrm{th}}C_p,$$

where B_{th} is the theoretical value of the proportionality constant in the $\alpha - C_p$ relation, i.e.,

$$B_{\mathrm{th}} = \frac{(m+n-3)W}{12mn\Delta H_s}.$$

The computed values of B_{th} are given in the bottom line of Table I for 13 elements. The m and n values are taken from Fürth (*2*) and the ΔH_s values are from Gschneidner (*5*). The experimental values of B are defined as

$$B_{\mathrm{exp}} = \left(\frac{\alpha}{C_p}\right)\mathrm{exp},$$

TABLE I

$B_{\mathrm{exp}} \times 10^6 = \dfrac{\alpha \times 10^6}{C_p}$ AS A FUNCTION OF TEMPERATURE

	Metal												
T°K	Al	Cr	Cu	Au	Fe	Mo	Ag	Ta	Ti	W	Pt	Pb	Be
25	4.55	1.82	2.60	2.56	1.82	—	3.27	—	1.33	—	—	4.21	—
50	3.85	1.33	2.59	2.29	1.78	—	2.83	—	1.06	—	—	4.24	—
100	3.85	1.05	2.75	2.32	1.98	0.87	3.00	1.10	1.28	0.68	1.44	4.34	3.02
200	3.91	1.06	2.81	2.33	1.97	0.89	3.10	1.09	1.39	0.76	1.44	4.46	2.95
300	3.95	0.90	2.86	2.34	1.97	0.88	3.14	1.10	1.52	0.78	1.44	4.51	2.85
400	3.98	1.33	2.89	2.38	2.02	0.86	3.22	1.06	1.49	0.77	1.46	4.69	2.88
500	4.12	1.40	2.92	2.42	2.01	0.83	3.29	1.08	1.52	0.76	1.48	4.89	2.92
600	4.20	1.44	2.96	2.47	1.98	0.85	3.35	1.09	1.54	0.76	1.48	—	2.96
700	4.34	1.49	3.01	2.51	1.95	0.85	3.41	1.10	1.53	0.77	1.49	—	3.04
800	4.54	1.51	3.08	2.57	1.82	0.87	3.48	1.10	1.52	0.75	1.50	—	3.14
1000	—	1.57	3.28	2.73	1.19α	0.90	3.64	1.11	1.50	0.76	1.53	—	3.30
Average	4.13	1.35	2.89	2.45	1.85	0.87	3.25	1.09	1.43	0.76	1.47	4.48	3.02
Theory	3.66	1.81	3.54	2.72	1.96	1.09	3.95	—	—	0.86	1.77	7.09	3.74

and are shown in the body of the table. The Institute of Physics Handbook furnished the experimental coefficients of expansion (*6*) and the heat capacities at constant pressure (*6*).

This work tends to show that there is both theoretical and experimental justification for the general belief that the coefficients of expansion of metals are approximately proportional to the heat capacities.

References

1. E. GRÜNEISEN Zustand der Festen Körper, *in* "Handbook of Physics", Julius Springer (Berlin) (1926).
2. R. FÜRTH, On the equation of State of Solids, *Proc. Roy. Soc. London* **A183**, 57–110 (1944).
3. G. MIE, Zur Kinetischen Theorie der Einatomigen Körper, *Ann. Phys. Lpz.* **11**, 657 (1903).
4. ROBERT A. LEVY, Principles of Solid State Physics, Academic Press, N.Y., pp. 141–144 (1968).
5. KARL A. GSCHNEIDER, JR., Physical properties and Interrelationships of Metallic and Semimetallic Elements *in* "Solid State Physics," (Seitz and Turnbull, Eds.) Vol. 16, pp. 275–426, Academic Press, N.Y. (1963).
6. Institute of Physics Handbook, Dwight E. Gray, coordinating Ed. 3rd Ed., pp. 4–106–4-108, Table 4e-2, and page 4-115, Table 4e-10 (1972).