VII. Specific Heat Data

13. ELECTRONIC SPECIFIC HEAT CONSTANT

The electronic specific heat constants were obtained directly from specific heat measurements at very low temperatures, $<10°\mathrm{K}$ ($-263°\mathrm{C}$). For most metals at these low temperatures, the specific heat is given by

$$C_p = C_v = \gamma T + 464.4(T/\theta_0^S)^3, \tag{13.1}$$

where C_p is the heat capacity at constant pressure, C_v is the heat capacity at constant volume, γ is the electronic specific heat constant, T is the absolute temperature, and θ_0^S is the Debye temperature.[59] The experimental data are usually plotted in the form C_v/T versus T^2, which yields an intercept equal to γ and a slope equal to $464.4/(\theta_0^S)^3$. Further discussion of θ_0^S is deferred until Section 16. For a few metals, magnetic and nuclear contributions may be equally important, and thus the simple expression given above (Eq. 13.1) then becomes invalid. The onset of superconductivity will also cause some problems, but these are usually solved by carrying out the measurements in a magnetic field that is large enough to destroy superconductivity. Since most of the authors evaluate their specific heat data, and since departures from Eq. (13.1) are taken into account by them, there is no need to discuss such anomalies here.

The electronic specific heat constant is directly proportional to the density of states of the electrons at the Fermi level. Thus it is seen that knowledge of the electronic specific heat constant is very desirable since it is a direct measurement of a fundamental property of a metal. For insulators there is no electronic contribution to the specific heat because all of the bands are completely filled; as a matter of fact, even semiconductors, which usually have a few electrons in an unfilled band (or a few holes in a filled band), generally do not have an electronic contribution.

The electronic specific heat constants are given in Table XIII. These values for γ vary from a minimum value of zero for diamond, germanium, selenium, gray tin, and tellurium to a maximum value of 58 mj/g-at/deg^2 for α-Ce. The mean value of γ for the elements, for which γ is less than 19 mj/g-at/deg^2 is 4.1 mj/g-at/deg^2. All of the estimated values lie between the two extremes cited.

A plot of the electronic specific heat constants of the elements of the fourth, fifth, and sixth periods of the Periodic Table is shown in Fig. 18.

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[59] The superscript and subscript after θ indicates that the Debye temperature was obtained from specific heat measurements (S) at zero degrees Kelvin (0). The need for these super- and subscripts will be apparent in Sections 16 to 21, which deal with the Debye temperature.

TABLE XIII. ELECTRONIC SPECIFIC HEAT CONSTANT

Element	γ $\left(\frac{\text{mjoules}}{\text{g-at.deg}^2}\right)$	$\gamma \times 10^4$ $\left(\frac{\text{cal}}{\text{g-at.deg}^2}\right)$	Ref.
3 Li	1.69 ±0.06	4.04	1, 2
4 Be	0.223 ±0.003	0.533	3, 4
5 B	1.26^{a}	3.01	5
6 C(g)	0.0138^{b}	0.0330	6
6 C(d)	~0	~0	7
11 Na	1.38 ±0.05^{a}	3.30	1, 8, 9, 10
12 Mg	1.30 ±0.08	3.11	3, 11, 12, 13
13 Al	1.36 ±0.01^{a}	3.25	14, 15, 16
14 Si	0.021	0.050	17, 18
15 P(w, r, b)	(0)^{c}	(0)^{c}	—
16 S(r, m)	(0)^{c}	(0)^{c}	—
19 K	2.11 ±0.11	5.04	1, 10, 19
20 Ca	2.90 ±0.18	6.93	20, 21
21 Sc	10.8 ±0.5	25.8	22, 23
22 Ti	3.41 ±0.10	8.15	11, 24, 25, 26
23 V	9.04 ±0.22	21.61	24, 27, 28, 29
24 Cr	1.46 ±0.06^{a,d}	3.49	30, 31, 32
25 Mn(α)	8.4^{e}	20	33
25 Mn(β)	9.7 ±0.3	23	33, 34
25 Mn(γ)	4.6 ±0.1^{a,f}	11	34, 35
25 Mn(δ)	9.42	22.5	34
26 Fe	4.98 ±0.06	11.9	36, 37, 38, 39
27 Co	4.73^{a}	11.3	36, 40
28 Ni	7.30 ±0.30^{a}	17.4	41, 42, 43
29 Cu	0.693 ±0.007^{a}	1.66	16, 21, 25, 44–51
30 Zn	0.643 ±0.012	1.54	3, 52–56
31 Ga	0.598 ±0.004	1.43	56, 57
32 Ge	0.000 ±0.001	0	18, 58, 59
33 As	(0.1)^{c}	(0.24)^{c}	—
34 Se	0	0	3, 60
37 Rb	2.52 ±0.07	6.02	19, 61
38 Sr	3.64 ±0.18	8.70	20
39 Y	10.1 ±0.1^{a}	24.1	22, 62
40 Zr	2.91 ±0.12	6.95	11, 24, 25
41 Nb	7.66 ±0.29^{d}	18.3	62, 63, 64
42 Mo	2.10 ±0.14	5.02	24, 62, 65–68
43 Tc	(4.06)^{c}	(9.7)^{c}	—
44 Ru	3.3	7.9	24
45 Rh	4.6 ±0.4	11.0	24, 69, 70
46 Pd	10.0 ±0.7^{a}	23.9	66, 71, 72
47 Ag	0.659 ±0.027	1.58	44, 66, 71, 73–76
48 Cd	0.674 ±0.036	1.61	3, 12, 77
49 In	1.70 ±0.11	4.06	48, 78, 79

TABLE XIII. ELECTRONIC SPECIFIC HEAT CONSTANT—*Continued*

Element	γ $\left(\frac{\text{mjoules}}{\text{g-at.deg}^2}\right)$	$\gamma \times 10^4$ $\left(\frac{\text{cal}}{\text{g-at.deg}^2}\right)$	Ref.
50 Sn(g)	0	0	58
50 Sn(w)	1.78 ±0.08	4.25	48, 79–83
51 Sb	(0.1)[c]	(0.24)[c]	—
52 Te	0	0	3, 60
55 Cs	3.55 ±0.08	8.48	19, 61
56 Ba	2.7 ±0.5	6.5	20
57 La	10.1[a]	24.1	22, 84
58 Ce(α)	58[g]	138	85
58 Ce(γ)	7.24	17.3	86
59 Pr	21.9 ±2.9	52.3	87, 88
60 Nd	8.92	21.3	86
61 Pm	(10)[c]	(24)[c]	—
62 Sm	10.6 ±1.5	25.3	86, 87, 89
63 Eu	(2.8)[c]	(6.7)[c]	—
64 Gd	(10)[c]	(24)[c]	—
65 Tb	9.05	21.6	90
66 Dy	9.25 ±0.25	22.1	87, 91
67 Ho	26 ±5	62	87
68 Er	13 ±1	31	87
69 Tm	19.7 ±1.8	47.1	87, 88
70 Yb	2.90	6.93	92
71 Lu	10.22 ±0.73	24.43	88, 93
72 Hf	2.40 ±0.24	5.74	24, 25
73 Ta	5.84 ±0.31	14.0	24, 29, 62, 94, 95
74 W	1.22 ±0.15[a]	2.92	24, 66, 67, 82, 96
75 Re	2.40 ±0.14	5.74	24, 62, 97
76 Os	2.35	5.62	24
77 Ir	3.15 ±0.05	7.53	24, 69
78 Pt	6.68 ±0.27	16.0	66, 70, 98
79 Au	0.748 ±0.013[a]	1.79	44, 55, 75
80 Hg	2.2	5.3	99
81 Tl	2.83 ±0.27	6.76	100, 101
82 Pb	3.14 ±0.15	7.50	102–105
83 Bi	0.049 ±0.029	0.12	106, 107, 108
84 Po	(0.1)[c]	(0.24)[c]	—
87 Fr	(4.2)[c]	(10)[c]	—
88 Ra	(3.1)[c]	(7.4)[c]	—
89 Ac	(9.6)[c]	(23)[c]	—
90 Th	4.69	11.2	109
91 Pa	(7.0)[c]	(16.7)[c]	—
92 U	10.9	26.1	109
93 Np	(10)[c]	(24)[c]	—
94 Pu	48.87	116.8	110

[a] See text for further discussion.

[b] Value obtained from Madagascar graphite. Value will vary with the degree of stacking faults in the specimen. In an earlier paper a value of 0.031 mj/g–at/deg² was found (Keesom and Pearlman[111]).

[c] Estimated value; see text for further discussion.

[d] Clusins and Franzosini[32] found that this value is valid below 20°K; at temperatures $> 100°\text{K}$ a value of $\gamma = 5.8$ mj/g–at/deg² is required to explain the experimental data in this region.

[e] Shinozaki *et al.*[33] also found linear magnetic contribution (4.2 mj/g–at/deg²) which might account for the high values ($\gamma \sim 13$) reported by other authors (Wolcott,[24] Weiss and Tauer,[34] Elson *et al.*[112] and Guthrie *et al.*[113]).

[f] Recent results indicate a γ value of 8.4 mj/g–at/deg² for γ-Mn[33]; however, complete details are not available to evaluate their results.

[g] Data of Parkinson and co-workers[114,115] and Lounasmaa[116] were analyzed by Gschneidner[35] correcting for the presence of other cerium phases assuming they had identical γ values of 7.24 mj/g–at/deg².

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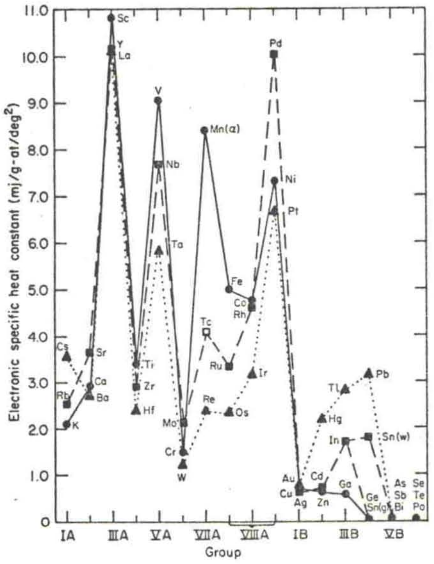
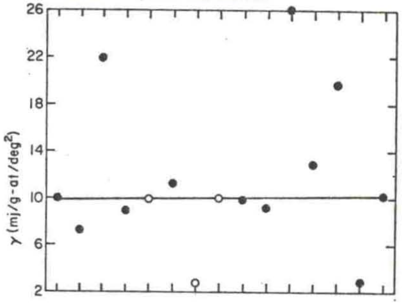


FIG. 18. Electronic specific heat constant of the elements of the fourth, fifth, and sixth periods of the Periodic Table. Open points are estimated values.

The variation of γ with the group number in this figure is much different from that seen in other plots of the physical properties of these same metals (Figs. 1, 3, 6, 12, 14, 15, and 17, or Figs. 9 and 11). The γ values of the elements (groups IA, IIA, and IB–VIB) that have no unpaired *d* electrons are generally low, i.e., lie below the mean value of 4.1 mj/g-at/deg^2. For the *d* transition metals such a general statement cannot be made. If we first examine the metals of groups IIIA through VIIA, we note that if the number of *d* electrons is odd, then the value of γ is large, and if the number is even, then γ is usually small. The γ values for the remaining elements, group VIIA, iron, and cobalt and their cogeners, are intermediate, but those for nickel and its cogeners are again quite large. From the above discussion it may be seen that if no unpaired *d* electrons are available, the electronic specific heat constant is always low. In order to have a large γ value it is a necessary, but not a sufficient condition, that unpaired *d* electrons must be available. As will be shown shortly the only elements which have been observed to have very high γ values (i.e., >15 mj/g-at/deg^2) are those which have, or are thought to have, unpaired *f* electrons. These observations also apply to the elements which are not shown in Fig. 18.

The variation of the electronic specific heat constant for the rare-earth

(a) Electronic specific heat constant



(b) Heat capacity at constant volume

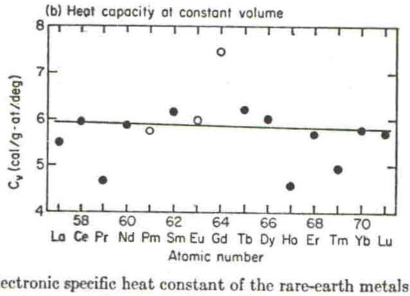


FIG. 19. (a) Electronic specific heat constant of the rare-earth metals. (b) The lattice contribution to the heat capacity at constant volume of the rare-earth metals. Open points are estimated data.

metals is shown in Fig. 19a. In general, most of the γ values lie quite close to 10 mj/g–at/deg^2, the value for lanthanum. The exceptions are the values for praseodymium, europium, holmium, thulium, ytterbium, and α-cerium (not shown in Fig. 19a, since its value is much larger than the range given in the figure). The values for europium (estimated) and ytterbium are low because these metals are divalent and have no d electrons.[13] The high values for the other four materials are not as easily explained. Since the rare earths have essentially the same valence band composed of $6s^25d^1$ electrons and since the $4f$ level is buried radially and shielded by the $5s^25p^6$ electrons from external forces, one would expect that the density of states (and thus the γ value) would be governed by the $6s^25d^1$ configuration; i.e., one would expect a constant value for the density of states for this series of elements. Since very large values are observed for the four elements, one might be tempted to suggest that there exists an f band which overlaps the $6s^25d^1$ bands and for a few elements the density of states is governed by the $4f$ band rather than by the $5d$ band, which leads to the very large γ values. This appears to be the situation for α-cerium,[60] but it is unclear for the other rare-earth exceptions (praseodymium, holmium, and thulium). The problem with these and also many of the other rare earths is that besides the normal lattice and electronic contributions to the specific heat (Eq. (13.1)) there are also magnetic and nuclear contributions which make it difficult to evaluate γ and $\theta_0{}^S$. Of these last two contributions the magnetic portion is by far the most uncertain from a theoretical standpoint, especially in view of the complex magnetic ordering which takes place in the rare-earth metals.[61–64] Much further research will be required before one can definitely conclude whether or not the $4f$ level is involved in determining the density of states of these metals.

Furthermore, if one attempts to calculate the lattice contribution to the heat capacity at constant volume, $C_v{}^e$, (see Section 15) he finds that $C_v{}^e$ is anomalously low for praseodymium, holmium, and thulium. This is due to the fact that the γ values for these metals are too large. Indeed, if one chooses a value of $\gamma = 10$ mj/g–at/deg^2 he obtains much more reasonable values for $C_v{}^e$ (also see the relevant discussion in Section 15). This also suggests that the high γ values for these three metals are suspect.

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[60] K. A. Gschneidner, Jr., *Proc. 4th Rare Earth Conf., Phoenix, Arizona, 1964*. Gordon & Breach, New York (to be published ca. 1965).

[61] W. C. Koehler, E. O. Wollan, M. K. Wilkinson, and J. W. Cable, *in* "Rare Earth Research" (E. V. Kleber, ed.), p. 149. Macmillan, New York, 1961.

[62] W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, *J. Phys. Soc. Japan* **17,** Suppl. B-III, 32 (1962).

[63] M. K. Wilkinson, H. R. Child, W. C. Koehler, J. W. Cable, and E. O. Wollan, *J. Phys. Soc. Japan* **17,** Suppl. B-III, 27 (1962).

[64] J. W. Cable, H. R. Child, W. C. Koehler, M. K. Wilkinson, and E. O. Wollan, *in* "Pile Neutron Research in Physics," p. 379. Intern. Atomic Energy Agency, Vienna, 1962.

The electronic specific heat constant for α-plutonium is only less high than that of α-cerium. It is quite likely that the $5f$ band is involved in determining the density of states in plutonium.

Boron. Kaufman and Clougherty[65] estimated the electronic specific heat constant from the low-temperature data (20° to 300°K) of Johnston *et al.*,[66] assuming γ to be linear and the lattice contribution to be given by the Debye model over this temperature range.

Sodium. The value given by Parkinson and Quarrington[67] is not included in the average value given in Table XIII, since it is significantly larger than any of the other values, i.e., 1.8 as compared with the mean of 1.38 ±0.05 mj/g–at/deg^2.

Aluminum. The value reported by Kok and Keesom[68] (1.46) is not included in the average (1.36 ±0.01) since it was higher than the other reported values.

Chromium. Edwards *et al.*[69] reviewed the literature up to 1958 and gave a best value for γ. This value was averaged with values which have been reported since then.

γ-Manganese. The mean value for γ-manganese was taken from the value calculated by Weiss and Tauer[70] from high-temperature specific heat data, and from the value obtained at low temperatures from γ-stabilized copper-manganese alloys (extrapolated to 100% Mn) reported by Zimmerman and Sato.[71] In view of the more recent data ($\gamma = 8.4$) published by Shinozaki *et al.*[72] the low given in Table XIII (4.6 ±0.1) may be incorrect. Since full details are presently not available, one can only point out this large difference.

Cobalt. The high value (5.02) reported by Duyckaerts[73] was omitted in calculating the average value (4.73) for cobalt.

Nickel. Recently Gupta *et al.*[74] obtained a value of 7.20 for nickel which

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[65] L. Kaufman and E. V. Clougherty, "Investigation of Boride Compounds for Very High Temperature Applications," Semi-Annual Rept. No. 2. Man Labs, Inc., April, 1963.

[66] H. L. Johnston, H. N. Hersh, and E. C. Kerr, *J. Am. Chem. Soc.* **73,** 1112 (1951).

[67] D. H. Parkinson and J. E. Quarrington, *Proc. Phys. Soc.* (*London*) **A68,** 762 (1955).

[68] J. A. Kok and W. H. Keesom, *Physica* **4,** 835 (1937).

[69] A. R. Edwards, J. I. Nish, and H. L. Wain, *Met. Rev.* **4,** 403 (1959).

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is very close to the mean value given in Table XIII and the value reported by Keesom and Clark[75] (Ref. 34 in Table XIII). This indicates that the value given in Table XIII is quite reliable, but that the error is probably less than that shown.

Copper. All of the γ values reported for copper having a total purity of less than 99.99% were not included in calculating the average value given in Table XIII. In general it was observed that γ increases with decreasing copper purity. Since the value given by du Chaterier and de Nobel[76] (0.721) was significantly higher than the other eleven literature values, it is not included in the average value (0.693 ±0.007) given in Table XIII.

Yttrium. Since the value (8.5) given by Jennings *et al.*[77] for yttrium is significantly lower than the other two values reported for that element, it is not included in the mean value (10.1 ±0.1).

Niobium. Since Boorse and co-workers[78] revised an earlier value for niobium,[79] and the revised value is in agreement with the value given by Morin and Maita,[80] the earlier value[79] is not considered in the present compilation.

Palladium. Since the value given by Pickard[81] (13.0) for palladium is significantly larger than the other literature values, it is not included in the average (10.0 ±0.7) given in Table XIII.

Lanthanum. Since the value (6.7) given by Parkinson *et al.*[82] for lanthanum is significantly smaller than the other values given in the literature, it is not included in the average (10.1) given in Table XIII.

Tungsten. The two different values reported by Daunt and co-workers for tungsten appear to be either too low (0.75)[83] or too high (21.4)[84] when compared with the mean value given here (1.22 ±0.15). For this reason they were omitted when the mean was calculated.

Gold. Since the value (0.87) given by Budworth *et al.*[85] for gold is significantly larger than the other literature values, it was not included in the average (0.748 ±0.013) given herein.

Estimated Data. Electrical resistivity and magnetic susceptibility data of the elements furnish some clues concerning the electronic specific heat constant. Since the resistivities of white and black phosphorus[86] and sulfur[50] indicate that these substances are insulators, it was assumed that the specific heat γ values for these substances would be zero.

In order to show how magnetic data may be used to estimate the electronic specific heat constant, we will quickly review the subject. The total magnetic susceptibility, χ_t, is given by

$$\chi_t = \chi_P + \chi_L + \chi_i + \chi_e + \chi_c + \chi_V, \tag{13.2}$$

where χ_P is the Pauli contribution, χ_L is the Landau contribution, χ_i is the ionic contribution, χ_e is the contribution due to exchange, χ_c is the contribution due to correlation, and χ_V is the Van Vleck temperature-independent orbital contribution. Usually χ_e is assumed to be equal to χ_c but of opposite sign. Thus, Eq. (13.2) is reduced to

$$\chi_t = \chi_P + \chi_L + \chi_i + \chi_V. \tag{13.3}$$

The χ_P and χ_V are paramagnetic contributions, while χ_L and χ_i are diamagnetic ones. The Van Vleck contribution is usually quite important for the transition metals with unfilled *d* levels, but for the other metals χ_V can be assumed to be zero. The Landau contribution for a free-electron gas model is equal to $-\frac{1}{3}\chi_P$. The ionic contribution is well known and can be found in the literature for most substances.[87–89] The Pauli contribution is directly proportional to the density of states at the Fermi level and, therefore, it is directly proportional to the electronic specific heat constant. Thus, in principle, one can evaluate γ from χ_t; for nontransition metals. For the transition metals there is another method one can employ to determine γ from χ_t; this method will be discussed shortly in connection with the estimation of the γ value for technetium.

The electrical resistivities of arsenic, antimony, and polonium are metallic in nature, suggesting that γ is greater than zero for these elements. The total magnetic susceptibility is negative for these three elements,[90] indicating that $|\chi_i|$ is greater than $|\chi_P + \chi_L| = |\frac{2}{3}\chi_P|$. This suggests that χ_P is small and, therefore, γ is small. From these two observations it was assumed that the γ is of the order of 0.1 mj/g–at/deg^2 for arsenic, antimony, and polonium.

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[90] The value for polonium is not known, but it is assumed to be negative.

Stoner[91] has shown that the total and Pauli susceptibilities are related by

$$1/\chi_t = (1/\chi_P) + \theta, \tag{13.4}$$

where θ is called the interaction term. If one knows θ, then it is possible to determine χ_P and, thus, γ from the measured χ_t. In general θ cannot be evaluated explicitly. The value of γ for technetium, however, was evaluated by making use of this equation. Nelson *et al.*[92] have measured the magnetic susceptibility of technetium and rhenium from 78° to 402°K (−195° to 129°C). The reviewer obtained the value of χ_t for technetium and rhenium at 0°K (−273°C) by extrapolation of their data. By using the known γ value for rhenium and χ_t at 0°K it was possible to determine θ for rhenium. The θ value for technetium was assumed to be equal to that of rhenium, which then permitted an evaluation of χ_P and γ of technetium. The value of γ obtained by this procedure is 4.06 mj/g–at/deg^2, which is a reasonable number. If one makes the assumption that χ_t at 0°K (−273°C) is equal to χ_P, then a γ equal to 21.5 mj/g–at/deg^2 is obtained, which is very unreasonable.

The γ values for promethium and gadolinium were estimated to be the same as for lanthanum and lutetium. The value of γ for europium was assumed to be equal to the mean value of barium and ytterbium. The γ values for francium and actinium were estimated from plots of the known electronic specific heat constants of their respective cogeners versus the period number. The γ values for radium and protactinium were assumed to be equal to the mean value of the alkaline-earth metals and the mean value of thorium and uranium, respectively. The γ value for neptunium was assumed to be the same as that for uranium.

14. HEAT CAPACITY AT CONSTANT PRESSURE

The heat capacity at constant pressure at 298°K (25°C) is shown in Table XIV. This value, C_p, is the usual quantity measured experimentally rather than the heat capacity at constant volume, C_v. For those involved in making thermodynamic calculations, C_p is of direct importance, but for those involved in studying the fundamental properties of solids, C_v, which must be calculated from the experimental value of C_p, is more useful.

The values of C_p are taken primarily from the reviews of Kelley[54] and of Stull and Sinke.[53] If more recent data were available to the reviewer, they are included in Table XIV. Since Stull and Sinke estimated the heat capacities of those elements for which no experimental values existed,

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TABLE XIV. HEAT CAPACITY AT CONSTANT PRESSURE AND AT CONSTANT VOLUME AND THE DILATION TERM[a]

Element	C_p (cal/g–at/deg)	Ref.	$A \times 10^5$ (g–at/cal)	C_v^l (cal/g–at/deg)	$C_v = C_v^l + C_v^e$ (cal/g–at/deg)
3 Li	5.65	1	2.056	5.34	5.46
4 Be	3.93	1, 2	0.9041	3.50	3.51
5 B	2.64	1, 2	1.666	2.52	2.61
6 C(g)	2.06	1, 2	0.1301	2.06	2.06
6 C(d)	1.462	3	0.2676	1.44	1.44
11 Na	6.745	1, 2	3.821	6.13	6.23
12 Mg	5.92	1, 2	2.011	5.62	5.71
13 Al	5.82	1, 2	2.445	5.48	5.57
14 Si	4.64	4	0.1124	4.62	4.63
15 P(w)	5.63	1	6.883	(4.98)[b]	4.98
15 P(r)	4.98	1, 2	(9.698)[b]	(4.26)[b]	(4.26)[b]
16 S(r)	5.40	1, 2	9.280	(4.59)[b]	4.59
16 S(m)	5.65	1	—	—	—
19 K	7.07	1	4.297	6.28	6.43
20 Ca	6.29	1, 2	1.086	5.96	6.16
21 Sc	6.09	5	(0.5004)[b]	(5.27)[b]	(6.03)[b]
22 Ti	5.98	1, 2	0.5316	5.68	5.92
23 V	5.905	1, 2	0.5756	5.20	5.85
24 Cr	5.57	1, 2	0.6731	5.40	5.51
25 Mn	6.285	1, 2	1.221	5.54	6.14
26 Fe	5.98	1, 2	0.9830	5.52	5.88
27 Co	5.95	1	1.196	5.49	5.82
28 Ni	6.23	1, 2	1.098	5.58	6.10
29 Cu	5.855	1, 2	1.630	5.65	5.69
30 Zn	6.07	1, 2	2.824	5.71	5.76
31 Ga	6.18	1	1.240	6.00	6.04
32 Ge	5.47	4	0.2518	5.45	5.45
33 As	5.895	1, 2	0.0579	(5.88)[b]	5.89
34 Se	6.075	1, 2	1.186	5.94	5.94
35 Rb	7.36	1	5.433	6.30	6.48
38 Sr	6.30	1, 2	0.8541	5.94	6.20
39 Y	6.34	6, 7	0.5608	5.55	6.27
40 Zr	6.12	1	0.2231	5.89	6.10
41 Nb	5.965	1, 2	0.5566	5.36	5.91
42 Mo	5.695	1, 2	0.4186	5.51	5.66
43 Tc	(5.80)[c]	—	(1.066)[b]	(5.40)[b]	(5.69)[b]
44 Ru	5.80	1	1.472	5.42	5.65
45 Rh	6.00	1	0.9456	5.57	5.90
46 Pd	6.21	1	1.185	5.36	6.07
47 Ag	6.095	1, 2	2.208	5.80	5.85
48 Cd	6.215	1, 2	3.168	5.80	5.85
49 In	6.39	1	3.357	5.86	5.98
50 Sn(g)	6.16	1	0.3627	5.75	5.75
50 Sn(w)	6.30	1, 2	2.151	5.92	6.05
51 Sb	6.03	1, 2	0.4198	(5.98)[b]	5.98
52 Te	6.145	1, 2	0.7542	6.06	6.06

TABLE XIV. HEAT CAPACITY AT CONSTANT PRESSURE AND AT CONSTANT VOLUME, AND THE DILATION TERM[a]—*Continued*

Element	C_p (cal/g-at/deg)	Ref.	$A \times 10^5$ (g-at/cal)	$C_v{}^l$ (cal/g-at/deg)	$C_v = C_v{}^l + C_v{}^e$ (cal/g-at/deg)
55 Cs	7.65	1	4.855	6.55	6.80
56 Ba	6.30	2	0.7510	6.02	6.21
57 La	6.25	7	0.3261	5.49	6.21
58 Ce(γ)	6.48	8	0.1833	5.94	6.46
59 Pr	6.45	7	0.1522	4.87	6.43
60 Nd	6.56	8	0.3340	5.88	6.52
61 Pm	(6.50)[c]	—	(0.2959)[b]	(5.75)[b]	(6.46)[b]
62 Sm	6.95	8, 9	0.2825	6.16	6.91
63 Eu	6.48	7	2.395	(5.98)[b]	6.18
64 Gd	8.72	2	0.1482	(7.97)[b]	8.69
65 Tb	6.92	1	0.3663	6.22	6.87
66 Dy	6.72	1	0.3475	6.01	6.67
67 Ho	6.49	1	0.4349	4.59	6.44
68 Er	6.72	1	0.5464	5.72	6.65
69 Tm	6.45	1, 2	0.6582	4.97	6.37
70 Yb	6.16	7	1.166	5.82	6.03
71 Lu	6.46	6	0.2492	5.70	6.43
72 Hf	6.10	1, 2	0.3047	5.90	6.07
73 Ta	6.07	1, 2	0.5440	5.59	6.01
74 W	5.84	1	0.4120	5.71	5.80
75 Re	6.14	1, 2	0.8267	5.88	6.05
76 Os	5.95	2	(0.4733)[b]	(5.89)[b]	(5.90)[b]
77 Ir	6.10	1	0.7697	5.79	6.02
78 Pt	6.185	1, 2	1.144	5.58	6.05
79 Au	6.065	1, 2	2.058	5.79	5.84
80 Hg	6.68[d]	1	7.138	5.81[d]	5.94
81 Tl	6.29	1, 2	2.907	5.75	5.95
82 Pb	6.39	1	3.478	5.74	5.97
83 Bi	6.20	1	0.6744	6.12	6.12
84 Po	(6.30)[c]	—	(1.710)[b]	(6.09)[b]	(6.10)[b]
87 Fr	(7.60)[c]	—	(5.538)[b]	(6.35)[b]	(6.65)[b]
88 Ra	(6.49)[c]	—	(1.071)[b]	(6.14)[b]	(6.36)[b]
89 Ac	(6.50)[c]	—	(0.6252)[b]	(5.74)[b]	(6.42)[b]
90 Th	6.53	1, 2	0.6797	6.11	6.44
91 Pa	(6.79)[c]	—	(0.2858)[b]	(6.25)[b]	(6.75)[b]
92 U	6.58	1	1.025	5.67	6.45
93 Np	7.02[e]	10	(2.946)[b]	(5.87)[b]	(6.59)[b]
94 Pu	8.50	11	5.816	3.77	7.25

[a] The dilation term, C^d, is given here in terms of a constant A, which is essentially independent of temperature. $C^d = AC_pT$. See text for further discussion.

[b] Estimated value; see text for further discussion.

[c] These data were estimated by Stull and Sinke.[2]

[d] This value corresponds to that of solid mercury at its melting point, 234°K.

[e] This value was obtained by the reviewer from the data given by Evans and Mardon[10] by extrapolation of the high-temperature specific heat from ~325° to 298°K.

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and since these values appear to be reasonable, the reviewer has included these in Table XIV instead of attempting to make his own estimates.

15. HEAT CAPACITY AT CONSTANT VOLUME AND THE DILATION TERM

The heat capacity at constant volume, C_v, is related to the heat capacity at constant pressure, C_p, by the following expression

$$C_p = C_v + C^d = C_v{}^l + C_v{}^e + C^d, \tag{15.1}$$

where $C_v = C_v{}^l + C_v{}^e$; $C_v{}^l$ is the lattice contribution to the heat capacity at constant volume; $C_v{}^e$ is the electronic contribution to the heat capacity at constant volume; and C^d is the dilation term. $C_v{}^e$ is given by

$$C_v{}^e = \gamma T, \tag{15.2}$$

where γ is the electronic specific heat constant listed in Table XIII, and T is the absolute temperature. The dilation term is given by

$$C^d = 9\alpha^2 TV/\chi, \tag{15.3}$$

where α is the linear coefficient of thermal expansion listed in Table VI, V is the atomic volume listed in Table VII, and χ is the isothermal compressibility listed in Table V. The difficulty in using Eq. (15.3) to determine the dilation term is that the coefficient of expansion, the atomic volume, and the compressibility must be known for each temperature at which one wishes to calculate C_v, and these quantities, especially the compressibility, are usually known over a small range of temperature. Fortunately this limitation can be overcome. If Eq. (15.3) is rewritten as

$$C^d = 9\alpha^2 TVC_p{}^2/\chi C_p{}^2 \tag{15.4}$$

and letting

$$A = 9\alpha^2 V/\chi C_p{}^2, \tag{15.5}$$

we have

$$C^d = AC_p^2T. \tag{15.6}$$

It has been found experimentally that A is almost constant over a wide range of temperatures. Thus one needs only to calculate A at a given temperature to determine C_v from C_p over a wide range of temperatures. Now rewriting Eq. (15.1) we have

$$C_v = C_p(1 - AC_pT), \tag{15.7}$$

or

$$C_v^l = C_p(1 - - AC_pT)\ C_v^e. \tag{15.8}$$

The values of A (defined by Eq. (15.5)), C_v^l and C_v (as given by Eqs. (15.7) and (15.8), respectively) are listed in Table XIV.

The value of C_v^l rather than the value of C_v should be compared with the Dulong and Petit value of $3R = 5.96$ because C_v also contains the electronic contribution. In general $C_v \simeq C_v^l$ since C_v^e is small, but for a few metals, primarily the group IIIA and VA metals, manganese, nickel, and its cogeners, the rare earths, uranium, and transuranium metals, C_v is significantly larger than C_v^l. The mean value of C_v^l for the elements is 5.80 ± 0.39 cal/g-at/deg if the values of beryllium, boron, graphite, diamond, and plutonium are omitted. This mean value is slightly less than the Dulong and Petit value. The error, ± 0.39, is equivalent to $\pm 6.7\%$ which suggests that C_v^l is reasonably constant for all of the elements, much more so than many of the other so-called "constants" of the elements (see Sections 5 and 22–29). The mean value of C_v is 6.05 ± 0.43 cal/g-at/deg if the values of beryllium, boron, graphite, diamond, and gadolinium are omitted. The error ± 0.43 is equivalent to $\pm 7.1\%$, which is slightly larger than the error for C_v^l.

The values for the heat capacities of gadolinium (C_p, C_v, C_v^l) are larger than one might expect, because of the ferromagnetic–paramagnetic transition at 289°K (16°C). No attempt has been made to subtract the magnetic contribution to these heat capacities.

The variation of the lattice contribution to the heat capacity at constant volume is shown in Fig. 20. In general C_v^l is almost always less than the Dulong–Petit value (shown as a dashed horizontal line in the figure) with the exception of the alkali and a few of the actinide elements. There is also a slight dependence on the location of the element in the Periodic Table. That is, the high values just mentioned for the alkali metals decrease as one proceeds to the group IIA elements, rise slightly at group IVA and then dip again at group VA. As one continues moving to the right the value of C_v^l slowly increases, with some small undulations, to the group VIB elements.

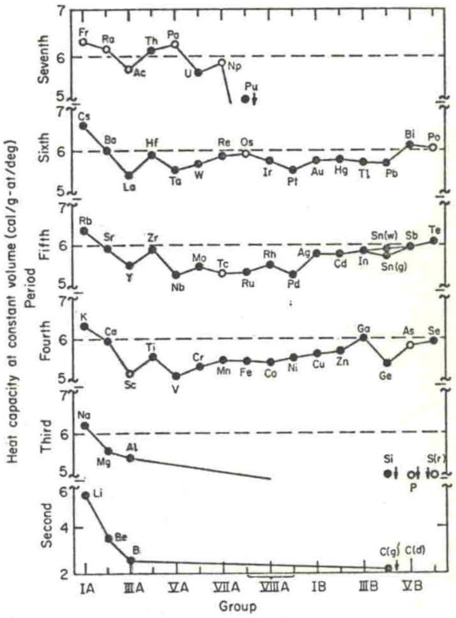

FIG. 20. Heat capacity at constant volume (lattice contribution only) of all of the elements considered in this review with the exception of the rare-earth metals. The horizontal dashed line represents the Dulong and Petit value of $3R = 5.96$. The open points are estimated values.

The heat capacities of the rare earths are shown in Fig. 19b. Except for the values for praseodymium, gadolinium, holmium, and thulium, the heat capacities are very close to the Dulong–Petit value. As noted earlier, the magnetic contribution to the heat capacity accounts for the anomalously high value for gadolinium. The low values for praseodymium, holmium, and thulium can be accounted for by the large electronic contribution which is subtracted from C_v. As mentioned in Section 13, it was thought that perhaps the electronic specific heat constant, γ, is too large for these three metals. If one assumes that $\gamma = 10$ mj/g-at/deg^2 then he obtains C_v^l values of 5.55, 5.72, and 5.65 for praseodymium, holmium, and thulium, respectively, which are much more reasonable. This anomaly in C_v^l for these three metals suggests that their measured electronic specific heat constants are too large, and that a value approximately equal to 10 mj/g–at/deg^2 is more reasonable.

Estimated Data. The data given in parentheses for the dilation term A, and the heat capacities C_v^l and C_v are the estimated values. If one of the quantities needed to calculate A, C_v^l, or C_v was estimated, then A, C_v^l, or C_v is considered to be an estimated value. For the elements white phosphorus, rhombic sulfur, arsenic, antimony, europium, and gadolinium the only estimated quantity was C_v^e. For scandium and osmium the compressibility was the only estimated quantity. For neptunium both C_v^e and the compressibility were estimates. For polonium C_p, C_v^e, and the compressibility were estimated. For white phosphorus both C_v^e and the thermal expansion were estimated. For technetium, actinium, and protactinium, estimated values were used for C_v^e, C_p, the compressibility, and the thermal expansion. For promethium, francium, and radium all quantities were estimates.

VIII. Debye Temperature

There is little need to dwell on the theory and the background of the Debye temperature, since these are usually well treated in the standard textbooks concerned with solids. More detailed discussions are found in the review papers by Blackman,[93] de Launay,[94] Keesom and Pearlman,[95] Herbstein,[96] and Mitra.[97]

The Debye temperature can be obtained from specific heat measurements, melting points (Lindemann equation), elastic constants, X-ray and neutron diffraction intensity data, electrical resistivities, and thermal-expansion data. Other techniques, which are not as generally applicable as those mentioned above, are of minor importance here. For those who are interested, these other techniques are summarized in some of the above reviews.[93,96,97]

Since the Debye temperatures vary with temperature, one must be careful when comparing the Debye temperature obtained by one method with a Debye temperature obtained by another method. That is, the Debye temperatures should only be compared when both were measured at the same or approximately the same temperature. This is especially important for low-temperature measurements, i.e., temperatures below 50° to 100°K (−223° to −173°C). Usually, the Debye temperatures do not show very large temperature variations above this temperature range, although exceptions may be encountered, particularly for those materials which have very large Debye temperatures, i.e., >800°K.

The Debye temperatures as determined by the methods mentioned above are discussed in Sections 16–21 and summarized in Tables XV through XVIII.

16. Debye Temperature from Specific Heat Data

The Debye temperature as determined from specific heat measurements is designated as θ^S, and any subscript which may be given indicates the particular temperature (absolute) at which θ^S was evaluated; e.g., θ_0^S indicates the Debye temperature was evaluated from specific heat data at 0°K (−273°C). The Debye theory of the lattice specific heat gives the following expression for the heat capacity of a solid:

$$C_V^l = 3R[J(y) - yJ'(y)], \tag{16.1}$$

where R is the gas constant, $y = \theta^S/T$ and $J(y)$ is given by

$$J(y) = \frac{3}{y^3}\int_0^y \frac{y^3\,dy}{e^y - 1}. \tag{16.2}$$

The integral in Eq. (16.2) has been solved, and tables of C_v^l versus θ^S/T may be found in a number of sources.[57,94,98,99] The tables given by de Launay[94] and Zemansky[98] are quite abbreviated compared with those of Simon,[99] and Lewis *et al.* (Appendix 5).[57] At low temperatures when $\theta^S/T \ll 1$, Eq. (16.1) can be written as

$$C_v^l = 464.4(T/\theta_0^S)^3, \tag{16.3}$$

which is seen to be identical to the last term in Eq. (13.1). It is appropriate to use the subscript 0 with θ^S in Eq. (16.3) since the Debye temperature and electronic specific heat constant, γ, are evaluated from a plot of C_v/T versus T^2, where γ is the intercept at $T = 0$°K and $464.4/(\theta_0^S)^3$ is the slope of the straight line.

Debye Temperature at 0°K. The Debye temperatures θ_0^S are listed in Table XV. The value of θ_0^S varies from a minimum value of 40°K for

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TABLE XV. DEBYE TEMPERATURES OBTAINED FROM SPECIFIC HEAT DATA (θ^{S}) AND FROM THE LINDEMANN EQUATION (θ^{M})^{a,b,c}

TABLE XV. DEBYE TEMPERATURES OBTAINED FROM SPECIFIC HEAT DATA (θ^{S}) AND FROM THE LINDEMANN EQUATION (θ^{M})^{a,b,c}—*Continued*

Element	$\theta_0^{S\ a}$ (°K)	Ref.	$\theta_{298}^{S\ b}$ (°K)	Ref.	$\theta^{M\ c}$ (°K)
3 Li	352 ±17	1, 2	448	—	476
4 Be	1160	3	1031	—	1062
5 B	1315^{d}	4	1362	—	1286
6 C(g)	402 ±11	5, 6	1550^{e}	—	1471
6 C(d)	2240 ±5	7	1874	—	—
11 Na	157 ±1	1, 8–11	155 ±5	96, 97	193
12 Mg	396 ±54	12–14	330	—	354
13 Al	423 ±5	15, 16	390	—	378
14 Si	647 ±11	17, 18	692	—	468
15 P(w)	(193)^{f}	—	(576)^{f}	—	184
15 P(r)	(325)^{f}	—	(800)^{f}	—	310
16 S(r)	250^{g}	19	527	19	202
16 S(m)	(200)^{f}	—	—	—	191
19 K	89.4 ±0.5	1, 11	100	96, 97	114
20 Ca	234 ±5	20, 21	230	96, 97	246
21 Sc	470 ±80	22	(476)^{f}	—	356
22 Ti	426 ±5^{e}	23–25	380	97	385
23 V	326 ±54	23, 26–28	390	97	446
24 Cr	598 ±32^{e}	23, 29, 30	424	—	460
25 Mn	418 ±32	23, 31, 32	363	—	374
26 Fe	457 ±12	33–35	373	—	410
27 Co	452 ±17	35, 36, 37	386	—	402
28 Ni	427 ±14	29, 38	345	—	401
29 Cu	342 ±2^{e}	21, 25, 39–43	310	—	333
30 Zn	316 ±20	44–48	237 ±3	96, 97	216
31 Ga	317	46, 49	240	97	127
32 Ge	378 ±22	18, 50, 51	403	—	237
33 As	(236)^{f}	—	275	98	225
34 Se	151.7 ±0.4	52	—	—	136
35 Rb	54 ±4	53, 54	59	99	69.1
38 Sr	147 ±1	20	148	99	158
39 Y	268 ±32	22, 55	214	100	229
40 Zr	289 ±24	12, 23, 25	250	97	277
41 Nb	241 ±13	55–57	260	55	340
42 Mo	459 ±11	23, 55, 58–60	377	—	360
43 Tc	(351)^{f}	—	(422)^{f}	—	335
44 Ru	600	23	415	—	345
45 Rh	480 ±32	23, 61, 62	350	—	319
46 Pd	283 ±16	63–65	275	97	277
47 Ag	228 ±3	39, 43, 65–68	221	—	216
48 Cd	252 ±48^{h}	14, 69	221	—	135
49 In	108.8 ±0.3	70, 71	129	97	107
50 Sn(g)	236 ±24	50, 72	254	—	330
50 Sn(w)	196 ±9	71, 73–75	170	97	356
51 Sb	(150)^{f}	—	200	97	143
52 Te	141 ±12	52, 76	—	—	121
55 Cs	40 ±5	53, 54	43	99	50.8
56 Ba	110.5 ±1.8	20	116	99	111
57 La	142 ±3	22	135 ±5	101	144
58 Ce(γ)	(146)^{f}	—	138	102	140
59 Pr	85 ±1	77	138	103	147
60 Nd	(159)^{f}	—	148 ±8	*i*	152
61 Pm	(158)^{f}	—	—	—	(151)^{f}
62 Sm	116	77	148 ±4	101, 102	153
63 Eu	(127)^{f}	—	—	—	121
64 Gd	(170)^{f}	—	155 ±3	101, 104	162
65 Tb	150	78	158	101	165
66 Dy	172 ±35	77, 79	158	101	167
67 Ho	114 ±7	77	161	101	169
68 Er	134 ±10	77	163	101	171
69 Tm	127 ±1	77	167	101	173
70 Yb	118	80	—	—	120
71 Lu	210	81	166	100, 101	176
72 Hf	256 ±5	23, 25	213	99	240
73 Ta	247 ±13	23, 26, 55, 82, 83	225	97	266
74 W	388 ±17^{e}	23, 59, 84	312 ±3	96, 97	291
75 Re	429 ±22	23, 85	275	99	287
76 Os	500	23	400	105	283
77 Ir	425 ±5	23, 61	228	—	255
78 Pt	234 ±1	62, 86	225 ±5	96, 97	215
79 Au	165 ±1	39, 43, 48, 62	178 ±8	96, 97	166
80 Hg	~75	76	92 ±8	96, 97	62.0
81 Tl	88 ±1	87, 88	96	97	90.1
82 Pb	102 ±5	89, 90	87 ±1	96, 97	89.5
83 Bi	119 ±2	91–93	116 ±5	96, 97	80.6
84 Po	(81)^{f}	—	—	—	77.1
87 Fr	(39)^{f}	—	—	—	(37.5)^{f}
88 Ra	(89)^{f}	—	—	—	(84.9)^{f}
89 Ac	(124)^{f}	—	—	—	118
90 Th	170	94	100	97	151
91 Pa	(159)^{f}	—	(262)^{f}	—	(152)^{f}
92 U	200	94	300	—	143
93 Np	(121)^{f}	—	(163)^{f}	—	115
94 Pu	171	95	176	95	118

[a] $\theta_0{}^S$ refers to the Debye temperature at 0°K or to a temperature which is as close to 0°K as possible. If the temperature is different from 0°K, it is noted in a footnote.

[b] $\theta_{298}{}^S$ refers to the Debye temperature at 298°K as calculated from the specific heat at constant volume (Table XIV), unless otherwise noted. The values taken from the references cited are generally for Debye temperatures determined at $\sim\frac{1}{2}\theta^S$.

[c] θ^M refers to the Debye temperature calculated from the Lindemann equation. using the constant 138.5; see text for further discussion.

[d] Calculated by Kaufman and Clougherty[4] from the data of Johnston *et al.*[106] This value applies to a temperature of 13°K.

[e] See text for further discussion.

[f] Estimated value; see text for further discussion.

[g] This value applies to 40°K. From an extrapolation of high-temperature data to 0°K a value of 105°K is obtained for $\theta_0{}^S$.

[h] Rajdev and Whitmore[107] re-evaluated Martin's data[14] and obtained a value of $\theta_0{}^S = 220$ which lies within the error listed above.

[i] Mean value of Debye temperature calculated from C_v (Table XIV) and Debye temperatures given by Murao[103] and Arajs and Colvin.[102]

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cesium to a maximum value of 2240°K for diamond. Most of the values for θ_0^S, however, are less than 600°K.

The variation of θ_0^S for the elements of the fourth, fifth, and sixth periods of the Periodic Table is shown in Fig. 21. The usual behavior as noted for other properties is seen in this figure, although there are some

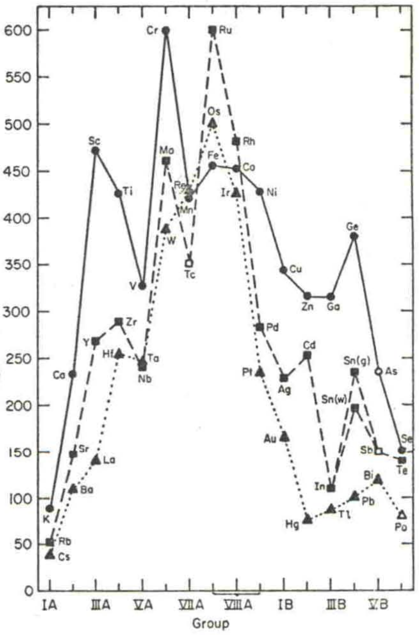
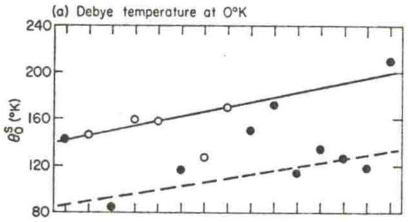


FIG. 21. Debye temperature at 0°K, as determined from specific heat data of the elements of the fourth, fifth, and sixth periods of the Periodic Table. Open points are estimated values.

significant differences. The similarity is shown by the low values at the beginning and end of each period; and by the major and the minor maxima and the minimum, near group VIIA, group IVB, and group IIIB, respectively. The major difference is that for most properties the values for the elements of the sixth period are larger than those of the fifth, which are larger than those of the fourth. For the Debye temperatures (Fig. 21) the reverse is generally observed. Other differences are that a maximum occurs near group IVA, and that the broad maximum near group VIIA, seen for other properties, splits up into two maxima and a minimum.

The $\theta_0{}^S$ values for the rare earths are shown in Fig. 22a. The data seem to lie on two different curves. The upper curve connects the experimental values obtained for lanthanum, terbium, dysprosium, and lutetium and the estimated values of cerium, neodymium, promethium, and gadolinium. The values for europium and ytterbium lie below this curve because they are divalent.[13] Unfortunately these two values (Eu and Yb) lie near the lower curve, and it should be pointed out that they are not related to it. The lower curve connects the values of praseodymium, samarium, holmium, erbium, and thulium. As noted earlier (Sections 13 and 15), the electronic contribution to the specific heat is anomalously high and is probably incorrect for praseodymium, holmium, and thulium. Because of this it is quite possible that the lattice contribution is also incorrect. The lattice and electronic contributions to the specific heat of these three metals and also samarium and erbium is difficult to evaluate, especially at low temperatures, because of the magnetic and nuclear contributions. Thus it appears that $\theta_0{}^S$ is also too low for samarium and erbium.

(a) Debye temperature at 0°K



(b) Debye temperature at 298°K

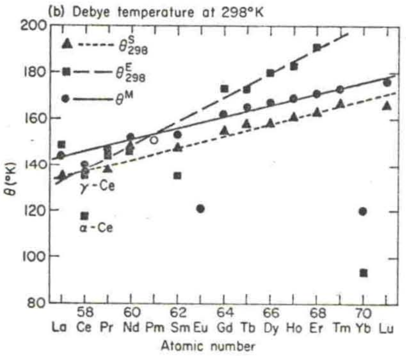


FIG. 22. (a) Debye temperature at 0°K, as determined from specific heat data of the rare-earth metals. (b) Debye temperature at 298°K of the rare-earth metals, as determined from the specific heat, $\theta_{298}{}^S$, from elastic constants, $\theta_{298}{}^E$, and from the Lindemann Equation, θ^M. Open points are estimated values.

Titanium. The value of $\theta_0{}^S$ given by Estermann, *et al.*[100] for titanium (280°) is not included in the average (426 ±5°) since it is significantly smaller than the other values given in the literature.

Chromium. Since the value of $\theta_0{}^S$ given by Estermann *et al.*[100] for chromium (418°) is significantly smaller than the other literature values (598 ±32°), it is not included in the average.

Copper. The value of $\theta_0{}^S$ was found in general to decrease with increasing total number of impurities in copper, if the purity was less than 99.99%. Therefore, only $\theta_0{}^S$ values for copper specimens which had a purity of 99.99% or greater are considered here. The value given by Franck *et al.*[101] (327°) is not considered in the average, since it is smaller than the seven other values given in literature (343° ±2°K).

Tungsten. The values given by Daunt and co-workers[83,84] for $\theta_0{}^S$ (250° and 169°) are much smaller than those given by others (388° ±17°) and therefore are not included in the average.

Estimated Data. The estimated $\theta_0{}^S$ values were calculated using the Lindemann equation and the constant 145.1 (the choice of this constant and further details are described in Section 17). The $\theta_0{}^S$ values were estimated for white and red phosphorus, monoclinic sulfur, arsenic, technetium, antimony, γ-cerium, neodymium, promethium, europium, gadolinium, polonium, francium, radium, actinium, protactinium, and neptunium.

Debye Temperature at 298°K. The Debye temperatures at 298°K, $\theta_{298}{}^S$ are also given in Table XV. They were evaluated from $C_v{}^l$ (Table XIV) by using the tables of $C_v{}^l$ versus θ^S/T given by Lewis *et al.*[57] For a few elements the values of $\theta_{298}{}^S$ obtained in this manner were quite unreasonable, primarily because $C_v{}^l$ was too large. These $\theta_{298}{}^S$ values were discarded and replaced by more reasonable values of $\theta_T{}^S$, where T refers

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[100] I. Estermann, S. A. Friedberg, and J. E. Goldman, *Phys. Rev.* **87,** 582 (1952).

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to the so-called high-temperature θ^S values found in the literature. The $\theta_{298}{}^S$ values obtained from the literature are identified by citations in the reference column for $\theta_{298}{}^S$.

Since the values of $\theta_{298}{}^S$ are usually large when $\theta_0{}^S$ values are large, and small when $\theta_0{}^S$ values are small, no plot of $\theta_{298}{}^S$ versus the group (similar to Fig. 21) is included here. The values of $\theta_{298}{}^S$ vary from a minimum of 43°K for cesium to a maximum of 1874°K for diamond.

A plot of $\theta_{298}{}^S$ for the rare earths (triangular points) is shown in Fig. 22b. It is seen that there is a small but smooth increase in $\theta_{298}{}^S$ with increasing atomic number, which is approximately parallel to the Lindermann value, θ^M. This smooth increase contrasts with the scattered data shown in Fig. 22a for $\theta_0{}^S$.

Graphite. Examination of $\theta_0{}^S$ and $\theta_{298}{}^S$ for graphite shows a very large difference ($\theta_0{}^S = 402$°K and $\theta_{298}{}^S = 1550$°K). DeSorbo[102] has plotted θ^S versus temperature, which shows that θ^S increases very rapidly with temperature from $\theta_{10}{}^S = 500$°K at 10°K to $\theta_{75}{}^S = 900$°K at about 75°K. The values given in Table XV and the curve given by DeSorbo are in reasonable agreement.

Estimated Data. The estimated values of $\theta_{298}{}^S$ for white and red phosphorus, scandium, technetium, protactinium, and neptunium are based on the estimated $C_v{}^l$ values listed in Table XIV. For those elements for which no values are listed (monoclinic sulfur, selenium, tellurium, promethium, europium, ytterbium, polonium, francium, radium, and actinium), reasonable estimates for $\theta_{298}{}^S$ may be obtained from the Lindemann equation, which is also listed in Table XV.

17. LINDEMANN EQUATION AND THE DEBYE TEMPERATURE

In 1910 Lindemann[103] showed that the Debye temperature θ^M is related to the melting point T_m, atomic mass M, and atomic volume V, of a substance, according to the following expression:

$$\theta^M = K(T_m/M)^{\frac{1}{2}}(1/V)^{\frac{1}{3}}. \qquad (17.1)$$

In Eq. (17.1) K is a constant approximately equal to 130. This expression is commonly called the Lindemann equation or the Lindemann law. Several values for K have appeared in the literature; Blackman[93] gives 115, Zemansky[104] gives 137, and Kaufman[105] gives 135.2. The value for K is determined by substituting experimental values of θ in Eq. (17.1) for as many substances as possible. The value of K depends on the number of Debye temperatures available, since T_m, M, and V are known for almost all the elements, and the value depends also on which Debye temperature one chooses, i.e., $\theta_0{}^S$, $\theta_{298}{}^S$, or some other θ. Because this information was not given for the above literature values, K was evaluated from both $\theta_0{}^S$ and $\theta_{298}{}^S$. Substituting $\theta_0{}^S$ into Eq. (17.1), K was found to be 145.1 ± 31.6 for 59 elements. The $\theta_0{}^S$ values for graphite, gallium, germanium, ruthenium, cadmium, osmium, and iridium were not used to evaluate K. Substituting $\theta_{298}{}^S$ into Eq. (17.1), K was found to be 138.5 ± 25.6 for 64 elements. The $\theta_{298}{}^S$ values for white and red phosphorus, rhombic sulfur, gallium, germanium, and cadmium were not used to evaluate K.

The standard deviations indicate that there is really not much difference between the two values of K obtained here. It is also seen that the range of the standard deviation for either K value includes the three literature values cited. The K value of 138.5 was used to calculate the θ^M values listed in Table XV, primarily because its standard deviation was less than that of the K value of 145.1. The K value of 145.1 was, however, used to estimate the $\theta_0{}^S$ values for those elements for which no experimental data existed.

Because of the relationship between $\theta_0{}^S$ and θ^M, and since $\theta_0{}^S$ is shown in Fig. 21, no plot of θ^M is shown for the elements of the fourth, fifth, and sixth periods of the Periodic Table. A plot, however, of θ^M versus the atomic number for the rare-earth elements is shown in Fig. 22b. The θ^M value increases smoothly with increasing atomic number, and with a slope similar to $\theta_{298}{}^S$. The low values for europium and ytterbium follow directly from the low melting points and the large atomic volumes of these two elements as compared with those of the other rare earths. Again this is a manifestation of the divalent character of these two elements.[13]

Estimated Data. The values for promethium and francium are shown as estimated data since their melting points and atomic volumes were both estimated. The values for radium and protactinium are shown as estimated data because the atomic volume of radium and the melting point of protactinium were estimated.

18. DEBYE TEMPERATURE FROM ELASTIC CONSTANTS

Debye temperatures can be calculated from the single-crystal elastic constants c_{ij} and from the polycrystalline elastic constants c_t and c_l. The details for determining Debye temperatures are given in the reviews of Blackman,[93] de Launay,[94] Herbstein,[96] and Mitra,[97] and are not discussed here. The Debye temperatures determined from elastic constants at 0°K, $\theta_0{}^E$, and at 298°K, $\theta_{298}{}^E$, are listed in Table XVI. For convenience in making

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TABLE XVI. DEBYE TEMPERATURES OBTAINED FROM SPECIFIC HEAT DATA (θ^S) AND FROM ELASTIC CONSTANTS (θ^E)[a,b,c]

Element	θ_0^S [a] (°K)	θ_0^E [b] (°K)	Ref.	θ_{298}^E [c] (°K)	Ref.
3 Li	352 ±17	336.3 ±2.1	1	350 ±9	6, 10, 18, 19
4 Be	1160	1462	2	1367	19
6 C(d)	2240 ±5	2240 ±5	3	2010 ±166[d]	6, 10
11 Na	—	—	—	164 ±19	6, 18–20
12 Mg	396 ±54	387 ±1	1, 4	363	19
13 Al	423 ±5	428	1, 5	403 ±8[d]	5, 6, 10, 18, 19
14 Si	647 ±11	649	6	576 ±71	6, 19
19 K	—	—	—	77	18
20 Ca	—	—	—	208	19
22 Ti	—	—	—	373	19
23 V	326 ±54	399	7	394 ±18	6, 7, 19
24 Cr	—	—	—	454 ±1	6, 19
25 Mn	—	—	—	461	19
26 Fe	457 ±12	477	8	466 ±2[d]	6, 19
27 Co	—	—	—	446	19
28 Ni	427 ±14	476.2 ±0.1	1	443 ±17	6, 19
29 Cu	342 ±2	345	1, 9	332 ±6[d]	6, 10, 18, 19
30 Zn	316 ±20	324 ±8	1, 10–12	231[d]	20
31 Ga	—	—	—	89	19
32 Ge	378 ±22	375	10	323 ±48	6, 19
37 Rb	—	—	—	55	19
38 Sr	—	—	—	133	19
39 Y	—	—	—	250	21
40 Zr	—	—	—	231	19
41 Nb	—	—	—	328	19
42 Mo	459 ±11	474	13	454 ±11	6, 19
44 Ru	—	—	—	512	19
45 Rh	—	—	—	478	19
46 Pd	283 ±16	275 ±8	14	264	6, 19
47 Ag	228 ±3	227	1, 9	213 ±2[d]	6 10, 18, 19
48 Cd	252 ±48	212 ±1	15	160 ±8	10, 20
49 In	108.8 ±0.3	111.3 ±1.1	16	85	19
50 Sn(w)	236 ±24	201.6 ±2.6	17	184 ±1	10, 19
51 Sb	—	—	—	187	19
55 Cs	—	—	—	40	19
56 Ba	—	—	—	97	19
57 La	—	—	—	149	21
58 Ce(α)	—	—	—	118[e]	22
58 Ce(γ)	—	—	—	135	21
59 Pr	—	—	—	144	21
60 Nd	—	—	—	147	21
62 Sm	—	—	—	135	21
64 Gd	—	—	—	173	21
65 Tb	—	—	—	173	21

TABLE XVI. DEBYE TEMPERATURES OBTAINED FROM SPECIFIC HEAT DATA (θ^S) AND FROM ELASTIC CONSTANTS (θ^E)[a,b,c]—*Continued*

Element	θ_0^S [a] (°K)	θ_0^E [b] (°K)	Ref.	θ_{298}^E [c] (°K)	Ref.
66 Dy	—	—	—	180	21
67 Ho	—	—	—	183	21
68 Er	—	—	—	191	21
70 Yb	—	—	—	94	21
72 Hf	—	—	—	181	19
73 Ta	247 ±13	262	13	257	19
74 W	388 ±17	384	13	370 ±4[d]	6, 19
75 Re	—	—	—	421	19
76 Os	—	—	—	431	19
77 Ir	—	—	—	414	19
78 Pt	—	—	—	229 ±6	6, 10, 19
79 Au	165 ±1	162	1, 9	160 ±4	6, 10, 18–20
80 Hg	—	—	—	167	19
81 Tl	—	—	—	55	19
82 Pb	102 ±5	105	6	81 ±9	6, 10, 18, 19
83 Bi	—	—	—	113 ±2	10, 19
90 Th	170	164.2	1	158 ±1	6
94 Pu	—	—	—	178 ±1	23

[a] θ_0^S is the Debye temperature at 0°K as determined from specific heat data; values are taken from Table XV.

[b] θ_0^E is the Debye temperature at 0°K as determined from elastic constants.

[c] θ_{298}^E is the Debye temperature at 298°K as determined from elastic constants.

[d] See text for further discussion.

[e] Extrapolated from high pressure data of Voronov *et al.*[22] to zero pressure.

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comparisons the θ_0^S value for each corresponding θ_0^E is listed in the second column of Table XVI. These θ_0^S values were taken from Table XV. Examination of θ_0^S and θ_0^E shows that $\theta_0^S = \theta_0^E$ within the experimental error given or within ±5%, whichever is greater, for all of the elements except beryllium, vanadium, nickel, and white tin. The reason for the discrepancies for vanadium and nickel[105a] is not understood, but the discrepancies for beryllium and white tin may be due to an anisotropic contribution to the specific heat[106] (which has a T^5 dependence) which had not been taken into account when the low-temperature data were evaluated. Because of the sparsity of data, no plot of θ_0^E values is given here; but such a plot would be expected to be similar to Fig. 21 since $\theta_0^E \simeq \theta_0^S$.

There are many more data available for θ_{298}^E than for θ_0^E. The corresponding θ_{298}^S values are not included in Table XVI, but a comparison of θ_{298}^E to θ_{298}^S is found in Table XVIII along with several other comparisons of Debye temperatures. Close examination of the data for $\theta_{298}^E/\theta_{298}^S$ shows that only about 42% of the experimental values of θ_{298}^E lie within 10% of θ_{298}^S and 70% lie within 20% of θ_{298}^S. This suggests that $\theta_{298}^S = \theta_{298}^E$ is a rather poor approximation, as compared with $\theta_0^S = \theta_0^E$. Further analysis reveals that 27 of the 60 θ_{298}^E values are smaller than the corresponding θ_{298}^S values. This indicates that there is no systematic discrepancy between θ_{298}^S and θ_{298}^E; e.g., θ_{298}^E is generally not smaller than θ_{298}^S.

The Debye temperatures obtained from elastic constants, θ_{298}^E, for the rare earths are shown in Fig. 22b. The agreement of θ_{298}^E with θ_{298}^S is reasonable for the rare earths lanthanum through samarium, and also for terbium. The agreement becomes poorer as the atomic number increases.

Diamond, Aluminum, Iron, Copper, Silver, and Tungsten. The Debye temperatures, θ_{298}^E, given by Post[107] for diamond, aluminum, iron, copper, silver, and tungsten are not included in the average values listed in Table XVI because Post's values are significantly smaller than the other values given in the literature.

Zinc. The Debye temperature given by Masing[108] for zinc (303°K) is significantly larger than Post's value (231°K),[107] but since Post's value is in much better agreement with θ_{298}^S than Masing's value, the lower value was listed in Table XVI.

19. Debye Temperature from Electrical Resistivity

The Debye temperature may be calculated from the temperature dependence of the electrical resistivity.[109] The values obtained in this manner are given in Table XVII under the heading θ_m^R. The subscript m signifies that θ^R is an average value which fits the experimental data over a wide range of temperatures. In general these ranges are as large as ~20°K to 500° or 600°K, and thus the values should correspond closely to those obtained by other techniques at 298°K, e.g., θ_{298}^S and θ_{298}^E.

In general the θ_m^R values obtained from different sources agree with one another within about ±25°K, which indicates that θ_m^R values are probably not more accurate than that. Because of the lack of sufficient data, no plots were made for these Debye temperatures. The θ_m^R values range from a minimum of 37°K for mercury to a maximum of 495°K for chromium. A comparison of θ_m^R with θ_{298}^S is given in Table XVIII. Close examination reveals that only about one-third (34%) of the θ_m^R values lie within ±10% of the corresponding θ_{298}^S values and that about two-thirds (68%) lie within ±25% of θ_{298}^S. Hence the agreement between θ_m^R and θ_{298}^S is poorer than it is between θ_{298}^E and θ_{298}^S (Section 18). Furthermore, there is a tendency for θ_m^R to be larger than θ_{298}^S, i.e., 71% of the θ_m^R values are larger than the corresponding θ_{298}^S values. Thus we find that $\theta_m^R > \theta_{298}^S$ is probably a better approximation than $\theta_m^R = \theta_{298}^S$.

20. Debye Temperature from Thermal Expansion

The derivation of the Debye temperature from thermal expansion measurements is discussed by Blackman[93] and therefore no details will be given here. The values for the Debye temperatures as determined from thermal expansion (dilatometric) data, θ_m^D, are listed in Table XVII. The subscript m has the same significance as mentioned above for θ_m^R

[105a] *Note added in proof*: J. A. Morrison and L. S. Salter (*Phys. Letters* **9,** 110 (1964)) have shown that if higher order terms (such as T^5, T^7, etc.) are included in Eq. (13.1), then the resulting θ_0^S value for vanadium is in agreement with the θ_0^E value.

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Table XVII. Debye Temperatures Obtained from Electrical Resistivity[a] (θ_m^R), Thermal Expansion[b] (θ_m^D), and X-Ray Intensities[c] Data (θ^I)

Element	$\theta_m^{R\,a}$ (°K)	Ref.	$\theta_m^{D\,b}$ (°K)	Ref.	$\theta_{298}^{I\,c}$ (°K)	Ref.
3 Li	356 ±26	1–3	—	—	306	13
6 C(d)	—	—	1860	9	1730 ±220[d]	14[d]
11 Na	205 ±28	1–3	—	—	114	15
12 Mg	357	1	—	—	307	16
13 Al	422 ±17	1, 2	390 ±11	10, 11	383	13
14 Si	—	—	—	—	555 ±39	17, 18
19 K	148 ±34	1, 3	—	—	—	—
21 Sc	275	4	—	—	—	—
22 Ti	342	5	270	12	—	—
23 V	—	—	—	—	337 ±25[e]	19
24 Cr	495	5	—	—	566	20
26 Fe	494 ±25	5, 6	418 ±3	10, 11	404 ±17	20, 21
27 Co	401	5	—	—	—	—
28 Ni	274	5	405 ±5	10, 11	341	20
29 Cu	336 ±19	1–3	320 ±5	9–11	308 ±4	13, 22
32 Ge	—	—	—	—	283 ±5	18
33 As	210	1	—	—	—	—
37 Rb	75 ±10	1, 3	—	—	—	—
38 Sr	171	1	—	—	—	—
39 Y	201 ±14	7, 8	—	—	—	—
40 Zr	281	5	—	—	—	—
42 Mo	—	—	388	10	389	20
44 Ru	426	5	—	—	341	16
45 Rh	394 ±25	2, 5	—	—	—	—
46 Pd	270	5	300	10	—	—
47 Ag	219 ±20	1–3, 9	209 ±12	10–12	211	23
48 Cd	158	1	—	—	—	—
49 In	198	1	—	—	—	—
50 Sn(w)	210	5	—	—	—	—
51 Sb	241	5	—	—	—	—
55 Cs	45	3	—	—	—	—
56 Ba	133	1	—	—	—	—
73 Ta	228	5	252	10	—	—
74 W	359 ±26	2, 5	310	10	—	—
75 Re	310	5	—	—	—	—
77 Ir	316	5	—	—	—	—
78 Pt	235 ±5	5, 6	233 ±3	9, 10	151 ±26	24
79 Au	189 ±14	1–3	183 ±7	9–11	—	—
80 Hg	37[f]	1	—	—	—	—
81 Tl	140	1	—	—	—	—
82 Pb	89 ±3	2, 5	88	10	67.0	13
83 Bi	62	5	—	—	—	—
90 Th	168	5	—	—	—	—

[a] θ_m^R is the Debye temperature determined from electrical resistivity data. These Debye temperatures usually correspond to an average value for a wide range of temperatures.

[b] θ_m^D is the Debye temperature determined from thermal expansion data. These Debye temperatures usually correspond to an average value for a wide range of temperatures.

[c] θ_{298}^I is the Debye temperature at 298°K as determined from X-ray intensity data.

[d] This value was calculated by Herbstein[14] from the data given by Carpenter[25] and Post.[26]

[e] Calculated from neutron diffraction data.

[f] This value corresponds to that for solid mercury.

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TABLE XVIII. COMPARISON OF DEBYE TEMPERATURES

Element	$\theta_{298}^{E}/\theta_{298}^{S}$	$\theta_{m}^{R}/\theta_{298}^{S}$	$\theta_{m}^{D}/\theta_{298}^{S}$	$\theta_{298}^{I}/\theta_{298}^{S}$
3 Li	0.781	0.795	—	0.683
4 Be	1.326	—	—	—
6 C(d)	1.073	—	0.992	0.923
11 Na	1.058	1.323	—	0.736
12 Mg	1.100	1.082	—	0.930
13 Al	1.033	1.082	1.000	0.982
14 Si	0.832	—	—	0.802
19 K	0.770	1.480	—	—
20 Ca	0.904	—	—	—
21 Sc	—	0.578	—	—
22 Ti	0.982	0.900	0.711	—
23 V	1.010	—	—	0.864
24 Cr	1.071	1.167	—	1.355
25 Mn	1.270	—	—	—
26 Fe	1.249	1.324	1.121	1.083
27 Co	1.155	1.039	—	—
28 Ni	1.284	0.794	1.174	0.988
29 Cu	1.071	1.084	1.032	0.994
31 Ga	0.371	—	—	—
32 Ge	0.802	—	—	0.702
33 As	—	0.764	—	—
37 Rb	0.932	1.271	—	—
38 Sr	0.899	1.155	—	—
39 Y	1.168	0.939	—	—
40 Zr	0.924	1.124	—	—
41 Nb	1.262	—	—	—
42 Mo	1.204	—	1.029	1.032
44 Ru	1.234	1.027	—	0.822
45 Rh	1.366	1.126	—	—
46 Pd	0.960	0.982	1.091	—
47 Ag	0.964	0.991	0.946	0.955
48 Cd	0.724	0.715	—	—
49 In	0.659	1.535	—	—
50 Sn(w)	1.082	1.235	—	—
51 Sb	0.935	1.205	—	—
55 Cs	0.930	1.047	—	—
56 Ba	0.836	1.147	—	—
57 La	1.104	—	—	—
58 Ce(γ)	0.978	—	—	—
59 Pr	1.043	—	—	—
60 Nd	0.993	—	—	—
62 Sm	0.912	—	—	—
64 Gd	1.116	—	—	—
65 Tb	1.095	—	—	—
66 Dy	1.139	—	—	—
67 Ho	1.137	—	—	—
68 Er	1.172	—	—	—
72 Hf	0.850	—	—	—
73 Ta	1.142	1.013	1.200	—
74 W	1.186	1.151	0.994	—
75 Re	1.531	1.127	—	—
76 Os	1.078	—	—	—
77 Ir	1.816	1.386	—	—
78 Pt	1.018	1.044	1.036	0.671
79 Au	0.899	1.062	1.028	—
80 Hg	1.815	0.402	—	—
81 Tl	0.573	1.458	—	—
82 Pb	0.931	1.023	1.011	0.770
83 Bi	0.974	0.535	—	—
90 Th	1.580	1.680	—	—
94 Pu	1.011	—	—	—

TABLE XVIII. COMPARISON OF DEBYE TEMPERATURES—*Continued*

(Section 19). In general, the temperatures range between ~20°K and ~400°K, and thus the θ_m^D values correspond more closely to θ_{298}^S than to θ_0^S.

Examination of the data given in Table XVII indicates that the values obtained from several sources are in very good agreement, usually within ±10°K. The θ_m^D values range from a minimum of 88°K for lead to a maximum of 1860°K for diamond. A comparison of θ_m^D and θ_{298}^S values is given in Table XVIII. These data show that two-thirds of the θ_m^D values lie within ±10% of the corresponding θ_{298}^S values, and that four-fifths of them lie within ±20%. This represents the best agreement between Debye temperatures measured by different techniques, except for the θ_0^S and θ_0^E values. Further examination reveals that θ_m^D is larger than θ_{298}^S for two-thirds of the values listed here. From these observations one would conclude that, in general, θ_m^D is slightly larger than θ_{298}^S.

21. DEBYE TEMPERATURE FROM X-RAY INTENSITY DATA

The determination of the Debye temperature from X-ray intensity data is described quite thoroughly by Herbstein[96] and Ibers *et al.*[110] For

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[110] J. A. Ibers, D. H. Templeton, B. K. Vainshtein, G. E. Bacon, and K. Lonsdale, *in* "International Tables for X-Ray Crystallography, III, Physical and Chemical Tables," p. 237. Kynoch, Birmingham, England, 1962.

this reason no further discussion is warranted here. The symbol $\theta_{298}{}^{I}$ is used herein to represent the Debye temperature determined from X-ray or neutron diffraction intensity data. The subscript refers to the temperature at which the experimental data were obtained. It should be noted that the experimentally measured θ^{Ie} value is not directly comparable with θ^{S}, because these two quantities are defined differently.[96,111] Zener and Bilinsky[111] showed that the ratio of θ^{Ie}/θ^{S} can be expressed as a function of Poisson's ratio; thus, from the known Poisson's ratio (Table III) of the material whose θ^{Ie} has been experimentally determined, one can calculate the θ^{I} value which should be compared with θ^{S}. All of the values given in Tables XVII and XVIII are θ^{I} values; that is, the experimental values θ^{Ie} have been converted to θ^{I} by the method of Zener and Bilinsky.

The $\theta_{298}{}^{I}$ values for 17 elements are listed in Table XVII and are compared with $\theta_{298}{}^{S}$ in Table XVIII. It is seen that the $\theta_{298}{}^{I}$ values range from a minimum of 67°K for lead to a maximum of 1730°K for diamond. Examination of the ratio of $\theta_{298}{}^{I}/\theta_{298}{}^{S}$ in Table XVIII indicates that only 47% of the $\theta_{298}{}^{I}$ values lie within ±10% of the corresponding $\theta_{298}{}^{S}$, and that about 70% lie within ±25%. Thus the agreement between $\theta_{298}{}^{I}$ and $\theta_{298}{}^{S}$ is poor. Furthermore, $\theta_{298}{}^{I}$ is less than $\theta_{298}{}^{S}$ for about 82% of the elements. Since, as noted earlier, $\theta_{298}{}^{E} \simeq \theta_{298}{}^{S}$ (i.e., approximately equal numbers of values of $\theta_{298}{}^{E}$ are larger and smaller than $\theta_{298}{}^{S}$) and since $\theta_{298}{}^{I} < \theta_{298}{}^{S}$, it is concluded that $\theta_{298}{}^{I}$ is generally less than $\theta_{298}{}^{E}$. This is in agreement with the observations of Blackman[93] and Herbstein.[96]

IX. Some Interrelationships and Derived Properties

22. RATIO OF YOUNG'S MODULUS TO THE SHEAR MODULUS

The ratio of Young's modulus to the shear modulus, Y/μ, is essentially a constant for all materials. This is quite easily seen from Eq. (II.1) or (5.1), which show that Y/μ is related to Poisson's ratio. Since Poisson's ratio is practically a constant, equal to 0.301 (see Section 5), we find $Y/\mu = 2.604$ from Eq. (5.1). Furthermore, since Poisson's ratio can only have values between 0 and 0.5, the minimum value for Y/μ is 2.0 and the maximum is 3.0. Poisson's ratio is usually measured directly and not calculated from the two moduli; thus the interrelationships, as given by Eq. (II.1) or (5.1), among the three quantities serve as a check on the consistency of the three measured values.

The Y/μ ratios, which are listed in Table XIX, were calculated from the values of Y and μ given in Tables I and II, respectively. The mean value for all of the experimental data is 2.60 ±0.17, which is identical to that calculated from the mean value of Poisson's ratio. The error, ±0.17, corresponds to a percentage error of ±6.5, which is misleadingly small. If Poisson's ratio and the corresponding error were to be calculated from the above numbers, it would be found that $\sigma = 0.300 \pm 0.080$. This error is equivalent to a percentage error of ±26.7. The ratio Y/μ varies from a minimum of 2.08 for beryllium and chromium to a maximum of 2.91 for lead, and lies within the minimum and maximum theoretical limits, 2.0 and 3.0.

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[111] C. Zener and S. Bilinsky, *Phys. Rev.* **50**, 101 (1936).

TABLE XIX. RATIO OF YOUNG'S MODULUS TO THE SHEAR MODULUS

Element	Y/μ	Element	Y/μ	Element	Y/μ
3 Li	2.72	38 Sr	(2.71)^a	65 Tb	2.52
4 Be	2.08	39 Y	2.51	66 Dy	2.49
5 B	2.17	40 Zr	2.70	67 Ho	2.52
6 C(g)	2.56	41 Nb	2.80	68 Er	2.48
6 C(d)	2.50	42 Mo	2.83	69 Tm	(2.48)^a
11 Na	2.61	43 Tc	(2.59)^a	70 Yb	2.56
12 Mg	2.55	44 Ru	2.58	71 Lu	(2.50)^a
13 Al	2.67	45 Rh	2.53	72 Hf	2.59
14 Si	2.59	46 Pd	2.42	73 Ta	2.64
15 P(w, r, b)	(2.67)^a	47 Ag	2.82	74 W	2.60
16 S(r)	2.69	48 Cd	2.58	75 Re	2.58
19 K	2.78	49 In	2.82	76 Os	(2.57)^a
20 Ca	2.67	50 Sn(g)	2.84	77 Ir	2.51
21 Sc	(2.54)^a	50 Sn(w)	2.64	78 Pt	2.80
22 Ti	2.69	51 Sb	2.74	79 Au	2.83
23 V	2.83	52 Te	2.68	80 Hg	2.74
24 Cr	2.08	55 Cs	(2.71)^a	81 Tl	2.89
25 Mn	2.59	56 Ba	2.58	82 Pb	2.91
26 Fe	2.58	57 La	2.55	83 Bi	2.66
27 Co	2.70	58 Ce(α)	2.31	84 Po	(2.68)^a
28 Ni	2.58	58 Ce(γ)	2.51	87 Fr	(2.71)^a
29 Cu	2.74	59 Pr	2.41	88 Ra	(2.61)^a
30 Zn	2.48	60 Nd	2.62	89 Ac	(2.54)^a
31 Ga	2.47	61 Pm	(2.53)^a	90 Th	2.68
32 Ge	2.52	62 Sm	2.70	91 Pa	(2.56)^a
33 As	(2.67)^a	63 Eu	(2.58)^a	92 U	2.53
34 Se	(2.68)^a	64 Gd	2.52	93 Np	(2.51)^a
37 Rb	(2.71)^a			94 Pu	2.21

[a] Estimated value; see text for further discussion.

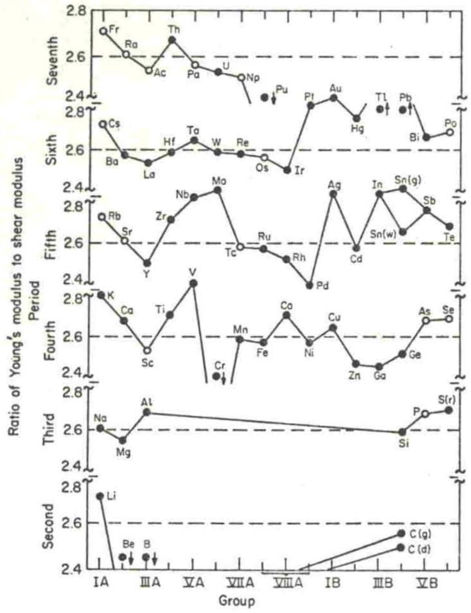


FIG. 23. The ratio of Young's modulus to the shear modulus of all of the elements considered in this review with the exception of the rare-earth elements. The horizontal dashed line represents the mean value of this ratio for these elements. Open points are estimated values.

The variation of Y/μ for all the elements is shown in Fig. 23. The similarity between Y/μ given in this plot and Poisson's ratio (Fig. 4) is quite close, as would be expected. The variation of Y/μ as one proceeds from one element to the next is more strikingly illustrated by the Y/μ ratio than by Poisson's ratio. The periodic dependence, such as is shown by the low values for the group IIIA metals and iron and its cogeners, and the higher-than-average values for the group IA, IIA, IVA, VA, IB, VB, and VIB elements, is obvious.

An attempt was made to determine whether or not the ratio of Y/μ has a crystal-structure dependence. It was found that the mean value was 2.64 for both the face-centered cubic, *A*1, and body-centered cubic, *A*2, metals; 2.62 for the diamond lattice, *A*4, elements; and 2.55 for the hexagonal close-packed, *A*3, metals. Hence the data do not seem to reveal any dependence on the crystal structure.

The variation of Y/μ for the rare earths is shown in Fig. 2c, where it is seen that the ratio decreases slightly with increasing atomic number. It should be observed, however, that the values for the ratio Y/μ are more scattered than are the values for either Young's modulus or the shear modulus alone (Figs. 2a and 2b).

Estimated Data. First, a value for Y/μ was estimated assuming that for a given element it was equal to the mean value obtained from the element's cogeners. Second, an estimated value of Y/μ was calculated from the estimated value of Poisson's ratio (see Section 5) by using Eq. (5.1). Third, these two estimated values were averaged to obtain the values shown in Table XIX and in Fig. 23. This procedure was used to estimate the values for phosphorus, scandium, arsenic, selenium, rubidium, strontium, technetium, cesium, osmium, polonium, francium, radium, and actinium. The estimated values for protactinium and neptunium for the first step were assumed to be equal to the mean value of thorium and uranium, and to the value of uranium, respectively. The other two steps of the procedure given above were followed exactly for estimating the value of Y/μ for protactinium and neptunium. The estimated values for Y/μ for the rare earths promethium, europium, thulium, and lutetium were calculated directly from the estimated values of Young's modulus (see Section 3) and the shear modulus (see Section 4).

The mean value of all the estimated Y/μ ratios is 2.603, which shows that mean value of the experimental Y/μ ratios would remain unchanged if the estimated values were included.

23. THE RATIO $(1 - \sigma)/(1 + \sigma)$

One of the steps in calculating the size factor involves the ratio $(1 - \sigma)/(1 + \sigma)$ (see Section 29), and because of this, these ratios are listed in Table XX.

The average value of Poisson's ratio for the elements is 0.301. If this value is substituted into the ratio $(1 - \sigma)/(1 + \sigma)$, a value of 0.536 is obtained. The minimum and maximum values possible for this ratio are 0.333 for $\sigma = 0.5$ and 1.000 for $\sigma = 0$. Furthermore, since σ is essentially a constant, the ratio $(1 - \sigma)/(1 + \sigma)$ would be expected to be a constant also. The average for all of the experimental values is 0.543 ±0.102. The values of beryllium and boron are anomalously large, and if they are excluded from the average, a value of 0.533 ±0.083 is obtained. The latter value is thought to be a more reliable average than the former.

TABLE XX. RATIO OF $(1 - \sigma)/(1 + \sigma)$

Element	$\frac{1 - \sigma}{1 + \sigma}$	Element	$\frac{1 - \sigma}{1 + \sigma}$	Element	$\frac{1 - \sigma}{1 + \sigma}$
3 Li	0.468	38 Sr	(0.534)[a]	65 Tb	0.586
4 Be	0.925	39 Y	0.590	66 Dy	0.609
5 B	0.837	40 Zr	0.493	67 Ho	0.594
6 C(g)	0.575	41 Nb	0.481	68 Er	0.616
6 C(d)	0.695	42 Mo	0.538	69 Tm	(0.619)[a]
11 Na	0.521	43 Tc	(0.547)[a]	70 Yb	0.558
12 Mg	0.563	44 Ru	0.555	71 Lu	(0.622)[a]
13 Al	0.493	45 Rh	0.575	72 Hf	0.538
14 Si	0.389	46 Pd	0.455	73 Ta	0.481
15 P(w, r, b)	(0.498)[a]	47 Ag	0.460	74 W	0.558
16 S(r)	0.489	48 Cd	0.538	75 Re	0.547
19 K	0.481	49 In	0.370	76 Os	(0.556)[a]
20 Ca	0.527	50 Sn(g)	0.408	77 Ir	0.587
21 Sc	(0.576)[a]	50 Sn(w)	0.504	78 Pt	0.449
22 Ti	0.487	51 Sb	0.527	79 Au	0.404
23 V	0.471	52 Te	0.504	80 Hg	0.466
24 Cr	0.654	55 Cs	(0.475)[a]	81 Tl	0.370
25 Mn	0.613	56 Ba	0.563	82 Pb	0.389
26 Fe	0.564	57 La	0.553	83 Bi	0.504
27 Co	0.499	58 Ce(α)	0.754	84 Po	(0.495)[a]
28 Ni	0.538	58 Ce(γ)	0.603	87 Fr	(0.475)[a]
29 Cu	0.487	59 Pr	0.533	88 Ra	(0.534)[a]
30 Zn	0.550	60 Nd	0.531	89 Ac	(0.576)[a]
31 Ga	0.619	61 Pm	(0.565)[a]	90 Th	0.556
32 Ge	0.575	62 Sm	0.479	91 Pa	(0.560)[a]
33 As	(0.498)[a]	63 Eu	(0.555)[a]	92 U	0.606
34 Se	(0.495)[a]	64 Gd	0.589	93 Np	(0.594)[a]
37 Rb	(0.475)[a]			94 Pu	0.739

[a] Estimated value; see text for further discussion.

The error ±0.083 is equivalent to ±15.6%. The values for the ratio $(1 - \sigma)/(1 + \sigma)$ vary from a minimum of 0.370 for indium and thallium to a maximum of 0.925 for beryllium. The estimated values lie well within this range.

The variation of the ratio $(1 - \sigma)/(1 + \sigma)$ for many elements is shown in Fig. 24. As would be expected, this plot is almost exactly the inverse of the plot of Poisson's ratio given in Fig. 4. The slight group dependence noted for Poisson's ratio (Section 5) is also obvious in Fig. 24.

The ratio $(1 - \sigma)/(1 + \sigma)$ for the rare earths, which is shown in Fig. 25a, is seen to increase with increasing atomic number. In general the points are scattered about the straight line shown in the figure, with large departures shown by cerium, samarium, and ytterbium. The anomaly for ytterbium may be due to its divalent nature,[13] but the departures shown by cerium and samarium are not understood.

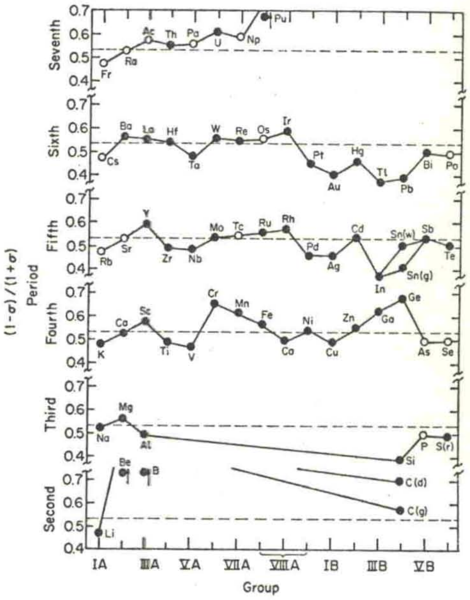
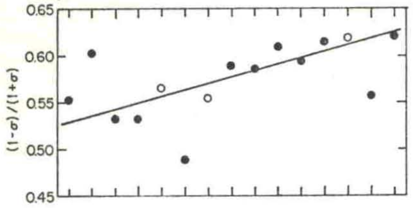


FIG. 24. The ratio $(1 - \sigma)/(1 + \sigma)$ of all of the elements considered in this review with the exception of the rare-earth elements. The horizontal dashed line represents the mean value of this ratio for these elements. Open points are estimated values.

Estimated Data. The values of $(1 - \sigma)/(1 + \sigma)$ are considered to be estimated if the value of Poisson's ratio was estimated. Estimated values are given for phosphorus, scandium, arsenic, selenium, rubidium, strontium, technetium, cesium, promethium, europium, thulium, lutetium, osmium, polonium, francium, radium, actinium, protactinium, and neptunium. The mean value of $(1 - \sigma)/(1 + \sigma)$ for the estimated data is 0.539, which indicates that the mean value of the experimental data would remain unchanged if the estimated values were included.

(a) Ratio of $(1-\sigma)/(1+\sigma)$



(b) Ratio of compressibility constants, b/a^2

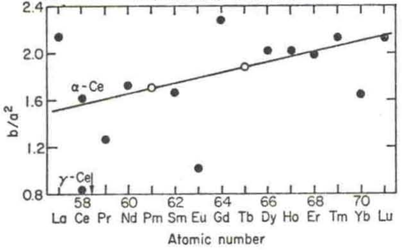


FIG. 25. (a) The ratio $(1 - \sigma)/(1 + \sigma)$ of the rare-earth metals. (b) The ratio of the compressibility constants, b/a^2, of the rare-earth metals. Open points are estimated values.

24. THE RATIO OF THE COMPRESSIBILITY CONSTANTS, b/a^2

Slater[17] has shown that the Grüneisen constant can be calculated from the compressibility constants, a and b, of Eq. (6.1). (See Section 28 for further details concerning this calculation.) The constants appear in Slater's expression (Eq. (28.2)) in the form b/a^2. Furthermore, Slater[17] points out that b/a^2 is approximately a constant equal to about 2.5, and thus this ratio can be used to check on the validity of the compressibility measurements. That is, if the ratio of b/a^2 departs considerably from 2.5, the compressibility data should be suspected. For the above reasons the b/a^2 values listed in Table XXI were calculated from the compressibility constants a and b given in Table IV.

Examination of the data given in Table XXI reveals negative values for the ratio b/a^2 for ruthenium, γ-cerium, and tungsten. The negative values mean that the compressibility increases with increasing pressure, which is, in general, unlikely. Cerium, because it undergoes an electronic transformation,[41] involving a large volume change ~13% at a moderately low pressure of 7720 kg/cm², may show an increase in compressibility with increasing pressure, because of some pretransformation. The compressibilities of ruthenium and tungsten cannot be so easily explained. Therefore, compressibility data for these two elements should be used with extreme caution. If the values in Table XXI are examined for other divergent ratios (assuming that those ratios greater than 4.17 or smaller than 0.83, i.e., $2.50 + (\frac{2}{3})2.50$, or $2.50 - (\frac{2}{3})2.50$, are divergent), we

TABLE XXI. RATIO OF THE COMPRESSIBILITY CONSTANTS, b/a^2

Element	b/a^2	Element	b/a^2	Element	b/a^2
3 Li	2.20	33 As	4.54	64 Gd	2.29
4 Be	4.11	34 Se	1.67	65 Tb	(1.88)[a]
5 B	2.13	37 Rb	1.57	66 Dy	2.02
6 C(g)	3.62	38 Sr	1.56	67 Ho	2.02
6 C(d)	(2.35)[a]	39 Y	1.98	68 Er	1.99
11 Na	1.85[b]	40 Zr	3.24	69 Tm	2.13
11 Na	1.79[c]	41 Nb	2.67	70 Yb	1.65
12 Mg	1.80	42 Mo	1.22	71 Lu	2.12
13 Al	2.63	43 Tc	(2.19)[a]	72 Hf	1.00
14 Si	2.48	44 Ru	−8.79	73 Ta	0.98
15 P(w)	(3.19)[a]	45 Rh	1.37	74 W	−0.97
15 P(r)	3.84	46 Pd	8.02	75 Re	(2.19)[a]
15 P(b)	2.47	47 Ag	0.35	76 Os	(2.19)[a]
16 S(r?)[d]	2.02[d]	48 Cd	2.77	77 Ir	5.25
16 S(r)	(1.94)[a]	49 In	2.26	78 Pt	0.72
19 K	1.96	50 Sn(g)	(2.35)[a]	79 Au	2.51
20 Ca	1.79	50 Sn(w)	2.52	80 Hg	(2.80)[a]
21 Sc	(2.20)[a]	51 Sb	2.47	81 Tl	2.17
22 Ti	2.71	52 Te	2.12	82 Pb	1.79
23 V	2.78	55 Cs	1.81	83 Bi	2.63
24 Cr	2.37	56 Ba	1.02	84 Po	(1.94)[a]
25 Mn	3.01	57 La	2.14	87 Fr	(1.84)[a]
26 Fe	2.35	58 Ce(α)	1.62	88 Ra	(1.54)[a]
27 Co	1.80	58 Ce(γ)	−5.60	89 Ac	(2.22)[a]
28 Ni	1.95	59 Pr	1.27	90 Th	3.03
29 Cu	3.60	60 Nd	1.73	91 Pa	(2.97)[a]
30 Zn	2.82	61 Pm	(1.71)[a]	92 U	4.70
31 Ga	(2.30)[a]	62 Sm	1.67	93 Np	(2.97)[a]
32 Ge	2.22	63 Eu	1.03	94 Pu	3.64

[a] Estimated value; see text for further discussion.

[b] Value obtained from parameters listed by Gilvarry[1] of Table IV.

[c] Value obtained from parameters listed by Beecroft and Swenson[6] of Table IV.

[d] See the text, Section 6, concerning the modification of Bridgman's sulfur.

find that arsenic, palladium, iridium, and uranium have too large a ratio and that silver and platinum have too small a ratio. Thus, if the criterion proposed by Slater is correct, it is likely that the compressibility data for these elements are incorrect and should be used with caution.

It should be possible to predict the pressure dependence of the compressibility if Slater's observation that b/a^2 is a constant is correct. Examination of the data in Table XXI or in Fig. 26 indicates that the ratio may not be a constant. Further investigation, however, reveals that $b/a^2 = 1.89 \pm 0.88$ for all the face-centered cubic metals, except palladium, γ-cerium, and iridium; 1.83 ± 0.63 for all the body-centered cubic metals, except tungsten; 2.19 ± 0.69 for all the hexagonal close-packed metals, except ruthenium; 2.35 ± 0.13 for the diamond-lattice-type elements, and **2.97** ± 0.95 for all the remaining elements which do not have any of the

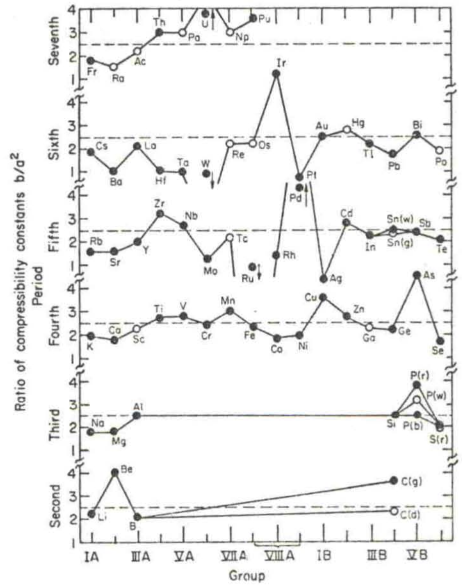


FIG. 26. The ratio of the compressibility constants, b/a^2, of all of the elements considered in this review with the exception of the rare-earth elements. The horizontal dashed line represents Slater's approximation that $b/a^2 = 2.5$. Open points are estimated values.

above crystal structures. Grouping these ratios according to crystal structures will probably give a better estimate for the b/a^2 value of an element rather than the more general value given by Slater.

Examination of Fig. 26 reveals that the ratio b/a^2 has a slight group dependence, especially for the IA, IIA, IIIA, IIB, IIIB, IVB, VB, and VIB elements. The mean value for a group may also be used to estimate the b/a^2 ratio for an element in that group. Similarly, the variation of b/a^2 with atomic number for the rare earths (Fig. 25b) was used to estimate the value of the ratio for promethium and terbium.

Estimated Data. Based on the observations described above, the b/a^2 ratios were estimated by using either the crystal-structure dependence (diamond, technetium, gray tin, rhenium, osmium, protactinium, and neptunium), or the group dependence (white phosphorus, rhombic sulfur, gallium, promethium, terbium, mercury, polonium, radium, and actinium), or both since the two techniques gave practically the same estimate (scandium and francium). The pressure dependence of the compressibility (the b term) can be estimated from this ratio and the known a values (given in Table IV or V) or the estimated a values (given in Table V only). This was done, and the results are given in the text of Section 6.

25. THE RELATIONSHIP BETWEEN THERMAL EXPANSION AND MELTING POINT

The relationship between the coefficient of thermal expansion and the absolute temperature of the melting point has been known for almost 85 years.[112] Carnelley noted that materials which have high melting points have low coefficients of thermal expansion, and those which have low melting points have high coefficients of expansion. Hidnert and Sonder[113] express the relationship as

$$\alpha = 0.020/T \tag{25.1}$$

for face-centered and body-centered cubic and hexagonal close-packed structures.

The data in Tables VI and IX were examined to see if Eq. (25.1) is valid for all materials. The product of αT was found to be 0.0186 ± 0.0080 for all of the elements for which experimental values are known. The error ± 0.0080 corresponds to a percentage error of ± 43. If, however, the data are grouped such that only the face-centered and body-centered cubic and hexagonal close-packed structures are considered, then the product of αT was found equal to 0.0197 ± 0.0051, and the percent error

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[112] T. Carnelley, *Ber. Deut. Chem. Ges.* **12**, 439 (1879).

[113] P. Hidnert and W. Sonder, *Natl. Bur. St.* (*U.S.*) *Circ.* **486**, (1950).

is reduced to ±26. Thus Eq. (25.1) is a fair approximation for these metals. The product αT was found to be 0.0049 ± 0.0018 for those elements which crystallize in a diamond-type lattice; 0.0073 ± 0.0026 for the group VB elements (arsenic, antimony, and bismuth); 0.0123 ± 0.0046 for those *metals* which do not crystallize in any of the above structures and which have four or less atoms per unit cell (gallium, indium, white tin, mercury, and uranium); and 0.0365 ± 0.0137 for those *metals* which do not crystallize in any of the above structures and which have more than four atoms per unit cell (manganese, neptunium, and plutonium). The semimetals—sulfur, selenium, tellurium, and polonium—showed a wide variation in their αT values, but it was noted that αT decreased in a nonlinear manner with increasing atomic number for these four elements. The elements boron, graphite, and white phosphorus could not be placed in any of they above categories.

The product of αT varies from a minimum value of 0.0027 for gray tin to a maximum value of 0.0502 for plutonium. The relationship between α and T has been used to estimate the coefficient of thermal expansion for a number of elements from the known or estimated melting points (see Part III).

26. LEIBFRIED, MODIFIED LEIBFRIED, AND BRAGG NUMBERS

In Leibfried's study of melting[114] he observed that for a number of metals (specifically aluminum, copper, palladium, silver, gold, and lead) the quantity $RT_m/\mu V = L \simeq 0.042$, where R is the gas constant, T_m is the melting point (Table IX), μ is the shear modulus (Table II), and V is the atomic volume (Table VII). The term RT_m is an approximation of the heat of fusion, which follows from Richard's rule (see Section 27). Bragg,[115] on the other hand, noted that $\Delta H_f/\mu V = \mathcal{B} \simeq 0.034$ for a few metals (specifically aluminum, iron, cobalt, nickel, copper, silver, gold, and lead), where ΔH_f is the heat of fusion (Table X). Since $\Delta H_f \simeq RT_m$ (Richard's rule) it is difficult to understand why such a large discrepancy exists between L (which will be referred to hereafter as the Leibfried number) and $\mathcal{B}$ (referred to hereafter as the Bragg number). Furthermore, since these approximations were based on only a very limited number of metals, it would be desirable to know if they are generally valid for all metals and semimetals. In order to investigate these two points, and since the Bragg and/or Leibfried numbers are necessary to calculate the size factor, these numbers were calculated for all the elements from the appropriate data given in the earlier tables. The results are shown in Table XXII.

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[114] G. Leibfried, *Z. Physik* **127**, 344 (1950).

[115] L. Bragg, *in* "Symposium on Internal Stresses," p. 221. Inst. Metals, London, 1948.

TABLE XXII. LEIBFRIED, MODIFIED LEIBFRIED, AND BRAGG NUMBERS

Element	L	L′	$\mathcal{B}$
3 Li	0.0686	0.0611	0.0512
4 Be	0.0185	0.0165	0.0197
5 B	0.0233	0.0233	(0.0252)[a]
6 C(g)	1.99	1.99	5.72
6 C(d)	0.0222	0.0728	0.0640
11 Na	0.0378	0.0336	0.0299
12 Mg	0.0316	0.0369	0.0345
13 Al	0.0292	0.0341	0.0378
14 Si	0.0292	0.0956	0.0983
15 P(w)	(0.1070)[a]	(0.1070)[a]	(0.0239)[a]
15 P(r)	(0.0765)[a]	(0.0765)[a]	—
16 S(r)	0.0293	0.0293	0.0118
19 K	0.0481	0.0429	0.0375
20 Ca	0.0480	0.0428	0.0421
21 Sc	(0.0320)[a]	(0.0285)[a]	(0.0308)[a]
22 Ti	0.0342	0.0304	(0.0284)[a]
23 V	0.0466	0.0415	(0.0386)[a]
24 Cr	0.0212	0.0188	0.0161
25 Mn	0.0224	0.0200	0.0244
26 Fe	0.0260	0.0232	0.0249
27 Co	0.0287	0.0335	0.0284
28 Ni	0.0290	0.0339	0.0334
29 Cu	0.0351	0.0410	0.0381
30 Zn	0.0169	0.0197	0.0203
31 Ga	0.0057	0.0057	0.0118
32 Ge	0.0188	0.0614	0.0557
33 As	(0.0479)[a]	(0.1290)[a]	(0.1370)[a]
34 Se	(0.0114)[a]	(0.0309)[a]	(0.0143)[a]
37 Rb	(0.0462)[a]	(0.0412)[a]	(0.0391)[a]
38 Sr	(0.0490)[a]	(0.0436)[a]	(0.0484)[a]
39 Y	0.0288	0.0256	0.0209
40 Zr	0.0369	0.0329	(0.0306)[a]
41 Nb	0.0562	0.0500	(0.0466)[a]
42 Mo	0.0221	0.0197	0.0240
43 Tc	(0.0165)[a]	(0.0193)[a]	(0.0173)[a]
44 Ru	0.0162	0.0190	(0.0170)[a]
45 Rh	0.0152	0.0178	(0.0159)[a]
46 Pd	0.0334	0.0390	0.0354
47 Ag	0.0349	0.0407	0.0370
48 Cd	0.0158	0.0184	0.0185
49 In	0.0610	0.0712	0.0522
50 Sn(g)	0.0111	0.0362	0.0177
50 Sn(w)	0.0126	0.0126	0.0202
51 Sb	0.0206	0.0556	0.0510
52 Te	0.0191	0.0515	0.0520
55 Cs	(0.0560)[a]	(0.0499)[a]	(0.0443)[a]

TABLE XXII. LEIBFRIED, MODIFIED LEIBFRIED, AND BRAGG NUMBERS—*Continued*

Element	L	L′	$\mathcal{B}$
56 Ba	0.0444	0.0396	0.0384
57 La	0.0295	0.0263	0.0173
58 Ce(α)	0.0627	0.0558	0.0342
58 Ce(γ)	0.0359	0.0320	0.0196
59 Pr	0.0356	0.0318	0.0230
60 Nd	0.0361	0.0321	0.0224
61 Pm	(0.0321)[a]	(0.0286)[a]	(0.0224)[a]
62 Sm	0.0443	0.0395	0.0320
63 Eu	(0.0536)[a]	(0.0477)[a]	(0.0507)[a]
64 Gd	0.0297	0.0264	0.0215
65 Tb	0.0308	0.0274	0.0219
66 Dy	0.0290	0.0258	(0.0202)[a]
67 Ho	0.0288	0.0257	0.0265
68 Er	0.0269	0.0240	(0.0188)[a]
69 Tm	(0.0274)[a]	(0.0244)[a]	(0.0300)[a]
70 Yb	0.0527	0.0469	0.0414
71 Lu	(0.0266)[a]	(0.0237)[a]	(0.0186)[a]
72 Hf	0.0291	0.0259	(0.0242)[a]
73 Ta	0.0367	0.0327	(0.0305)[a]
74 W	0.0208	0.0185	0.0226
75 Re	0.0180	0.0211	(0.0195)[a]
76 Os	(0.0155)[a]	(0.0181)[a]	(0.0167)[a]
77 Ir	0.0126	0.0147	(0.0136)[a]
78 Pt	0.0306	0.0357	0.0332
79 Au	0.0394	0.0461	0.0411
80 Hg	0.0138	0.0138	0.0153
81 Tl	0.1013	0.0902	0.0846
82 Pb	0.0507	0.0592	0.0454
83 Bi	0.0165	0.0446	0.0372
84 Po	(0.0201)[a]	(0.0201)[a]	(0.0167)[a]
87 Fr	(0.0548)[a]	(0.0488)[a]	(0.0454)[a]
88 Ra	(0.0348)[a]	(0.0310)[a]	(0.0289)[a]
89 Ac	(0.0360)[a]	(0.0421)[a]	(0.0389)[a]
90 Th	0.0305	0.0272	(0.0253)[a]
91 Pa	(0.0241)[a]	(0.0241)[a]	(0.0200)[a]
92 U	0.0121	0.0107	(0.0100)[a]
93 Np	(0.0145)[a]	(0.0129)[a]	(0.0120)[a]
94 Pu	0.0144	0.0128	0.0050

[a] Estimated value; see text for further discussion.

Also shown in Table XXII are the modified Leibfried numbers, L'. The modified Leibfried number differs from the Leibfried number in that the term RT_m in L is replaced by the term KT_m, where the value of K depends on the crystal structure of the element just below its melting point. The values of K are 1.76 for body-centered cubic metals; 2.29 for face-centered cubic or hexagonal close-packed metals; 5.36 for the $A7$ arsenic-type elements (arsenic, antimony, and bismuth); 4.22 for the $A8$ selenium-type elements (selenium and tellurium); 6.50 for the $A4$ diamond-type elements (diamond, silicon, germanium, and gray tin); and 1.978 for the elements which do not fit into the above groups.

The results of a detailed examination of these three numbers is shown in the accompanying tabulation. These results indicate that Leibfried's conclusion is incorrect that $L \simeq 0.042$, but that Bragg's conclusion that $\mathcal{B} \simeq 0.034$ is in agreement with the results shown here, and that $L \simeq L' \simeq \mathcal{B}$, which is to be expected. The percentage deviation from the mean for these three quantities is quite large, which raises the question—should this percentage deviation be used as a criterion for determining whether or not something is or is not a constant, and, if so, then at what percentage does the distinction occur, at 25%, 33⅓%, 50%, or even higher? This question, of course, has no single answer since any answer will depend greatly on the individual's background and philosophy. It should be mentioned in this connection that the percentage deviation from the mean for the Grüneisen constant is larger than it is for L or L' or $\mathcal{B}$; and if one accepts the premises that the Grüneisen constant is a constant and that the percentage error is a valid criterion for determining this, then L, L', and $\mathcal{B}$ must also be constants of the elements. The percentage deviations for the other constants of the elements are less than 25%, except Poisson's ratio (26.2%).

Number	L	L′	$\mathcal{B}$
Mean value	0.0305	0.0334	0.0312
Standard deviation from mean	0.0135	0.0145	0.0127
Percentage deviation from mean	44.3	43.4	40.7
Elements excluded from averaging process	C(g), Ga, Tl	C(g), Si, Ga, Tl	C(g), Si, Tl, Pu
Minimum value	0.0057	0.0057	0.0050
Element for which minimum occurs	Ga	Ga	Pu
Maximum value	1.99	1.99	5.72
Element for which maximum occurs	C(g)	C(g)	C(g)

A comparison of L and L' with $\mathcal{B}$ revealed, as would be expected if Richard's rule is a poor approximation, that L' was in better agreement with $\mathcal{B}$ for 32 of the elements (72.7%), but in poorer agreement for 12 of the elements. There were 5 elements for which L and L' were identical

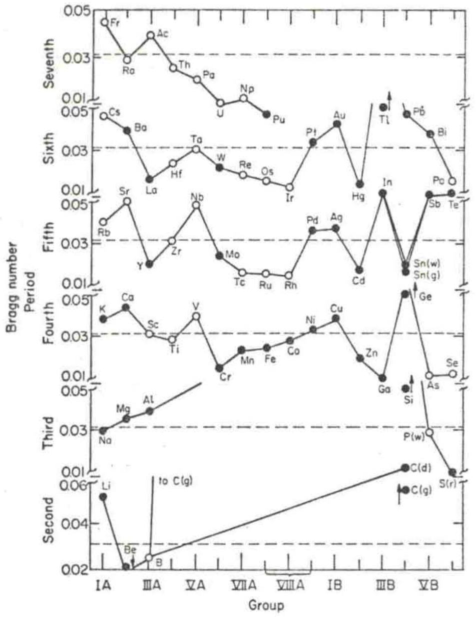


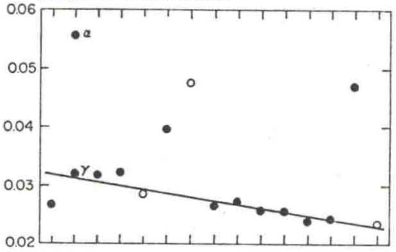
FIG. 27. The Bragg number of all of the elements considered in this review with the exception of the rare-earth metals. The horizontal dashed line represents the mean value. Open points are estimated values.

and thus agreed equally well with ℬ. It is felt that L' is more characteristic of the element than L, primarily because L depends on the validity of Richard's rule. For this reason L' rather than L was used in calculating the size factor (see Section 29).

The variation of the Bragg number with the group is shown in Fig. 27, and again a group dependence is noted: ℬ is high for the alkali and alkaline-earth metals, group VA metals, nickel and its cogeners, and group IB metals; and low for the group IIIA, IVA, VIA, VIIA metals, iron and cobalt and their cogeners, and group IIB metals. Since $L \simeq L' \simeq \mathcal{B}$ the plots for L and L' are not shown, but in general they are quite similar.

The modified Leibfried and Bragg numbers for the rare earths are shown in Fig. 28. In general both L' and ℬ decrease with increasing atomic number. The anomalies at europium and ytterbium are undoubtedly due to the divalent nature of these elements.[13] The value for α-cerium is included only for comparative purposes and is not expected to lie near the straight line established for the normal trivalent rare earths. The anomalous behavior of lanthanum and samarium is not understood, but seems to follow the tendency of these two metals to deviate from the trend established by the other rare earths for some of the other properties (Figs. 2 and 25).

(a) Modified Leibfried number



(b) Bragg number

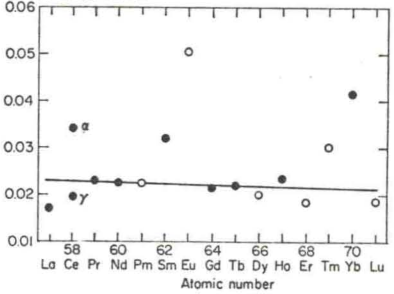


FIG. 28. (a) The modified Leibfried number of the rare-earth metals. (b) The Bragg number of the rare-earth metals. Open points are estimated data.

Estimated Data. The values considered to be estimated in Table XXII are those for which at least one quantity used in calculating L, L', or ℬ was estimated. In general the shear modulus, μ, was the quantity which was least known experimentally for the elements. If the melting point or the atomic volume was an estimated value for a given element, the shear modulus was also an estimated quantity. For the Bragg number considerable experimental data concerning the heats of fusion were lacking.

and in general this quantity determined whether $\mathcal{B}$ was considered to be an estimated value. For the elements white phosphorus, scandium, arsenic, selenium, rubidium, strontium, cesium, and thulium the heat of fusion is known experimentally but the shear modulus is not.

27. Entropies of Fusion and Vaporization

Entropy of Fusion. The entropy of fusion, ΔS_f, is defined as

$$\Delta S_f = \Delta H_f / T_m, \qquad (27.1)$$

where ΔH_f is the heat of fusion (Table X) and T_m is the melting point in degrees Kelvin (Table IX). Richard's rule states that the entropy of fusion is approximately equal to a constant (2.0 e.u.). Often the approximation is given as $\Delta S_f \simeq R$, where R is the gas constant. Generally this rule is used to estimate the heat of fusion of an element from the known melting point. Kelley,[54] however, used a value of 2.3 e.u. for estimating heats of fusion; and Stull and Sinke[53] used two values, 2.3 e.u. for elements which crystallize as close-packed structures (face-centered cubic and hexagonal) and 1.9 e.u. for elements which exhibit body-centered cubic structures. These results suggest that Richard's rule may not be a valid approximation, and therefore the ΔS_f values were calculated for all the known elements.

The entropies of fusion are shown in Table XXIII. The ΔS_f values vary from a minimum 0.47 e.u. for white phosphorus to a maximum of 7.13 e.u. for silicon. This is a very wide variation of values for a quantity which is supposed to be constant. However, if the values are grouped according to the crystal structure of the phase just prior to melting, several interesting things are seen. The entropy of fusion for 26 body-centered cubic metals is 1.76 ±0.34 e.u.; for 9 face-centered cubic metals, 2.28 ±0.23 e.u.; for 5 hexagonal close-packed metals, 2.33 ±0.23; or, for 14 metals with a close-packed structure (face-centered cubic and hexagonal) 2.29 ±0.23; for 3 elements which have the diamond structure, 6.50 +0.63; for 3 elements which have the *A*7 arsenic structure, 5.36 ±0.71; and 2 elements which have the *A*8 selenium structure, 4.22 ±1.57. Thus one notes that ΔS_f has a strong crystal-structure dependence and, therefore, Richard's rule is a poor approximation.

The variation of the entropy of fusion for the elements is shown in Fig. 29. Because of the sparsity of data for the transition metals (groups IVA, VA, VIIA, and VIIIA) it is not clear that there is a group dependence in this portion of the diagram. A group dependence is noted, however, near both ends of the plot shown in Fig. 29.

TABLE XXIII. ENTROPIES OF FUSION AND VAPORIZATION

Element	ΔS_f (e.u./g-at)	ΔS_v (e.u./g-at)
3 Li	1.58	21.5
4 Be	2.26	22.1
5 B	(2.29)[a]	29.6
6 C(g)	6.10	42.1
11 Na	1.68	20.5
12 Mg	2.32	22.2
13 Al	2.74	30.4
14 Si	7.13	34.1
15 P(w)	0.47	136.
16 S(m)	0.86	90.4
19 K	1.65	18.8
20 Ca	1.86	20.3
21 Sc	2.04	19.8
22 Ti	(1.76)[a]	28.6
23 V	(1.76)[a]	30.7
24 Cr	1.62	28.6
25 Mn	2.31	22.3
26 Fe	2.03	26.6
27 Co	2.10	28.4
28 Ni	2.44	29.7
29 Cu	2.30	25.9
30 Zn	2.55	23.4
31 Ga	4.41	24.3
32 Ge	6.28	25.6
33 As	6.07	32.6
34 Se	2.65	48.5
37 Rb	1.80	18.6
38 Sr	2.10	20.2
39 Y	1.54	24.3
40 Zr	(1.76)[a]	29.9
41 Nb	(1.76)[a]	34.2
42 Mo	2.30	24.1
43 Tc	(2.29)[a]	(25.5)[a]
44 Ru	(2.29)[a]	33.7
45 Rh	(2.29)[a]	30.0
46 Pd	2.25	27.1
47 Ag	2.25	24.7
48 Cd	2.49	23.0
49 In	1.82	23.9
50 Sn	3.39	25.2
51 Sb	5.25	28.5
52 Te	5.78	37.0
55 Cs	1.68	17.0
56 Ba	1.83	19.3

TABLE XXIII. ENTROPIES OF FUSION AND VAPORIZATION—*Continued*

Element	ΔS_f (e.u./g-at)	ΔS_v (e.u./g-at)
57 La	1.24	26.3
58 Ce	1.16	23.3
59 Pr	1.37	22.3
60 Nd	1.32	23.1
61 Pm	(1.48)[a]	(22.1)[a]
62 Sm	1.53	(22.1)[a]
63 Eu	2.01	18.1
64 Gd	1.54	(22.1)[a]
65 Tb	1.51	(22.1)[a]
66 Dy	(1.48)[a]	19.7
67 Ho	1.95	19.3
68 Er	(1.48)[a]	(22.1)[a]
69 Tm	2.32	21.9
70 Yb	1.67	(18.1)[a]
71 Lu	(1.48)[a]	(22.1)[a]
72 Hf	(1.76)[a]	29.8
73 Ta	(1.76)[a]	31.2
74 W	2.31	31.8
75 Re	(2.29)[a]	28.0
76 Os	(2.29)[a]	33.4
77 Ir	(2.29)[a]	29.6
78 Pt	2.30	29.8
79 Au	2.21	24.8
80 Hg	2.34	22.6
81 Tl	1.77	19.9
82 Pb	1.90	21.2
83 Bi	4.77	24.0
84 Po	(1.76)[a]	23.8
87 Fr	(1.76)[a]	(15.8)[a]
88 Ra	(1.76)[a]	(19.9)[a]
89 Ac	(2.29)[a]	(25.5)[a]
90 Th	(1.76)[a]	(25.5)[a]
91 Pa	(1.76)[a]	(25.5)[a]
92 U	(1.76)[a]	27.7
93 Np	(1.76)[a]	(25.5)[a]
94 Pu	0.74	21.6

[a] Estimated value; see text for further discussion.

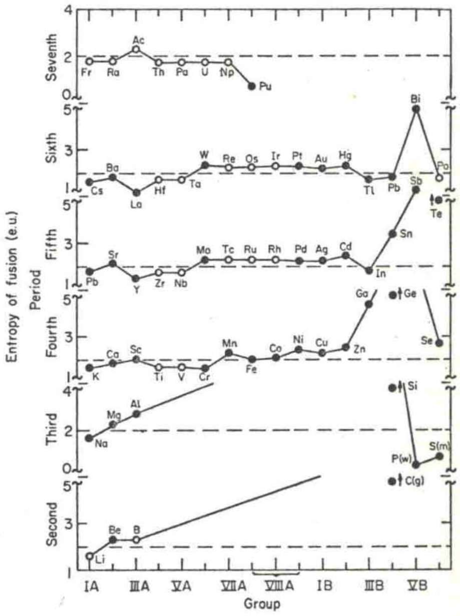
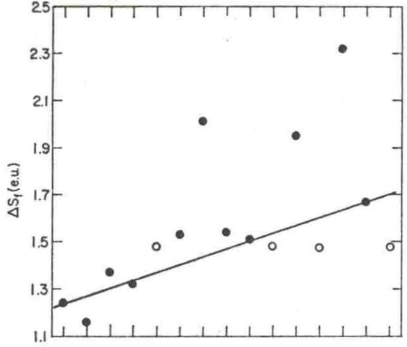


FIG. 29. Entropy of fusion of all of the elements considered in this review with the exception of the rare-earth metals. The horizontal dashed line represents Richard's constant, 2.0 e.u. Open points are estimated data.

The variation of the entropy of fusion for the rare earths is given in Fig. 30a. It is seen that ΔS_f slowly increases with increasing atomic number. The estimated entropies were assumed to be equal to the mean value for these metals and, therefore, deviate from the line drawn through the points. The high ΔS_f values for holmium and thulium are probably due to the fact that the measured heat of fusion includes both the α–β heat of transition and the heat of fusion, because the α–β transformation lies so near the melting point that these two heats cannot be resolved experimentally. The value for europium is also anomalous, but the reason for its behavior is not clear. It should be mentioned that europium has only one allotropic form, body-centered cubic, but the other rare earths have a close-packed structure which transforms, usually within 100°C of their melting points, to the body-centered cubic modification. Perhaps this may be a partial explanation for this anomaly.

Estimated Data. From the above-mentioned crystal-structure dependence of the entropy of fusion, ΔS_f was estimated to be 1.76 e.u. for the body-centered cubic elements titanium, vanadium, zirconium, niobium,


(a) Entropy of fusion

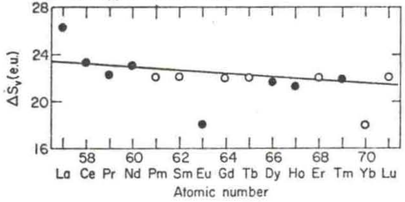

(b) Entropy of vaporization

FIG. 30. (a) Entropy of fusion of the rare-earth metals. (b) Entropy of vaporization of the rare-earth metals. Open points are estimated data.

hafnium, tantalum, thorium, uranium, and neptunium; for the assumed body-centered cubic metals francium and radium; and for the metals polonium and protactinium, which have open structures. For the close-packed elements technetium, ruthenium, rhodium, rhenium, osmium, iridium, and actinium, and also for boron, the entropy of fusion was estimated to be 2.29 e.u. The entropy of fusion for the rare earths promethium, dysprosium, erbium, and lutetium was estimated to be 1.48 e.u., the mean value for the normal rare-earth elements.

Entropy of Vaporization. The entropy of vaporization, ΔS_v, is defined as

$$\Delta S_v = \Delta H_v / T_b, \tag{27.2}$$

where ΔH_v is the heat of vaporization at the normal boiling point T_b (T_b is given in degrees Kelvin). The heat of sublimation at 298°, ΔH_s^{298},

which is given in Table XII, cannot be used in Eq. (27.2) as such, but must be corrected by using the high-temperature heat capacity data to obtain ΔH_v at T_b. Extensive use was made of the thermodynamic tables of Stull and Sinke[53] to convert ΔH_s^{298} to ΔH_v at T_b. If T_b was greater than the maximum temperature given in their compilation (3000°K), the data were extrapolated to T_b. The entropy of vaporization, like the entropy of fusion, is thought to be approximately constant for all materials (Trouton's rule), and the constant generally given is 23.5 i.e., $\Delta S_v \simeq 23.5$ e.u.

The entropies of vaporization are listed in Table XXIII. Examination of these values reveals that in general they lie between 15 and 35 e.u.; the minimum experimental value is 17.0 e.u. for cesium and the maximum is 136 e.u. for phosphorus. If the estimated data are considered, then the minimum value is 15.8 e.u. for francium, but the maximum remains unchanged. The average value for ΔS_f is 25.5 ±4.5 e.u. if one excludes the values of carbon, phosphorus, sulfur, and selenium. The percentage error is ±17.6%, which is moderately good. Thus it would appear that Trouton's rule is valid, except the constant should be 25.5. However, the value commonly quoted as 23.5 lies well within the range of the error.

The variation of ΔS_v as a function of the group is shown in Fig. 31. There is certainly a marked dependence on an element's location in the Periodic Table. The low values for the alkali metals increase slowly as one moves across the Periodic Table and reach a maximum at about the group VA metals, beyond which they decrease sharply at about the group VIIA metals, increase suddenly at about iron or cobalt and their cogeners, gradually decrease to a minimum at about the group IIB metals, and finally increase as one moves to the end of each row.

The ΔS_v of the rare earths is shown in Fig. 30b, where it is seen that the entropy of vaporization decreases with increasing atomic number. The anomalies at europium and ytterbium are probably due to the divalent nature of these metals.

Estimated Data. The entropies of vaporization for technetium, actinium, thorium, protactinium, and neptunium are assumed to be equal to the mean value. Although ΔH_s^{298} and T_b are known for thorium, the heat capacity of the gaseous phase is not known and therefore ΔH_v cannot be calculated. Instead of estimating a value for the heat capacity of thorium gas, Trouton's rule was applied, which probably gave as reliable results. The mean value for the experimentally determined ΔS_v for the rare earths is 22.1 e.u., and this value was assumed to apply to those rare earths for which ΔS_v was unknown. The entropy of vaporization for the alkali metals decreases with increasing atomic number; thus, an estimate for francium was obtained by extrapolating the straight line established for the other alkali metals

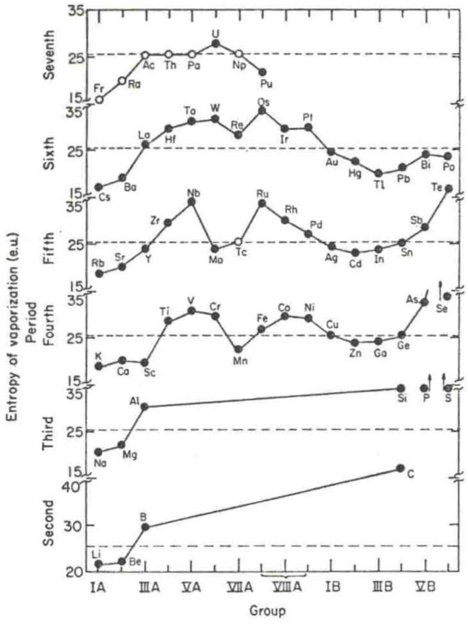


FIG. 31. Entropy of vaporization of all of the elements considered in this review with the exception of the rare-earth metals. The horizontal dashed line represents the mean value. Open points are estimated data.

in a plot of ΔS_v versus the period. The mean value of ΔS_v of the alkaline-earth metals was assumed to be the value for radium.

28. GRÜNEISEN CONSTANT

Grüneisen[116] showed that a quantity γ_G, which is defined as

$$\gamma_G = \frac{\alpha_v V}{\chi C_v{}^l}, \tag{28.1}$$

is a constant of a material, and that it is about equal to 1.8 for most substances. In Eq. (28.1) γ_G is now known as the Grüneisen constant, α_v is the volume coefficient of thermal expansion and is equal to 3α (α is the linear coefficient of thermal expansion in Table VI), V is the atomic volume (Table VII), χ is the compressibility (Table V), and $C_v{}^l$ is the lattice contribution to the heat capacity at constant volume (Table XIV). In most of the previous calculations the total heat capacity at constant volume $C_v = C_v{}^l + C_v{}^e$, was used in the denominator of Eq. (28.1). For most substances the inclusion of $C_v{}^e$ makes only a small difference in γ_G. For a few materials, however, $C_v{}^e$ is large enough to have a significant effect on γ_G. Since most of the literature values are based on C_v, these values have also been included in Table XXIV for convenience in comparing the value calculated herein with those previously given in the literature. The values calculated from Eq. (28.1) (that is, by using $C_v{}^l$) are also given in Table XXIV.

Slater[17] has shown that the Grüneisen constant may be given also by the compressibility constants a and b (see Table IV). The constant is given by the symbol γ_S and is defined as

$$\gamma_S = b/a^2 - \tfrac{2}{3}. \tag{28.2}$$

According to Slater, γ_G should equal γ_S; however, he found that a large discrepancy existed between these values for manganese, molybdenum, tantalum, and gold. Gilvarry,[117] by using Bridgman's more recent data, found that γ_G and γ_S are in good agreement for gold, in fair to poor agreement for molybdenum, and in very poor agreement for tantalum. The results were inconclusive for manganese. Since much more information is presently available for the compressibility constants, the analysis of Slater and Gilvarry was extended to all of the elements for which data exist. The γ_S values are also shown in Table XXIV.

The Grüneisen constant can also be calculated from shock wave data.[26] Since these data are somewhat limited, the reader is referred to the review by Rice *et al.*[26] concerning the details of this method for obtaining the Grüneisen constant. The Grüneisen constant obtained from shock wave data is represented by the symbol γ_{SW}, and values thus obtained for this constant are listed in Table XXIV.

Grüneisen Constant γ_G. The mean value of γ_G (as calculated from $C_v{}^l$) is 1.57 ±0.72 excluding the value for plutonium. The error ±0.72 corresponds to a percentage error of 45.8. The values of γ_G vary from a minimum of 0.25 for graphite to a maximum of 6.76 for plutonium. The estimated data also lie within this range.

The variation of γ_G for the elements is shown in Fig. 32, and the dependency of that constant on an element's position in the Periodic Table is

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[116] E. Grüneisen, *in* "Handbuch der Physik" (H. Geiger and K. Scheel, eds.), Vol. 10, p. 1. Springer, Berlin, 1926; *NASA (Natl. Aeron. Space Admin.), Rept. (Engl. Transl.)* NASA-RE-2-18-59W.

[117] J. J. Gilvarry, *J. Chem. Phys.* **23**, 1925 (1955).

TABLE XXIV. GRÜNEISEN CONSTANT

Element	γ Calculated from C_v data (γ_G)				γ Calculated from compressibility data (γ_S)	γ Calculated from shock wave data	
	(This paper)						
	C_v^l	C_v	(Literature)	Ref.		γ_{SW}	Ref.
3 Li	0.91	0.89	1.18 ±0.02	1, 2	1.53	—	—
4 Be	1.16	1.15	1.18 ±0.01	3, 4	3.44	1.18	4
5 B	1.85	1.79	—	—	1.47	—	—
6 C(g)	0.24	0.23	—	—	2.96	—	—
6 C(d)	1.10	1.10	—	—	—	—	—
11 Na	1.33	1.31	1.31 ±0.06	1, 2	1.16 ±0.04	—	—
12 Mg	1.63	1.60	1.48 ±0.03	4, 5	1.14	1.32	4
13 Al	2.18	2.14	2.19 ±0.10	1–3, 6	1.96	2.09	7
14 Si	0.57	0.57	—	—	1.81	—	—
15 P(w)	(1.17)^a	1.17	—	—	—	—	—
15 P(r)	(2.83)^a	(2.83)^a	—	—	3.17	—	—
15 P(b)	—	—	—	—	1.80	—	—
16 S(r)	(3.11)^a	3.11	—	—	1.35	—	—
19 K	1.37	1.34	1.37 ±0.04	1, 2	1.30	—	—
20 Ca	1.07	1.04	1.16	3	1.12	—	—
21 Sc	(1.17)^a	(1.03)^a	—	—	—	—	—
22 Ti	1.33	1.28	1.18	4	2.04	1.13	4
23 V	1.55	1.38	1.05	3	2.11	1.42	8
24 Cr	1.53	1.51	1.30	3	1.70	2.07	4
25 Mn	1.28	1.16	2.07 ±0.86	1–3	2.34	—	—
26 Fe	1.81	1.70	1.66 ±0.06	1, 3, 6	1.69	—	—
27 Co	2.07	1.95	1.93 ±0.06	1, 4	1.14	2.01	4
28 Ni	2.00	1.83	1.88 ±0.08	1, 3, 6	1.28	2.00 ±0.19	4, 11
29 Cu	1.97	1.96	2.00 ±0.08	1, 3, 4, 6, 9	2.93	2.00 ±0.06	4, 7, 11
30 Zn	2.05	2.03	2.01 ±0.14	3–5	2.15	2.24 ±0.14	4, 11
31 Ga	1.45	1.44	—	—	—	—	—
32 Ge	0.80	0.80	—	—	1.56	—	—
33 As	(0.27)^a	0.27	0.19	5	3.87	—	—
34 Se	0.67	0.67	—	—	1.00	—	—
35 Rb	1.85	1.80	1.67 ±0.19	2, 5	0.90	—	—
38 Sr	0.95	0.91	—	—	0.89	—	—
39 Y	1.13	1.00	0.89	10	1.31	—	—
40 Zr	0.82	0.71	0.83 ±0.06	4, 9	2.57	0.87	4
41 Nb	1.74	1.58	1.58 ±0.11	3, 4, 9	2.00	1.42	4
42 Mo	1.65	1.61	1.60 ±0.08	1–4	0.56	1.41	4
43 Tc	(2.75)^a	(2.61)^a	—	—	—	—	—
44 Ru	3.25	3.12	—	—	−9.46	—	—
45 Rh	2.43	2.29	2.23 ±0.03	3, 4	0.71	2.29	4
46 Pd	2.47	2.18	2.28 ±0.10	1, 3, 4, 9	7.35	2.84	4
47 Ag	2.46	2.44	2.36 ±0.12	1, 3, 4, 6	−0.32	2.29	4
48 Cd	2.30	2.28	2.23 ±0.04	4, 5	2.10	2.33 ±0.11	4, 11
49 In	2.48	2.43	2.37 ±0.16	4, 9	1.60	2.24	4
50 Sn(g)	1.51	1.51	—	—	—	—	—
50 Sn(w)	2.27	2.22	2.00 ±0.14	3–5, 12	1.85	1.93 ±0.08	4, 11
51 Sb	(0.84)^a	0.84	0.92	3, 5	1.80	—	—
52 Te	0.93	0.93	—	—	1.45	—	—
55 Cs	1.49	1.44	1.44 ±0.16	1, 2	1.14	—	—
56 Ba	0.88	0.85	—	—	0.35	—	—
57 La	0.74	0.66	0.32	10	1.47	—	—
58 Ce(α)	—	—	—	—	0.96	—	—
58 Ce(γ)	0.51	0.47	0.50	10	−6.27	—	—
59 Pr	0.64	0.49	0.37	10	0.60	—	—
60 Nd	0.82	0.74	0.52	10	1.06	—	—
61 Pm	(0.81)^a	(0.72)^a	—	—	—	—	—
62 Sm	0.71	0.63	—	—	1.00	—	—
63 Eu	(1.69)^a	1.64	2.26	10	0.36	—	—

TABLE XXIV. GRÜNEISEN CONSTANT—*Continued*

Element	γ Calculated from C_v data (γ_G)				γ Calculated from compressibility data (γ_S)	γ Calculated from shock wave data	
	(This paper)						
	C_v^l	C_v	(Literature)	Ref.		γ_{SW}	Ref.
64 Gd	(0.57)[a]	0.52	0.55	10	1.62	—	—
65 Tb	0.91	0.83	0.61	10	—	—	—
66 Dy	0.87	0.78	0.68	10	1.35	—	—
67 Ho	1.24	0.89	0.80	10	1.35	—	—
68 Er	1.17	1.01	0.88	10	1.33	—	—
69 Tm	1.38	1.08	0.94	10	1.47	—	—
70 Yb	1.02	0.98	0.95	10	0.98	—	—
71 Lu	0.75	0.66	1.15	10	1.45	—	—
72 Hf	1.07	1.04	—	—	0.34	—	—
73 Ta	1.82	1.69	1.70 ±0.06	1–4, 9	0.32	0.31	4
74 W	1.78	1.76	1.68 ±0.06	1, 3	−1.64	1.54	8
75 Re	2.66	2.59	—	—	—	—	—
76 Os	(2.02)[a]	(2.02)[a]	—	—	—	—	—
77 Ir	2.49	2.39	—	—	4.58	—	—
78 Pt	2.92	2.69	2.56 ±0.12	1, 3, 4, 9	0.05	1.81	4
79 Au	3.09	3.06	3.04 ±0.04	1–4, 6	1.84	2.22	4
80 Hg	3.00	2.93	—	—	—	—	—
81 Tl	2.27	2.19	2.73	5	1.51	2.13	4
82 Pb	2.84	2.74	2.62 ±0.27	1, 3, 4	1.12	2.38 ±0.35	4, 7, 11
83 Bi	1.05	1.05	1.13 ±0.01	3, 5	1.96	—	—
84 Po	(1.62)[a]	(1.61)[a]	—	—	—	—	—
87 Fr	(1.65)[a]	(1.57)[a]	—	—	—	—	—
88 Ra	(1.21)[a]	(1.17)[a]	—	—	—	—	—
89 Ac	(1.03)[a]	(0.92)[a]	—	—	—	—	—
90 Th	1.41	1.34	1.21 ±0.09	3, 4	2.37	1.76	4
91 Pa	(0.96)[a]	(0.89)[a]	—	—	—	—	—
92 U	2.07	1.82	—	—	4.03	—	—
93 Np	(3.00)[a]	(2.67)[a]	—	—	—	—	—
94 Pu	6.76	3.51	—	—	2.98	—	—

[a] Estimated value; see text for further discussion.

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seen, especially for the elements in the fourth, fifth, and sixth periods. The value for the alkali metals, which is close to the mean for all the metals, decreases as one moves along the period, with a minimum occurring at about the group IIIA elements. The value then gradually rises to a maximum at about the group IB metals, with a few minor oscillations between the group IIIA and IB metals. From the maximum at group IB, γ_G decreases almost steadily until the end of the row is reached.

The Grüneisen constants for the rare earths are shown in Fig. 33a, and it is seen that γ_G increases with increasing atomic number. The values for γ_G scatter considerably about the straight line drawn through the points.

The Grüneisen constant, γ_G, as calculated from the total heat capacity at constant volume, C_v, is always equal to, or less than, that calculated from $C_v{}^l$. The mean value of γ_G (from C_v) is 1.50 ±0.78. The error ±0.78 corresponds to a percentage error of ±52.0%. Comparing these calculated γ_G values with the literature values we find that 33 out of 51 of these values agree with one another within ±10%. Most of the differences between the other 18 sets of values can be explained on the basis of revised thermal expansion and compressibility data. Such differences are to be expected, since many of the γ_G literature values are based on data over 30 years old. Thus, the agreement between literature values and those calculated herein seem to be reasonably good.

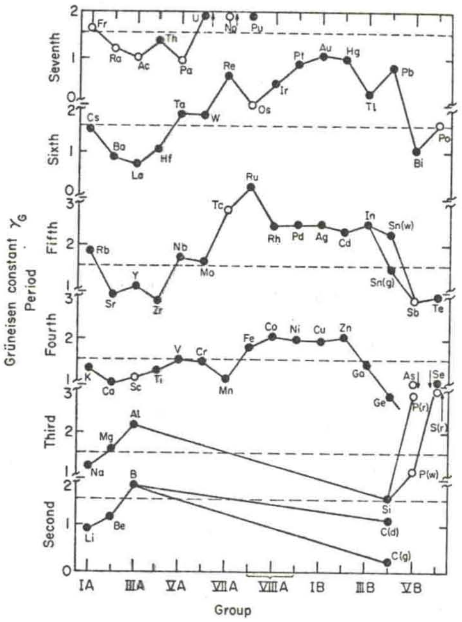
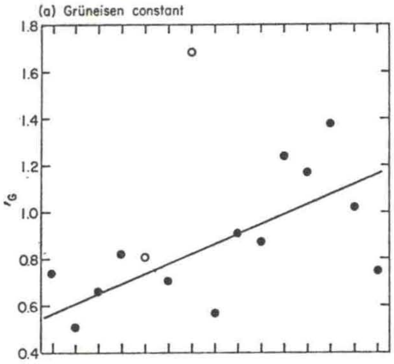


FIG. 32. Grüneisen constant, γ_G, as calculated from $C_v{}^l$, of all of the elements considered in this review with the exception of the rare-earth metals. The horizontal dashed line represents the mean values. Open points are estimated data.

Grüneisen Constant γ_S. A comparison of γ_G (from $C_v{}^l$) and γ_S was made, thus extending analysis of Slater[17] and of Gilvarry[117] to all of the elements for which experimental data exist. Arbitrarily the following criteria were used in assessing the data: (1) if γ_S lies within ±25% of γ_G, then the agreement was considered to be very good; if γ_S lies between ±25 and ±50% of γ_G, then the agreement was considered to be good; (3) if γ_S lies between ±50 and ±80%, the agreement was considered fair; and (4) if it was more than ±80%, the agreement was considered to be poor. This scale is about the same as Gilvarry used.[117] It was found that for 18 elements the agreement was very good (B, Na, Al, K, Ca, Fe, Zn, Sr, Y, Nb, Cd, Sn(w), Cs, Pr, Ho, Er, Tm, and Yb); for 11 elements the agreement was good (Mg, V, Cr, Ni, Cu, Se, In, Nd, Sm, Au, and Tl); for 11 elements the agreement was fair (Li, Ti, Mo, Rh, Te, Ba, Dy, Hf, Pb, Th, and Pu); and for 20 elements the agreement was

(a) Grüneisen constant



(b) Size factor

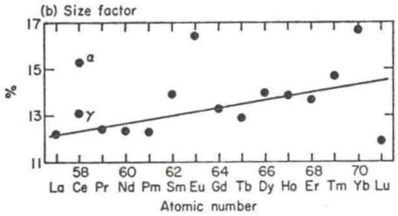


FIG. 33. (a) Grüneisen constant, γ_G, as calculated from $C_v{}^l$, of the rare-earth metals. (b) Size factor of the rare-earth metals. Open points are estimated data.

poor (Be, C(g), Si, Mn, Co, Ge, Rb, Zr, Ru, Pd, Ag, La, Ce(γ), Lu, Ta, W, Ir, Pt, Bi, and U). Of the elements which are included in the "poor" category, the compressibility data for 8 of the metals (Ru, Pd, Ag, γ-Ce, W, Ir, Pt, and U) was suspected of being incorrect (see Section 24). The compressibility data of Mn and Rb had been questioned by Gilvarry,[117] and this may explain the poor agreement for these two elements. If these elements are excluded from the above analysis, then we would have 18 very good, 11 good, 11 fair, and 10 poor. Thus it would appear that one finds reasonable agreement between γ_G and γ_S, as had been proposed by Slater.

The mean value for γ_S was found to be 1.64 ± 0.91, if the value for the elements Ru, Ag, γ-Ce, Pd, and W are excluded from the average. The error ± 0.91 corresponds to the percentage error of ± 55.5, which is slightly poorer than that for γ_G.

Grüneisen Constant γ_{SW}. The Grüneisen constant as determined from shock wave data, γ_{SW}, was also compared with γ_G. It was found that γ_{SW} was smaller than γ_G for 17 elements and greater for 9 elements (almost 2 to 1). By using the same criteria as given above, it was found that very good agreement was obtained for 22 elements (Be, Na, Mg, Ti, V, Co, Ni, Cu, Zn, Zr, Nb, Mo, Rh, Pd, Ag, Cd In, Sn(w), W, Tl, Pb, and Th); good agreement for 3 elements (Cr, Pt, and Au); and poor agreement only for tantalum. This indicates that $\gamma_G = \gamma_{SW}$ is a very good approximation.

Since the agreement between γ_G and γ_{SW} is good for Be, Co, and Zr (3 of the 10 remaining elements for which γ_S is in poor agreement with γ_G), this places a higher degree of confidence on γ_G for these 3 elements and therefore suggests that γ_S may be unreliable because of inaccuracy in the compressibility data, especially in the b (pressure-dependence) term.

It is interesting to find that $\gamma_{SW} \simeq \gamma_S$ for tantalum and that both of these values are very much smaller than γ_G. Perhaps the value for γ_G is incorrect, although this seems unlikely since the values of α, V, χ, and C_v are reasonably well established.

The mean value for γ_{SW} is 1.76, which is somewhat larger than the mean value of γ_G, 1.57. Since it was mentioned above that γ_{SW} is usually smaller than γ_G, the reverse relationship between the means is somewhat surprising. However, if one takes the average for the same elements for which γ_G, γ_S, and γ_{SW} are all known (Be, Mg, Al, Ti, V, Cr, Co, Ni, Cu, Zn, Zr, Nb, Mo, Rh, Cd, In, Sn(w), Ta, Pt, Au, Tl, Pb, and Th), we find the mean values to be 1.98, 1.67, and 1.76, respectively.

Gschneidner and Vineyard[4] have used the Grüneisen constant to predict departures from Vegard's law (which states that the lattice constants of binary alloys vary linearly between the two end-menbers). They found that their method, based on second-order elasticity, described the sign and order of magnitude of departures from Vegard's law in binary alloy systems better than did previous techniques given in the literature.

Estimated Data. In calculating γ_G from $C_v{}^l$ and C_v, there are a few elements for which the coefficient of expansion, the compressibility, or the heat capacity at constant volume ($C_v{}^l$ and C_v) were not known experimentally. If any one of these quantities was estimated, then γ_G was considered to be estimated also.

29. SIZE FACTOR

Eshelby's Approach. Eshelby[118] has pointed out in his review paper on the continuum theory of lattice defects that it is possible to derive

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[118] J. D. Eshelby, *Solid State Phys.* **3**, 79 (1956).

Hume-Rothery's 15% size rule for the solid solubility of metallic phases.[119,120] Hume-Rothery's empirical size rule states that if two substances differ in size by more than ±15%, very limited solid solubility is to be expected; but if they differ by less than 15%, then solid solubility is expected *if other factors* are favorable.[119,120] Waber *et al.*[5] have shown, considering only the size factor, that for 619 binary alloy systems where the size difference is greater than ±15%, 90% of these systems exhibited very limited solid solubilities, and for 804 systems where the size difference is less than ±15%, only 50% of these systems exhibited extensive solid solutions. This is a very striking confirmation of Hume-Rothery's size rule, proposed almost 30 years ago.

Eshelby noted that the size factor, S.F., is given by

$$\text{S.F.} = \left[\left(\frac{RT_m}{\mu V}\right)\left(\frac{1-\sigma}{1+\sigma}\right)\right]^{\frac{1}{2}}, \qquad (29.1)$$

where R is the gas constant, T_m is the melting point, μ is the shear modulus, V is the atomic volume, and σ is Poisson's ratio. It should be noted that the term $RT_m/\mu V$ is the Leibfried number, L, which was discussed in Section 26. Since $L \simeq 0.030$ and $(1-\sigma)/(1+\sigma) \simeq 0.5$ (Section 23), we find S.F. $\simeq 0.13$ or 13%. Eshelby explained that if the size difference, $|r_A - r_B/r_A| = \epsilon$, is smaller than the size factor calculated for the solvent, A, no solid miscibility gap is expected; but if ϵ is greater than the size factor, then the formation of two phases, i.e., limited solid solubility, is expected.

As mentioned in Section 26, it was thought that the modified Leibfried number, L', was more accurate than L, and accordingly L' was used in calculating the size factor. Furthermore, it was mentioned in Section 26 that $L' \simeq \mathcal{B}$, where $\mathcal{B}$ is the Bragg number, and therefore a second set of size factors was calculated by using $\mathcal{B}$ instead of L'. The size factors calculated from L' and $\mathcal{B}$ (Table XXII) and the term $(1-\sigma)/(1+\sigma)$ (Table XX) are listed in Table XXV. From these two, L' and $\mathcal{B}$, a size factor, called the "best value," was chosen, which is also given in Table XXV. This best value is thought to represent the best size factor for a given element as calculated by Eshelby's method.

Friedel's Approach. Friedel independently suggested another method for determining the size factor for each element.[121] He gave the following expression:

$$\text{S.F.} = \left[\frac{RT_m\chi}{\pi r^3 N}\right]^{\frac{1}{2}} = \left[\frac{4RT_m\chi}{3V}\right]^{\frac{1}{2}}, \qquad (29.2)$$

where χ is the compressibility and r is the atomic radius. Since it has been shown that Richard's rule is a poor approximation, the constant K was substituted for R in Eq. (29.2) (see Section 27). The value of the constant K depends on the crystal structure of the element just prior to melting. The size factor determined in this manner is also shown in Table XXV, under the column heading "Calculated from Friedel's approach."

Discussion. The values determined from the two approaches were then averaged (except for a few elements) to give the final value, which is believed to best represent the size factor for a given element. If the size factors differed by more than ±6.00 from one another, the two values were not averaged but the lower value of the two was chosen to be the representative value for that particular element. This lower value was chosen for graphite, diamond, white and red phosphorus, manganese, selenium, and thallium. Since there was only one value for black phosphorus, it necessarily was used.

The mean value for the size factor based on L' is 12.97 ±2.49; based on $\mathcal{B}$ it is 12.71 ±2.58; based on the best value from Eshelby's approach it is 12.50 ±2.48; and based on Friedel's approach it is 13.92 ±3.63. The mean value of the final best representative values is 12.88 ±2.73. The error for the final best representative value ±2.73 corresponds to a percentage error of ±21.2, which is quite good. The final best representative value varies from a minimum of 7.81 for gallium to a maximum of 50.56 for graphite. These values for the elements are shown in Fig. 34. The dependence on the location of the element in the Periodic Table is again evident. The large values for the alkali and alkaline-earth metals decrease slowly as one moves across each period, reach a minimum near iron and its cogeners, increase to a maximum at the group IB elements, decrease to a minimum near the group IIB elements, and finally attain a maximum near the group VB elements.

The size factors for the rare earths show a steady increase with increasing atomic number (Fig. 33b). The large values for europium and ytterbium correspond to the large values of the alkaline-earth metals; again this shows the divalent nature of these two rare-earth metals.[13] The value for α-Ce is included for comparative purposes; this value, because of its higher valence, would not necessarily be expected to lie on the same curve with the other rare earths.

Preliminary results from an extension of the study of the prediction of solid solubility in metallic alloys[5] indicated that a slight improvement could be gained by using the individual size factors from Eshelby's approach

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[119] W. Hume-Rothery, G. W. Mabbott, and K. M. Channel-Evans, *Phil. Trans. Roy. Soc. London* **A223**, 1 (1934).

[120] W. Hume-Rothery, "Structure of Metals and Alloys," 1st ed. (1939); and W. Hume-Rothery and G. V. Raynor, *ibid.*, 3rd ed. Inst. Metals, London, 1954.

[121] J. Friedel, *Advan. Phys.* **3**, 504 (1954).

TABLE XXV. SIZE FACTOR[a]

Element	Calculated from Eshelby's approach: From modified Leibfried No.	Calculated from Eshelby's approach: From Bragg No.	Calculated from Eshelby's approach: Best value	Calculated from Friedel's approach	Mean or chosen value[b]
3 Li	16.91[a]	15.48[a]	15.48[a]	17.25[a]	16.37 ±0.89[a]
4 Be	12.34	13.50	13.50	17.70	15.60 ±2.10
5 B	13.97	(14.51)[c]	13.97	18.78	16.38 ±2.41
6 C(g)	107.0	181.4	181.4	50.56	50.56[d]
6 C(d)	22.49	21.00	21.00	28.34	21.00[d]
11 Na	13.24	12.46	12.46	15.02	13.74 ±1.28
12 Mg	14.41	13.94	13.94	15.52	14.73 ±0.79
13 Al	12.97	13.65	13.65	12.94	13.30 ±0.36
14 Si	19.28	19.55	19.55	22.63	21.09 ±1.54
15 P(w)	(23.08)[c]	(10.90)[c]	(10.90)[c]	23.17	10.90[d]
15 P(r)	(19.52)[c]	—	(19.52)[c]	11.79	11.79[d]
15 P(b)	—	—	—	10.02	10.02[d]
16 S(r)	11.98	7.61	7.61	12.59[e]	10.10 ±2.49
19 K	14.36	13.43	13.43	15.15	14.29 ±0.86
20 Ca	15.01	14.90	14.90	16.61	15.76 ±0.86
21 Sc	(12.81)[c]	(13.32)[c]	(13.32)[c]	(14.39)[c]	13.86 ±0.52
22 Ti	12.17	(11.76)[c]	12.17	12.32	12.25 ±0.08
23 V	13.98	(13.49)[c]	13.98	12.60	13.29 ±0.69
24 Cr	11.10	10.26	10.26	12.41	11.34 ±1.08
25 Mn	11.06	12.22	12.22	18.48	12.22[d]
26 Fe	11.43	11.85	11.85	12.21	12.03 ±0.18
27 Co	12.93	11.90	11.90	13.35	12.63 ±0.73
28 Ni	13.50	13.40	13.40	13.48	13.44 ±0.04
29 Cu	14.15	13.65	13.65	13.73	13.69 ±0.04
30 Zn	10.42	10.57	10.57	12.78	11.68 ±1.11
31 Ga	5.93	8.56	8.56	7.06	7.81 ±0.75
32 Ge	18.80	17.89	17.89	20.40	19.15 ±1.26
33 As	(25.36)[c]	(26.12)[c]	(26.12)[c]	25.16	25.64 ±0.48
34 Se	(12.36)[c]	(8.42)[c]	(8.42)[c]	31.31	8.42[d]
37 Rb	(13.98)[c]	(13.63)[c]	(13.63)[c]	13.21	13.42 ±0.21
38 Sr	(15.27)[c]	(16.08)[c]	(16.08)[c]	16.19	16.41 ±0.33
39 Y	12.30	11.11	11.11	15.52	13.32 ±2.21
40 Zr	12.73	(12.29)[c]	12.73	13.40	13.07 ±0.34
41 Nb	15.51	(14.97)[c]	15.51	9.58	12.55 ±2.97
42 Mo	10.29	11.37	11.37	10.55	10.96 ±0.41
43 Tc	(10.28)[c]	(9.73)[c]	(9.73)[c]	(11.10)[c]	10.42 ±0.69
44 Ru	10.26	(9.71)[c]	10.26	11.22	10.74 ±0.48
45 Rh	10.11	(9.57)[c]	10.11	11.35	10.73 ±0.62
46 Pd	13.33	12.70	12.70	12.13	12.42 ±0.29
47 Ag	13.69	13.05	13.05	12.43	12.74 ±0.31
48 Cd	9.95	9.98	9.98	11.25	10.62 ±0.64
49 In	16.23	13.89	13.89	9.28	11.59 ±2.31
50 Sn(g)	12.15	8.49	8.49	8.95	8.72 ±0.23
50 Sn(w)	7.98	10.08	10.08	7.96	9.02 ±1.06
51 Sb	17.12	16.40	16.40	19.69	18.05 ±1.65
52 Te	16.11	16.19	16.19	21.42	18.81 ±2.62
55 Cs	(15.40)[c]	(14.51)[c]	(14.51)[c]	14.57	14.54 ±0.03
56 Ba	14.93	14.71	14.71	15.85	15.28 ±0.57
57 La	12.06	9.78	9.78	14.67	12.23 ±2.45
58 Ce(α)	20.52	16.05	16.05	14.60	15.33 ±0.73
58 Ce(γ)	13.89	10.87	10.87	15.38	13.13 ±2.26
59 Pr	13.01	11.07	11.07	13.69	12.38 ±1.31
60 Nd	13.07	10.89	10.89	13.80	12.35 ±1.46
61 Pm	(12.71)[c]	(11.26)[c]	(11.26)[c]	(13.42)[c]	12.34 ±2.54
62 Sm	13.75	12.38	12.38	15.50	13.94 ±1.56
63 Eu	(16.28)[c]	(16.77)[c]	(16.77)[c]	15.95	16.36 ±0.41

Table XXV. Size Factor[a]—*Continued*

Element	Calculated from Eshelby's approach: From modified Leibfried No.	Calculated from Eshelby's approach: From Bragg No.	Calculated from Eshelby's approach: Best value	Calculated from Friedel's approach	Mean or chosen value[b]
64 Gd	12.48	12.26	12.26	14.31	13.29 ±1.03
65 Tb	12.67	11.33	11.33	14.47	12.90 ±1.57
66 Dy	12.53	(11.10)[c]	12.53	15.08	13.96 ±1.43
67 Ho	12.35	12.55	12.55	15.17	13.86 ±1.31
68 Er	12.15	(10.76)[c]	12.15	15.19	13.67 ±1.52
69 Tm	(12.30)[c]	(13.63)[c]	(13.63)[c]	15.79	14.71 ±1.08
70 Yb	16.18	15.21	15.21	18.12	16.67 ±1.46
71 Lu	(12.14)[c]	(10.75)[c]	(10.75)[c]	13.13	11.94 ±1.19
72 Hf	11.82	(11.40)[c]	11.82	12.95	12.39 ±0.57
73 Ta	12.54	(12.10)[c]	12.54	12.21	12.38 ±0.17
74 W	10.17	11.23	11.23	10.81	11.02 ±0.21
75 Re	10.74	(10.32)[c]	10.74	11.61	11.18 ±0.44
76 Os	(10.03)[c]	(9.63)[c]	(9.64)[c]	(11.01)[c]	10.32 ±0.69
77 Ir	9.30	(8.94)[c]	9.30	10.77	10.04 ±0.74
78 Pt	12.67	12.21	12.21	10.22	11.22 ±1.00
79 Au	13.64	12.89	12.89	9.88	11.39 ±1.51
80 Hg	8.03	8.43	8.43	8.07	8.25 ±0.18
81 Tl	18.27	17.69	17.69	9.59	9.59[d]
82 Pb	15.17	13.28	13.28	9.95	11.62 ±1.67
83 Bi	14.99	13.69	13.69	15.58	14.64 ±0.95
84 Po	(9.98)[c]	(9.09)[c]	(9.09)[c]	(9.81)[c]	9.45 ±0.36
87 Fr	(15.22)[c]	(14.69)[c]	(14.69)[c]	(14.31)[c]	14.50 ±0.19
88 Ra	(12.88)[c]	(12.34)[c]	(12.34)[c]	(13.68)[c]	13.01 ±0.67
89 Ac	(15.57)[c]	(14.97)[c]	(14.97)[c]	(17.59)[c]	16.28 ±1.31
90 Th	12.30	(11.87)[c]	12.30	13.64	12.97 ±0.67
91 Pa	(11.61)[c]	(10.58)[c]	(10.58)[c]	(12.88)[c]	11.73 ±1.15
92 U	8.07	(7.79)[c]	8.07	10.33	9.20 ±1.13
93 Np	(8.76)[c]	(8.45)[c]	(8.45)[c]	(10.03)[c]	9.24 ±0.79
94 Pu	9.73	6.09	6.09	11.81	8.95 ±2.86

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[a] All values given in percent.

[b] Mean or chosen value determined from "Best value, Eshelby's approach" and from "Friedel's approach" (columns 4 and 5, respectively). Most values are means; chosen values are indicated.

[c] Estimated value; see text for further discussion.

[d] Chosen value; see text for further discussion.

[e] Using the larger value for the compressibility of sulfur, the size factor is 16.02%. See discussion concerning the choice of compressibility value.

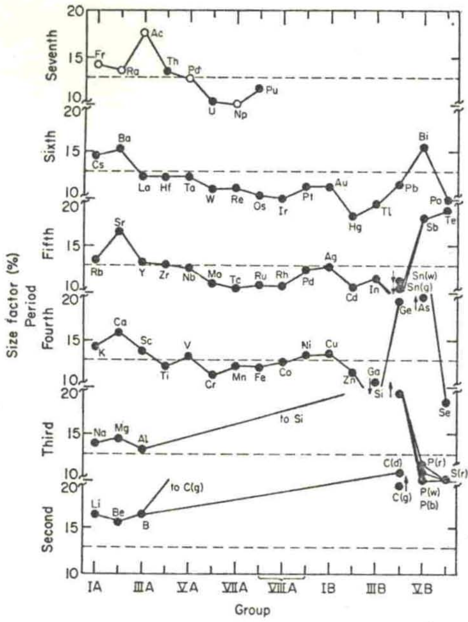

FIG. 34. Size factor (final best representative value) of all of the elements considered in this review with the exception of the rare-earth metals. The horizontal dashed line represents the mean value. Open points are estimated data.

rather than the 15% criterion of Hume-Rothery for all of the metals. In the near future we plan to analyze the same data by using the final best representative value of the size factor.

Estimated Data. The data shown in Table XXV are considered to be estimated if one or more of the quantities (shear modulus, Poisson's ratio, compressibility, atomic volume, melting point, and heat of fusion) were estimated.

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Author Index

Numbers in parentheses are reference numders and indicate that an author's work is referred to although his name is not cited in the text. Numbers in italics show the page on which the complete reference is listed.

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Physical Properties and Interrelationships of Metallic and Semimetallic Elements*

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I. Introduction

For a number of years the author and his co-workers have been interested in alloying theory. Initially we were concerned with the rare earths[1] and the actinide elements,[2,3] but more recently we extended our range of interest to include most of the metallic and semimetallic elements of the Periodic Table.[4,5] Soon after we had become involved in this enlarged field, it became apparent that no extensive listing of many of the physical properties and some of the derived properties of the elements, such as the Grüneisen constant, could be found in the commonly available handbooks or reference books. Although some books and review articles contained selected values for a few of these properties of many of the metals, there were still a small number of elements for which data were not available. Furthermore, a number of values listed in the handbooks were found to be outdated and needed to be replaced by more recent data. For these reasons we found it necessary to make our own compilation of data to facilitate furthering our study of the alloying behavior of the elements. It was then felt that these data would not only be of interest to us but also to other scientists actively engaged in the studies of solids; therefore, these values are being presented in the hope that they will be useful to a large segment of research workers.

1. General Description of the Tables of Physical Properties

The physical properties given in this compilation are listed in the accompanying tabulation according to the table in which they can be found. Values for two quantities that have frequently been used in alloying-theory studies, viz., the metallic radius and electronegativity, are not included here. Such data have been compiled and published fairly recently.[6] Other properties, such as magnetic susceptibility, electrical resistivity, and thermal conductivity, which are generally of interest to those studying solids, are not included in this compilation primarily because such properties do not appear to be important in alloying theory.

Table number	Table title
I	Young's (Elastic) Modulus
II	Shear Modulus
III	Poisson's Ratio
IV	Isothermal Compressibility
V	Compressibility at Zero Pressure and the Bulk Modulus
VI	Linear Coefficient of Thermal Expansion
VII	Atomic Volume
VIII	Primary and Secondary Fixed Points of the International Practical Temperature Scale
IX	Melting Point
X	Heat of Fusion
XI	Boiling Point at 1 Atmosphere
XII	Cohesive Energy and Heat of Sublimation at 298°K
XIII	Electronic Specific Heat Constant
XIV	Heat Capacity at Constant Pressure and at Constant Volume and the Dilation Term
XV	Debye Temperatures Obtained from Specific Heat Data and from the Lindemann Equation
XVI	Debye Temperatures Obtained from Specific Heat Data and from Elastic Constants
XVII	Debye Temperatures Obtained from Electrical Resistivity, Thermal Expansion, and X-Ray Intensity Data
XVIII	Comparison of Debye Temperatures

The values of the properties given in the tables, unless otherwise noted, are for the common modifications of the elements existing at 298°K (25°C). Specifically, these are the following: the crystalline forms of boron, carbon (see below), sulfur (see below), arsenic ($A7$)[6a], selenium ($A8$),[6a] and tellurium ($A8$)[6a]; the hexagonal closest-packed ($A3$)[6a] forms of beryllium, scandium, titanium, cobalt, yttrium, zirconium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, lutetium, hafnium, and thallium; the face-centered cubic ($A1$)[6a] forms of calcium, strontium,

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[1] K. A. Gschneidner, Jr. and J. T. Waber, *in* "The Rare Earths" (F. H. Spedding and A. H. Daane, eds.), p. 386. Wiley, New York, 1961.

[2] J. T. Waber, *in* "Extractive and Physical Metallurgy of Plutonium and Its Alloys" (W. H. Wilkinson, ed.), p. 111. Wiley (Interscience), New York, 1960.

[3] J. T. Waber and K. A. Gschneidner, Jr., *in* "Plutonium 1960" (E. Grison, W. B. H. Lord, and R. D. Fowler, eds.), p. 109. Cleaver-Hume, London, 1961.

[4] K. A. Gschneidner, Jr. and G. H. Vineyard, *J. Appl. Phys.* **33,** 3444 (1962).

[5] J. T. Waber, K. A. Gschneidner, Jr., A. C. Larson, and M. Y. Prince, *Trans. AIME* **227,** 717 (1963).

[6] E. Teatum, K. Gschneidner, Jr., and J. Waber, *U.S. At. Energy Comm.* Rept. LA-2345 (June, 1960).

[6a] *Strukturbericht* notation.

cerium (see below), ytterbium, and thorium; the complex crystal-structure forms designated as α-Mn, α-U, α-Np, and α-Pu; the body-centered cubic $(A2)^{6a}$ form of iron (α-Fe); the hexagonal (with a double *c*-axis) form of lanthanum, praseodymium, and neodymium; the rhombohedral form of mercury and samarium; and the simple cubic form of polonium. The remaining elements, except phosphorus and tin (see below), are known to have only one crystalline modification. The data for mercury are for the solid at its melting point of 234°K (−39°C) instead of 298°K. Some of the properties, such as the melting point, heat of fusion, boiling point, etc., obviously do not pertain to this temperature, or to the allotrope which exists at 298°K.

For five of the elements, viz., carbon, phosphorus, sulfur, tin, and cerium, data are given for more than one allotrope. In the tables, the following nomenclature is used to identify the various allotropes of these five elements: C(g) refers to graphite, which is the standard reference state at 298°K; C(d) refers to diamond; P(w) refers to white phosphorus; P(r) refers to red phosphorus, which is the standard reference state at 298°K; P(b) refers to black phosphorus; S(r) refers to orthorhombic sulfur, commonly called "rhombic" sulfur, which is the standard reference state at 298°K; S(m) refers to monoclinic sulfur; Sn(w) refers to white or metallic tin, which is the standard reference state at 298°K; Sn(g) refers to gray or diamond tin; Ce(α) refers to the collapsed face-centered cubic form of cerium, which exists below 116°K at 1 atm, or above 7470 atm at 298°K; and Ce(γ) refers to the normal face-centered cubic form of cerium, which is the standard reference state at 298°K.

A list of references is given for each table, so one does not have to thumb back and forth to find the source of information. In some instances where no experimental data exist, an estimated value is given. The estimated value is always given in parentheses, and the manner in which the value was derived is discussed in the text.

2. GENERAL DESCRIPTION OF THE DERIVED PROPERTIES

The derived properties and some interrelationships of the physical properties are examined and discussed in Part IX of this chapter. Those subjects which also appear in tabulated form are listed in the accompanying tabulation.

Table number	Table title
XIX	Ratio of Young's Modulus to the Shear Modulus
XX	Ratio of $(1 - \sigma)/(1 + \sigma)$ (where σ is Poisson's ratio)
XXI	Ratio of the Compressibility Constants, b/a^2
XXII	Leibfried, Modified Leibfried, and Bragg Numbers
XXIII	Entropies of Fusion and Vaporization
XXIV	Grüneisen Constant
XXV	Size Factor

The initial goal in our alloy-theory program was a set of Grüneisen constants[4] and a set of size factors.[7] In order to calculate these quantities, almost all of the physical properties given herein are needed in the computations. Some of the other derived quantities are not only intermediate steps in the computations of the Grüneisen constant and size factor, but also serve as checks on the consistency of initial data (i.e., the measured physical properties of the elements). Furthermore, some of the "constants" of the elements—i.e., the Grüneisen constant, entropy of fusion, etc., which have been derived for a few elements and then generally assumed to apply to all elements—are examined to see if this generalization is valid. No attempt is made to discuss these properties in detail, since most of them are discussed in textbooks and in many instances in detailed review papers recently published.

II. Elastic Properties

The four elastic properties listed here, Young's (elastic) modulus, the shear modulus, Poisson's ratio, and the compressibility, are for bulk, polycrystalline materials. At the time of writing, single-crystal elastic constants were available for about half of the elements considered herein. It is because of this sparsity of data that single-crystal values are not included in this review. Hearmon[8,9] and Huntington[10] have included in their review papers extensive listings of elastic constants derived from single crystals. Almost all of the more recent single-crystal data (since 1957–1958) have generally been published in either the *Physical Review* or the *Journal of Applied Physics*.

In a few instances where reliable polycrystalline data are lacking but single-crystal data are available, the reviewer has used the method of Voigt[11] to calculate the four elastic properties from the single-crystal data Values so obtained are identified as such in the tables.

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[7] J. T. Waber, A. C. Larson, and K. A. Gschneidner, Jr., to be published (1965).

[8] R. F. S. Hearmon, *Rev. Mod. Phys.* **18,** 409 (1946).

[9] R. F. S. Hearmon, *Advan. Phys.* **5,** 323 (1956).

[10] H. B. Huntington, *Solid State Phys.* **7,** 213 (1958).

[11] W. Voigt, "Lehrbuch der Kristalphysik," Teubner, Leipzig, 1928; also see Huntington,[10] p. 317.

For an isotropic medium the four elastic properties are related to one another by the following equations:

$$Y = 2\mu(1 + \sigma) \tag{II.1}$$

and

$$\frac{1}{\chi} = B = \frac{Y}{3(1 - 2\sigma)} \tag{II.2}$$

where Y is Young's modulus, μ is the shear modulus, σ is Poisson's ratio, χ is the compressibility, and B is the bulk modulus. The compressibility and the bulk modulus are considered to be one elastic property, since one is the reciprocal of the other. It is seen from Eqs. (II.1) and (II.2) that if two of the elastic properties are known, the other two may be calculated; i.e., any one of the four elastic properties may be expressed in terms of two of the remaining three. The twelve possible equations have been summarized by Köster and Franz[12] and therefore are not repeated here.

In general the values listed for each of the four elastic properties were obtained experimentally. In a few instances when an experimental value was not available, and when values of two of the other elastic properties were given, the values for the other two properties were calculated. This procedure is valid if the two experimental values pertain to the same material; if, however, they pertain to different samples, then the above procedure may not be valid. Values calculated from data taken from different samples are identified by footnotes in the tables. Fortunately, this procedure led to consistent results for all but selenium (this is discussed in Section 5).

3. Young's Modulus

Values for Young's modulus, also known as the elastic modulus, are listed in Table I, and are shown in Fig. 1 for the elements of the fourth, fifth, and sixth periods of the Periodic Table. It should be noted that Young's modulus varies between 0.0361×10^6 kg/cm^2 for potassium to 11.5×10^6 kg/cm^2 for diamond. Estimated values, however, would indicate that the lower limit is probably 0.017×10^6 for francium. The magnitude of Young's modulus appears to be dependent on the electronic configuration of the element, i.e., the group in which it lies. The maximum value encountered in a given period is associated with the elements having the maximum number of unpaired d electrons. As will be noted, this behavior is observed in a number of other physical properties. The anomalous behaviors of manganese, iron, cobalt, and nickel (Fig. 1), as compared with those of their cogeners of the fifth and sixth periods, are also evident

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[12] W. Köster and H. Franz, *Met. Rev.* **6**, 1 (1961).

TABLE I. YOUNG'S (ELASTIC) MODULUS

Element	$Y \times 10^{-6}$ (kg/cm^2)	Ref.
3 Li	0.117[a,b]	1
4 Be	3.04 ±0.12	2, 3, 4
5 B	4.50	5
6 C(g)	0.0849 ±0.0025	6
6 C(d)	11.5 ±1.3[b]	7
11 Na	0.0912[b,c]	1
12 Mg	0.452	3
13 Al	0.724	3, 8, 9
14 Si	1.05 ±0.10	10, 11
15 P(w)	(0.047)[d]	—
15 P(r)	(0.194)[d]	—
15 P(b)	(0.307)[d]	—
16 S(r)	0.198[b]	7
19 K	0.0361[b,c]	1
20 Ca	0.200	3
21 Sc	0.809	12
22 Ti	1.08 ±0.4	3, 4, 13
23 V	1.34 ±0.05	4, 14
24 Cr	2.48 ±0.04	15
25 Mn	2.02	3
26 Fe	2.14 ±0.03	3, 16, 17
27 Co	2.10 ±0.02	3, 17
28 Ni	1.97	17
29 Cu	1.26 ±0.06	3, 9, 16
30 Zn	0.940	3
31 Ga	0.944[b,e]	18
32 Ge	1.01	19
33 As	(0.398)[d]	—
34 Se	0.591[f]	20
37 Rb	(0.0277)[d]	—
38 Sr	(0.139)[d]	—
39 Y	0.661 ±0.015	21, 22
40 Zr	0.939 ±0.004	4, 23, 24
41 Nb	1.07 ±0.01	4, 25, 26
42 Mo	3.34 ±0.10	3, 16, 27, 28
43 Tc	(3.76)[d]	—
44 Ru	4.20 ±0.02	20, 29
45 Rh	3.80 ±0.06	3, 16
46 Pd	1.26 ±0.02	3, 16
47 Ag	0.822 ±0.010	3, 16, 30
48 Cd	0.635	3
49 In	0.107	3
50 Sn(g)	0.534	31
50 Sn(w)	0.550	3
51 Sb	0.560	3
52 Te	0.42	32

TABLE I. YOUNG'S (ELASTIC) MODULUS—*Continued*

Element	$Y \times 10^{-6}$ (kg/cm^2)	Ref.
55 Cs	(0.0179)[d]	—
56 Ba	0.129	3
57 La	0.387 ±0.005	3, 21
58 Ce(α)	0.196[g]	33
58 Ce(γ)	0.306	21
59 Pr	0.332	21
60 Nd	0.387	21
61 Pm	(0.43)[d]	—
62 Sm	0.348	21
63 Eu	(0.155)[d]	—
64 Gd	0.573	21
65 Tb	0.586	21
66 Dy	0.644	21
67 Ho	0.684	21
68 Er	0.748	21
69 Tm	(0.77)[d]	—
70 Yb	0.182	21
71 Lu	(0.86)[d]	—
72 Hf	1.40 ±0.01	34, 35
73 Ta	1.85 ±0.07	3, 16, 25
74 W	4.05 ±0.10	3, 16, 24, 36, 37
75 Re	4.7 ±0.2	38
76 Os	(5.50)[d]	—
77 Ir	5.38	3, 16
78 Pt	1.74	3, 16
79 Au	0.794 ±0.008	3, 9, 16, 39
80 Hg	0.279[a,b]	7
81 Tl	0.081	3
82 Pb	0.160	3
83 Bi	0.348	3
84 Po	(0.26)[d]	—
87 Fr	(0.017)[d]	—
88 Ra	(0.16)[d]	—
89 Ac	(0.35)[d]	—
90 Th	0.76 ±0.04	3, 4, 40
91 Pa	(1.02)[d]	—
92 U	1.90 ±0.10	4, 41
93 Np	1.02	42
94 Pu	0.984	43

[a] Value obtained at 83°K.

[b] Single-crystal data.

[c] Value obtained at 90°K.

[d] Estimated value; see text for further discussion.

[e] Value obtained at 273°K.

[f] See text for further discussion.

[g] Extrapolated from high-pressure data of Voronov *et al.*[33] to zero pressure.

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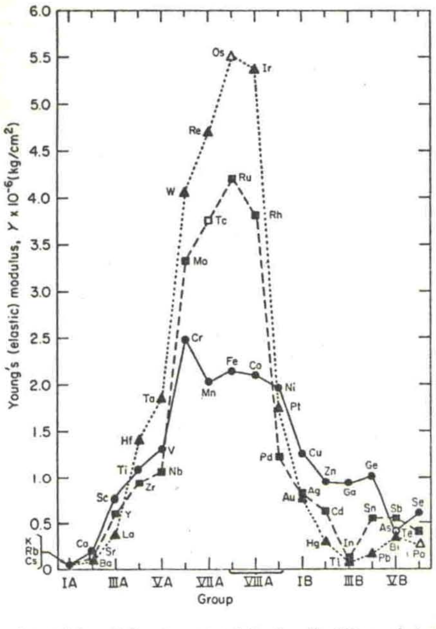

FIG. 1. Young's modulus of the elements of the fourth, fifth, and sixth periods of the Periodic Table. Open points are estimated values.

in many of their physical properties and in their alloying behaviors. Although the values for the elements in the second and third periods are not shown in Fig. 1, Young's modulus increases as one proceeds from lithium to beryllium to boron (or sodium to magnesium to aluminum) and decreases on going from silicon to sulfur, in a manner similar to that shown for the corresponding elements of the fourth, fifth, and sixth periods.

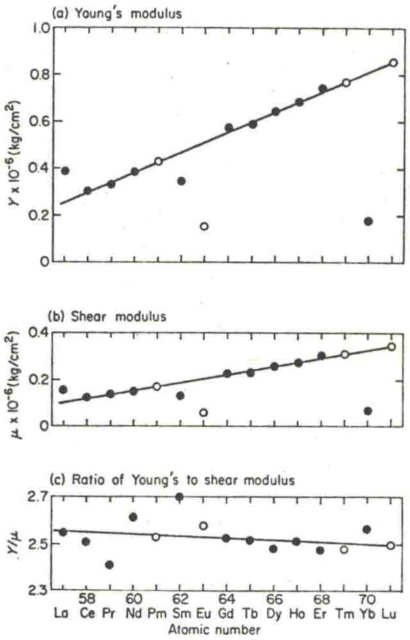

FIG. 2. (a) Young's modulus of the rare-earth metals. (b) Shear modulus of the rare-earth metals. (c) The ratio of Young's modulus to the shear modulus of the rare-earth metals. Open points are estimated values.

The variation of Young's modulus for the rare earths lanthanum (atomic number 57) through lutetium (atomic number 71) is shown in Fig. 2a. The points for lanthanum, samarium, and ytterbium were ignored in drawing the straight line. The value for ytterbium is low because that element is divalent in the metallic state while the other rare earths are normally trivalent in the metallic state; but there seems to be no simple explanation for the lesser deviations of the values for lanthanum and samarium.

Selenium. Although the value listed here for Young's modulus for selenium appears to be reasonable when compared with the data shown in Fig. 1, if one uses it and the bulk modulus given in Table V, which also appears to be reasonable, to calculate Poisson's ratio, a negative value for Poisson's ratio is obtained. This indicates that one or both values are probably incorrect. If the relationships between the four elastic properties are valid, then in order to make the data compatible, assuming that all of the discrepancy does *not* lie in the bulk modulus, the correct Young's modulus value for selenium must be less than 0.591×10^6 kg/cm², the value given in Table I.

Estimated Data. As will be shown later in Section 22 and in Table XIX, the ratio of Young's modulus to the shear modulus, Y/μ, is very nearly a constant and therefore may be quite reliably estimated for elements for which this ratio is unknown. This ratio and the value for the bulk modulus (experimental or estimated value) may be used to calculate the estimated value of Young's modulus by means of the following equation:

$$Y = [9 - 3(Y/\mu)]B, \tag{3.1}$$

which is obtained by simple algebra from Eqs. (II.1) and (II.2). The bulk modulus was used in the calculations since it has been determined experimentally for more elements than any of the other elastic properties. Furthermore, because of this reason it was felt that unknown values of the bulk modulus could be better estimated from the periodic relationships of the elements (see Section 6). The estimated values of Young's modulus for white, red, and black phosphorus, arsenic, rubidium, strontium, and cesium were calculated by using the experimental value of the bulk modulus (Table V) and the estimated value of Y/μ (Table XIX); and for technetium, osmium, polonium, francium, radium, actinium, and protactinium by using the estimated values of both the bulk modulus and Y/μ. The estimated values of Young's modulus for promethium, thulium, and lutetium were estimated from the plot shown in Fig. 2a. The value for europium was estimated to be equal to the mean value for barium and ytterbium, since europium is also known to be divalent in the metallic state[13]; thus these three elements are respectively the initial, end, and middle members of the divalent $4f$ series.[13]

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[13] Europium and ytterbium have been considered to be divalent because most of their physical properties, such as the atomic volumes, metallic radii, melting and boiling points, heats of sublimation, compressibilities, and coefficients of expansion are more like those of the alkaline-earth metals, calcium, strontium, and barium, than those of the rare-earth metals. This is confirmed by magnetic data, which indicate that europium has a $4f^7$ configuration and ytterbium a $4f^{14}$ configuration; in both instances this leaves only two electrons remaining beyond the xenon core, and presumably they are in the $6s^2$ state. Thus, since barium has a $4f^0 6s^2$ configuration, these three elements are the first (barium), mid (europium), and end (ytterbium) members of the divalent $4f$ transition series. Values for most of the above-mentioned properties are given in the following sections; those which are not may be found in K. A. Gschneidner, Jr., "Rare Earth Alloys," pp. 3–66. Van Nostrand, Princeton, New Jersey, 1961.

4. SHEAR MODULUS

The shear modulus is also known as the torsion modulus and modulus of rigidity. The values of the shear moduli are listed in Table II, and are shown in Fig. 3 for the elements of the fourth, fifth, and sixth periods of the Periodic Table. The shear modulus varies between 0.13×10^6 kg/cm² for potassium and 4.6×10^6 kg/cm² for diamond. The estimated value for francium, however, indicates that the lower limit should be extended to 0.0063×10^6 kg/cm². The shear modulus, like Young's modulus, has a marked dependence on the electronic configuration of the element (Fig. 3). The similar shape of Figs. 1 and 3 is not surprising since $Y \simeq 2.6\mu$ (see Section 22 and Table XIX). The maximum value of the shear modulus encountered in a given period is associated with the elements having the maximum number of unpaired d electrons. The minimum near the end of each period occurs for the elements that have an s^2p^1 configuration. The anomalous behavior of the fourth-period elements as compared with those in the fifth and sixth periods is again evident. The behavior of the elements in the second and third periods is similar to that of their cogeners in the fourth through sixth period; e.g., the shear modulus increases as one proceeds from the alkali metals to the alkaline-earth metals to the group IIIA elements.

The variation in the shear modulus for the rare earths is shown in Fig. 2b. The point for ytterbium was ignored in drawing the straight line. The value for ytterbium is low because ytterbium is divalent.[13]

Boron, Selenium, Ruthenium, and Rhenium. No experimental values of the shear modulus exist for boron, selenium, ruthenium, and rhenium. However, from the experimental values of the bulk modulus (Table V) and Young's modulus (Table I) it was possible to calculate the shear modulus. For boron, ruthenium, and rhenium reasonable values were obtained for both the shear modulus and Poisson's ratio. For selenium, on the other hand, a negative value was obtained for Poisson's ratio, indicating that the calculated value for the shear modulus is probably incorrect. Therefore, the value for selenium given here was estimated (see below).

Estimated Data. From an estimated value of the ratio of Young's modulus to the shear modulus (see Section 22 and Table XIX) and the known values of Young's modulus, the estimated shear modulus was calculated for scandium, selenium, and neptunium. Since Young's modulus for selenium is probably too large (see Section 3), the estimated shear modulus is probably too large also. The estimated shear moduli for white, red, and black phosphorus, arsenic, rubidium, strontium, technetium, cesium, osmium, polonium, francium, radium, actinium, and protactinium are based both on estimated values of Young's modulus and on the ratio Y/μ.

TABLE II. SHEAR MODULUS

TABLE II. SHEAR MODULUS—*Continued*

Element	$\mu \times 10^{-6}$ (kg/cm^2)	Ref.
3 Li	0.0431[a,b]	1
4 Be	1.46 ±0.04	2, 3
5 B	2.07[c]	—
6 C(g)	0.0332 ±0.0006	4
6 C(d)	4.6 ±1.0[b]	5
11 Na	0.035[b,d]	1
12 Mg	0.177	6
13 Al	0.271 ±0.001	7, 8, 9
14 Si	0.405	6
15 P(w)	(0.018)[e]	—
15 P(r)	(0.073)[e]	—
15 P(b)	(0.115)[e]	—
16 S(r)	0.0737[b]	5
19 K	0.013[b,d]	1
20 Ca	0.075	6
21 Sc	(0.319)[e]	—
22 Ti	0.401 ±0.005	2, 10
23 V	0.474 ±0.001	2, 11
24 Cr	1.19[b]	12
25 Mn	0.78	6
26 Fe	0.831 ±0.006	8, 13
27 Co	0.779	13
28 Ni	0.765	13
29 Cu	0.460 ±0.015	7, 8, 14
30 Zn	0.379	6
31 Ga	0.382[b,f]	15
32 Ge	0.40	6
33 As	(0.149)[e]	—
34 Se	(0.221)[e]	—
37 Rb	(0.0102)[e]	—
38 Sr	(0.0533)[e]	—
39 Y	0.263 ±0.004	16, 17
40 Zr	0.348 ±0.008	2, 18, 19
41 Nb	0.382 ±0.001	2, 20
42 Mo	1.18	21
43 Tc	(1.45)[e]	—
44 Ru	1.63[c]	—
45 Rh	1.50 ±0.03	6, 14
46 Pd	0.521	7
47 Ag	0.292 ±0.007	7, 14, 22
48 Cd	0.246	6
49 In	0.038	6
50 Sn(g)	0.188	23
50 Sn(w)	0.208	6
51 Sb	0.204	24
52 Te	0.157	24
55 Cs	(0.0066)[e]	—
56 Ba	0.050	6
57 La	0.152	17
58 Ce(α)	0.085[g]	25
58 Ce(γ)	0.122	17
59 Pr	0.138	17
60 Nd	0.148	17
61 Pm	(0.17)[e]	—
62 Sm	0.129	17
63 Eu	(0.060)[e]	—
64 Gd	0.227	17
65 Tb	0.233	17
66 Dy	0.259	17
67 Ho	0.272	17
68 Er	0.302	17
69 Tm	(0.31)[e]	—
70 Yb	0.071	17
71 Lu	(0.345)[e]	—
72 Hf	0.540	6
73 Ta	0.700	6
74 W	1.56 ±0.04	14, 19, 26, 27
75 Re	1.82[c]	—
76 Os	(2.14)[e]	—
77 Ir	2.14	6, 14
78 Pt	0.622	7
79 Au	0.281 ±0.003	7, 8, 14
80 Hg	0.102[a,b]	5
81 Tl	0.028	6
82 Pb	0.055	28
83 Bi	0.131	6
84 Po	(0.097)[e]	—
87 Fr	(0.0063)[e]	—
88 Ra	(0.061)[e]	—
89 Ac	(0.138)[e]	—
90 Th	0.284 ±0.002	2, 29
91 Pa	(0.398)[e]	—
92 U	0.75 ±0.04	2, 30
93 Np	(0.406)[e]	—
94 Pu	0.446	31

[a] Value obtained at 83°K.

[b] Single-crystal data.

[c] Calculated from Young's modulus and the bulk modulus.

[d] Value obtained at 90°K.

[e] Estimated value; see text for further discussion.

[f] Value obtained at 273°K.

[g] Extrapolated from high-pressure data of Voronov *et al.*[25] to zero pressure.

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The estimated shear moduli for promethium, thulium, and lutetium were estimated from the straight line shown in Fig. 2b. The estimated value for europium was assumed to be equal to the mean value of barium and ytterbium, because europium is the mid-member of the divalent 4*f* series and barium and ytterbium are, respectively, the first and last members of this series.[13]

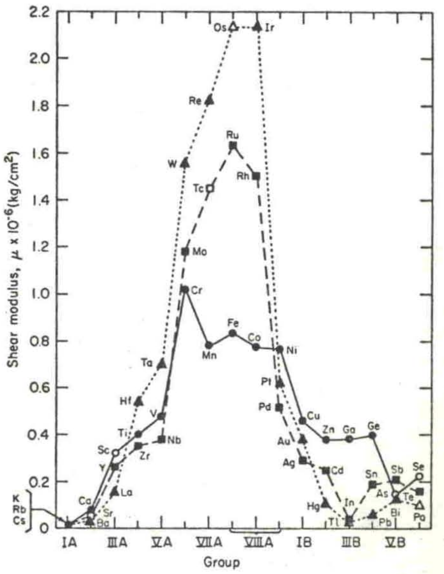

FIG. 3. Shear modulus of the elements of the fourth, fifth, and sixth periods of the Periodic Table. Open points are estimated values.

5. Poisson's Ratio

The values of Poisson's ratio are listed in Table III, and are shown in Fig. 4 for all the elements. Köster and Franz[12] recently reviewed this subject quite thoroughly.

The minimum and maximum values for Poisson's ratio are zero and 0.5. It was noted more than a century ago that Poisson's ratio is approximately a constant for most materials; the standard textbooks usually give a value of $\frac{1}{3}$ for this constant. Examination of Table III shows that the minimum value experimentally determined is 0.039 for beryllium and the maximum is 0.46 for indium and thallium. The estimated values all lie within this range. The mean value of Poisson's ratio for the 64 experimental values is 0.301 ±0.079. The standard deviation is equivalent to

TABLE III. POISSON'S RATIO

Element	σ	Ref.
3 Li	0.362^{a,b}	1
4 Be	0.039 ±0.011	2, 3
5 B	0.089^{c}	—
6 C(g)	0.27 ±0.06	4
6 C(d)	0.18 ±0.08^{b}	5
11 Na	0.315^{b,d}	1
12 Mg	0.28	6
13 Al	0.34 ±0.01	7, 8, 9
14 Si	0.44	6
15 P(w, r, b)	(0.335)^{e}	—
16 S(r)	0.343^{b}	5
19 K	0.35^{b,d}	1
20 Ca	0.31	6
21 Sc	(0.269)^{e}	—
22 Ti	0.345 ±0.005	2, 10
23 V	0.36	2
24 Cr	0.209^{b}	11
25 Mn	0.24	6
26 Fe	0.279 ±0.013	7, 9, 12, 13
27 Co	0.334	13
28 Ni	0.30 ±0.01	12, 13
29 Cu	0.345 ±0.005	7, 9
30 Zn	0.29	14
31 Ga	0.235^{b,f}	15
32 Ge	0.27	6
33 As	(0.335)^{e}	—
34 Se	(0.338)^{e}	—
37 Rb	(0.356)^{e}	—
38 Sr	(0.304)^{e}	—
39 Y	0.258 ±0.008	16, 17
40 Zr	0.34	2, 18
41 Nb	0.35 ±0.03	2, 19
42 Mo	0.30	9
43 Tc	(0.293)^{e}	—
44 Ru	0.286^{c}	—
45 Rh	0.27	9
46 Pd	0.375 ±0.015	9, 12
47 Ag	0.37	9, 12
48 Cd	0.30	12
49 In	0.46	6
50 Sn(g)	0.42	20
50 Sn(w)	0.33	12
51 Sb	0.31 ±0.06^{g}	—
52 Te	0.33	21
55 Cs	(0.356)^{e}	—
56 Ba	0.28	6

TABLE III. POISSON'S RATIO—*Continued*

Element	σ	Ref.
57 La	0.288	17
58 Ce(α)	0.14^{h}	22
58 Ce(γ)	0.248	17
59 Pr	0.305	17
60 Nd	0.306	17
61 Pm	(0.278)^{e}	—
62 Sm	0.352	17
63 Eu	(0.286)^{e}	—
64 Gd	0.259	17
65 Tb	0.261	17
66 Dy	0.243	17
67 Ho	0.255	17
68 Er	0.238	17
69 Tm	(0.235)^{e}	—
70 Yb	0.284	17
71 Lu	(0.233)^{e}	—
72 Hf	0.30	6
73 Ta	0.35	9
74 W	0.284 ±0.004	9, 23, 24, 25
75 Re	0.293^{c}	—
76 Os	(0.285)^{e}	—
77 Ir	0.26	9
78 Pt	0.38 ±0.01	9, 12
79 Au	0.425 ±0.010	7, 9, 12
80 Hg	0.364^{a,b}	5
81 Tl	0.46	6
82 Pb	0.44	12
83 Bi	0.33	12
84 Po	(0.338)^{e}	—
87 Fr	(0.356)^{e}	—
88 Ra	(0.304)^{e}	—
89 Ac	(0.269)^{e}	—
90 Th	0.285 ±0.015	2, 26
91 Pa	(0.282)^{e}	—
92 U	0.245 ±0.005	2, 27
93 NP	(0.255)^{e}	—
94 Pu	0.15	28

[a] Value obtained at 83°K.

[b] Single-crystal data.

[c] Calculated from Young's modulus and bulk modulus.

[d] Value obtained at 90°K.

[e] Estimated value; see text for further discussion.

[f] Value obtained at 273°K.

[g] Calculated from the three moduli; see text for further details.

[h] Extrapolated from high-pressure data of Voronov *et al.*[22] to zero pressure.

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an error of ±26.2% from the mean. The mean value for the 19 estimated values is 0.300, which indicates that if the estimated values were included, the over-all mean value for Poisson's ratio would not change. These data suggest that it might be more accurate to use $\frac{3}{10}$ for the mean value of Poisson's ratio for the metals rather than $\frac{1}{3}$.

Examination of Fig. 4 shows that the value of Poisson's ratio for a given element depends on the element's position in the Periodic Table. For example, the values of Poisson's ratio exceed the mean value for the alkali metals; for the group IVA, VA, VB, and VIB elements; for nickel, palladium, and platinum; and for the noble metals. For the group IIIA, VIA, and VIIA metals, and iron, ruthenium, and osmium, Poisson's ratio is less than the mean; and for the alkaline-earth metals and group IIB metals it is approximately equal to the mean.

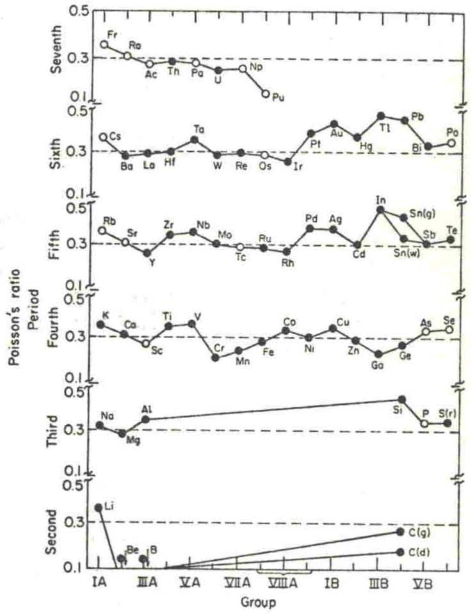

FIG. 4. Poisson's ratio of all of the elements considered in this review with the exception of the rare-earth metals. Open points are estimated values. The horizontal dashed line represents the mean value for these elements.

The variation of Poisson's ratio for the rare earths is shown in Fig. 5a. The point for ytterbium was ignored in drawing the straight line through the solid points. The data show considerably more scatter here than the corresponding plots of Young's modulus or the shear modulus (Figs. 2a and 2b, respectively) for these metals. The scatter may be emphasized by the expanded scale in Fig. 5a. However, the ratio Y/μ (Fig. 2c), which is

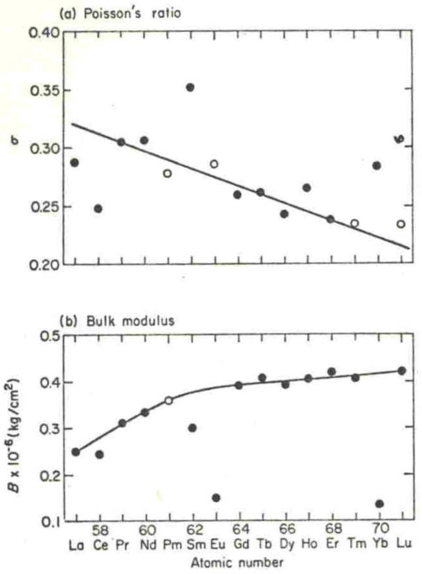

FIG. 5. (a) Poisson's ratio of the rare-earth metals. (b) Bulk modulus of the rare-earth metals. Open points are estimated values.

directly related to Poisson's ratio, also shows more scatter than does either Young's modulus or the shear modulus.

Boron, Ruthenium, and Rhenium. Since no experimental value exists for Poisson's ratio for boron, ruthenium, and rhenium, this ratio was calculated from the experimental values of Young's and the bulk moduli. The values so obtained appear to be reasonable.

Antimony. No experimental value exists for Poisson's ratio for antimony, but from the experimental values of Young's, the shear, and the bulk moduli three different values for Poisson's ratio were calculated. By using Young's and the shear moduli, a value of 0.371 was obtained; by using Young's and the bulk moduli, 0.284 was obtained; and by using the shear and the bulk moduli, 0.277 was obtained. A mean value of 0.31 ±0.06 was thus chosen to represent Poisson's ratio for antimony. This situation clearly illustrates the difficulties involved when the elastic properties are not measured on the same sample.

Selenium. Since Poisson's ratio has not been experimentally determined for selenium, an attempt was made to calculate it by using the experimental values of Young's modulus and the bulk modulus and Eq. (II.2), which gave a value of -0.562. This negative value indicates that possibly Young's modulus or the bulk modulus or both are in error. This situation, and that as noted with antimony, clearly shows that elastic properties should be measured on the same specimen if one uses these data to calculate the remaining one or two elastic properties. The value for selenium given herein has been estimated (see below).

Estimated Data. As noted earlier, the ratio of Young's modulus to the shear modulus, Y/μ (see Section 22 and Table XIX), is nearly a constant for all materials, the mean value being 2.60. By simple algebra Eq. (II.1) can be rewritten as

$$Y/\mu = 2(1 + \sigma). \tag{5.1}$$

This indicates that Poisson's ratio, σ, and the ratio Y/μ are essentially the same quantity. However, since the data for most of the values of Poisson's ratio, Young's modulus, and the shear modulus have been measured independently and directly, the value of the ratio Y/μ gives us an independent check on the measured value of Poisson's ratio. Thus the estimated values of Poisson's ratio given in Table III are the average values obtained by estimating both Poisson's ratio (see below) and the ratio Y/μ (see Section 22).

It was mentioned above that the value of Poisson's ratio is dependent on the atomic structure (Fig. 4). Thus, instead of assuming a value of 0.301 for those elements for which Poisson's ratio is unknown, an average value for each group was assumed to be a better estimate. The mean value of Poisson's ratio of antimony and bismuth was assumed for phosphorus and arsenic; the mean value of yttrium and lanthanum, for scandium and actinium; the mean of rhombohedral sulfur and tellurium, for selenium and polonium; the mean of lithium, sodium, and potassium, for rubidium, cesium, and francium; the mean of calcium and barium, for strontium and radium; the mean of molybdenum and ruthenium, for technetium; the mean of barium and ytterbium, for europium[13]; the mean of ruthenium and iron, for osmium; the mean of thorium and uranium, for protactinium; and the value of neptunium was assumed to be identical with that of uranium. The values of the rare earths, promethium, thulium, and lutetium, were estimated from the straight line shown in Fig. 5a. Since these latter three values were averaged with the σ values calculated from the estimated Y/μ values (Eq. (5.1)) to give the "best" estimated value, the open points for promethium, thulium, and lutetium do not lie on the straight line shown in Fig. 5a.

6. Compressibility (Bulk Modulus)

The compressibility, which is the reciprocal of the bulk modulus, has been measured more extensively than has any other elastic property. Over 90% of the values listed in Tables IV and V are based on the extensive work of Bridgman. Bridgman's data were carried to quite high pressures (especially for his day), which were sufficient to determine the pressure dependence of the compressibility. Bridgman's early work was conveniently summarized as analytical fits of the experimental data, usually of the form

$$\Delta V/V = aP + bP^2 \tag{6.1}$$

where $\Delta V/V$ is the compression for a given pressure P (in kg/cm^2), and a and b are constants fitted to the experimental data. The isothermal compressibility at zero pressure is given by a, and the pressure dependence of the compressibility is given by b. Bridgman's later data, however, were not fitted to an expression such as Eq. (6.1); instead, the $\Delta V/V$ values were tabulated for a number of convenient pressures.

All of the data given by Bridgman are relative to the compressibility of iron, which he measured absolutely. In the late 1930's and early 1940's he redetermined the compressibility of iron[14–16] and found that the older values were incorrect, especially the value of the b term in Eq. (6.1). Unfortunately, considerable confusion has arisen regarding the redetermination, and therefore an attempt will be made here to clarify the situation.

In 1940 Bridgman[14] published a paper in which he noted that the absolute compressibility of iron previously used was incorrect. He expressed the revised data for iron in terms of $\Delta l/l$ rather than $\Delta V/V$:

$$\Delta l/l = -1.942 \times 10^{-7}\,P + 0.23 \times 10^{-12}\,P^2. \tag{6.2}$$

Slater,[17] who had derived an expression for the Grüneisen constant (see Section 28) based only on the a and b constants of Eq. (6.1), needed to know the revised values of a and b. Therefore, from the data given by Bridgman,[14] Slater[17] found that

$$-a_{\text{new}} = -a_{\text{old}} + 0.04 \times 10^{-7}, \tag{6.3a}$$

and

$$b_{\text{new}} = b_{\text{old}} - 1.30 \times 10^{-12}. \tag{6.3b}$$

In 1946 Bridgman[15] reviewed the recent developments in the high-pressure field. Therein, he gave the revised compressibility for iron as

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[14] P. W. Bridgman, *Phys. Rev.* **57**, 235 (1940).

[15] P. W. Bridgman, *Rev. Mod. Phys.* **18**, 23 (1946).

[16] P. W. Bridgman, "Physics of High Pressure," pp. 416–417. Bell, London, 1949.

[17] J. C. Slater, *Phys. Rev.* **57**, 744 (1940).

$$\Delta V/V = -5.826 \times 10^{-7}\,P + 0.80 \times 10^{-12}\,P^2, \tag{6.4}$$

and furthermore he pointed out that the data published prior to 1940 must be corrected by using the following relations:

$$-a_{\text{new}} = -a_{\text{old}} + 0.033 \times 10^{-7}, \tag{6.5a}$$

and

$$b_{\text{new}} = b_{\text{old}} - 1.56 \times 10^{-12} - (0.022 \times 10^{-7})\,a_{\text{old}}. \tag{6.5b}$$

A comparison of Eqs. (6.3a) and (6.3b) with Eqs. (6.5a) and (6.5b) reveals that the value suggested by Slater for correcting the a parameter is almost the same as that given by Bridgman, but that the corrections for the b parameter are quite different. Since Bridgman's and Slater's corrections are based on the same measurements, it is difficult to see why this discrepancy arose. Neither Bridgman's articles[14,15] nor his book[16] give further clues which might shed some light on this discrepancy. Perhaps Bridgman found another error in his measurements before 1940 which he did not discuss. In any event, since only Bridgman had intimate knowledge of his experimental techniques, it is felt that his values for correcting a_{old} and b_{old} are probably correct. Fortunately, almost all of the data Bridgman obtained for the pure elements prior to 1940 were redetermined. The only exceptions are boron, red phosphorus, vanadium, chromium, nickel, and hafnium. For these six elements Eqs. (6.5a) and (6.5b) were used to convert a_{old} and b_{old} into a_{new} and b_{new}.

It is also unfortunate that Bridgman's book,[18] which was reprinted in 1949, contains a tabulation of the *old* a and b values for a large number of elements, but no remark was made to warn the reader that they, especially the b values, are incorrect. Examination of the literature indicates that most authors are not aware of this.

For the above reasons and because almost all the compressibility data published by Bridgman after 1940 are available only in tabular form, and not as analytical fits,[19] all of Bridgman's data for the elements have been reduced to an equation of the form

$$\Delta V/V = aP + bP^2 + cP^2 + \cdots \tag{6.6}$$

by the method of least squares. In most instances only the first two terms of Eq. (6.6) were necessary to obtain a satisfactory fit. The elements which required more than two terms to fit the experimental data are,

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[18] P. W. Bridgman, "Physics of High Pressure." Bell, London, 1949.

[19] J. J. Gilvarry fitted Bridgman's data for Li, Na, Al, K, Mn, Rb, Mo, Cs, Ta, and Au to an equation of the form of Eq. 6.6. In some instances more terms containing powers higher than P^3 were required (*J. Chem. Phys.* **23**, 1925 (1955)).

TABLE IV. ISOTHERMAL COMPRESSIBILITY

Element	$\Delta V/V_0 = aP + bP^2 + cP^3$				Pressure range $P \times 10^3$ (kg/cm^2)	Ref.
	$-a \times 10^7$	$b \times 10^{12}$	$-c \times 10^{15}$	$\sigma \times 10^4$		
3 Li	84.83	158.0	2.936[a]	—	0–40	1
4 Be	9.772	3.921	—	0.99	0–40	2
5 B	5.48[b]	0.64[b]	—	—	0–12	3
6 C(g)	29.01	30.50	—	1.36	0–25	4
6 C(d)	1.80	—	—	—	0–30	5
11 Na	141.9	373.4	7.390[c]	—	0–40	1
11 Na	145.9[d]	381[d]	5.1[d]	—	0–20	6
12 Mg	27.68	13.82	—	0.56	0–30	7
13 Al	13.59	4.864	—	0.27	0–30	8
14 Si	9.924	2.442	—	0.23	0–30	8
15 P(w)	209	—	—	—	0–0.5	9
15 P(r)	51.13[b]	100.4[b]	—	1.86	0–12	10
15 P(b)	32.23	25.66	—	4.42	0–40	11
16 S(r?)[e]	100.8[e]	204.9[e]	1.64[e]	11.34	0–50	12
16 S(r)	55.0[f]	—	—	—	—	13
19 K	308.7	1870	71.40[g]	—	0–40	1
20 Ca	64.51	74.36	0.46	6.62	0–40	14
Sc 22 Ti	9.328	2.358	—	1.85	0–30	8
23 V	6.057[b]	1.02[b]	—	—	0–12	10
24 Cr	5.154[b]	0.63[b]	—	—	0–12	10
25 Mn	16.44	8.125	—	15.97	0–100	11
26 Fe	5.826	0.798	—	2.69	0–30	8, 15, 16
27 Co	5.122	0.473	—	0.22	0–30	8
28 Ni	5.26[b,e]	0.54[b,e]	—	—	0–12	17
29 Cu	7.490	2.018	—	0.08	0–30	8, 18
30 Zn	16.39	7.575	—	0.76	0–30	8
31 Ga	17.2[f,h]	—	—	—	—	19
32 Ge	12.70	3.588	—	0.22	0–30	8
33 As	24.89	28.11	—	0.90	0–25	4
34 Se	107.8	193.9	1.38	4.01	0–50	12
Br 37 Rb	311.9	1524	39.87[i]	—	0–40	1
38 Sr	84.48	111.2	—	18.74	0–25	14
39 Y	26.79	14.22	—	7.60	0–40	5
40 Zr	11.77	4.484	—	2.10	0–40	2
41 Nb	5.761[e]	0.886[e]	—	0.19	0–30	8
42 Mo	3.598	0.158	—	0.10	0–30	8
Tc 44 Ru	3.057	−0.821	—	0.16	0–30	8
45 Rh	3.626	0.180	—	0.07	0–30	8
46 Pd	5.423[e]	2.358[e]	—	0.15	0–15	8
47 Ag	9.740	0.330	—	0.50	0–30	8
48 Cd	20.98	12.20	—	1.13	0–25	4, 20
49 In	23.87[e]	12.90[e]	—	1.01	0–50	12
50 Sn(g)	8.83	—	—	—	—	21
50 Sn(w)	18.10	8.259	—	0.46	0–30	8
51 Sb	25.62	16.19	—	1.21	0–30	8
52 Te	42.60	38.38	—	2.91	0–30	8
I 55 Cs	483.3	4226	221.1[j]	—	0–20	1
56 Ba	95.2	92.4	—	0	0–17	14
57 La	40.37	34.88	—	1.86	0–23.4	2
58 Ce(α)	[e, k]	[e, k]	—	76.0	7.72–100	2, 11
58 Ce(γ)	40.97[e]	−94.00[e]	4.53[e]	0.98	0–7.72	2
59 Pr	32.08	13.03	—	38.15	0–40	2
60 Nd	30.02	15.60	—	5.22	0–40	2
Pm 62 Sm	33.36	18.57	—	6.54	0–40	22
63 Eu	66.63	45.76	—	15.85	0–12.4	23
64 Gd	25.59	14.98	—	0.85	0–40	24
65 Tb	24.6	—	—	—	—	25
66 Dy	25.52	13.14	—	3.50	0–40	22

TABLE IV. ISOTHERMAL COMPRESSIBILITY—*Continued*

	Element	$\Delta V/V_0 = aP + bP^2 + cP^3$ $-a \times 10^7$	$b \times 10^{12}$	$-c \times 10^{15}$	$\sigma \times 10^4$	Pressure range $P \times 10^3$ (kg/cm²)	Ref.
	67 Ho	24.72	12.35	—	4.30	0–40	22
	68 Er	23.88	11.37	—	2.62	0–40	22
	69 Tm	24.71	13.03	—	3.88	0–40	22
	70 Yb	73.93	60.66	—	12.44	0–40	22
	71 Lu	23.85	12.03	—	1.62	0–40	22
	72 Hf	8.98[b]	0.81[b]	—	—	0–12	26
	73 Ta	4.89[e]	0.235[e]		0.06	0–30	8
	74 W	3.034	−0.0897	—	0.17	0–30	8
Os	75 Re	2.64	—	—	—	0–30	5
	77 Ir	2.76[l]	0.4[l]	—	0	0–10	8
	78 Pt	3.523	0.0893	—	0.09	0–30	8
	79 Au	5.664	0.805	—	0.07	0–30	8
	80 Hg[m]	34.7[m]	—	—	—	—	27
	81 Tl	27.30	16.20	—	0.79	0–25	4, 20
	82 Pb	22.82	9.319	—	0.18	0–30	5
Po	83 Bi	31.16	25.55	—	2.44	0–20	12, 20
	90 Th	18.07	9.906	—	3.12	0–30	8
	92 U	9.926	4.626	—	0.73	0–40	2
	94 Pu	18.3	12.2	—	—	0–40	28

[a] The remaining terms of this fit are: $d = 1.12 \times 10^{-20}$, $e = 1.00 \times 10^{-24}$, and $f = -1.48 \times 10^{-29}$; see Gilvarry[1] and Ref. 29.

[b] The original data as given in the reference cited was corrected as suggested by Bridgman.[15,30]

[c] The remaining terms of this fit are: $d = 1.21 \times 10^{-21}$, $e = 5.56 \times 10^{-24}$, $f = -1.54 \times 10^{-28}$, and $g = 1.38 \times 10^{-33}$; see Gilvarry[1] and Ref. 29.

[d] Swenson (private communication, 1963) noted an error in the press calibration and thus the values given in Beecroft and Swenson[6] are incorrect. The correct values are listed here.

[e] See text for further discussion.

[f] Single-crystal data.

[g] The remaining terms of this fit are: $d = 2.34 \times 10^{-20}$, $e = 7.99 \times 10^{-23}$, $f = -2.02 \times 10^{-28}$, $g = -1.24 \times 10^{-31}$, $h = 3.55 \times 10^{-36}$, and $i = -3.03 \times 10^{-41}$; see Gilvarry[1] and Ref. 29.

[h] Value obtained at 273°K.

[i] The remaining terms of this fit are: $d = 7.57 \times 10^{-21}$, $e = -2.81 \times 10^{-24}$, $f = 1.64 \times 10^{-27}$, $g = -5.42 \times 10^{-32}$, and $h = 5.20 \times 10^{-37}$; see Gilvarry[1] and Ref. 29.

[j] The remaining term of this fit is: $d = 4.38 \times 10^{-18}$; see Gilvarry[1] and Ref. 29.

[k] The analytical expression for α-Ce is $\Delta V/V = -0.1706 - 37.4 \times 10^{-7} (P - P_0) + 22.8 \times 10^{-12} (P - P_0)^2$, where $P_0 = 7720$ kg/cm², over the range 7720 to 100,000 kg/cm².

[l] At higher pressures compressibility increases with increasing pressure, for the range 0 to 30,000 kg/cm², $a = -2.721 \times 10^{-7}$, $b = -0.0259 \times 10^{-12}$ and $\sigma = 0.07$.

[m] Solid mercury.

References to Table IV

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28. P. W. Bridgman, *J. Appl. Phys.* **30,** 214 (1959).
29. Only the first two constants were listed in Gilvarry[1]; the remainder were graciously furnished by J. J. Gilvarry. Further details concerning these fits are given in footnote 8, p. 1926 of Gilvarry.[1]
30. P. W. Bridgman, "Physics of High Pressure," pp. 416–417. Bell, London, 1949.

in general, the more compressible ones. The standard deviation of a fit was taken as an indication of its accuracy. That is, if the two-parameter fit had a lower standard deviation than the three-parameter fit, the two-parameter fit was chosen to represent the data. The fits for the alkali metals were kindly furnished by Dr. J. J. Gilvarry of General Dynamics/Astronautics.

The compressibility constants, the standard deviation of the fit, the pressure range, and references are given in Table IV. Slater[17] has pointed out that the ratio of b/a^2 is approximately equal to 2.5 for most substances, and thus it would appear possible to estimate the b term for those substances for which only a is known. This point is discussed later in Section 24. The relationship of the compressibility constants to the Grüneisen constant is discussed in Section 28. Furthermore, Slater[17] suggested that if the ratio of b/a^2 differed considerably from 2.5, then the compressibility data might be erroneous. By applying Slater's criterion to these data, it is found that one should be suspicious of the values given for arsenic, ruthenium, palladium, silver, γ-cerium, tungsten, iridium, platinum, and uranium. (This point is discussed in more detail in Section 24.) Furthermore, from an analysis of the Grüneisen constant, it was noted that the a and b values for beryllium, manganese, cobalt, rubidium, and zirconium may also be incorrect.

All of the values in Table IV are given as isothermal compressibilities (χ_T). A few of these, however, were calculated from the adiabatic values (χ_S) by using the following relationship:

$$\chi_T = \chi_S + \frac{9\alpha^2 TV}{C_P}, \tag{6.7}$$

where α is the linear coefficient of expansion (see Table VI), T is the temperature in °K, V is the atomic volume (Table VII) and C_P is the heat capacity at constant pressure. In general the second term on the right-hand side of Eq. (6.7) is quite small, usually slightly less than 1% of the value of χ_S.

Sulfur. In Tables IV and V two different values are given for rhombic sulfur. In Table IV, the values for the a parameters differ by a factor of almost 2. (The χ values in Table V are identical with the a values in Table IV.) The smaller value (55.0) was obtained from single-crystal measurements on orthorhombic ("rhombic") sulfur using Voigt's method to obtain the bulk adiabatic compressibility. This bulk value was converted to the isothermal compressibility by using Eq. (6.7). The larger value was obtained by Bridgman on a crystalline form of sulfur which he stated had been crystallized from a carbon disulfide solution. Usually sulfur obtained in this manner is rhombic sulfur, but since Bridgman did not give further details, one cannot be absolutely certain that his compressibility data listed in Tables IV and V are for rhombic sulfur. For this reason the question mark was placed after the identification of the element and its modification. Since the two compressibilities listed in these tables differ by a factor of almost 2, and since one of the values is known to have been measured on rhombic sulfur, it would appear that Bridgman's data for sulfur are for a modification other than rhombic sulfur.

Nickel. Bridgman's latest results[20] for nickel show a cusp at 10,500 kg/cm² in the $\Delta V/V$ versus pressure curve. By using his data points for pressures less than 10,500 kg/cm², a very unrealistic value for the b param-

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[20] P. W. Bridgman, *Daedalus* **77,** 187 (1949).

eter was obtained (15×10^{-12}), and a value somewhat too large for the a parameter (6.29×10^{-7}). Primarily because of the unrealistic b value, these data were felt to be erroneous. The data used in this compilation were Bridgman's pre-1940 data,[21] which were then corrected as outlined above.

Niobium. Bridgman[20] found considerable hysteresis between the $\Delta V/V$ values obtained on increasing pressure and those obtained on decreasing pressure. The data given in Tables IV and V are based on the increasing pressure values only.

Palladium. Bridgman[20] found a cusp in the $\Delta V/V$ versus pressure measurements at a pressure of 16,500 kg/cm². Because of this, only the data given up to 15,000 kg/cm² were used in obtaining the data given in Tables IV and V.

Indium. Bridgman has reported compressibility data for indium on four different occasions.[22–25] The earliest results[22] differ considerably from the latter three measurements,[23–25] which are in substantial agreement with each other. Since the former results[22] are in better agreement with the shock wave data from indium,[26] the compressibility data given in that paper were chosen for this compilation.

α and γ-Cerium. Bridgman's compressibility data[27,28] for α- and γ-cerium indicate that the $\gamma \rightarrow \alpha$ transformation occurs substantially above the presently accepted value of 7720 kg/cm² at 298°K.[29–38] (See Section 1 for a description of the α- and γ-cerium phases.) Therefore, the compressibility data of γ-Ce given by Bridgman[27,28] were fitted to Eq. (6.6) up to a maximum pressure of 7720 kg/cm², rather than to the transformation pressure which he gave. The volume change at the $\gamma \rightarrow \alpha$ transformation, 7720 kg/cm², was taken to be 13.0%.[33,36,38] The compressibility data for α-Ce were then extrapolated back to 7720 kg/cm², so that the $\Delta V/V$ point for α-Ce was 13.0% larger than the $\Delta V/V$ point for γ-Ce at this transformation pressure. Because of these modifications of Bridgman's data, care should be exercised in using the cerium data tabulated in Tables IV and V.

Tantalum. Bridgman[20] gave two sets of compressibility data for tantalum. One specimen was reported to be 99.9% pure and the second 99.95% pure. In his paper, however, Bridgman indicated that he believed that the data for the 99.9% specimen were more reliable, and for this reason the parameters given herein are based on his 99.9% pure specimen.

Estimated a and b Values. The data listed in Table IV are for experimentally measured values only. For seven elements only the a parameter is known, and for eleven others none of the compressibility parameters are known. The derivation of the estimated a parameter is described later in this section and that of the estimated b parameter is given in Section 24. For convenience, these estimated values are listed below:

	a	b
Diamond	1.80×10^{-7}	$(0.076) \times 10^{-12}$
White phosphorus	209	(1.39)
Rhombic sulfur	100.8	(197.)
Scandium	(17.1)	(6.43)
Gallium	17.2	(6.80)
Technetium	(3.30)	(0.238)
Gray tin	8.83	(1.83)
Promethium	(27.8)	(13.2)
Terbium	(24.6)	(11.4)
Rhenium	2.64	(0.153)
Osmium	(2.35)	(0.121)
Mercury	34.7	(33.7)
Polonium	(37)	(26.6)
Francium	(500)	(4600)
Radium	(74.1)	(84.6)
Actinium	(40)	(35.5)
Protactinium	(13)	(5.02)
Neptunium	(14.4)	(6.16)

Table V. The isothermal compressibility as the pressure approaches the limit of zero is given in Table V and is taken directly from the a parameter in Table IV. The bulk modulus given in Table V is the reciprocal

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[21] P. W. Bridgman, *Daedalus* **58,** 166 (1923).
[22] P. W. Bridgman, *Daedalus* **74,** 21 (1940).
[23] P. W. Bridgman, *Daedalus* **76,** 1 (1945).
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TABLE V. COMPRESSIBILITY (χ) AT ZERO PRESSURE AND THE BULK MODULUS (B)[a]

Element	$\chi \times 10^6$ (cm²/kg)	$B \times 10^{-6}$ (kg/cm²)
3 Li	84.83	0.118
4 Be	9.772	1.023
5 B	5.48	1.82
6 C(g)	29.01	0.3447
6 C(d)	1.80	5.56
11 Na	143.9 ±2.0[b]	0.06949
12 Mg	27.68	0.3613
13 Al	13.59	0.7358
14 Si	9.924	1.008
15 P(w)	209	0.0478
15 P(r)	51.13	0.1956
15 P(b)	32.23	0.3103
16 S(r?)[c]	100.8[c]	0.0992[c]
16 S(r)	55.0	0.182
19 K	308.7	0.0324
20 Ca	64.51	0.1550
21 Sc[h]	(17.1)[d,h]	(0.584)[d,h]
22 Ti	9.328	1.072
23 V	6.057	1.651
24 Cr	5.154	1.940
25 Mn	16.44	0.6083
26 Fe	5.826	1.716
27 Co	5.122	1.952
28 Ni	5.26[c]	1.90[c]
29 Cu	7.490	1.335
30 Zn	16.39	0.6101
31 Ga	17.2[e]	0.580[e]
32 Ge	12.70	0.7874
33 As	24.89	0.4018
34 Se	107.8	0.09276
37 Rb	311.9	0.03206
38 Sr	84.48	0.1184
39 Y	26.79	0.3733
40 Zr	11.77	0.8496
41 Nb	5.761[c]	1.736[c]
42 Mo	3.598	2.779
43 Tc	(3.30)[d]	(3.03)[d]
44 Ru	3.057	3.271
45 Rh	3.626	2.758
46 Pd	5.423[c]	1.844[c]
47 Ag	9.740	1.027
48 Cd	20.98	0.4766
49 In	23.87[c]	0.4189[c]
50 Sn(g)	8.83	1.13
50 Sn(w)	18.10	0.5525
51 Sb	25.62	0.3903
52 Te	42.60	0.2347
55 Cs	483.3	0.02069
56 Ba	95.2	0.105

TABLE V. COMPRESSIBILITY (χ) AT ZERO PRESSURE AND THE BULK MODULUS (B)[a]—*Continued*

Element	$\chi \times 10^6$ (cm²/kg)	$B \times 10^{-6}$ (kg/cm²)
57 La	40.37	0.2477
58 Ce(α)	37.4[c,f]	0.267[c,f]
58 Ce(γ)	40.97[c]	0.2441[c]
59 Pr	32.08	0.3117
60 Nd	30.02	0.3331
61 Pm	(27.8)[d]	(0.360)[d]
62 Sm	33.36	0.2998
63 Eu	66.63	0.1501
64 Gd	25.59	0.3908
65 Tb	24.6	0.407
66 Dy	25.52	0.3918
67 Ho	24.72	0.4045
68 Er	23.88	0.4188
69 Tm	24.71	0.4047
70 Yb	73.93	0.1353
71 Lu	23.85	0.4193
72 Hf	8.98	1.11
73 Ta	4.89[c]	2.04[c]
74 W	3.034	3.296
75 Re	2.64	3.79
76 Os	(2.35)[d]	(4.26)[d]
77 Ir	2.76	3.62
78 Pt	3.523	2.838
79 Au	5.664	1.766
80 Hg	34.7[g]	0.288[g]
81 Tl	27.30	0.3663
82 Pb	22.82	0.4382
83 Bi	31.16	0.3209
84 Po	(37)[d]	(0.27)[d]
87 Fr	(500)[d]	(0.020)[d]
88 Ra	(74.1)[d]	(0.135)[d]
89 Ac	(40)[d]	(0.25)[d]
90 Th	18.07	0.5534
91 Pa	(13)[d]	(0.78)[d]
92 U	9.926	1.007
93 Np	(14.4)[d]	(0.694)[d]
94 Pu	18.3	0.546

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[a] References for the compressibility values are given in Table IV.

[b] Mean value of the two entries cited in Table IV.

[c] See text for further discussion.

[d] Estimated value; see text for further discussion.

[e] Value obtained at 273°K.

[f] This value corresponds to the compressibility or bulk modulus at 7720 kg/cm², the pressure at which α-Ce is formed from γ-Ce.

[g] Value for solid mercury.

[h] *Note added in proof*: C. E. Monfort, III, and C. A. Swenson found the compressibility of Sc to be 22.5×10^{-7} cm²/kg and $B = 0.444 \times 10^6$ kg/cm² (*Phys. Chem. Solids*, to be published).

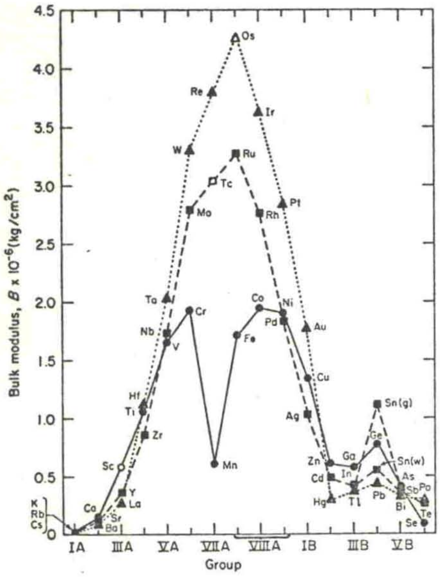

FIG. 6. Bulk modulus of the elements of the fourth, fifth, and sixth periods of the Periodic Table. Open points are estimated values.

of the isothermal compressibility as the pressure approaches zero. Also included in Table V are the estimated values for the elements for which these two quantities are unknown.

The bulk modulus for the fourth, fifth, and sixth periods is shown in Fig. 6. The general trend as one proceeds across one period is similar to that noted for Young's modulus and the shear modulus. The one anomaly, which is very evident, is that manganese has a much smaller bulk modulus than its neighbors. The bulk modulus for the rare-earth series of metals is shown in Fig. 5b. It is evident that a smooth curve can be drawn through the data points if the data points for cerium, samarium, europium, and ytterbium are ignored. The low values for europium and ytterbium are not surprising since these metals are divalent.[13] The value for cerium is probably anomalous because cerium undergoes a polymorphic transition at moderately low pressures—at 7720 kg/cm². There is no apparent explanation for samarium's anomalous behavior.

Estimated Data. Of the four elastic properties the bulk modulus (or compressibility) has been determined for more elements than any of the remaining three. Because of this, the bulk modulus was estimated using various extrapolation and interpolation techniques based on the periodic nature of the physical properties of the elements. From the estimated and experimental bulk moduli the other elastic properties were then estimated by making use of the interrelationships among these properties, as described earlier in Sections 3–5.

From the variation of the bulk modulus with the group number in the Periodic Table (Fig. 6) the bulk modulus was estimated for technetium and osmium. If one assumes that the bulk modulus increases between molybdenum and technetium at the same rate that it does between tungsten and rhenium, then an estimated value of 3.19×10^6 kg/cm² is obtained for technetium. The mean value of the bulk moduli of molybdenum and ruthenium leads to another estimated value for the bulk modulus of technetium, 3.02×10^{-6}. These two values, when averaged with a third estimated value (see below), give the final estimated value shown in Table V. The percent increase technique was also used to obtain one of the estimated values for osmium; in this instance the percent increase between iridium and osmium was assumed to be identical to that between rhodium and ruthenium. The bulk modulus for promethium was estimated from the plot shown in Fig. 5b for the rare-earth metals. The value for pro-

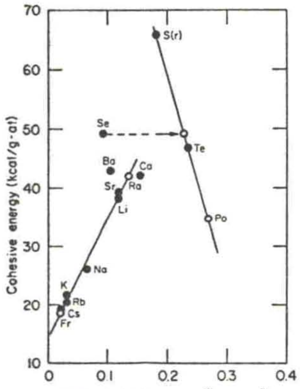

FIG. 7. Bulk modulus versus the cohesive energy of the alkali and alkaline-earth metals, and the calcogens. Open points are estimated values.

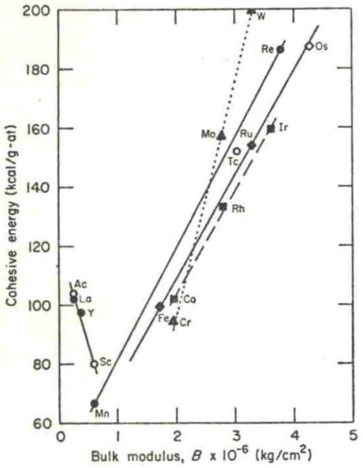

FIG. 8. Bulk modulus versus the cohesive energy of a number of transition metals. Open points are estimated values.

tactinium was assumed to be equal to the mean value of thorium and uranium.

Examination of the values of a number of physical properties indicated that the cohesive energy or the heat of sublimation (see Sections 11 and 12 and Table XII) has roughly a one-to-one correspondence to the bulk modulus. That is, if the bulk modulus is small, the cohesive energy is small; and when the former is large, the latter is also large. Unfortunately this correspondence is not exactly the same for all the elements in the Periodic Table, although it does appear to be the same for all elements in each group. This is shown in Figs. 7 and 8. In Fig. 7 it is seen that alkali and alkaline-earth metals seem to have the same slope; i.e., their bulk moduli are related to their cohesive energies by a constant value. This type of relationship is seen in Fig. 8, where it holds for chromium, molybdenum, and tungsten, and for cobalt, rhodium, and iridium. Assuming that this type of relationship holds for the other groups, it is possible to obtain the slope if both the cohesive energy and the bulk modulus are known for only two elements in a given group. Thus the bulk moduli for technetium, osmium, polonium, francium, radium, and actinium have been estimated from their known or estimated cohesive energies (see Table XII). The value shown for technetium in Fig. 8 is the final estimated value chosen for this element, not the value derived from this plot.

The values for scandium and neptunium were calculated from the experimental value of Young's modulus and the estimated value of Y/μ by use of Eq. (3.1).

Selenium. As has been mentioned in Sections 3–5, the bulk modulus for selenium is probably incorrect. If one were to shift the experimental value for selenium, as shown in Fig. 7, so that it falls on the curve established by rhombic sulfur and tellurium, a much larger bulk modulus would be obtained. By using this value of the bulk modulus, reasonable values for the compressibility, Young's modulus, the shear modulus, and Poisson's ratio are obtained. Since this is quite speculative, this point will not be discussed further.

III. Coefficient of Thermal Expansion

The linear coefficients of thermal expansion at 298°K (25°C) are listed in Table VI for all the elements, and are shown for the elements in the fourth, fifth, and sixth periods of the Periodic Table in Fig. 9 and for the rare earths in Fig. 10. The values of the coefficient of expansion given herein for the noncubic elements are average values. In a few instances the values for the various crystallographic directions of a noncubic crystal have been given in the literature. Such data were averaged by the usual techniques to obtain an average value for the thermal expansion. Most of the values listed here are based on measurements of polycrystalline bulk material. In some instances values based on X-ray measurements are given as the best values for the thermal expansion; these data are identified in Table VI by a footnote.

The experimental values of the coefficient of thermal expansion vary between a minimum value of 1.19×10^{-6} for diamond and a maximum of 124.5×10^{-6} for white phosphorus. The estimated values also lie well within this range.

In Fig. 9 it is noted that the coefficients of thermal expansion when plotted as a function of atomic number show a behavior which is approximately the opposite of that shown by Young's, the shear, and the bulk moduli (Figs. 1, 3, and 6), the melting and boiling points (Figs. 12 and 15), and the cohesive energy (Fig. 17). The coefficient of expansion is very large for the alkali metals but it decreases rapidly as one proceeds through the alkaline-earth and group IIIA metals. The minimum value for each period is attained in the element which has the s^2d^4 configuration, i.e., chromium, molybdenum, and tungsten. As one proceeds beyond these

TABLE VI. LINEAR COEFFICIENT OF THERMAL EXPANSION

Element	$\alpha \times 10^{6}$ (°C^{-1})	Ref.
3 Li	45	1
4 Be	11.5	2, 3
5 B	8.3	3, 4, 5
6 C(g)	3.8 ±3.1	4, 5, 6
6 C(d)	1.19 ±0.01	5, 6
11 Na	70.6 ±0.6	1, 4, 5
12 Mg	25.7 ±0.7	1, 5, 6
13 Al	23.1 ±0.5	1, 7, 8, 9
14 Si	3.07 ±0.07[a]	10, 11
15 P(w)	124.5 ±0.5	4, 6
15 P(r)	(66.5)[b]	—
16 S(r)	64.1 ±0.1	4, 6
16 S(m)	(63)[b]	—
19 K	83.0	1, 4
20 Ca	22.4 ±0.1	1, 4
21 Sc	10.0[a]	12
22 Ti	8.35 ±0.15	13
23 V	8.3	14
24 Cr	8.4[c]	15
25 Mn	22.6 ±0.3	16
26 Fe	11.7	1, 4, 8
27 Co	12.4	1, 5, 6
28 Ni	12.7 ±0.2	1, 6, 8
29 Cu	16.7 ±0.3	1, 4, 5, 6, 8
30 Zn	29.7	1
31 Ga	18.1 ±0.2	1, 3, 4
32 Ge	5.75	7
33 As	4.28 ±0.42	4, 6
34 Se	36.9 ±0.1	4, 6
37 Rb	88.1 ±1.9	4, 6
38 Sr	20	17
39 Y	12.0[a]	12
40 Zr	5.78 ±0.07	18, 19
41 Nb	7.07 ±0.05	1, 20, 21
42 Mo	4.98 ±0.15	1, 4, 6, 22
43 Tc	(8.06)[b]	—
44 Ru	9.36 ±0.27	4, 6
45 Rh	8.40 ±0.10	1, 4, 6
46 Pd	11.5 ±0.4	1, 4, 6
47 Ag	19.2 ±0.4	1, 4, 5, 6, 8
48 Cd	30.6 ±1.3	1, 4, 5, 6
49 In	31.4 ±1.4	1, 4, 5
50 Sn(g)	5.3[d]	23
50 Sn(w)	21.2[a]	24
51 Sb	10.9	1, 6

TABLE VI. LINEAR COEFFICIENT OF THERMAL EXPANSION—*Continued*

Element	$\alpha \times 10^{6}$ (°C^{-1})	Ref.
52 Te	16.77 ±0.03	4, 5, 6
55 Cs	97	1, 3, 4
56 Ba	18.8 ±0.8	5, 25
57 La	10.4[a]	12
58 Ce(γ)	8.5	26
59 Pr	6.79[a]	12
60 Nd	9.98[a]	12
61 Pm	(9.0)[b]	—
62 Sm	10.4	27
63 Eu	33.1[a]	12
64 Gd	8.28[a,e]	12
65 Tb	10.3[a]	12
66 Dy	10.0[a]	12
67 Ho	10.7[a]	12
68 Er	12.3[a]	12
69 Tm	13.3[a]	12
70 Yb	24.96 ±0.04	12, 26
71 Lu	8.12[a]	12
72 Hf	6.01 ±0.16	3, 19, 28, 29
73 Ta	6.55 ±0.05	1, 4, 20, 29
74 W	4.59 ±0.03	1, 4, 29, 30
75 Re	6.63 ±0.06	1, 4, 31
76 Os	4.7 ±0.1	1, 4
77 Ir	6.63 ±0.12	1, 4, 5
78 Pt	8.95 ±0.05	1, 4, 6, 25
79 Au	14.1 ±0.1	1, 4, 5, 25, 32
80 Hg	61[f]	1, 25
81 Tl	29.4 ±1.0	1, 4, 5, 6
82 Pb	29.0 ±0.3	1, 4, 5, 25, 33
83 Bi	13.41 ±0.09	4, 5, 6, 25
84 Po	23.0 ±1.5	34
87 Fr	(102.)[b]	—
88 Ra	(20.2)[b]	—
89 Ac	(14.9)[b]	—
90 Th	11.2 ±0.4	35
91 Pa	(7.3)[b]	—
92 U	12.6 ±0.4	1, 36
93 Np	27.5	37
94 Pu	55	38

[a] X-ray data.

[b] Estimated value; see text for further discussion.

[c] See text for details concerning the derivation of this value.

[d] Value at 215°K.

[e] Value at 361°K; see text for more details.

[f] Value for solid mercury at its melting point, 234°K.

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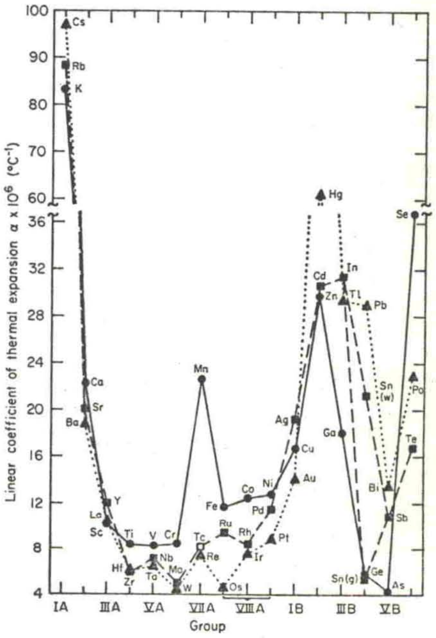

FIG. 9. Linear coefficient of thermal expansion of the elements of the fourth, fifth, and sixth periods of the Periodic Table. Open points are estimated values.

elements the coefficient of expansion increases, slowly at first, reaching a maximum at approximately the configuration s^2d^{10}, i.e., zinc and its cogeners. As one moves further along in the respective periods, another minimum is reached when the p level is half filled, i.e., at arsenic, antimony, and

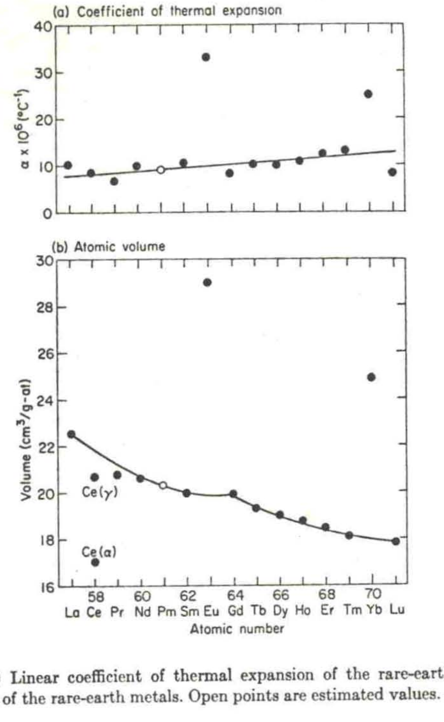

FIG. 10. (a) Linear coefficient of thermal expansion of the rare-earth metals. (b) Atomic volume of the rare-earth metals. Open points are estimated values.

bismuth. The anomalous behavior of manganese is evident. The variation of the coefficient of expansion with atomic number for the rare earths (Fig. 10a) is quite normal. The large values for europium and ytterbium are, as noted earlier, a manifestation of their divalent character as opposed to the normally trivalent rare earths.[13]

Chromium. The literature value given for the coefficient of thermal expansion of chromium is about $3 \times 10^{-6}(°C^{-1})$ at 298°K (25°C). Because of the paramagnetic–antiferromagnetic transition at about 310°K (37°C), this coefficient is much lower in the region between about 290°K and 330°K (17°C and 57°C) than it is below 280°K (7°C) and above 340°K (67°C). In order to obtain a value which is not affected by this magnetic ordering, the values of the coefficient of thermal expansion well below the magnetic transition temperature have been connected by a straight line with those well above this transition in a plot of the coefficient of thermal expansion versus the temperature. The coefficient of expansion given in this review was estimated from the interpolated line at 298°K. It is noted that this value is almost three times as large as the experimentally determined value. The reviewer, however, believes that it is more representative of chromium when one is not concerned with its magnetic properties.

Examination of the elastic properties given by Bolef and de Klerk[39] indicates that these properties are only slightly affected (about 3% at the most) by the magnetic transition in chromium. This is compared with a factor of about *3* for the thermal expansion coefficient. Because of the small variation of the elastic properties, no attempt was made to correct them for this magnetic transition.

Gadolinium. As does chromium, gadolinium undergoes a magnetic transition near room temperature. At 289°K (16°C) gadolinium undergoes a paramagnetic–ferromagnetic transition. Because of the strong influence of magnetic transitions on the coefficient of thermal expansion, the X-ray value given by Spedding *et al.*[40] at 361°K (88°C) is considered to be representative of the coefficient of expansion of gadolinium at 298°K (25°C) uninfluenced by the magnetic transition.

Estimated Data. Most of the estimated values of the coefficient of thermal expansion are based on the relationship between the coefficient and the melting point (see Section 25). The product of the coefficient of expansion, α, and the melting point, T, for red phosphorus is assumed to be the same as it is for white phosphorus ($\alpha T = 0.0395$); for monoclinic sulfur, the same as rhombic sulfur (0.0248); for technetium, radium, and actinium, the same as the average value for the face-centered cubic, body-centered cubic, and hexagonal closest-packed metals (0.0197); and for protactinium, the same as the mean for gallium, indium, white tin, mercury, and uranium (0.0123). The product of α and T for the alkali metals increases with increasing atomic number, and for that reason the value of αT for francium (0.0304) was obtained by extrapolation from the values for lower-atomic-number alkali metals. By using this value of αT the coefficient of expansion is estimated to be 102×10^{-6} (°C⁻¹). The value for promethium was estimated from the straight line in a plot of the coefficient of expansion versus the atomic number of the rare-earth metals (Fig. 10a).

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[39] D. I. Bolef and J. de Klerk, *Phys. Rev.* **129**, 1063 (1963).

[40] F. H. Spedding, J. J. Hanak, and A. H. Daane, *J. Less-Common Metals* **3**, 110 (1961).

TABLE VII. ATOMIC VOLUME[a]

Element	Atomic volume (cm^3/g-at)	Element	Atomic volume (cm^3/g-at)
3 Li	13.02	50 Sn(g)	20.59
4 Be	4.891	50 Sn(w)	16.30
5 B	4.388[b]	51 Sb	18.21
6 C(g)	5.260[c]	52 Te	20.46
6 C(d)	3.397[c]	55 Cs	69.19
11 Na	23.79	56 Ba	38.08
12 Mg	14.00	57 La	22.54[e]
13 Al	10.00	58 Ce(α)	17.03
14 Si	12.07	58 Ce(γ)	20.69[g]
15 P(w)	13.96	59 Pr	20.82[e]
15 P(r)	13.18[d]	60 Nd	20.59[e]
15 P(b)	11.51[d]	61 Pm	(20.33)[h]
16 S(r)	17.41	62 Sm	19.95[e]
16 S(m)	16.36[d]	63 Eu	28.98[e]
19 K	45.61	64 Gd	19.94[e]
20 Ca	26.19	65 Tb	19.26[e]
21 Sc	15.06[e]	66 Dy	18.99[e]
22 Ti	12.01	67 Ho	18.75[e]
23 V	8.365	68 Er	18.46[e]
24 Cr	7.231	69 Tm	18.13[e]
25 Mn	7.357	70 Yb	24.87[e]
26 Fe	7.094	71 Lu	17.77[e]
27 Co	6.689	72 Hf	13.45
28 Ni	6.593	73 Ta	10.80
29 Cu	7.114	74 W	9.551
30 Zn	9.165	75 Re	8.860
31 Ga	11.81	76 Os	8.441
32 Ge	13.64	77 Ir	8.524
33 As	12.96	78 Pt	9.094
34 Se	16.43	79 Au	10.22
37 Rb	56.07	80 Hg	14.09
38 Sr	33.93	81 Tl	17.22
39 Y	19.88[e]	82 Pb	18.27
40 Zr	14.02	83 Bi	21.33
41 Nb	10.83	84 Po	22.53
42 Mo	9.387	87 Fr	(73.0)[h]
43 Tc	8.635[f]	88 Ra	(38.8)[h]
44 Ru	8.178	89 Ac	22.56
45 Rh	8.292	90 Th	19.79
46 Pd	8.879	91 Pa	15.03
47 Ag	10.27	92 U	13.16
48 Cd	13.00	93 Np	13.11
49 In	15.73	94 Pu	12.06

[a] The atomic volumes were calculated from the lattice constants of the elements as listed by Pearson[1] unless otherwise noted.

[b] Calculated from X-ray density given by Du Mond *et al.*[2] for the α-(rhombohedral)-boron modification.

[c] Calculated from the lattice constants given by Hodgman.[3]

[d] Calculated from the pycnometric density given by Hodgman.[3]

[e] Atomic volumes as given by Gschneidner.[4]

[f] Calculated from lattice constants given by Lam *et al.*[6]

[g] Atomic volume given by Gschneidner *et al.*[5]

[h] Estimated value; see text for further discussion.

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IV. Atomic Volume

The atomic volume is used in many calculations involving solid state physics and physical metallurgy and, therefore, it is one of the more important quantities. In this compilation the atomic volume was needed to calculate the heat capacity at constant volume (Section 15), the Debye temperature from the Lindemann equation (Section 17), the Leibfried and Bragg numbers (Section 26), the Grüneisen constant (Section 28) and the size factor (Section 29).

The atomic volume (Table VII) was calculated from the lattice constant(s) of the pure element, except for the three phosphorus and two sulfur allotropes. For these five substances the atomic volume was obtained by dividing the atomic weight by the pycnometric density.

The variation of the atomic volume with the atomic number for the elements of the fourth, fifth, and sixth periods of the Periodic Table are shown in Fig. 11. It is seen that the atomic volume decreases smoothly as one proceeds from the alkali metals to about the location where the *d* level is slightly more than half filled, after which the volume increases as one approaches the end of the period. As mentioned in earlier discussions concerning the variation of some of these properties as a function of

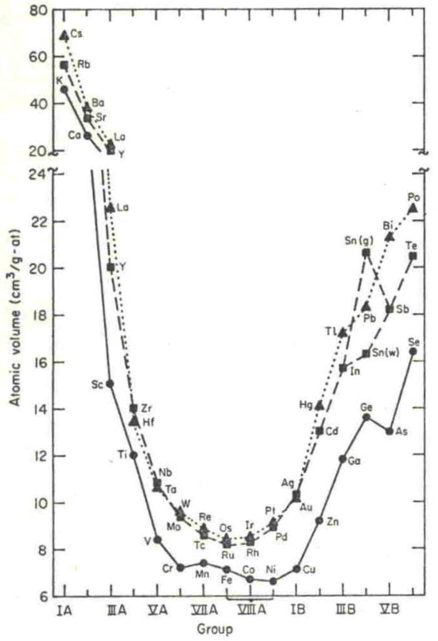

FIG. 11. Atomic volume of the elements of the fourth, fifth, and sixth periods of the Periodic Table.

atomic number, the elements in the fourth period appear to behave slightly differently from those in the fifth and sixth periods. This is especially evident for the atomic volumes of manganese, iron, cobalt, and nickel.

The atomic volumes of the rare-earth metals are shown in Fig. 10b. It is noted that the atomic volumes decrease in a smooth fashion with increasing atomic number except for cerium, europium, and ytterbium. The large anomalous values for the atomic volumes of europium and ytterbium reflect the divalent nature of these two metals. The anomaly at cerium is probably due to the tendency of cerium to become tetravalent.[41] The atomic volumes for both γ-Ce (the normal room-temperature face-centered cubic form) and α-Ce (the low-temperature or high-pressure denser face-centered cubic form) are shown in Fig. 10b. The large difference in volume (17.7%) between these two phases is immediately evident in this plot. The cusp at gadolinium, which is quite obvious in this plot, is found in almost all of the plots of the lattice parameter (which is directly related to the volume) versus atomic number.[42,43]

The atomic volume varies between 3.397 cm³/g-at for diamond and 69.19 cm³/g-at for cesium if one considers only the measured or experimental values. However, the estimated value for francium, 73 cm³/g-at, is even larger than that of cesium.

Estimated Data. The atomic volumes of promethium, francium, and radium were estimated from plots of the atomic volume versus the atomic number of the rare-earth, alkali, and alkaline-earth metals, respectively. The first is an interpolated value and the latter two are extrapolated estimates.

V. Melting Point and Heat of Fusion

7. INTERNATIONAL PRACTICAL TEMPERATURE SCALE

The international practical temperature scale was first recommended in 1927 by the International Committee on Weights and Measures, and since then has been universally accepted. In 1948 this scale was revised and in 1960 the text of the 1948 agreement was revised, which resulted in a few minor changes in the 1948 scale. These changes included the addition of indium as a secondary fixed point, the deletion of antimony, the revision of the melting points of tin, cadmium, and zinc, and the change of the melting point of zinc from a secondary fixed point to a fundamental and primary fixed point. The data in Table VIII reflect the 1960 revisions, except for the standards that have transition temperatures below the mercury point. The low-temperature standards were omitted, since Table VIII is intended to show only those elements which have been designated as practical temperature standards from the elements which are considered in this review.

At the time the 1927 international practical temperature scale was adopted, it was in very close agreement with the thermodynamic scale. Because of improvements in determining the thermodynamic scale, the difference between these scales is now measurable and significant. At the zinc and sulfur points 0.07° must be added to the international practical

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[41] K. A. Gschneidner, Jr. and R. Smoluchowski, *J. Less-Common Metals*, **5**, 374 (1963).

[42] K. A. Gschneidner, Jr., "Rare Earth Alloys," p. 10. Van Nostrand, Princeton, New Jersey, 1961.

[43] K. A. Gschneidner, Jr., *in* "Progress in the Science and Technology of the Rare Earths," Vol. 1, p. 222. Pergamon Press, New York, 1963.

TABLE VIII. PRIMARY AND SECONDARY FIXED POINTS OF THE INTERNATIONAL PRACTICAL TEMPERATURE SCALE

Element	Temperature		Point[a]	Transformation[b]	Ref.
	(°K)	(°C)			
80 Hg	234.28	−38.87	S	M	1
49 In[c]	429.76[c]	156.61[c]	S	M	2
50 Sn[c]	505.06[c]	231.91[c]	S	M	1, 2
48 Cd[c]	594.18[c]	321.03[c]	S	M	1, 2
82 Pb[d]	600.4[d]	327.3[d]	S	M	1
80 Hg	629.73	356.58	S	B	1
30 Zn[c]	692.655[c]	419.505[c]	P	M	1, 2
16 S	717.75	444.60	P	B	1
13 Al	933.2	660.1	S	M	1
47 Ag	1234.0	960.8	P	M	1
79 Au	1336.2	1063.0	P	M	1
29 Cu	1356	1083	S	M	1
28 Ni	1726	1453	S	M	1
27 Co	1765	1492	S	M	1
46 Pd	1825	1552	S	M	1
78 Pt	2042	1769	S	M	1
45 Rh	2233	1960	S	M	1
77 Ir	2716	2443	S	M	1
74 W	3653	3380	S	M	1

[a] The letter P signifies a primary fixed point, and S a secondary fixed point.

[b] The letter B signifies a boiling point at 1 atm pressure, and M a melting point at 1 atm.

[c] As a result of the 1960 revision of the text of the 1948 international practical temperature scale the melting point of In has been added as a fixed point, and the melting points of Sn, Cd, and Zn have been revised. In addition, Zn has been changed from a secondary fixed point to a primary one.[2] See text for further discussion.

[d] In view of the recent results of McLaren[3] the melting point of lead will probably be revised. McLaren gives 600.576°K (327.426°C) for the melting point of lead.

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2. H. F. Stimson, *in* "Temperature, Its Measurement and Control in Science and Industry" (C. M. Herzfeld, ed.), Vol. 3, Part 1, p. 59. Reinhold, New York, 1962.
3. E. H. McLaren, *in* "Temperature, Its Measurement and Control in Science and Industry (C. M. Herzfeld, ed.), Vol. 3, Part 1, p. 185. Reinhold, New York, 1962.

temperature scale to make it agree with the thermodynamic scale; at the antimony point 0.17° must be added; at the silver point 1.13° must be added; and at the gold point 1.48° must be added.[44–47] If these differences continue to increase with increasing temperature at about the same rate as those mentioned above, then one would expect that the international practical temperature scale lies below the thermodynamic temperature scale by as much as 25° at the melting point of tungsten. The changes cited above, or changes of about this order of magnitude, are expected to be made in 1966, thus revising the practical temperature scale upwards from that given in Table VIII. Other changes, which will probably be made in 1966 as a result of the excellent work of McLaren,[48] are the revision of the value for the melting point of lead (see footnote *d* of Table VIII), and the addition of the melting point of bismuth to the list of standards (this value is given in Table IX). A value of 273.15° was used to convert the temperatures from degrees Kelvin to degrees Centigrade or vice versa.

8. MELTING POINT

The melting points of the elements are listed in Table IX and are shown for the elements of the fourth, fifth, and sixth periods of the Periodic Table in Fig. 12, and for the rare-earth metals in Fig. 13a. The melting point and also the atomic volume are the two properties for which the most experimental data are available. For each of these properties experimental data are avilable for 77 elements of the 80 considered in this review.

The variation of the melting point with the atomic number (Fig. 12) is similar to that shown in several of the previous plots (Figs. 1, 3, and 6). The alkali metals and those elements near the end of the fourth, fifth, and sixth periods have low melting points. A maximum melting point occurs in each period for the metals with a s^2d^4 configuration. The minimum near the end of each period occurs at or near the elements having the $s^2p^1d^{10}$ configuration. The anomalous behavior of germanium is probably due to its diamond structure as compared with the more normal behavior of tin and lead, which have metallic structures.

The melting points of the rare earths increase in a smooth manner with increasing atomic number (Fig. 13a). Small deviations from this curve are found for the experimental value of lanthanum, cerium, and

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[44] H. Moser, *in* "Temperature, Its Measurement and Control in Science and Industry" (C. M. Herzfeld, ed.), Vol. 3, Part. 1, p. 167. Reinhold, New York, 1962.

[45] Anonymous, *Chem. Eng. News* **41,** No. 2, 39 (1963).

[46] F. G. Brickwedde, *Phys. Today* **16,** No. 5, 24 (1963).

[47] Anonymous, Nature **197,** 1055 (1963).

[48] E. H. McLaren, *in* "Temperature, Its Measurement and Control in Science and Industry" (C. M. Herzfeld, ed.), Vol. 3, Part 1, p. 185. Reinhold, New York, 1962.

TABLE IX. MELTING POINT

Element	Melting point		Ref.
	(°K)	(°C)	
3 Li	454 ±1	181 ±1	1, 2, 3
4 Be	1557 ±1	1284 ±1	4, 5, 6
5 B	2498 ±75	2225 ±75	4, 6
6 C(g)	4100[a]	3827[a]	7
11 Na	370.8 ±0.3	97.6 ±0.3	8, 9, 10
12 Mg	923 ±1	650 ±1	4, 8, 9, 10
13 Al	933.2	660.1	*b*
14 Si	1685 ±3	1412 ±3	4, 8, 11, 12
15 P(w)[c]	317.2 ±0.2	44.0 ±0.2	8, 9, 10
16 S(m)[d]	392	119	4, 8, 9, 13
19 K	336.6 ±0.2	63.4 ±0.2	8, 9
20 Ca	1112 ±4	839 ±4	8, 14, 15
21 Sc	1812	1539	16
22 Ti	1941 ±5	1668 ±5	4, 8, 17
23 V	2178 ±14	1905 ±14	4, 8, 18, 19
24 Cr	2148 ±25	1875 ±25	4, 8, 20
25 Mn	1517 ±3	1244 ±3	4, 8, 21
26 Fe	1808 ±1	1535 ±1	4, 8, 9, 10
27 Co	1765	1492	*b*
28 Ni	1726	1453	*b*
29 Cu	1356	1083	*b*
30 Zn	692.655	419.505	*b*
31 Ga	302.8 ±0.1	29.6 ±0.1	6, 8, 9
32 Ge	1209 ±2	936 ±2	4, 8, 12
33 As	1090[e]	817[e]	4, 8, 9
34 Se	490	217	4, 8, 9
37 Rb	311.8 ±0.3	38.6 ±0.3	4, 8, 9, 10
38 Sr	1045 ±2	772 ±2	3, 4, 9, 14
39 Y	1775 ±7	1502 ±7	22
40 Zr	2123 ±5	1850 ±5	23
41 Nb	2741 ±27	2468 ±27	24, 25
42 Mo	2888 ±5	2615 ±5	4, 8, 26, 27
43 Tc	2443 ±30	2170 ±30	27, 28
44 Ru	2553 ±30	2280 ±30	27, 29, 30, 31
45 Rh	2233	1960	*b*
46 Pd	1825	1552	*b*
47 Ag	1234.0	960.8	*b*
48 Cd	594.18	321.03	*b*
49 In	429.76	156.61	*b*
50 Sn	505.06	231.91	*b*
51 Sb	903.6[f]	630.5[f]	32
52 Te	722.8 ±0.3	449.6 ±0.3	8, 9
55 Cs	301.8 ±0.2	28.6 ±0.2	6, 8, 9, 10
56 Ba	998 ±5	725 ±5	2, 15, 33
57 La	1193 ±5	920 ±5	22
58 Ce	1070 ±3	797 ±3	22
59 Pr	1208 ±5	935 ±5	22
60 Nd	1297 ±5	1024 ±5	22
61 Pm[i]	(1308)[g,i]	(1035)[g,i]	22
62 Sm	1345 ±5	1072 ±5	22
63 Eu	1099 ±10	826 ±10	22
64 Gd	1585 ±15	1312 ±15	22
65 Tb	1629 ±5	1356 ±5	22
66 Dy	1680 ±5	1407 ±5	22
67 Ho	1734 ±5	1461 ±5	22
68 Er	1770 ±15	1497 ±15	22
69 Tm	1818 ±5	1545 ±5	22
70 Yb	1097 ±5	824 ±5	22
71 Lu	1925 ±5	1652 ±5	22
72 Hf	2495 ±30	2222 ±30	4, 8, 34
73 Ta	3271 ±30	2998 ±30	4, 8, 24
74 W	3653	3380	*b*
75 Re	3433 ±20	3160 ±20	35, 36
76 Os	3300 ±18	3027 ±18	29, 35
77 Ir	2716	2443	*b*
78 Pt	2042	1769	*b*
79 Au	1336.2	1063.0	*b*
80 Hg	234.28	−38.87	*b*
81 Tl	576 ±1	303 ±1	4, 8, 9, 10
82 Pb	600.576[h]	327.426[h]	37
83 Bi	544.525	271.375	37
84 Po	519	246	38
87 Fr	(297)[g]	(24)[g]	—
88 Ra	973	700	8, 9, 10
89 Ac	1323 ±50	1050 ±50	39
90 Th	2024 ±4	1751 ±4	4, 8, 40, 41
91 Pa	(1698)[g]	(1425)[g]	—
92 U	1404 ±2	1131 ±2	4, 8, 40, 42
93 Np	910 ± 2	637 ±2	43
94 Pu	913 ±1	640 ±1	44

[a] Value obtained by extrapolation of the melting point versus pressure curve to zero pressure.

[b] Value taken from Table VIII.

[c] P(r) melts at 868 ±5°K (595 ±5°C) at ~45 atm pressure (Farr[45]).

[d] S(r) melts at 386°K (113°C) (Brasted[13]).

[e] Under 36 atm pressure.

[f] Antimony's melting point was a secondary fixed point on the international practical temperature scale, but it was deleted in the 1960 revision.

[g] Estimated value; see text for further discussion.

[h] See footnote *d* of Table VIII and text.

[i] *Note added in proof*: F. Weigel found melting point of Pm to be 1353 ± 10°K (1080 ± 10°C) [*Angew. Chem.* **75,** 451 (1963)].

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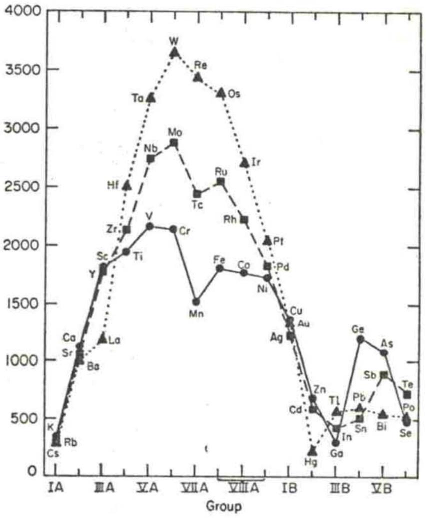
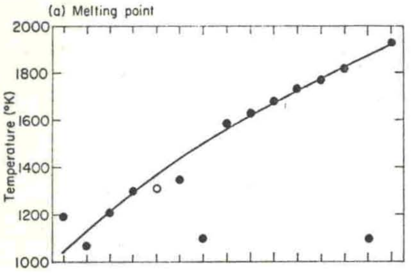


FIG. 12. Melting point of the elements of the fourth, fifth, and sixth periods of the Periodic Table.



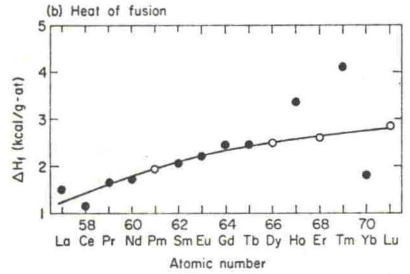


FIG. 13. (a) Melting point of the rare-earth metals. (b) Heat of fusion of the rare-earth metals. Open points are estimated values.

samarium, and for the estimated value of promethium. The large departures from this curve for europium and ytterbium again confirm the divalent nature of these two metals.[13]

The melting points are found to range from 234.28°K (−38.87°C) for mercury to 4100°K (3827°C) for carbon (graphite). The three estimated values fall well within this range. Of the true metallic elements tungsten has the highest melting point, 3653°K (3380°C). The melting points for graphite, red phosphorus, and arsenic all lie above their respective sublimation points at 1 atm pressure.

Estimated Data. The melting points of promethium, francium, and protactinium are estimated values. The estimated value for promethium is taken from Gschneidner's review.[49] He estimated the melting point of promethium by assuming that it lies about midway between those of neodymium and samarium, the immediate neighbors of promethium. The melting point of francium was estimated from a plot of the melting points versus the atomic numbers of the alkali metals and extrapolation to the atomic number of francium. In this manner a value of 297°K (24°C) was obtained, which compares favorably to the estimated value of 300°K (27°C) given by Lyman.[50] In a similar manner the melting point of protactinium was obtained by interpolation from a plot of the melting points versus atomic numbers of thorium, uranium, and neptunium. This gives a value of 1698°K (1425°C), which is larger than the estimated values given by Lyman[50] (1503°K or 1230°C) and Hansen[51] (1573°K or 1300°C).

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[49] K. A. Gschneidner, Jr., "Rare Earth Alloys," p. 24. Van Nostrand, Princeton, New Jersey, 1961.

9. HEAT OF FUSION

The heat of fusion, which is given in Table X, is one of the lesser known properties of the elements. This area, which also includes high-temperature specific heat data, will require considerably more experimental work before we have a reasonably complete set of reliable data.

In 1936 Kelley[52] thoroughly reviewed the existing heats of fusion as determined from direct measurements, phase diagrams, and vapor pressure data. Since that time, many of these data have been redetermined and are summarized in the reviews by Stull and Sinke[53] and Kelley.[54] If no better value has been determined since Kelley's 1936 review,[52] this paper is cited as the reference rather than later reviews of Stull and Sinke[53] and Kelley.[54] More recent experimental data (published since 1960) which have come to the reviewer's attention, are also included in Table X.

The variation of the heat of fusion of the elements of the fourth, fifth, and sixth periods of the Periodic Table as a function of atomic number is shown in Fig. 14. This plot is very similar to those seen earlier. Low values for the heats of fusion are found for the alkali metals and for most of the group IIB, IIIB, IVB, and VIB elements. The maximum value occurs at approximately the s^2d^4 configuration, and the minimum near the end of each period occurs at approximately the $s^2p^1d^{10}$ configuration. The large value for germanium as compared with those of tin and lead is probably related to germanium's diamond structure, while tin and lead are more nearly metallic elements. The large value for arsenic may be incorrect; Kelley[52] also questioned its large magnitude. It should be noted

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TABLE X. HEAT OF FUSION

TABLE X. HEAT OF FUSION—*Continued*

Element	ΔH_F (kcal/g-at)	Ref.
3 Li	0.719 ±0.004	1, 2
4 Be	3.52 ±0.08	3
5 B	(5.72)[a]	—
6 C(g)	25[b]	4
11 Na	0.622	1, 2
12 Mg	2.14	1, 2
13 Al	2.56 ±0.01	1, 2
14 Si	12.02 ±0.08	1, 5
15 P(w)	0.15	6
16 S	0.336 ±0.001	1, 2
19 K	0.556 ±0.002	1, 2
20 Ca	2.07 ±0.08	2
21 Sc	3.70	7
22 Ti	(3.42)[a]	—
23 V	(3.83)[a]	—
24 Cr	3.47 ±0.17	2, 8
25 Mn	3.50	1, 2
26 Fe	3.67	1, 2
27 Co	3.70 ±0.06	2, 9
28 Ni	4.21	1, 2, 9
29 Cu	3.12	1, 2
30 Zn	1.765	1, 2
31 Ga	1.335	1, 2, 9
32 Ge	7.6 ±0.5	2
33 As	6.62[c,d]	6
34 Se	1.30	1, 2
37 Rb	0.56	1, 2
38 Sr	2.19[c]	6
39 Y	2.732 ±0.025	10
40 Zr	(3.74)[a]	—
41 Nb	(4.82)[a]	—
42 Mo	6.66[e]	6
43 Tc	(5.42)[a]	—
44 Ru	(5.67)[a]	—
45 Rh	(4.96)[a]	—
46 Pd	4.10 ±0.10	1, 2
47 Ag	2.78 ±0.08	1, 9
48 Cd	1.48 ±0.05	1, 2, 9
49 In	0.78	1, 2, 9
50 Sn	1.71 ±0.02	6, 9
51 Sb	4.74 ±0.01	1, 2, 9
52 Te	4.18 ±0.13	2
55 Cs	0.506 ±0.006	1, 2, 9
56 Ba	1.83 ±0.07	2
57 La	1.482 ±0.002	10
58 Ce	1.238 ±0.004	11
59 Pr	1.652 ±0.003	10
60 Nd	1.705 ±0.019	11
61 Pm	(1.94)[a]	—
62 Sm	2.061 ±0.015	11
63 Eu	2.204 ±0.018	10
64 Gd	2.438	7
65 Tb	2.46	7
66 Dy	(2.49)[a]	—
67 Ho	3.38[f]	7
68 Er	(2.62)[a]	—
69 Tm	4.22[f]	7
70 Yb	1.830 ±0.008	10
71 Lu	(2.85)[a]	—
72 Hf	(4.39)[a]	—
73 Ta	(5.76)[a]	—
74 W	8.42[e]	6
75 Re	(7.86)[a]	—
76 Os	(7.56)[a]	—
77 Ir	(6.22)[a]	—
78 Pt	4.70[c]	6
79 Au	2.955	1, 2
80 Hg	0.5486	2
81 Tl	1.02 ±0.01	1, 2, 9
82 Pb	1.14 ±0.01	1, 2, 9
83 Bi	2.60 ±0.05	2, 9
84 Po	(0.91)[a]	—
87 Fr	(0.52)[a]	—
88 Ra	(1.71)[a]	—
89 Ac	(3.03)[a]	—
90 Th	(3.56)[a]	—
91 Pa	(2.99)[a]	—
92 U	(2.47)[a]	—
93 Np	(1.60)[a]	—
94 Pu	0.676 ±0.010	12

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[a] Estimated value; see text for further discussion.

[b] Value obtained at 48 kilobars ($\sim 48 \times 10^3$ kg/cm^2); see text for further discussion.

[c] Calculated from binary phase diagram data.

[d] Kelley[6] thought this value might be too large.

[e] Calculated from vapor pressure data.

[f] This value is probably the sum of the heat of transformation (hcp → bcc) and the heat of fusion, since they occur close to one another.

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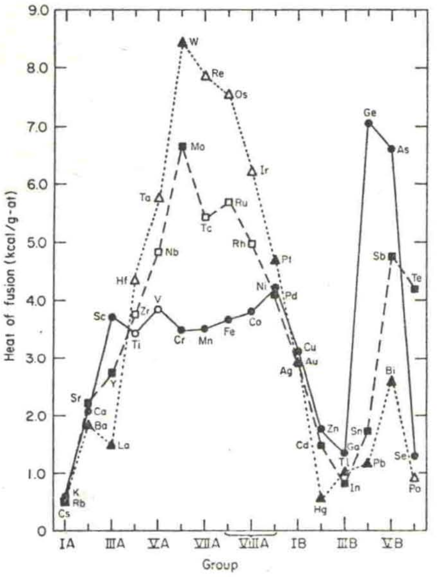

FIG. 14. Heat of fusion of the elements of the fourth, fifth, and sixth periods of the Periodic Table. Open points are estimated values.

that the entropy of fusion for arsenic, which is 6.07 compared with a mean value of 5.02 ±0.24 for antimony and bismuth (see Table XXIII), also indicates that the heat of fusion of arsenic may be too large. The anomalous behavior of the transition elements of the fourth period, from chromium through cobalt, as compared with their cogeners in fifth and sixth periods is evident.

A comparison of the plot of the heat of fusion versus the group (Fig. 14) with that of the melting point versus the group (Fig. 12) shows a striking similarity, except for one or two elements, notably manganese. Of course one would expect this since the entropy of fusion (the heat of fusion divided by the absolute melting point) is supposed to be equal to about 2. This point will be discussed in Section 27.

The heat of fusion for the rare earths is shown in Fig. 13b, where it is seen to vary smoothly as a function of atomic number. The rare-earth metals in general transform from their normal room-temperature close-packed structures to another modification just below (within 100°) their melting points. For about half of these metals it has been shown that the high-temperature allotrope has the body-centered cubic structure. For those rare earths for which the specific heat has been measured up into the liquid region, except for holmium and thulium, the heat of transformation (closed-packed to body-centered cubic) and the heat of fusion have been measured independently. For holmium and thulium the solid state transformation temperatures and the melting points lie so close together that it was not possible to separate the effects of these two heats and, therefore, the values given in Table X and shown in Fig. 13b for these two elements are the sum of the heat of transition and the heat of fusion. This accounts for the anomalously high heat of fusion of these two metals. Although the heat of fusion appears to be too low for ytterbium, it is only a consequence of the low melting point of ytterbium, since its entropy of fusion is in accord with those of the other rare earths.

The heats of fusion range from a low value of 0.15 kcal/g-at for phosphorus to a high value of 25 kcal/g-at for carbon (graphite). All of the estimated values lie well within this range.

Carbon (Graphite). In a study of the carbon pressure–temperature, diagram, Bundy[55] was able to determine the heat of fusion of graphite at a pressure of 48 kilobars. It was assumed that this value for the heat of fusion, 25 kcal/g-at, was independent of both temperature and pressure; i.e., the heat of fusion is the same at 1 atm pressure and 4100°K (3827°C) as at 48 kilobars pressure and 5600°K (5327°C).

Estimated Data. Most of the values of the heats of fusion were obtained

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[55] F. P. Bundy, *J. Chem. Phys.* **38,** 618 (1963).

by multiplying an assumed estimated value for the entropy of fusion and the known melting point. As will be shown in Section 27, the entropy of fusion for body-centered cubic metals is 1.76 e.u. and for close-packed structures (face-centered cubic and hexagonal) it is 2.29 e.u. The entropy of fusion was assumed to be 1.76 e.u. for titanium, vanadium, zirconium, niobium, hafnium, tantalum, polonium, francium, radium, thorium, protactinium, uranium, and neptunium. Most of these metals are known or thought to be body-centered cubic just below their melting points. For the remaining elements, it was assumed that 1.76 was more representative of the entropy of fusion than was 2.29. The value 2.29 e.u. was assumed to be the entropy of fusion for boron, technetium, ruthenium, rhodium, rhenium, osmium, iridium, and actinium. All of these elements, except boron, are thought to have the closed-packed structure up to their melting points. This value of 2.29 e.u. for the entropy of fusion for boron was thought to be more representative than 1.76 e.u. The mean value for the entropy of fusion for the rare earths, which are known or thought to melt from the body-centered cubic form, is 1.48 e.u. By use of this value the heat of fusion was calculated for promethium, dysprosium, erbium, and lutetium. It should be mentioned that Kelley[54] used a value of 2.3 e.u. for the entropy of fusion to estimate the heat of fusion of any element for which the heat of fusion was not known, but Stull and Sinke[53] used 1.9 and 2.3 e.u. for body-centered cubic and close-packed metals, respectively. The technique used herein and that used by Stull and Sinke are essentially the same, except for the value used for the body-centered cubic metals. Presumably the present value is more accurate since more heats of fusion are available today than seven years ago.

VI. Boiling Point and Heat of Sublimation

10. BOILING POINT

The boiling points of the elements are listed in Table XI and are shown for the elements of the fourth, fifth, and sixth periods of the Periodic Table and for the rare-earth metals in Figs. 15 and 16a, respectively.

Most of the boiling points were calculated from vapor pressure data obtained at pressures substantially below 1 atm pressure. For many elements the original investigators calculated the boiling points, but for a few the reviewer calculated the value from the low-pressure data, which were usually given in the form

$$\log p_{mm} = -(A/T) + B, \tag{10.1}$$

TABLE XI. BOILING POINT AT 1 ATMOSPHERE

Element	Boiling point (°K)	Boiling point (°C)	Ref.
3 Li	1600	1327	1
4 Be	3142 ±100^{a}	2869^{a}	2, 3
5 B	4050 ±100	2777	4
6 C	4000^{b}	3727^{b}	5
11 Na	1154^{c}	881^{c}	6
12 Mg	1385	1112	5, 7
13 Al	2333	2060	7, 8
14 Si	2753	2480	9
15 P	553	280	7, 9
16 S	717.75^{c}	444.60^{c}	*d*
19 K	1027^{c}	754^{c}	6
20 Ca	1765	1492	5, 7
21 Sc	3537 ±30^{a}	3264^{a}	10, 11
22 Ti	3586^{a}	3313^{a}	12
23 V	3582 ±42	3309	13, 14
24 Cr	2918 ±35	2645	12, 15, 16
25 Mn	2368	2095	17
26 Fe	3160	2887	5
27 Co	3229^{a}	2956^{a}	18, 19
28 Ni	3055^{a}	2782^{a}	20
29 Cu	2811 ±20^{c}	2583^{c}	21
30 Zn	1175^{a}	902	22
31 Ga	2510	2237	5, 9
32 Ge	3100	2827	5, 9
33 As	886^{b}	613^{b}	5, 7, 9
34 Se	958	685	5, 9
37 Rb	959^{c}	686^{c}	6
38 Sr	1645	1372	5, 9
39 Y	3670^{a}	3397^{a}	11
40 Zr	4650	4377	5
41 Nb	4813^{a}	4540^{a}	23
42 Mo	5785 ±175	5512	12, 24
43 Tc	(5300)^{e}	(5030)^{e}	—
44 Ru	4325 ±25	4052	4, 25
45 Rh	3960 ±60	3687	26, 27, 28
46 Pd	3200	2927	29, 30
47 Ag	2468 ±15^{c}	2195^{c}	21
48 Cd	1038	765	5, 7
49 In	2279 ±6^{c}	2006^{c}	21, 31, 32
50 Sn	2766 ±14^{c}	2493^{c}	21, 33
51 Sb	1907 ±10^{c}	1634^{c}	21
52 Te	1163 ±1^{c}	890^{c}	34
55 Cs	939^{c}	666^{c}	6

TABLE XI. BOILING POINT AT 1 ATMOSPHERE—*Continued*

Element	Boiling point		Ref.
	(°K)	(°C)	
56 Ba	1910	1637	5, 7, 9
57 La	3713 ±70[a]	3440[a]	11, 35
58 Ce	3972[a]	3699[a]	35
59 Pr	3616[a]	3343[a]	36
60 Nd	2956[a]	2683[a]	37
61 Pm	(2730)[e]	(2460)[e]	—
62 Sm	(2140)[e]	(1870)[e]	—
63 Eu	1971[a]	1698[a]	38
64 Gd	(3540)[e]	(3270)[e]	—
65 Tb	(3810)[e]	(3540)[e]	—
66 Dy	3011[a]	2738[a]	39
67 Ho	3228[a]	2955[a]	40
68 Er	(3000)[e]	(2730)[e]	—
69 Tm	2266[a]	1993[a]	41
70 Yb	(1970)[e]	(1700)[e]	—
71 Lu	(4140)[e]	(3870)[e]	—
72 Hf	4575 ±150	4302	42
73 Ta	5760 ±60	5487	5, 12
74 W	6000 ±200	5727	5, 7
75 Re	6035 ±135	5762	5, 9
76 Os	5300 ±100	5027	25
77 Ir	4820 ±30	4547	4, 27, 28
78 Pt	4100	3827	27, 29
79 Au	3240	2967	7, 9
80 Hg	629.73[c]	356.58[c]	*d*
81 Tl	1939	1666	43
82 Pb	2022 ±10[c]	1749[c]	21
83 Bi	1824 ±8[c]	1551[c]	21, 44
84 Po	1235	962	5
87 Fr	(1020)[e]	(750)[e]	—
88 Ra	(1900)[e]	(1630)[e]	—
89 Ac	3200 ±300	2927	45
90 Th	4500	4227	5
91 Pa	(4680)[e]	(4410)[e]	—
92 U	3950 ±250	3677	46
93 Np	(4150)[e]	(3880)[e]	—
94 Pu	3727	3454	47

[a] Calculated by reviewer from vapor pressure data given in reference(s) cited.
[b] Sublimation point at 1 atm.
[c] Direct observation.
[d] Value taken from Table VIII.
[e] Estimated value; see text for further discussion.

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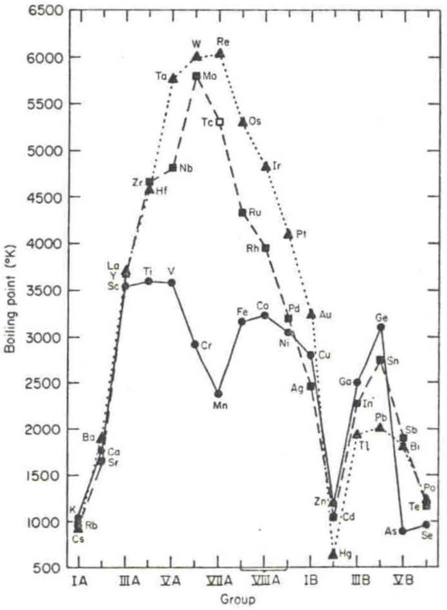
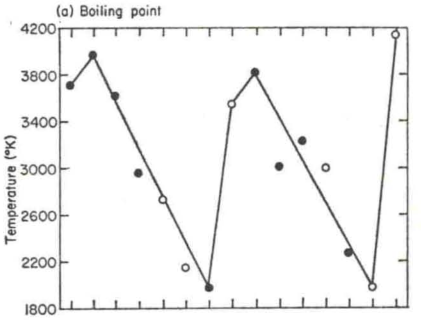


FIG. 15. Boiling point of the elements of the fourth, fifth, and sixth periods of the Periodic Table. Open points are estimated values.


(a) Boiling point

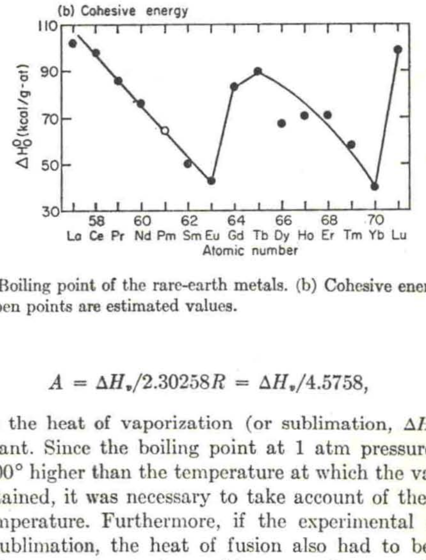

(b) Cohesive energy

FIG. 16. (a) Boiling point of the rare-earth metals. (b) Cohesive energy of the rare-earth metals. Open points are estimated values.

where

$$A = \Delta H_v/2.30258R = \Delta H_v/4.5758, \tag{10.2}$$

where ΔH_v is the heat of vaporization (or sublimation, ΔH_s) and R is the gas constant. Since the boiling point at 1 atm pressure may be as much as a 1000° higher than the temperature at which the vapor pressure data were obtained, it was necessary to take account of the variation of ΔH_v with temperature. Furthermore, if the experimental data yielded the heat of sublimation, the heat of fusion also had to be considered. These corrections were made by making extensive use of Stull's and Sinke's compilation of high-temperature specific heat data[53] and the heats of fusion listed in Table X. Values which were calculated by the reviewer according to the above procedure are so identified in Table XI.

Perhaps as many as one-fourth of the boiling points listed in Table XI are the result of direct observations. These values were assumed to be more accurate than those calculated from the low-pressure data. It was found, however, that for most of the elements for which reliable data exist from both types of experiments the two values usually agreed within ±25°. It should be noted that the direct-observation data are usually available for only the lower boiling elements.

The boiling points range from a low value of 553°K (280°C) for phosphorus to a high value of 6035°K (5762°C) for rhenium. Tungsten, however, may actually have a higher boiling point than that of rhenium because of the errors associated with calculating the boiling point from low-temperature vapor pressure data. The boiling points only differ by 35°, and the error associated with the boiling point of rhenium is ±135° and that for tungsten is ±200°.

The variation of the boiling points of the elements of the fourth, fifth, and sixth periods of the Periodic Table with the group location of the element (Fig. 15) shows a behavior very similar to those previously noted for many of the other physical properties: notably the large peak near the group VIA elements, the minimum at the group IIB elements, the second, but smaller, peak at the group IVB elements, and the anomalous behavior of the fourth-period transition elements, chromium through cobalt.

The variation of the boiling points of the rare earths as a function of atomic number is shown in Fig. 16a. This plot is very much different from those given in Figs. 2, 5, 10, and 13. The difference is probably due to the fact that in the condensed state the normal electronic configuration is $4f^n5d^16s^2$, where n varies from 0 for lanthanum to 14 for lutetium, but in the gaseous (isolated atoms) state the normal configuration is $4f^{n+1}6s^2$. If one makes a more thorough examination, one notes that for lanthanum, gadolinium ($n = 7$), and lutetium the condensed-state and gaseous-state configurations are the same, $4f^n5d^16s^2$, i.e., they are trivalent in both states. For europium ($n = 6$) and ytterbium ($n = 13$), the configurations in the two states are also the same, but they are $4f^{n+1}6s^2$, i.e., these two metals are divalent in both the gaseous and condensed states. For the other elements, praseodymium ($n = 2$), neodymium ($n = 3$), promethium ($n = 4$), samarium ($n = 5$), dysprosium ($n = 9$), holmium ($n = 10$), erbium ($n = 11$), and thulium ($n = 12$), the condensed-state configuration is $4f^n5d^16s^2$ and the gaseous-state configuration is $4f^{n+1}6s^2$. The gradual decrease in the boiling point as one proceeds from the maxima near lanthanum and gadolinium to the minima at europium and ytterbium may be due to the tendency towards a divalent character at high temperature in the condensed state as n increases. It is interesting to note that there is much doubt concerning the electronic configuration of gaseous cerium ($n = 1$) and terbium ($n = 8$); that is, the configuration is thought to be $4f^n5d^16s^2$ or $4f^{n+1}6s^2$ or a mixture of both. It is difficult to see how this might explain the fact that the observed boiling point of cerium is higher than that of lanthanum or that of terbium is higher than that of gadolinium. If, on the other hand, the gaseous configuration were $4f^{n-1}5d^26s^2$ or a mixture of this and the $4f^n5d^16s^2$ configuration, this might account for a higher boiling point, since the tetravalent transition metals have higher boiling points than the trivalent transition metals (Fig. 15). Apparently not many have considered the tetravalent state a possibility for cerium and terbium. In support of the possibility of a tetravalent character are Waber's Hartree calculations[56] for cerium which indicate that the $4f^15d^36s^2$ configuration has a lower energy than either the $4f^15d^16s^2$ or the $5d^26s^2$ configurations.

Estimated Data. The boiling points were estimated by using the known or estimated heats of sublimation at 298°K (25°C) (see Table XII), and by assuming Trouton's rule to be valid (except that the constant used herein was different from that normally associated with this rule; see Section 27). The heats of sublimation were corrected to the corresponding heats of vaporization at the boiling point as outlined above. The mean value of the entropy of vaporization (Trouton's constant) for all of the elements is 25.5 e.u. (see Section 27). This value was used to estimate the boiling point of technetium, protactinium, and neptunium. The mean value for the trivalent rare earths (22.3 e.u.) was used for the estimated entropy of vaporization of promethium, samarium, gadolinium, terbium, erbium, and lutetium. The entropy of vaporization for ytterbium was assumed to equal that of europium (18.1 e.u.), and that for radium was assumed to equal the mean value of those of the three other alkaline-earth metals (19.9 e.u.). The entropy of vaporization of the alkali metals decreases linearly with increasing atomic number; therefore, this straight line was extrapolated to obtain an entropy of 15.8 e.u. for francium.

11. HEAT OF SUBLIMATION

The heats of sublimation at 298°K (25°C), ΔH_s^{298}, which are listed in Table XII, were obtained from vapor pressure data by use of Eqs. (10.1) and (10.2), or directly from high-temperature mass spectrometric data. The value, in general, is usually obtained at some temperature other than 298°K (25°C) regardless of technique. The measured value was corrected to 298°K (25°C) either by the authors of the original paper or by the reviewer. The reviewer has made extensive use of the thermodynamic data given by Stull and Sinke[53] in making these corrections.

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TABLE XII. COHESIVE ENERGY AND HEAT OF SUBLIMATION AT 298°K

Element	ΔH_0° (kcal/g-at)	ΔH_s^{298} (kcal/g-at)	Ref.
3 Li	38.20	38.58 ±0.40	1
4 Be	76.9	77.9	2, 3
5 B	130.8	132.0 ±2.3	4–9
6 C	169.6	170.9	2, 3, 10
11 Na	26.02	25.92 ±0.15	1
12 Mg	35.3	35.6	2, 3
13 Al	76.9	77.5 ±1.5	2, 3
14 Si	107.4	108.4 ±3.0	11
15 P	75.0[a]	75.3	10
16 S	65.9	66.4	2, 10
19 K	21.69	21.48 ±0.06	1, 12
20 Ca	42.1	42.2	2, 3
21 Sc	80.06	80.45 ±0.35	13, 14
22 Ti	112.2	112.7	2, 3, 10
23 V	122.0	122.8 ±5.0	2, 3
24 Cr	94.5	95.0 ±1.0	2, 3, 15
25 Mn	66.9	67.2	2, 3
26 Fe	99.4	100.0 ±1.0	2, 3, 15
27 Co	101.7	102.1 ±0.9	2, 3, 16
28 Ni	102.3	102.8	2, 3
29 Cu	80.8	81.1	2, 3
30 Zn	31.0	31.1	2, 3, 10, 17
31 Ga	64.7	64.9	3
32 Ge	88.8	89.5	3, 10
33 As	28.7	29.0	10
34 Se	49.2	49.4	10
37 Rb	20.2	19.9 ±0.5	2, 3, 10, 18
38 Sr	39.3[a]	39.2	10
39 Y	97.6	97.8	14
40 Zr	145.7	146.0 ±1.0	2, 3
41 Nb	174.3	175.0 ±2.5	3, 19
42 Mo	157.1	157.5	2, 3
43 Tc	(152)[b]	(152)[b,c]	—
44 Ru	154.0[a]	154.2 ±0.7	7, 20
45 Rh	133.0[a]	133.2 ±1.0	21–24
46 Pd	89.9	90.1 ±0.9	24, 25
47 Ag	68.3	68.4	2, 3
48 Cd	26.8	26.8	2, 3
49 In	57.4	57.3 ±0.3	3, 26
50 Sn(w)	72.0	72.0	2, 3, 10
51 Sb	62.3	62.6[d]	2, 3, 17
52 Te	46.6	46.6 ±2.0	2, 3, 10
55 Cs	19.22	18.84 ±0.29	2, 3, 18

TABLE XII. COHESIVE ENERGY AND HEAT OF SUBLIMATION AT 298°K—*Continued*

Element	ΔH_0° (kcal/g-at)	ΔH_s^{298} (kcal/g-at)	Ref.
56 Ba	42.8	42.5 ±0.5	2, 3
57 La	101.9	101.8 ±2.2	14, 27
58 Ce(γ)	97.9[a]	97.6	27
59 Pr	85.8[a]	85.5 ±1.2	28–30
60 Nd	75.9	75.6 ±0.6	29, 31, 32
61 Pm	(64)[b]	(64)[b,c]	—
62 Sm	50.2[a]	49.9	33
63 Eu	42.9[a]	42.6 ±0.5	34, 35
64 Gd	82.7	82.4 ±1.2	31, 35
65 Tb	89.9[a]	89.6 ±2.2	31, 36
66 Dy	66.9[a]	66.6 ±4.8	31, 33
67 Ho	70.5[a]	70.2 ±0.6	31, 37
68 Er	70.7[a]	70.4 ±5.0	31, 35
69 Tm	58.3[a]	58.0 ±0.4	33, 38
70 Yb	40.3[a]	40.0	33
71 Lu	98.8	98.8 ±4.0	31, 36
72 Hf	145.5	145.5 ±3.0	39
73 Ta	186.7	186.8	2, 3
74 W	199.7	200.0 ±1.0	2, 3
75 Re	186.2	186.4 ±0.6	3, 10
76 Os	187.2[a]	187.4 ±0.9	20
77 Ir	158.9[a]	159.1 ±0.8	7, 21, 22
78 Pt	134.8	135.0 ±0.2	21, 24
79 Au	87.6	87.6 ±0.7	2, 3, 40
80 Hg	15.41	14.66 ±0.01	1
81 Tl	43.39	43.24 ±0.24	2, 3, 26, 41, 42
82 Pb	47.0	46.8	2, 3, 43
83 Bi	50.01	49.95 ±0.27	44–46
84 Po	34.6[a]	34.5	3, 10
87 Fr	(18.6)[b]	(18.1)[b,c]	—
88 Ra	(42)[b]	(42)[b,c]	—
89 Ac	(104)[b]	(104)[b,c]	—
90 Th	136.7	136.6	2, 10
91 Pa	(132)[b]	(132)[b,c]	—
92 U	125	125 ±3	2
93 Np	(113)[b]	(113)[b,c]	—
94 Pu	91.8	91.8[c]	47

[a] Estimated the value for $(\Delta H_0^\circ - \Delta H_s^{298})$ to obtain ΔH_0° from given ΔH_s^{298}.

[b] Estimated value; see text for further discussion.

[c] Estimated the value for $(\Delta H_0^\circ - \Delta H_s^{298})$ to obtain ΔH_s^{298} from given ΔH_0°.

[d] The data given by Rosenblatt and Birchenall[17] corresponded to the process $4\,Sb(s) = Sb_4(g)$. The reviewer used 13.7 kcal for the dissociation of $Sb_4(g)$ into $Sb(g)$ to determine the heat of sublimation given here.

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Two sets of heats of sublimation for the elements are listed in Table XII. One corresponds to the value at 0°K, and is commonly called the cohesive energy, $\Delta H_0°$. The cohesive energy is discussed in Section 12. The second set of values is the heat of sublimation at 298°K (25°C). This value is more important than the cohesive energy for those involved in making thermodynamic calculations, since almost all thermodynamic data are based on the standard state at 298°K (25°C). As a first approximation $\Delta H_0° \simeq \Delta H_s^{298}$, and for many applications knowledge of one or the other is sufficient. Since there is a difference between the two quantities, both are listed for convenience.

To convert $\Delta H_0°$ to ΔH_s^{298} or vice versa the reviewer made use of the tabulations of $(H_{298}° - H_0°)$ for the solid and for the gas as given by Lewis *et al.*[57] and Stull and Sinke.[53] That is,

$$\Delta H_0° - \Delta H_s^{298} = (H_{298}° - H_0°)_{(s)} - (H_{298}° - H_0°)_{(g)}. \quad (11.1)$$

If either or both values for $(H_{298}° - H_0°)$ were not available, then the reviewer estimated them; data so estimated are identified in Table XII.

Since $\Delta H_s^{298} \simeq \Delta H_0°$, the discussion concerning the periodic variation of this quantity and its relationship to other properties is deferred until Section 12.

Estimated Data. The heats of sublimation at 298°K (25°C) that were not experimentally determined were estimated from the cohesive energies.

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[57] G. N. Lewis, M. Randall, K. S. Pitzer, and L. Brewer, "Thermodynamics," 2nd ed. McGraw-Hill, New York, 1961.

The techniques used to estimate the cohesive energy are discussed in Section 12.

12. Cohesive Energy

The cohesive energy is of much more interest to the theoretical and solid state physicists than is the heat of sublimation at 298°K (25°C), because the cohesive energy is the energy required to dissociate 1 g-at of a solid substance into free atoms at 0°K (−273°C). Much work has been and is being done by theoretical physicists to attempt to calculate the cohesive energy of a solid from first principles.[58] Most of their success, however, has been limited to the alkali metals.

The derivation of the data shown in Table XII has been discussed in the previous section on the heat of sublimation and therefore will not be repeated here.

The cohesive energy varies from a minimum value of 15.41 kcal/g-at for mercury to a maximum value of 199.7 kcal/g-at for tungsten. The estimated values fall well within this range.

The cohesive energies for the elements of the fourth, fifth, and sixth periods of the Periodic Table are shown in Fig. 17. This figure is similar to those given previously. The major maximum in the cohesive energy occurs at the d^3s^2 configuration (except for the sixth period, where it is d^4s^2); the minimum occurs at the $d^{10}s^2$ configuration; and the smaller maximum at the $d^{10}s^2p^2$ configuration (except for the sixth period, where it is $d^{10}s^2p^3$). The anomalous behavior of the fourth-period transition metals observed in many of the other physical properties is not as evident in this plot, except for the pronounced drop as one proceeds from chromium to manganese.

The cohesive energy for rare-earth metals is shown in Fig. 16b. A comparison of this plot with the plot of the boiling points versus the atomic numbers, Fig. 16a, shows that the two plots are very similar. The discussion given in Section 10 concerning this unusual behavior of the boiling points of the rare earths is also applicable to the cohesive energy, since the cohesive energy divided by the boiling point is approximately a constant (Trouton's rule).

The relationship between the bulk modulus, B, and the cohesive energy was discussed earlier in Section 6 (also see Figs. 7 and 8), where it was found that for a given group

$$\Delta H_0{}^\circ = mB + b, \tag{12.1}$$

where m is the slope (both positive and negative values were found) and

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[58] J. Callaway, *Solid State Phys.* **7**, 99 (1958).

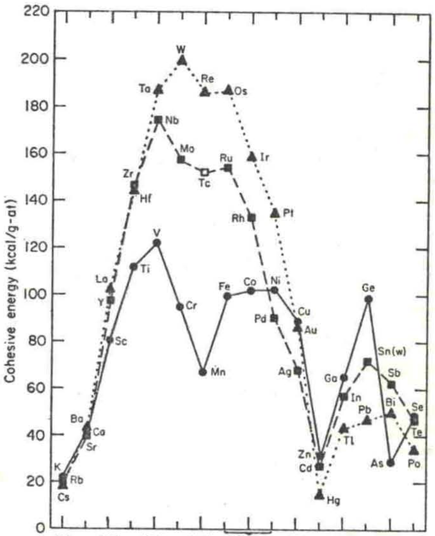

Fig. 17. Cohesive energy of the elements of the fourth, fifth, and sixth periods of the Periodic Table. Open points are estimated values.

b is the intercept. The values for m and b were found to be different for each particular group. This relationship was used to estimate some of the unknown bulk moduli.

Estimated Data. The value for technetium was estimated in two ways: it was assumed (1) to be equal to the mean value for molybdenum and ruthenium, and (2) to be smaller than the value for ruthenium by the same percent as the value of rhenium is smaller than that of osmium. The mean value of these two estimated numbers was chosen as the value for this compilation. The value for promethium was estimated from the straight line of Fig. 16b. The values for francium, radium, and actinium were estimated from plots of the known cohesive energy of their respective cogeners versus the period number. The values for these three elements were all obtained by extrapolation. The values for protactinium and neptunium were estimated by interpolation from a plot of the cohesive energy versus the atomic number of thorium, uranium, and plutonium.