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 ±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 ±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.

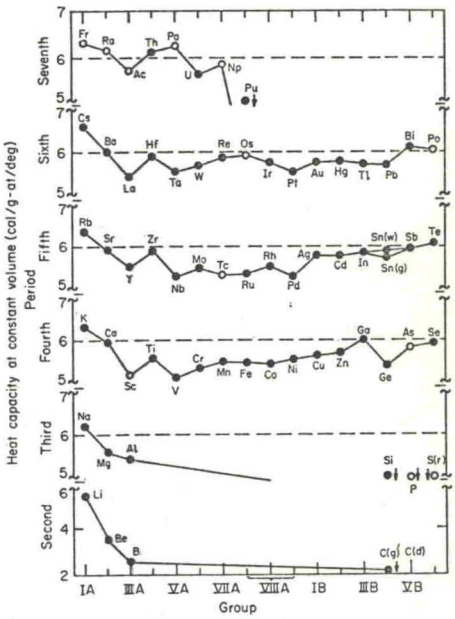

FIG. 20. Heat capacity at constant volume (lattice contribution only) of all of the elements considered in this review with the exception of the rare-earth metals. The horizontal dashed line represents the Dulong and Petit value of $3R = 5.96$. The open points are estimated values.

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