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 $\pm 25°$. 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 $\pm135°$ and that for tungsten is $\pm200°$.

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 $4f^15d^16s^2$ 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.

[56] J. T. Waber, *Proc. 3rd Rare Earth Conf.*, *Clearwater, Florida, 1963*. Gordon & Breach, New York, 1964 (to be published).