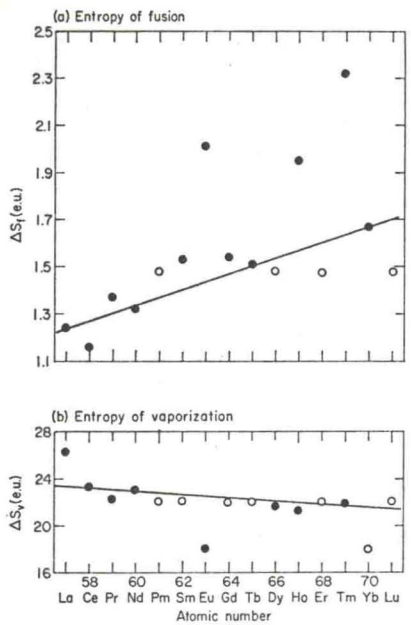

FIG. 30. (a) Entropy of fusion of the rare-earth metals. (b) Entropy of vaporization of the rare-earth metals. Open points are estimated data.

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 $\pm$4.5 e.u. if one excludes the values of carbon, phosphorus, sulfur, and selenium. The percentage error is $\pm$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