The experimental vapor density is practically equal to the ideal-gas density of mercury up to about 85 percent of the critical temperature. By extrapolating from the curve for the ideal-gas density to the rectilinear diameter, one obtains a temperature which always lies above the critical point. Furthermore, it is known that the density of the saturated vapor is only a fraction of the density of the liquid below the critical temperature. Thus, the measurements of Julie Bender, which were made up to 1650°K, were not far from the critical point (see Fig. 2). The $T_c$ and $P_c$ were actually measured for the first time by Birch (*18*) in Bridgeman's laboratory at Harvard University.

It was assumed that the law of Cailletet and Mathias holds for other metals also, and on this basis I developed a semi-empirical method of estimating the critical temperatures of all metals for which density data for the liquid state are available over a substantial temperature range.

Use of the method is illustrated in Fig. 3, with silver as the example (*19*). Here, $T_c$ is estimated to be 7500°K, and $D_c$, to be 1.85 g/cm$^3$. Diagrams of the temperature range for the liquid phase of many other metals, such as lead, tin, bismuth, magnesium, sodium, potassium, and gallium, were constructed in the same way, and it was found that the critical density of metals is usually about one-fourth the density at the normal boiling point.

The big differences in density between liquid metals and gases, at a given temperature and pressure, may be illustrated by comparing the density of liquid tungsten at 6000°K and the density of argon at the same temperature and at pressure of 1 atmosphere. The density of tungsten is estimated to be 16.40 g/cm$^3$ and that of argon, 8.10 $\times$ 10$^{-5}$ g/cm$^3$; the ratio of the densities is 200,000 to 1!

A second and independent semi-empirical method for estimating critical temperatures is based on van der Waals's theorem of corresponding states. The theorem requires (*20*) that, for example, the entropy of vaporization of various liquids should be equal at corresponding temperatures, and vice versa.

The heat of vaporization of mercury, $\Delta H_{vap}$, is known over an appreciable temperature range and the entropy of vaporization, $\Delta S_{vap}$ (or $\Delta H_{vap}\ T$), can be readily extrapolated to the critical temperature on a reduced temperature plot. Figure 4 is a plot of the entropy curve and the reduced-temperature curve for mercury and of corresponding curves for a number of well-known normal liquids, such as carbon dioxide, carbon tetrachloride, ammonia, benzene, and water. Mercury has a markedly distinct behavior. Let us assume for the present that other metals behave in the same manner. By assuming the principle of corresponding states to be valid for other metals and by using the experimentally determined values for entropy of vaporization of other metals—for example, at their normal boiling points—we can, from Fig. 4, derive their reduced temperatures and thus their approximate critical temperatures. Table 3 contains a summary of critical temperatures of a number of metals, arranged, in ascending order, from 1733°K for mercury to 23,000°K for tungsten.

Data on liquid sodium (*21*) have recently become available which give $\Delta H_{vap}$ and $\Delta S_{vap}$ over the whole range from 800°R (445°K) to 3000°R (1667°K). In the case of liquid sodium, a close fit to the mercury curve can be obtained only if the critical temperature for sodium is assumed to be 2800°K. Usually the critical temperatures estimated by the two methods are in good agreement (*22*). They cover a wide temperature range, and many metals—for example, uranium, zirconium, molybdenum, rhenium, tantalum, and tungsten—have critical temperatures above 10,000°K. The predicted critical constants of the alkali metals, based on a combination of the two methods, are given in Table 4.

The important point is not so much the particular critical temperature of a metal as the fact that many metals can be heated to over 10,000°K and still remain liquid (at saturated-vapor pressure).

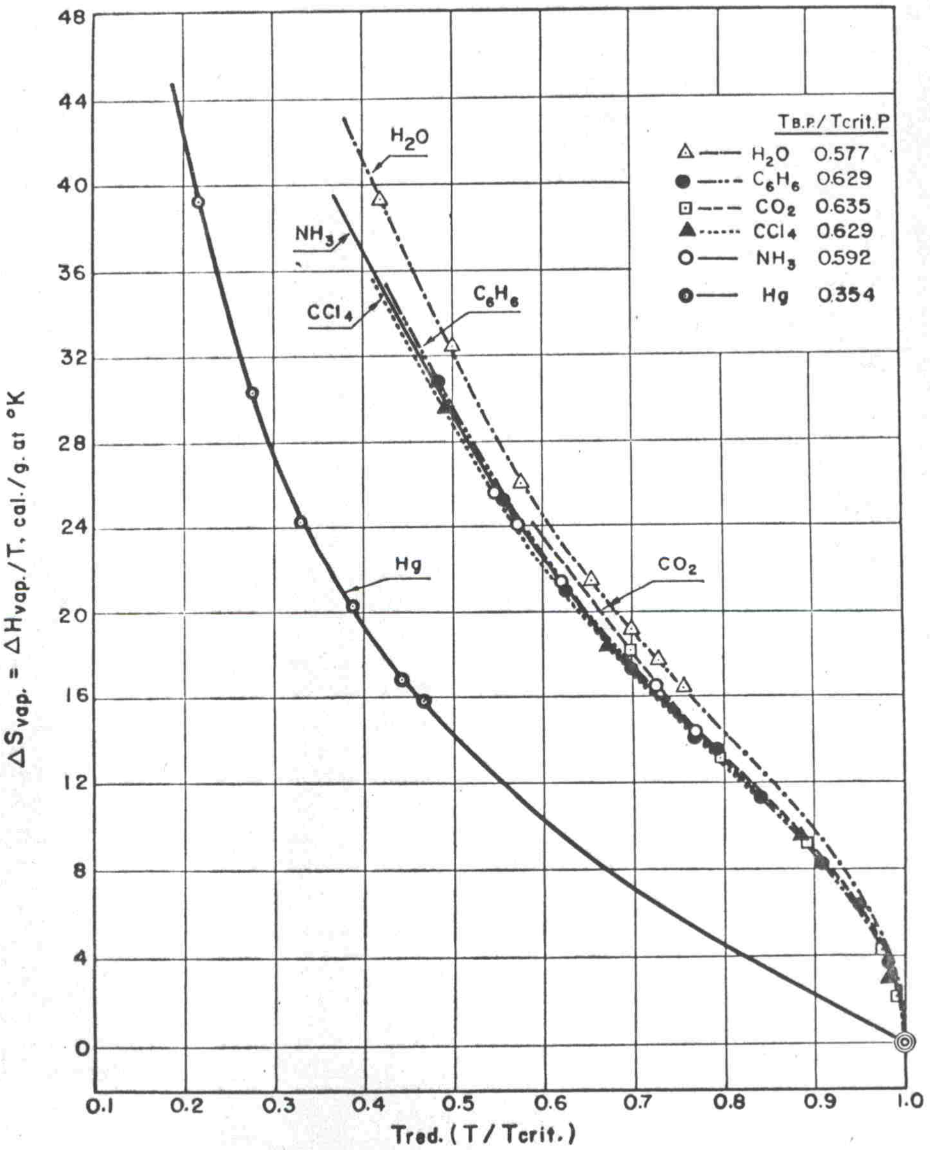

Fig. 4. Entropy plotted against reduced-temperature curve for mercury and other liquids.