

direct determination of the critical data of a metal. In view of their importance and because mercury is the lowest boiling metal and thus the easier with which to experiment, these measurements should be repeated to insure maximum reliability.

The *complete* range of saturated vapour-pressure of liquid mercury, over the whole range from the melting point to the critical point, is a straight line on a logarithmic plot,<sup>(1)</sup> over a  $10^{12}$ -fold increase in pressure from  $1.91 \times 10^{-9}$  atm at the melting point, i.e.,  $234.3^\circ\text{K}$ , to  $1587 \pm 50$  atm at the critical point ( $1733^\circ\text{K}$ ).

The vapour-pressure from the melting point to about 2 atm are known with great precision.<sup>(12)</sup> Two sets of data are available for the range of 2–140 atm.; the older data are due to CAILLETET<sup>(13)</sup>, and the more recent to BERNHARDT<sup>(14)</sup>. The latter extended his measurement to  $1708^\circ\text{K}$ , and to a pressure of 1955 atm. Both CAILLETET and BERNHARDT observed the actual boiling of the mercury in a pressure vessel; the measurements became progressively more difficult and less accurate at the higher pressures and temperatures.

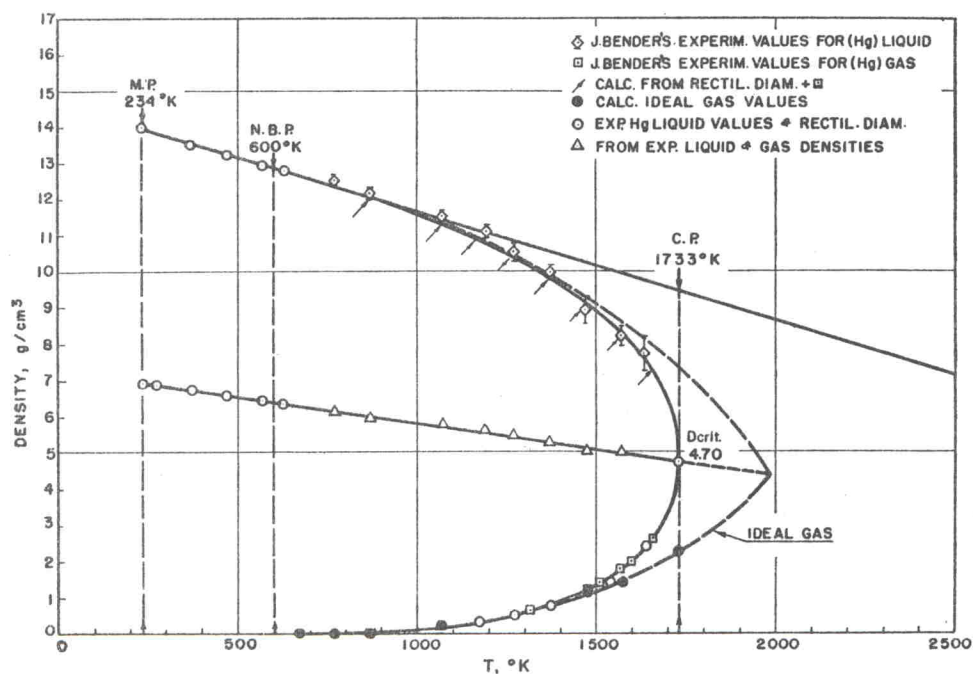


FIG. 1.

*The liquid and saturated vapour density of mercury over the whole liquid temperature range*

Fig. 1 shows a summary of mercury data on the density of both liquid and vapour and demonstrates that the law of rectilinear diameter is fulfilled. Because of the importance of these data they will be discussed in detail. They are due to the observations of BENDER<sup>(15,16)</sup> who measured the density of both liquid and saturated vapour

<sup>(12)</sup> See, for example, *Handbook of Chemistry and Physics*, (40th Ed.), p. 2331. (1959).

<sup>(13)</sup> CAILLETET, COLARDEAU and RIVIERE, *C.R. Acad. Sci., Paris* **130**, 1585 (1900).

<sup>(14)</sup> F. BERNHARDT, *Phys. Z.*, **26**, 265–275 (1925).

<sup>(15)</sup> J. BENDER, *Phys. Z.*, **16**, 246–247 (1915).

<sup>(16)</sup> J. BENDER, *Phys. Z.*, **19**, 410–414 (1918).

in the range of 500–1380°C, i.e., up to 60°C of the critical point, in sealed quartz vessels. The liquid densities from the melting point to the normal boiling point are known<sup>(17)</sup> with great accuracy and were also used in Fig. 1; they are indicated by  $\odot$ ; BENDER's values for the saturated vapour are shown by  $\bullet$ , while the liquid densities together with their error range are indicated by  $\diamond$ . The calculated values for the vapour density, assuming ideal gas laws and the vapour-pressure of mercury, are shown as  $\square$ ; up to about 1200°C there is no significant deviation between the ideal and actual values.

Values for the liquid density, calculated from this law and the experimental vapour density, are indicated with  $\nearrow$  on the liquid curve; values for  $\frac{1}{2}(D_{\text{liq.}} + D_{\text{vap.}})$ , calculated from the experimental data, are shown in triangles  $\triangle$  on the rectilinear diameter. The vapour densities, because of their lower absolute values, can be determined with greater accuracy; the liquid values show appreciable scatter because of experimental difficulties.

Using BENDER's smoothed values, we obtain for the equation of mercury's rectilinear diameter, the expression:

$$D_{\text{rec.}} \delta = 6.7978 - 14.30 \times 10^{-4} T (^{\circ}\text{C}).$$

Based on this equation the critical density of mercury, at 1460°C., equals 4.70 g/cm<sup>3</sup>, whereas BIRCH<sup>(11)</sup> estimated a value of 5 g/cm<sup>3</sup>.

We see further, from Fig. 1, that the two legs of the Cailletet–Mathias curve have two envelopes, (shown in dotted lines). The *first envelope* is the curve of the *ideal gas density*, the latter being always *less* than the actual saturated vapour density. The *second envelope* of the liquid leg is obtained by deducting the ideal saturated vapour density, in line with the rectilinear law, from the straight liquid density line. The two envelopes meet at a point which sets an *upper limit for the critical temperature*; in the case of mercury this limit is about 2000°K (see Fig. 1.)

Since the rectilinear diameter law is fulfilled for liquid mercury, as the only metal among many other liquids, *we will assume* it to hold for other metals also. It would be highly desirable if critical data for other metals were obtained so that the experimental evidence for the validity of the law can be put on as broad a foundation as possible.

#### THE TEMPERATURE RANGE OF OTHER LIQUID METALS

We are now interested in estimating, even if only approximately, the temperature range of other liquid metals. Usually, for most homopolar compounds, as has been mentioned, the normal boiling point corresponds to approximately two-thirds of the critical temperature.

As can be seen, this is not the case for the only known metal, mercury, where the ratio of the critical point to the normal boiling point

$$1733^{\circ}\text{K}/629.9^{\circ}\text{K} = 2.75$$

In order to estimate critical temperatures it is best to choose those physical properties which equal zero at the critical temperature and apply the principle of

<sup>(17)</sup> Data of THIESSEN and SCHEEL, *Handbook of Chemistry and Physics*, (40th Ed.) p. 2115. (1959).