Construction of the temperature range diagrams of liquid lead and silver

The whole temperature range of a liquid metal, i.e., the spread from the melting point to the critical point and an estimate of the critical data are of theoretical and practical importance.

One can now proceed with the construction of the liquid range diagrams of lead and silver. They are shown in Figs. 1 and 2.

From the vapour pressure data of both metals we can calculate the ideal gas density of their saturated vapours. It was demonstrated many years ago by WARTENBERG[6] that the vapours of Pb and Ag are monatomic. The density was determined directly in an iridium flask at a temperature close to the boiling point. In the case of mercury[1,2] it was shown that the ideal gas density equals the experimental saturated vapour density up to $\simeq$85 per cent of the critical point. It is only above a reduced temperature of $\simeq$0·85 that the actual saturated vapour density increases rapidly and of course equals the liquid density at the critical point.

As one will see later the ideal gas density at the normal boiling points (see Table 2) is still so small that it can be neglected. Thus, the rectilinear diameter density:

$$D_{\text{Ø}^{\nearrow}} = \tfrac{1}{2} D_{\text{liq.}}$$

and the equation of the rectilinear diameter is, for Pb:

$$D^{\text{Pb}}_{\text{Ø}^{\nearrow}} = 5{\cdot}339\text{-}6{\cdot}587 \times 10^{-4}(T\text{-}600{\cdot}6^{\circ})$$

or

$$= 5{\cdot}734\text{-}6{\cdot}587 \times 10^{-4} \cdot T$$

and for Ag:

$$D^{\text{Ag}}_{\text{Ø}^{\nearrow}} = 4{\cdot}673\text{-}4{\cdot}534 \times 10^{-4}(T\text{-}1234{\cdot}0^{\circ})$$

or

$$= 5{\cdot}232\text{-}4{\cdot}534 \times 10^{-4}T,$$

where again D is in g/cm^3 and T in °K.

The rectilinear diameter is extrapolated in Figs. 1 and 2 to the critical region. The probable error is indicated by a dotted line "error cone."

Estimate of the critical temperatures of lead and silver from the theorem of corresponding states

The pertinent data are taken from reference 3. The entropy of vaporization curve for mercury is given in references 1 and 2, and permits one to obtain the reduced temperature of Pb and Ag at their normal boiling points.

	Pb	Ag
Heat of vaporization at normal b.p. (cal/g atom)	42,880	60,960
Normal b.p. (°K)	2024	2450
Entropy of vaporization at normal b.p. (cal g atom^{-1} °K^{-1})	21·2	24·9
Reduced temperature ($T_{\text{red.}}$)	0·375	0·327
Critical temperature, T_c (°K)	5400	7500

These critical temperatures are estimated to be accurate to $\pm$10 per cent. This is indicated in Figs. 1 and 2 by the shaded area in the critical region. We will see later that these critical temperatures are bracketed on both the high and low

[6] H. V. WARTENBERG, *Z. Anorg. Chem.* **56**, 320–336 (1908).

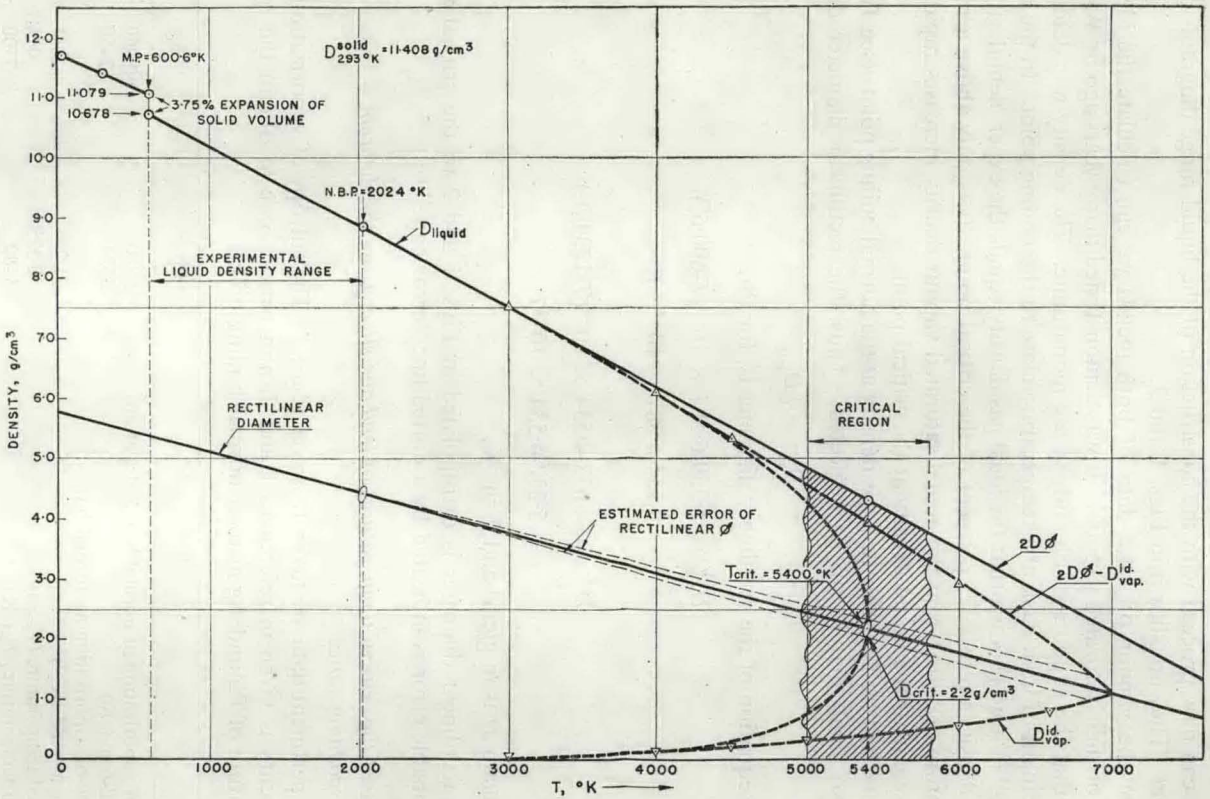

FIG. 1.—Liquid temperature range diagram of lead.