

The temperature range of liquid lead and silver and an estimate of their critical constants 745

WARTENBERG.<sup>(6)</sup> They show appreciable scatter around 2400°K, and additional experimental work in this pressure range and above is recommended. STULL and SINKF'S vapour-pressure data lead to the following expressions, for

Pb:

$$\log_{10} P_{\text{atm}} = -9.596/T + 4.74043 \quad (T \text{ in } ^\circ\text{K})$$

or in exponential form:  $P_{\text{atm}} = 5.5009 \times 10^4 \cdot \exp(-22,100/T)$ , and for

Ag:

$$\log_{10} P_{\text{atm}} = -13.388/T + 5.46223 \quad (T \text{ in } ^\circ\text{K})$$

or in exponential form:  $P_{\text{atm}} = 2.8989 \times 10^5 \cdot \exp(-30,827/T)$

Since the density of the ideal saturated vapour,  $D_{\text{vap}} = A/V_A$ , where  $A$  and  $V_A$  are

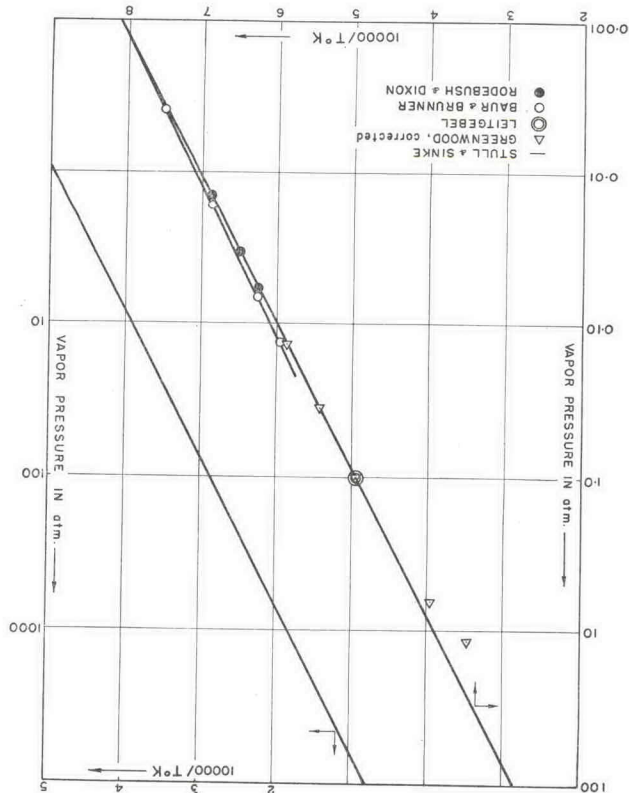


FIG. 3.—Vapour-pressure of lead.

atomic weight and volume respectively, it follows, from the ideal gas laws, that:

$$D_{\text{vap}} = A \cdot P/R \cdot T$$

thus,  $D_{\text{vap}}$ , for Pb =  $1.38920/T \times 10^5 \cdot \exp(-22,100/T)$  and for Ag =  $3.8145/T \times 10^5 \cdot \exp(-30,827/T)$

The values so obtained for lead and silver are tabulated in Table 2.

TABLE 2.— $D_{\text{vap}}^{\text{id}}$  IN G/CM<sup>3</sup> CALCULATED FROM VAPOUR-PRESSURE EQUATIONS AND IDEAL GAS LAWS

$T$ (°K)	Pb		Ag	
	$D$ (g/cm <sup>3</sup> )	$P$ (Atm)	$D$ (g/cm <sup>3</sup> )	$P$ (Atm)
2024	0.00124	1.00	—	—
2500	0.00805	7.97	0.000681	1.28
3000	0.0292	34.7	0.004340	10.00
3500	0.0722	100.1	0.01629	43.4
4000	0.1381	219	0.04286	130.0
4500	0.2276	406	0.08967	307
5000	0.3344	662	0.1601	610
5500	—	—	0.2549	1067
6000	—	—	0.3730	1700
6500	—	—	0.5111	2527
7000	—	—	0.6658	3500

Calculations of the liquid densities of Pb and Ag above their normal boiling point

From the law of rectilinear diameter it follows that:

$$D_{\text{liq.}} = 2D_{\text{g}}^{\text{r}} - D_{\text{vap.}}^{\text{id.}}$$

up to about  $T_{\text{red.}} = 0.85$ , i.e., 4500°K for Pb and 6300°K for Ag. Above these temperatures, as was shown in the case of mercury,<sup>(1,2)</sup> the *real* saturated vapour density begins to digress appreciably from the ideal density. This can be readily seen from the anticipated liquid and gas densities in the critical and near critical regions of Figs. 1 and 2.

Up to  $T_{\text{red.}} = 0.85$  and based on the above general equation, the specific and exact equations for the densities of Pb and Ag are respectively:

$D_{\text{liq.}}^{\text{r}}$  of Pb, in g/cm<sup>3</sup> =

$$11.4692 - 13.174 \times 10^{-4}T - \frac{1.3892}{T} \times 10^5 \cdot \exp(-22,100/T)$$

and for Ag =

$$10.465 - 9.067 \times 10^{-4}T - \frac{3.8145}{T} \times 10^5 \cdot \exp(-30,827/T)$$

where  $T$  is in °K.

In the classical work on the densities of liquids it has been the custom to express the liquid density in power series in  $T$  (see for example International Critical Tables, Volumes 1, 2 and 3). Using the method of least squares the following expressions have been obtained for  $D_{\text{liq.}}$  of Pb and Ag:

$$D_{\text{liq.}} \text{ of Pb (g/cm}^3\text{)} = 11.3039 - 1.1576 \times 10^{-3}T - 3.847 \times 10^{-8}T^2$$

and

$$D_{\text{liq.}} \text{ of Ag (g/cm}^3\text{)} = 10.1667 - 6.9155 \times 10^{-4}T - 3.7996 \times 10^{-8}T^2 \text{ (} T \text{ in } ^\circ\text{K)}$$

The calculated liquid densities up to  $T_{\text{red.}} = 0.85$ , using the exact or exponential equations given above, are shown in Table 3 and reproduced in Figs. 1 and 2.

The calculated *ideal* liquid and vapour densities cross the rectilinear diameter at a point which gives a maximum limit of the critical temperature (7000°K for Pb and 8500°K for Ag). The lower limit of critical temperature is a range where the vapour density is about 20–25 per cent of the liquid density, i.e., about 5000°K for Pb and