TABLE 3.—$D_{\text{liq.}}$ IN G/CM^3 CALCULATED FROM THE RECTILINEAR DIAMETER AND IDEAL GAS DENSITY (SEE TABLE 2), *i.e.* $D_{\text{liq.}} = 2D_{\varnothing}^{*} - D_{\text{vap.}}^{\text{id.}}$.

	Pb		Ag	
T (°K)	$D_{\text{liq.}}$ (g/cm³)	Estimate of probable error (g/cm³)	$D_{\text{liq.}}$ (g/cm³)	Estimate of probable error (g/cm³)
2500	8·17	±0·02	8·20	±0·01
3000	7·49	±0·03	7·74	±0·02
3500	6·79	±0·04	7·28	±0·02
4000	6·06	±0·06	6·80	±0·03
4500	5·31	±0·1	6·30	±0·05
5000	—	—	5·77	±0·06
6000	—	—	4·65	±0·08
6500	—	—	4·06	±0·09
7000	—	—	3·4	±0·1

7000°K for Ag. The errors rapidly increase in the critical range, which is represented by the shaded area in Figs. 1 and 2. This is due both to the inaccuracy of T_c, assumed to be about ±10 per cent, and our experimental error in the rectilinear diameter. We estimate the critical constants of Pb and Ag to be as follows:

	Pb	Ag
T_c (°K)	5400 ± 10%	7500 ± 10%
D_c (g/cm³)	2·2 ± 0·3	1·85 ± 0·3
V_c (cm³/g atom)	$94 \left(^{+15}_{-10}\right)$	58·3 (±10)
P_c (atm)	$850 \left(^{+450}_{-250}\right)$	5000 (±560)

In order to pin down the critical data further it would be particularly desirable to extend liquid density determinations of lead and silver to about 3500°K (vapour-pressure $\simeq$100 atm for Pb and $\simeq$40 atm for Ag), and extend entropy of vaporization data similarly to those of sodium (see Fig. 2 of reference 2). It will be many years before lead or silver will be observed under critical conditions experimentally.

It is of interest to compare our semiempirical estimates with theory. The theory of liquids, in contrast to the solid and gaseous state is the least developed. Recently EYRING and his associates[15] have calculated some properties of liquid metals, including Hg and Pb, by EYRING's method of significant structures. In general the theory uses two adjustable parameters: n and a to obtain agreement with experimental data. The advantage of the theory is that various properties, such as liquid density, vapour pressure, viscosity, self-diffusion and others are developed from a consistent viewpoint.

A comparison of our results and the experimental data for Hg with those of EYRING's theory are presented in Table 4. Comments on the comparison are as follows:

1. *Critical density.* In the case of Hg, EYRING's value (=3·15) is lower than the experiment, in the case of Pb (=3·04) higher than our estimate.* In either case the

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* EYRING's calc. D-value for Pb at the normal b.p. = 9·59, whereas our experimental density = 8·803.

[15] C. C. CARLSON, H. EYRING and T. REE, *Proc. Nat. Acad. Sci.* **46,** 649–659 (1960); see there for earlier literature.

theoretical values seem to be outside the experimental error (see Fig. 1 in citation 1 and Fig. 1 of this paper) of the rectilinear diameter.

TABLE 4.—COMPARISON OF SEMIEMPIRICAL DATA WITH THEORETICAL CALCULATIONS

		Experimental for Hg (see reference 1 and 2) or this paper for Pb and Ag	EYRING's theoretical calculations[15]	
Hg	Parameter n		11	
	T_c (°K)	1733 ± 50	1552	
	V_c (cm³/g atom)	$42 \cdot 7 \pm 3 \cdot 0$	$63 \cdot 7$	
	D_c (g/cm³)	$4 \cdot 70 \pm 0 \cdot 20$	$3 \cdot 15$	
	P_c (atm)	1587 ± 50	610	
Pb	Parameter n	—	11	6
	T_c (°K)	5400 ± 540	8390	6266
	V_c (cm³/g atom)	$94 \left(\begin{smallmatrix}+15\\-10\end{smallmatrix}\right)$	$68 \cdot 2$	$68 \cdot 3$
	D_c (g/cm³)	$2 \cdot 2 \pm 0 \cdot 3$	$3 \cdot 04$	$3 \cdot 04$
	P_c (atm)	$850 \left(\begin{smallmatrix}+450\\-250\end{smallmatrix}\right)$	3500	2530
Ag				
	T_c (°K)	$7500\ (\pm 750)$		
	V_c (cm³/g atom)	$58 \cdot 3\ (\pm 10)$	No data	
	D_c (g/cm³)	$1 \cdot 85\ (\pm 0 \cdot 3)$		
	P_c (atm)	$5000\ (\pm 560)$		

2. *Critical temperature.* We believe our value for Pb to be closer to the true value of Pb. The theoretical value with $n = 11$ is definitely far outside the maximum shown in Fig. 1; the value with $n = 6$ is closer to our estimate.

3. *Critical pressure.* P_c is the most doubtful of the critical constants. The theoretical values are much lower in the case of Hg and by approximately the same factor higher in the case of Pb.

In comparing the two methods it should be kept in mind that in the case of Pb both represent extrapolations of 3000°K or more beyond the present experimental range. Obviously both methods should be improved.

The critical scientist should remember, however, that in this case we are in a realm of temperatures at which *all* of the few million inorganic and organic compounds cease to exist and that only a few metals exist as liquids, since they are elementary and monatomic substances. The only thermal reaction possible is ionization. The present view on solid and liquid metals is that at room temperature they are already ions surrounded by a sea of electrons. The amount of ionization in the saturated metal vapour can be accurately calculated from the Saha equation and their well known ionization potentials; for metals like Ta and W, even at 20,000°K, the ionization is only a few per cent, due primarily to the high saturation vapour-pressures.