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THE TEMPERATURE RANGE OF LIQUID LEAD AND SILVER AND AN ESTIMATE OF THEIR CRITICAL CONSTANTS*

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Abstract—The temperature range diagrams of liquid Pb and Ag are constructed from experimental density data, from their melting points to their normal boiling points, the law of rectilinear diameter and the theorem of corresponding states. From these diagrams or the equations on which they are based, the critical constants are estimated as follows:

	For Pb	For Ag
T_c (°K)	5400	7500
D_c (g/cm^3)	2·2	1·85
V_c (cm^3/g atom)	94	58·3
P_c (atm)	850	(5000)

Liquid densities below the critical range can be calculated with much greater reliability and are as follows:

T (°K)	Pb	Ag
2024	8·801	—
2500	8·167	8·197
3000	7·488	7·741
3500	6·786	7·276
4000	6·061	6·795
4500	5·313	6·295
5000	—	5·771
5500	—	5·223
6000	—	4·652
6500	—	4·060

IT was shown recently(1,2) that the critical constants of metals could be estimated consistently by two independent semi-empirical methods.

Of all the known eighty metals, mercury is the only one whose critical constants have been determined experimentally

$$(T_c = 1733°\text{K};\ P_c = 1587 \pm 50 \text{ atm},\ D_c = 4{\cdot}70 \pm 0{\cdot}20 \text{ g/cm}^3).$$

It was demonstrated that mercury, like all other thermally stable liquids, follows the law of Cailletet and Mathias or the law of rectilinear diameter.(1,2) The average density of liquid mercury and its saturated vapour, i.e. $\frac{1}{2}(D_1 + D_v)$, is a straight line function of temperature. This is the basis of the *first method.* A liquid range diagram of the metal obtained by plotting or calculating the *experimental liquid density* and

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(1) A. V. GROSSE, *J. Inorg. Nucl. Chem.* **22,** 23 (1961).

(2) A. V. GROSSE, "The Liquid Range of Metals and Some of Their Physical Properties at High Temperatures," Research Institute of Temple University, Sept. 5, 1960.

the ideal vapour density vs. temperature. The maximum possible critical temperature (and the minimum critical density) is the point where the ideal vapour density crosses the rectilinear diameter. Actually, the real vapour density is always greater than the ideal, so that the real critical temperature is lower than the one obtained in the above manner. The lower limit of the critical temperature (and conversely the maximum critical density) is set by the fact that the real saturated vapour density has to approach the liquid density near T_c.

The *second method* is based on the theorem of corresponding states. The theorem requires that at corresponding or reduced temperatures, i.e. $T_{red} = T/T_c$, liquid metals have the same entropy of vaporization,

$$\Delta S_{vap} = \Delta H_{vap}/T$$

So far the entropy vs. T function has been established experimentally only for one metal—mercury.(1,2) Since the heats of vaporization of nearly all metals are known at their normal boiling points, or can be reliably extrapolated,(3) one can estimate from the mercury curve and the ΔS value at the temperature T the reduced temperature, and thus the critical temperature, of any metal. Critical temperatures of about 15 metals, together with their ΔS_{vap}, and other data were given before;(1,2) the critical temperatures range from 1733°K for mercury to about 23,000°K for tungsten.

In two recent experimental investigations the liquid densities of lead(4) and silver(5) were determined over a much wider temperature range than heretofore, namely, from their melting points (600·6° and 1234·0°K, respectively) up to their normal boiling points (2024° and 2450°K, respectively). The densities are straight line functions of temperature and are as follows:

for Pb:

$$D_T = 10{\cdot}678\text{-}13{\cdot}174 \times 10^{-4}(T\text{-}600{\cdot}6^{\circ}),$$

and for Ag:

$$D_T = 9{\cdot}346\text{-}9{\cdot}067 \times 10^{-4}(T\text{-}1234{\cdot}0^{\circ}),$$

where T is in °K and D in g/cm^3.

Values of the density of liquid lead and silver at their melting and normal boiling points as well as at some set temperatures are given in Table 1.

TABLE 1.—EXPERIMENTAL DENSITIES OF LIQUID LEAD(4) AND SILVER(5) IN G/CM^3

	Pb	Ag
M.P. (°K)	600·6	1234·0
D at M.P. (g/cm^3)	10·678	9·346 ± 0·009
Normal b.p. (°K)	2024	2450
D at normal b.p. (g/cm^3)	8·803 ± 0·009	8·244 ± 0·009
D at 1000°K	10·152	(solid)
1500°K	9·493	9·105
2000°K	8·834	8·652
2500°K	(see Table 2)	8·198

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(3) D. R. STULL and G. C. SINKE, *Thermodynamic Properties of the Elements*, No. 18 of the *Advances in Chemistry* Series, American Chemical Society, Washington, D.C. (1956).

(4) A. D. KIRSHENBAUM, J. A. CAHILL and A. V. GROSSE, *J. Inorg. Nucl. Chem.* **22**, 33 (1961).

(5) A. D. KIRSHENBAUM, J. A. CAHILL and A. V. GROSSE, *J. Inorg. Nucl. Chem.* In press (1962).

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 $\simeq 0{\cdot}85$ 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:

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

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

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

or

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

and for Ag:

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

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 ±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

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

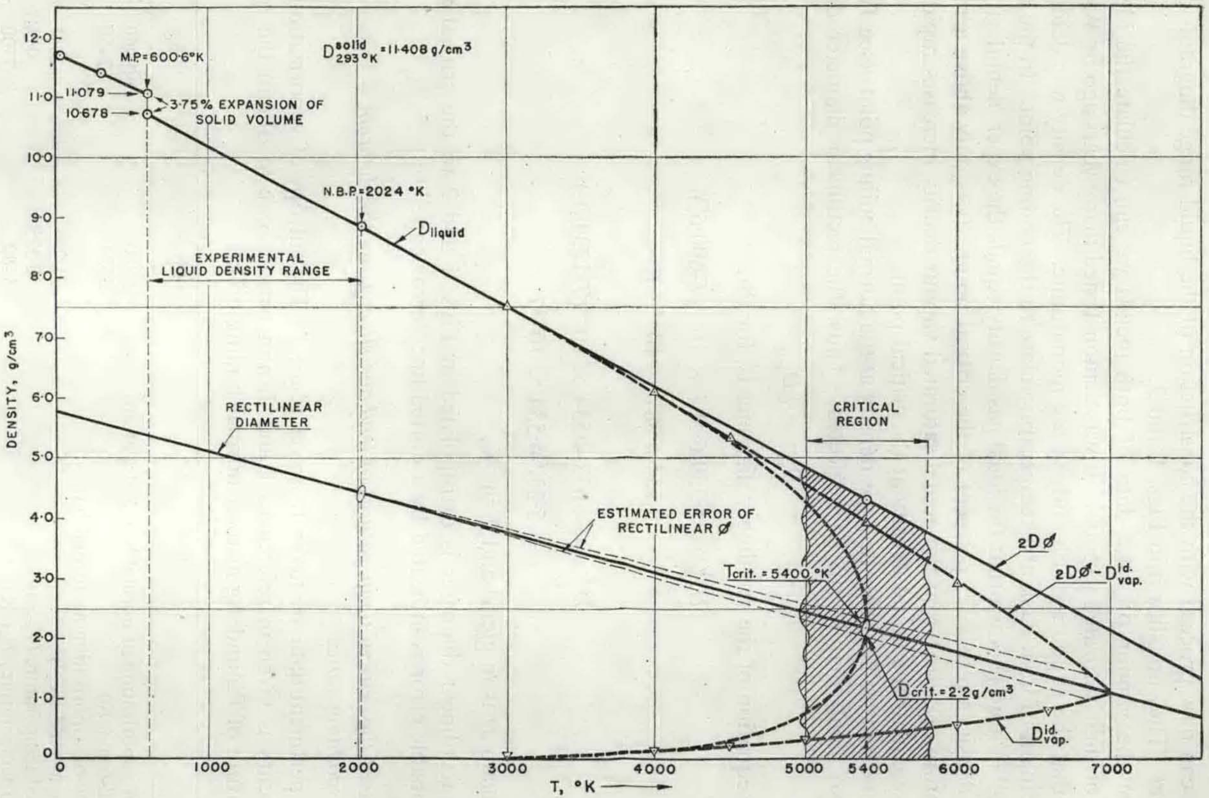

FIG. 1.—Liquid temperature range diagram of lead.

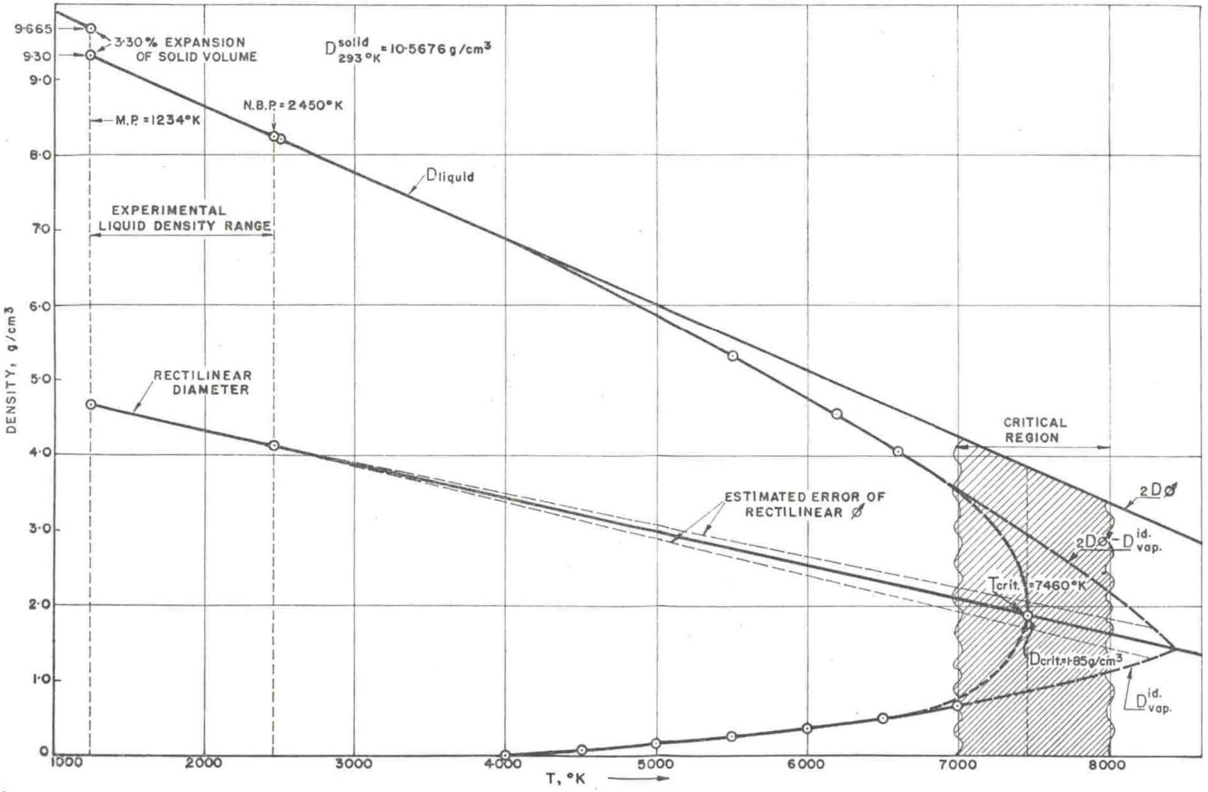

FIG. 2.—Liquid temperature range diagram of silver.

temperature sides by the considerations from the law of rectilinear diameter and the saturated vapour densities of the two metals.

The liquid densities beyond our experimental determinations can be calculated from the law of rectilinear diameter if the saturated vapour densities are known. As mentioned previously, the real densities should be equal to the ideal densities up to about 85 per cent of the critical temperature. The ideal densities can be easily obtained from the vapour pressure data of the two metals.

Saturated vapour densities of Pb *and* Ag

The vapour pressures used in these calculations were the most recent compilation of thermodynamic properties of the elements, tabulated by STULL and SINKE.(3)

We have reviewed the original literature, however, particularly in view of our interest in vapour-pressure at atmospheric pressure or above.

The vapour-pressure of lead was determined over fifty years ago by GREENWOOD(7, 8) up to 12 atm, far beyond the range of any other experimenters. KELLEY, a very careful worker, failed to notice, in referring to GREENWOOD's work, in his well known compilation(9) of vapour-pressure data, that the latter had a "self-correcting" temperature scale. He calibrated his Wanner optical pyrometer using pure Pt, Rh and Ir, "specially prepared of a high degree of purity by Messrs. Johnson, Matthey & Co.," and used Holborn & Henning's 1905 black body values of their melting points, i.e., Pt = 1545°C (1818°K), Rh = 1650°C (1923°K), and Ir = 2000°C (= 2273°K). We know now, 55 years later, that the *correct* melting points are: Pt = 2043°K, Rh = 2239°K and Ir = 2727°K. GREENWOOD's three melting points lie on a straight line; using their true melting points GREENWOOD's temperature scale can be corrected in a straightforward manner. GREENWOOD's true temperature, T_{true} in °K.

$$T_{\text{true}} = 1{\cdot}502 \cdot T_{\text{Greenwood}} - 682^\circ,$$

where $T_{\text{Greenwood}}$ are the original temperatures given by GREENWOOD *in* °K.

STULL and SINKE base their selection on KELLEY's review, who in turn picked Harteck's low temperature data as being the most reliable.

In Fig. 3 we compare STULL and SINKE's straight line with GREENWOOD's corrected data which extend to $\simeq$2900 K, and also of BAUR and BRUNNER,(10) RODEBUSH and DIXON,(11) and LEITGEBEL.(12) It can be readily seen that all of the experimental measurements are now in close agreement, except GREENWOOD's values at 6 and 12 atm. As mentioned by him(8) observations of the boiling lead surface becomes increasingly difficult at higher pressures. From 1·00 atm at 2024°K down to a vapour-pressure of $5{\cdot}6 \times 10^{-8}$ atm at 800°K (measured by EGERTON(13) (800–1000°K)), i.e., over a hundred million-fold pressure range, the log of vapour-pressure is a straight-line function of $1/T$°K. The same observation was made in the case of mercury(1, 2) up to the critical point. We are thus justified in making the assumption that the straight line log P vs. $1/T$ relationship can be extended to the critical point also in the case of Pb and Ag.

The data for silver do not extend beyond 1 atm. The only data available at one atmosphere are old measurements of GREENWOOD (corrected), RUFF(14) and

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(7) H. C. GREENWOOD, *Proc. Roy. Soc.* **82** A, 396–408 (1909).

(8) H. C. GREENWOOD, *Proc. Roy. Soc.* **83** A, 483–491, particularly p. 488 (1910).

(9) K. K. KELLEY, *U.S. Bureau of Mines, Bull.* 383, 59–60 (1935).

(10) E. BAUR and R. BRUNNER, *Helv. Chim. Acta* **17**, 958 (1934).

(11) W. H. RODEBUSH and A. L. DIXON, *J. Amer. Chem. Soc.* **47**, 1036 (1925).

(12) W. LEITGEBEL, *Z. Anorg. Chem.* **202**, 305 (1931).

(13) A. C. G. EGERTON, *Proc. Roy. Soc.* A **103**, 469 (1923).

(14) O. RUFF and B. BERGDAHL, *Z. Anorg. Chem.* **106**, 91 (1919).

WARTENBERG.(6) They show appreciable scatter around 2400°K, and additional experimental work in this pressure range and above is recommended.

STULL and SINKE's vapour-pressure data lead to the following expressions, for Pb:

$$\log_{10} P_{\text{atm}} = -9{,}596/T + 4{\cdot}74043 \ (T \text{ in } {}^\circ\text{K})$$

or in exponential form: $P_{\text{atm}} = 5{\cdot}5009 \times 10^4 \,.\, \exp(-22{,}100/T)$, and for Ag:

$$\log_{10} P_{\text{atm}} = -13{,}388/T + 5{\cdot}46223 \ (T \text{ in } {}^\circ\text{K})$$

or in exponential form: $P_{\text{atm}} = 2{\cdot}8989 \times 10^5 \,.\, \exp(-30{,}827/T)$

Since the density of the ideal saturated vapour, D_{vap}, $= A/V_A$, where A and V_A are atomic weight and volume respectively, it follows, from the ideal gas laws, that:

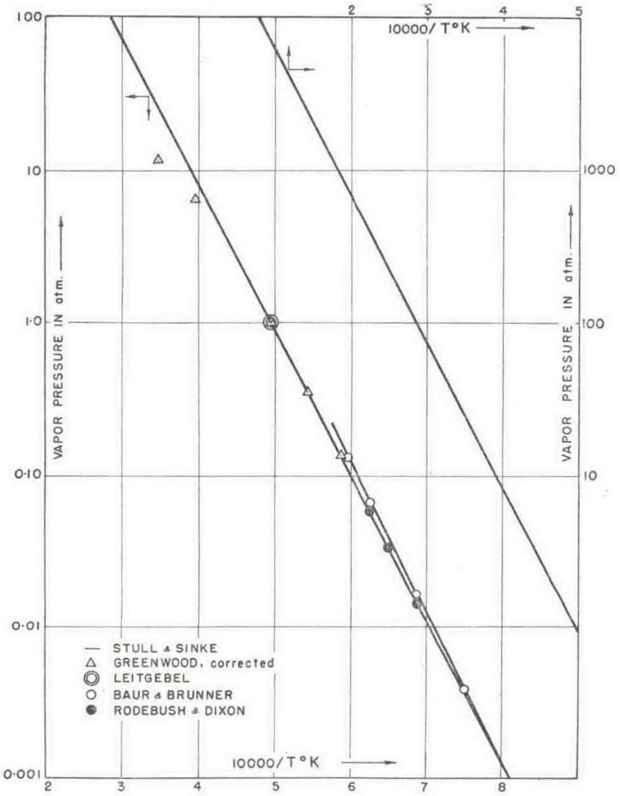

FIG. 3.—Vapour-pressure of lead.

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

thus, D_{vap}, for Pb $= 1{\cdot}38920/T \times 10^5 \,.\, \exp(-22{,}100/T)$
and for Ag $= 3{\cdot}8145/T \times 10^5 \,.\, \exp(-30{,}827/T)$

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

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

T (°K)	Pb		Ag	
	D (g/cm^3)	P (Atm)	D (g/cm^3)	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:

$$D_{\text{liq.}} = 2D_{\varnothing\nearrow} - D^{\text{id.}}_{\text{vap.}}$$

up to about $T_{\text{red.}} = 0{\cdot}85$, i.e., 4500°K for Pb and 6300°K for Ag. Above these temperatures, as was shown in the case of mercury,(1,2) 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 $T_{\text{red.}} = 0{\cdot}85$ and based on the above general equation, the specific and exact equations for the densities of Pb and Ag are respectively:

$D^{T}_{\text{liq.}}$ of Pb, in g/cm^3 =

$$11{\cdot}4692 - 13{\cdot}174 \times 10^{-4}T - \frac{1{\cdot}3892}{T} \times 10^{5}\,.\,\exp\,(-22{,}100/T)$$

and for Ag =

$$10{\cdot}465 - 9{\cdot}067 \times 10^{-4}T - \frac{3{\cdot}8145}{T} \times 10^{5}\,.\,\exp\,(-30{,}827/T)$$

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:

$$D_{\text{liq.}} \text{ of Pb (g/cm}^3) = 11{\cdot}3039 - 1{\cdot}1576 \times 10^{-3}T - 3{\cdot}847 \times 10^{-8}T^2$$

and

$$D_{\text{liq.}} \text{ of Ag (g/cm}^3) = 10{\cdot}1667 - 6{\cdot}9155 \times 10^{-4}T - 3{\cdot}7996 \times 10^{-8}T^2 \ (T \text{ in °K})$$

The calculated liquid densities up to $T_{\text{red.}} = 0{\cdot}85$, 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

TABLE 3.—$D_{\mathrm{liq.}}$ IN G/CM³ CALCULATED FROM THE RECTILINEAR DIAMETER AND IDEAL GAS DENSITY (SEE TABLE 2), *i.e.* $D_{\mathrm{liq.}} = 2D_{\varnothing}^{\nearrow} - D^{\mathrm{id.}}_{\mathrm{vap.}}$

T (°K)	Pb		Ag	
	$D_{\mathrm{liq.}}$ (g/cm³)	Estimate of probable error (g/cm³)	$D_{\mathrm{liq.}}$ (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)	$94\begin{pmatrix}+15\\-10\end{pmatrix}$	58·3 (±10)
P_c (atm)	$850\begin{pmatrix}+450\\-250\end{pmatrix}$	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 ≃100 atm for Pb and ≃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 (cm^3/g atom)	42·7 ± 3·0	63·7	
	D_c (g/cm^3)	4·70 ± 0·20	3·15	
	P_c (atm)	1587 ± 50	610	
Pb	Parameter n	—	11	6
	T_c (°K)	5400 ± 540	8390	6266
	V_c (cm^3/g atom)	$94\begin{pmatrix}+15\\-10\end{pmatrix}$	68·2	68·3
	D_c (g/cm^3)	2·2 ± 0·3	3·04	3·04
	P_c (atm)	$850\begin{pmatrix}+450\\-250\end{pmatrix}$	3500	2530
Ag				
	T_c (°K)	7500 (±750)		
	V_c (cm^3/g atom)	58·3 (±10)	No data	
	D_c (g/cm^3)	1·85 (±0·3)		
	P_c (atm)	5000 (±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.

Acknowledgement—Acknowledgement is due to P. J. McGONIGAL for a number of density equation calculations.