J. Inorg. Nucl. Chem., 1962, Vol. 24, pp. 739 to 748. Pergamon Press Ltd. Printed in Northern Ireland

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

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(*Received* 13 *October* 1961)

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/cm³)	2·2	1·85
V_c (cm³/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

* This research was supported in part by Grant 15540 of the National Science Foundation.

[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:

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

and for Ag:

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

where T is in °K and D in g/cm³.

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/CM³

	Pb	Ag
M.P. (°K)	600·6	1234·0
D at M.P. (g/cm³)	10·678	9·346 ± 0·009
Normal b.p. (°K)	2024	2450
D at normal b.p. (g/cm³)	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

[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).