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.

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

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 $5·6 \times 10^{-8}$ 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

[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).