Critical Temperatures of Metals and their Estimates by Gates and Thodos

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Sir:

In recent papers[1-3] it was shown that the temperature range of *liquid metals, i.e.,* the range from the melting to the critical point, is far greater than for any other type of substance. It extends, in view of their elementary and atomic nature, far beyond the thermal limits of existence of any other solid or liquid; even the stablest of the latter dissociate into atoms at about 5000–6000°K. In contrast, the refractory metals such as Re, Ta, and W will be liquids up to a critical temperature of about 20,000, 22,000, and 23,000°K., respectively.

It also was shown[1-3] that one can construct a liquid temperature range diagram of metals demonstrating the relationship between liquid (and saturated vapor) density *vs.* temperature over the whole liquid temperature range, from the melting point to the critical point, by using the theorem of corresponding states of van der Waals, the law of rectilinear diameter of Cailletet and Mathias, and experimental data on heats and entropies of vaporization, vapor pressure, and particularly experimental liquid density data over as wide a temperature range as possible.

Subsequently it has come to our attention that Gates and Thodos[4] estimated the critical temperatures of metals, but arrived at values that differed substantially from ours, as the comparison in Table I shows.

TABLE I

COMPARISON OF THE CRITICAL TEMPERATURE OF METALS ESTIMATED BY THE METHOD OF GATES AND THODOS[4] *vs.* THE INSTITUTE'S

	Normal b.p.,[5] °K.	Critical temp., °K. Gates and Thodos	R. I. T. U.
W	5800	11500	23000
Mo	5100	9880	17000
Sn	2960	5809	8700
Pb	2024	3584	5400
Na	1163	2124	2800

(1) A. V. Grosse, "The Liquid Range of Metals and Some of Their Physical Properties at High Temperatures," Report of the Research Institute of Temple University, September, 1960; see also *Nuclear Sci. Abstr.*, **15**, 4018, 31197 (1961).

(2) A. V. Grosse, American Rocket Society, Space Flight Report to the Nation, New York Coliseum, Oct. 9–15, 1961, Paper No. 2159-61.

(3) A. V. Grosse, *J. Inorg. & Nuclear Chem.*, **22**, 23 (1961).

(4) D. S. Gates and G. Thodos, *A.I.Ch.E. Journal*, **6**, 50 (1960).

(5) All data on normal boiling points and ΔH_{vap} are taken from D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Advances in Chemistry Series No. 18, 1956.

As one can see our critical temperatures are greater than the normal boiling points of the metals by a factor of 4 (W) to 2.5 (Na).

Gates and Thodos plotted all the known critical temperatures (T_c) of the elements *vs.* their normal boiling points (T_b) and arrived at the simple relationship

$$T_c = 1.4732\, T_b^{1.0818}\ (T \text{ in } °K.)$$

This is a similar relationship to an earlier one of Meissner and Redding,[6] supposedly applicable to all elements, namely

$$T_c = 1.70\, T_b - 2.0\ (T \text{ in } °K.)$$

Both of these empirical relationships, however, are based on the experimental critical temperatures of *the noble gases and non-metals only*.

From the T_c so obtained and the vapor pressure equation, Gates and Thodos extrapolated the critical pressure, P_c. Using both these critical constants, the constants a and b of the van der Waals equation of state were obtained. The critical volume $V_c = 3b$.

The relationship of Gates and Thodos and the previous one of Meissner and Redding, however, *do not apply to metals*.

Two basic facts have to be considered. The nature of the attractive forces in a liquid between atoms of the noble gases or the diatomic molecules of such elements as H, O, N, and all the halogens, which were used to estimate the empirical relationships, on the one hand, and the metals, on the other, are quite different. In the first case we have weak van der Waals forces and in the second much stronger metallic bonds. This is forcefully demonstrated by comparing the energy necessary to separate a gram atom of the liquid into separated atoms or molecules in the gas phase, *i.e.,* the heat of vaporization, ΔH_{vap}, for example at the normal boiling point, as shown in Table II.

The decisive piece of evidence, however, is the following one. Gates and Thodos, in their extensive literature survey on the subject, unfortunately missed the experimental determination of the critical constants of mercury, *the only metal* for which such constants are known.

Bender,[7,8] during World War I, measured the density of both liquid and saturated vapor of Hg up to 1380°, or 1650°K. Later, Bernhardt[9] de-

(6) H. P. Meissner and E. M. Redding, *Ind. Eng. Chem.*, **34**, 521 (1942).

(7) J. Bender, *Physik. Zeit.*, **16**, 246 (1915).

(8) J. Bender, *ibid.*, **19**, 410 (1918).

(9) F. Bernhardt, *ibid.*, **26**, 265 (1925).