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THE TEMPERATURE RANGE OF LIQUID METALS AND AN ESTIMATE OF THEIR CRITICAL CONSTANTS

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Abstract—It is shown that the temperature range of liquid metals extends in the case of the "refractory" metals, tungsten, tantalum and rhenium, to over 20,000°K. Methods are described that show how, based on the law of rectilinear diameter, and available experimental data, such as density vs. temperature, and vapour-pressures, heats and entropies of vaporization, liquid temperature diagrams for various metals, may be constructed. Estimates for the critical temperature, pressure and density of various metals, for example, sodium, lead and tin, have been made.

THE strength of even the strongest chemical bonds is not sufficient to hold atoms together in molecules at temperatures above 5000–6000°K. Even such thermally stable molecules as carbon monoxide and nitrogen, which exist in the atmosphere of the sun are atomized above 6000°K. Thus chemical substances, as they are known in inorganic and physical chemistry, cease to exist above this temperature range. As will be shown in this paper[1] exceptions are the liquid metals. The temperature range of the liquid state of metals extends in the case of the so-called refractory metals, such as tungsten, rhenium and tantalum, to over 20,000°K. In comparison, the solid metal state ranges from absolute zero to a maximum of 3650°K, i.e., the melting point of the highest melting metal—tungsten. Thus the liquid range is about six times greater!

Since the metals are *elementary monatomic* substances they are not subject to chemical decomposition or dissociation at extremely high temperatures. Even above 20,000°K the only possible change is ionization to positive ions and electrons. The amount of ionization in the saturated vapour of the metal can be readily calculated by the use of Saha's equation or the TOLMAN[2] procedure since the ionization potentials of most metals are accurately known.[3] The amount of this ionization is small, of the order of a few per cent, particularly in view of the high saturated vapour-pressure.

In the liquid (as well as the solid) metal the present-day quantum-mechanical theory assumes that *all the metal atoms are ionized*, i.e., present as cations, and the electrons are moving freely between the ions, thus accounting for most of the characteristic metallic properties. Thus an increase in temperature does not change the basic chemical nature of the liquid metal.

The limits of the liquid state or the critical temperature of a large number of chemical substances investigated are usually about one and one-half times their absolute boiling points. This is true for ideal liquids such as argon, for example, most homopolar inorganic compounds typified by water, carbon dioxide and carbon tetrachloride and most organic substances such as methane and benzene; the forces among the above molecules are the *weak Van der Waals forces*. It does not seem to be true for metals, however, although so far only one metal, namely, mercury, has

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(2) R. C. TOLMAN, *J. Amer. Chem. Soc.* **43**, 1630–32 (1921).
(3) See, for example, *Handbook of Chemistry and Physics* (40th Ed.), pp. 2546–47. (1959).

June 25–27, 1956, Berkeley, California, pp. 59–68, see Fig. 7 and 8, p. 63.
(6) A. V. Grosse and J. B. Conway, *Ind. Eng. Chem.*, **50**, 663 (1958), see Fig. 5 and 6.
(11) A. D. Kirshenbaum and J. A. Cahill, *J. Inorg. Nucl. Chem.*, **14**, 285–287 (1960).
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