

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

⁽¹⁾ A. V. GROSSE, *The Liquid Range of Metals and Some of Their Physical Properties at High Temperature*. The Research Institute of Temple University (1960).

⁽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).

been investigated experimentally. This is to be anticipated because in metals we have the characteristic *metallic bond*⁽⁴⁾ as distinguished from the homopolar bond as in the case of the inorganic and organic substances mentioned above, or the ionic bond as it exists in typical salts such as sodium chloride or calcium fluoride. Theoretically, the liquid state is the least understood state of matter, as compared to our knowledge of solids or gases. Of all liquids the liquid metal should represent, from the theoretical point of view, a particularly simple case since all metals are monatomic.

In the last two years particularly, advances in the theory of liquids have been made by EYRING and his associates⁽⁵⁻⁹⁾ in this country, and by BERNAL⁽¹⁰⁾ in England. Theoreticians, however, still need some arbitrary parameters to adjust the theory to experimentally available data. The main advantage is that they give a deeper insight into the structural, geometric, molecular and atomic factors involved and will give a much deeper understanding as to what makes a liquid liquid.

We will proceed on a semiempirical basis. A sufficiently accurate estimate of critical temperatures, pressures and densities can be made by using well established empirical relationships as well as presently available experimental data on liquid densities and vapour pressures and their temperature dependence.

Of special assistance for the evaluation of the liquid range or estimation of critical constants is the *empirical* law of Cailletet and Mathias, or the law of rectilinear diameter which states that "the average density or half the sum of the densities of a liquid and its saturated vapour decrease linearly with temperature; at the critical point the densities of liquid and saturated vapour are equal."

This law has been tested experimentally on a large variety of *thermally stable* organic and inorganic liquids. Examples are hydrocarbons, such as benzene, methane, pentane, ethyl ether, inorganic compounds such as water, sulphur dioxide, carbon dioxide, carbon tetrachloride, carbon monoxide and elements such as argon, krypton, xenon, nitrogen, oxygen, hydrogen and even such quantum liquids as helium-4 and helium-3. The early and very precise work of Young showed extremely small deviations from additivity and linearity in the case of some hydrocarbons near the critical region; even these deviations, in our opinion, may be due to thermal decomposition and/or impurities. Although about 80 per cent of the chemical elements are metals, only *one*, namely, *mercury*, has been heated to the critical point. Liquid and vapour densities, as well as vapour-pressure data, are available and, as we shall see, the law of Cailletet and Mathias is fulfilled for mercury. For these reasons a detailed summary of all data on liquid mercury will be discussed here.

Temperature range of liquid mercury and its critical data

The critical point of mercury was determined for the first and only time by BIRCH⁽¹¹⁾ in Bridgman's laboratory at Harvard, by measuring the electrical resistance of liquid mercury, under pressure, up to about 1800°K. He found the critical temperature to = 1733°K ($\pm 50^\circ$) and the critical pressure to = 1587 (± 50) atm. This is the only

(4) See L. PAULING, *The Nature of the Chemical Bond*, (3rd Ed.) Chap. 11. Cornell Univ. Press (1960).

(5) H. EYRING, T. REE and N. HIRAI, *Proc. Natl. Acad. Sci.* **44**, 683 (1958).

(6) E. J. FULLER, T. REE and H. EYRING, *Proc. Natl. Acad. Sci.* **45**, 1594 (1959).

(7) C. M. CARLSON, H. EYRING and T. REE, *Proc. Natl. Acad. Sci.* **46**, 333 (1960).

(8) T. R. THOMSON, H. EYRING and T. REE, *Proc. Natl. Acad. Sci.* **46**, 336 (1960).

(9) C. M. CARLSON, H. EYRING and T. REE, *Proc. Natl. Acad. Sci.* **46**, 649 (1960).

(10) J. D. BERNAL, *Proc. Royal Inst. of Gr. Britain* **37**, 380 (1959).

(11) F. BIRCH, *Phys. Rev.* **41**, 641-48 (1952).