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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-pressure, 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).

direct determination of the critical data of a metal. In view of their importance and because mercury is the lowest boiling metal and thus the easier with which to experiment, these measurements should be repeated to insure maximum reliability.

The *complete* range of saturated vapour-pressures of liquid mercury, over the whole range from the melting point to the critical point, is a straight line on a logarithmic plot,⁽¹⁾ over a 10^{12} -fold increase in pressure from 1.91×10^{-9} atm at the melting point, i.e., 234.3°K , to 1587 ± 50 atm at the critical point (1733°K).

The vapour-pressures from the melting point to about 2 atm are known with great precision.⁽¹²⁾ Two sets of data are available for the range of 2–140 atm.; the older data are due to CAILLETET⁽¹³⁾, and the more recent to BERNHARDT⁽¹⁴⁾. The latter extended his measurement to 1708°K , and to a pressure of 1955 atm. Both CAILLETET and BERNHARDT observed the actual boiling of the mercury in a pressure vessel; the measurements became progressively more difficult and less accurate at the higher pressures and temperatures.

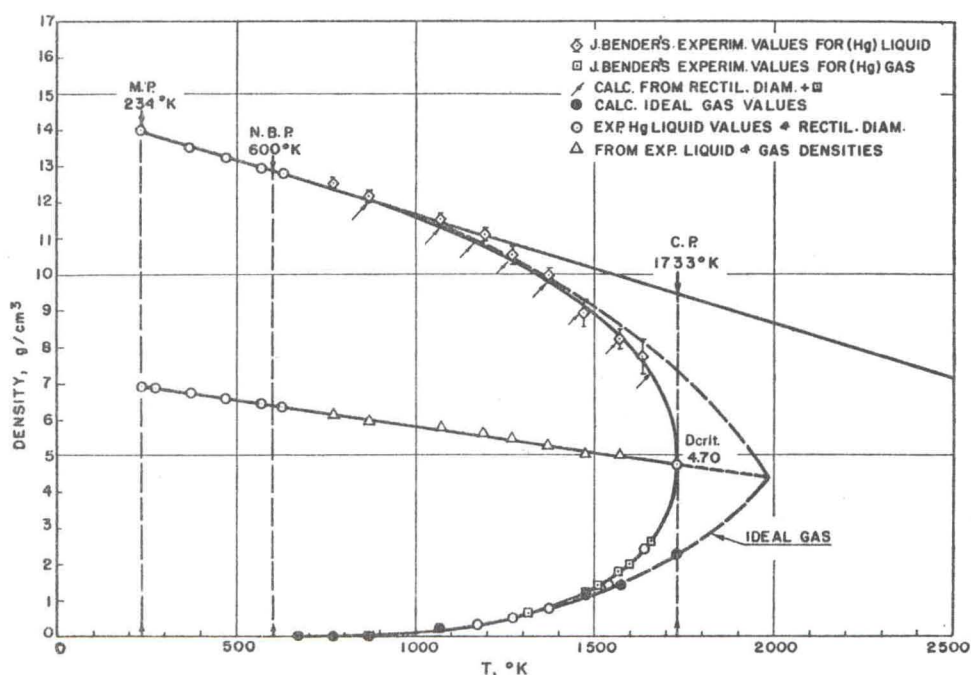


FIG. 1.

The liquid and saturated vapour density of mercury over the whole liquid temperature range

Fig. 1 shows a summary of mercury data on the density of both liquid and vapour and demonstrates that the law of rectilinear diameter is fulfilled. Because of the importance of these data they will be discussed in detail. They are due to the observations of BENDER^(15,16) who measured the density of both liquid and saturated vapour

⁽¹²⁾ See, for example, *Handbook of Chemistry and Physics*, (40th Ed.), p. 2331. (1959).

⁽¹³⁾ CAILLETET, COLARDEAU and RIVIERE, *C.R. Acad. Sci., Paris* **130**, 1585 (1900).

⁽¹⁴⁾ F. BERNHARDT, *Phys. Z.*, **26**, 265–275 (1925).

⁽¹⁵⁾ J. BENDER, *Phys. Z.*, **16**, 246–247 (1915).

⁽¹⁶⁾ J. BENDER, *Phys. Z.*, **19**, 410–414 (1918).

in the range of 500–1380°C, i.e., up to 60°C of the critical point, in sealed quartz vessels. The liquid densities from the melting point to the normal boiling point are known⁽¹⁷⁾ with great accuracy and were also used in Fig. 1; they are indicated by \odot ; BENDER's values for the saturated vapour are shown by \bullet , while the liquid densities together with their error range are indicated by \diamond . The calculated values for the vapour density, assuming ideal gas laws and the vapour-pressure of mercury, are shown as \square ; up to about 1200°C there is no significant deviation between the ideal and actual values.

Values for the liquid density, calculated from this law and the experimental vapour density, are indicated with \nearrow on the liquid curve; values for $\frac{1}{2}(D_{\text{liq.}} + D_{\text{vap.}})$, calculated from the experimental data, are shown in triangles \triangle on the rectilinear diameter. The vapour densities, because of their lower absolute values, can be determined with greater accuracy; the liquid values show appreciable scatter because of experimental difficulties.

Using BENDER's smoothed values, we obtain for the equation of mercury's rectilinear diameter, the expression:

$$D_{\text{rec.}} \delta = 6.7978 - 14.30 \times 10^{-4} T (\text{°C}).$$

Based on this equation the critical density of mercury, at 1460°C., equals 4.70 g/cm³, whereas BIRCH⁽¹¹⁾ estimated a value of 5 g/cm³.

We see further, from Fig. 1, that the two legs of the Cailletet–Mathias curve have two envelopes, (shown in dotted lines). The *first envelope* is the curve of the *ideal gas density*, the latter being always *less* than the actual saturated vapour density. The *second envelope* of the liquid leg is obtained by deducting the ideal saturated vapour density, in line with the rectilinear law, from the straight liquid density line. The two envelopes meet at a point which sets an *upper limit for the critical temperature*; in the case of mercury this limit is about 2000°K (see Fig. 1.)

Since the rectilinear diameter law is fulfilled for liquid mercury, as the only metal among many other liquids, we will assume it to hold for other metals also. It would be highly desirable if critical data for other metals were obtained so that the experimental evidence for the validity of the law can be put on as broad a foundation as possible.

THE TEMPERATURE RANGE OF OTHER LIQUID METALS

We are now interested in estimating, even if only approximately, the temperature range of other liquid metals. Usually, for most homopolar compounds, as has been mentioned, the normal boiling point corresponds to approximately two-thirds of the critical temperature.

As can be seen, this is not the case for the only known metal, mercury, where the ratio of the critical point to the normal boiling point

$$1733^{\circ}\text{K}/629.9^{\circ}\text{K} = 2.75$$

In order to estimate critical temperatures it is best to choose those physical properties which equal zero at the critical temperature and apply the principle of

⁽¹⁷⁾ Data of THIESSEN and SCHEEL, *Handbook of Chemistry and Physics*, (40th Ed.) p. 2115. (1959).

corresponding states. Such properties are, for example, heat of vaporization, *entropy of vaporization* or surface tension.

The principle of corresponding states⁽¹⁸⁾ requires that the molar entropies of vaporization of various liquids should be equal at corresponding temperatures and vice versa.

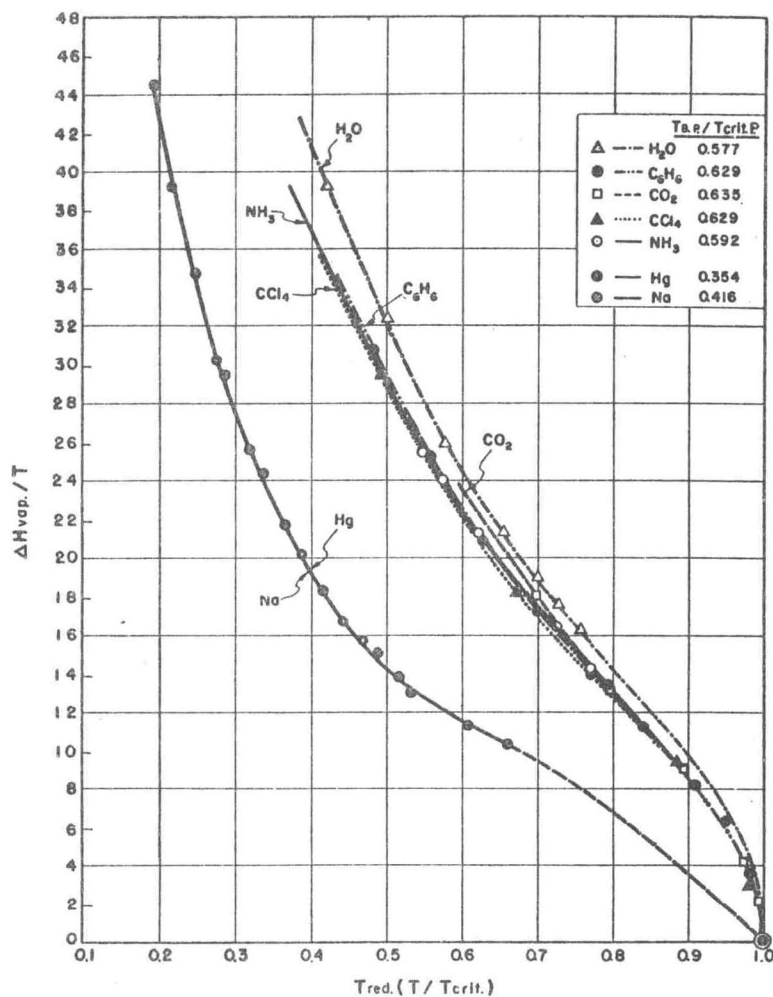


FIG. 2.

The heat of vaporization of mercury, $\Delta H_{\text{vap.}}$, is known over an appreciable range and can be readily extrapolated to the critical temperature; the same applies to the entropy, $\Delta S_{\text{vap.}} = \Delta H_{\text{vap.}}/T$. Fig. 2 shows the *entropy curve of mercury* and compares it with a number of well known normal liquids, such as carbon dioxide, carbon tetrachloride, ammonia, benzene and water. It will be noticed that mercury, the only known metal, shows a markedly different behaviour. We will assume for the present that other metals will behave in the same manner. By assuming the principle of corresponding states to be valid for other metals and using the experimentally

⁽¹⁸⁾ For example, E. A. GUGGENHEIM, *J. Chem. Phys.* 13, 253-261 (1945).

determined entropy of vaporization of other metals, for example, at their normal boiling points, we can, by using Fig. 2, arrive at their *reduced temperatures* and thus also at their approximate critical temperatures. Table 1 contains a summary of critical temperatures of a number of metals, arranged in ascending order from 1733°K, for mercury up to 23,000°K for tungsten. These critical temperatures (see last column of Table 2), were estimated, based on ΔS_{vap} , only at the boiling point.

TABLE 1.—CRITICAL TEMPERATURES, HEATS OF VAPORIZATION AND ENTROPIES AT NORMAL BOILING POINTS FOR VARIOUS METALS⁽²¹⁾

Metal	Boiling point at 1 atm. (°K)	ΔH_{vap} . (cal/g atom)	ΔS_{vap} . (cal/g atom °K)	$T_{\text{red.}}$ from Hg-curve Fig. 2	$T_{\text{crit.}}$ °K
Cs	958	15,750	16.95	0.445	2150
Rb	974	16,540	16.99	0.445	2190
K	1039	18,530	17.88	0.425	2440
Na	1163	21,280	18.40	0.415	2800
Bi	1832	36,200	19.75	0.397	4620
Pb	2024	42,880	21.15	0.375	5400
Ga	2510	61,200	24.40	0.330	7620
Sn	2960	69,400	23.42	0.340	8720
Fe	3160	83,900	26.55	0.305	10,000
U	4200	101,000	24.05	0.333	12,500
Mo	5100	142,000	27.85	0.295	17,000
Re	5900	169,000	28.63	0.287	20,500
Ta	5700	180,000	31.60	0.260	22,000
W	5800	191,000	32.90	0.250	23,000

Data on liquid sodium^(19,20) have recently become available which gives ΔH_{vap} , and ΔS_{vap} , over the whole range from 800° (445°K) to 3000°R (1667°K). Thus in the case of liquid sodium a close fit to the mercury curve can be obtained only if the critical point of sodium is assumed to equal 2800°K (see Fig. 2 data for sodium).

The most interesting point revealed by the data of Table 1 is the wide temperature range of the liquid state of metals. Such metals as molybdenum, tantalum and tungsten will exist as liquids well over 10,000°K.

Vapour and critical pressures

Mercury is the only metal for which saturated vapour-pressures have been measured all the way to the critical point (see p. 25). For sodium and lead experimental data are available up to 15 and 12 atm, respectively.⁽¹⁾ For most other metals vapour-pressures have been measured below 1 atm. They have been critically evaluated in the well known contribution of KELLEY⁽²²⁾. The vapour-pressure data on all elements have been brought up to date and published by STULL and SINKE⁽²¹⁾. As a first approximation, however, it can be assumed that the logarithm of the vapour-pressure is a straight line function of the reciprocal absolute temperature. Thus from the estimated critical

⁽¹⁹⁾ C. T. EWING, J. P. STONE and R. R. MILLER, Report NRL 1069 (1960).

⁽²⁰⁾ M. MAKANSI, W. A. SELKE and C. F. BONILLA, *J. Chem. Engng. Soc. Imp. Coll. Data*, **5**, 441-452 (1960).

⁽²¹⁾ All data on normal boiling points and ΔH_{vap} taken from D. R. STULL and G. C. SINKE, *Thermodynamic Properties of the Elements, Advances in Chemistry Series, Vol. 19*. American Chemical Society, (1956).

⁽²²⁾ K. K. KELLEY, *U.S. Bur. Min. Bull.* **383** (1935).

temperatures from the preceding section we can obtain the critical pressure by extrapolation of the logarithmic vapour-pressure line.

Our estimates⁽¹⁾ of the critical pressures are as follows:

Sodium	490 atm
Lead	850 atm
Tin	2100 atm
Tungsten	> 10000 atm

Liquid range diagrams of typical metals

We have constructed liquid range diagrams of typical metals in analogy to mercury (Fig. 1) based on the estimates of critical temperatures and pressures given in the preceding sections. In addition, experimental data on the densities of liquid metals are available. We have selected such metals for which liquid density measurements have been made over as wide a temperature range as possible. In addition to mercury, these metals are *sodium*, *gallium*, *lead* and *tin*. The available data on these metals, particularly their liquid densities, temperature coefficients and the experimental temperature ranges where they have been determined, are all given in Table 2.

TABLE 2.—EXPERIMENTAL DENSITIES OF LIQUID METALS AT VARIOUS TEMPERATURES

Metal	Reference	Melting point (°K)	Normal boiling point (°K)	D at normal boiling point (estimate) (g/cm ³)	Experimental range of D -measurements (°C)	Experimental $-dD/dT$ (g/cm ³ °K)	$D_{crit.}$ (estimate) (g/cm ³)	$D_{b.p.}/D_{crit.}$
Hg	This paper 23	234.3	629.9	12.7374	-39-480	$28.6 \cdot 10^{-4}$	4.70	2.72
Na	24	371.0	1163	0.740	97.8-800	$2.43 \cdot 10^{-4}$	0.18	4.1
Ga	25	303.1	2510	4.55	29.9-1100	$6.07 \cdot 10^{-4}$	0.95	4.8
Pb	26	600.6	2024	8.85	327-850	$11.62 \cdot 10^{-4}$	2.1	4.2
Sn	26	505.1	2960	5.55	232-1600	$6.05 \cdot 10^{-4}$	1.3	4.3

In the case of mercury (see Fig. 1), we see that the actual vapour density *begins to differ* appreciably from the ideal gas density only above a $T_{red.} = 0.8$, i.e., above 80 per cent of the liquid range, in contrast to most inorganic and organic compounds. Knowing the vapour-pressure of the metal we can readily calculate the ideal density of the saturated vapour as a function of temperature and correct the liquid density in line with the rectilinear diameter law, up to about $T_{red.} = 0.8$. Thus, if the vapour density of the metal, $D_{vap.}$ is expressed as a function of the type:

$$D_{vap.} = K + aT + bT^2 + cT^3 + \dots,$$

while the liquid density, $D_{liq.}^{(0)}$, in the range where $D_{vap.}$ is 0 or negligible, is given by:

$$D_{liq.}^{(0)} = M + nt$$

⁽²³⁾ Data of THIESEN and SCHEEL, *Handbook of Chemistry and Physics*, (40th Ed.), p. 2115. (1959). *International Critical Tables*, Vol. 2 p. 456. (1928).

⁽²⁴⁾ C. E. JACKSON, *Liquid-Metals Handbook, Sodium-NaK Supplement*, p. 26. (Editor-in-Chief) Sponsored by The Atomic Energy Commission and The Bureau of Ships Department of the Navy, Washington, D.C. (1955).

⁽²⁵⁾ W. H. HOATHER, *Proc. Roy. Soc.* 48, 699 (1936).

⁽²⁶⁾ DAY, SOSMAN and HOSTETTER, *Amer. J. Sci.* 37, 1 (1914).

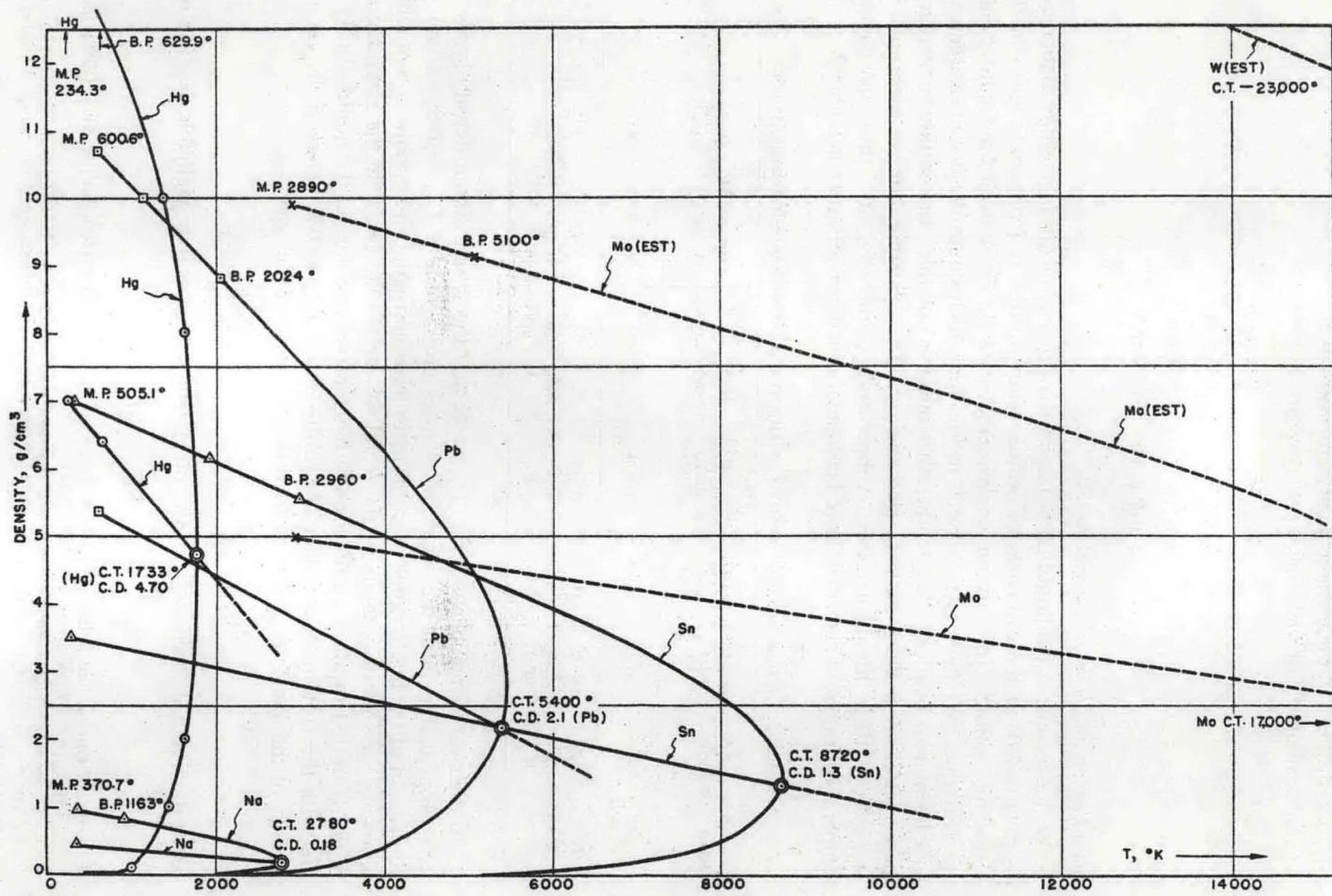


FIG. 3.

the correct density of the liquid metal, $D_{\text{liq.}}$, up to about 80 per cent of the critical temperature, will be given by the equation:

$$D_{\text{liq.}} = D_{\text{liq.}}^{(0)} - D_{\text{vap.}} = M - K + (n - a)T - bT^2 - cT^3 - \dots$$

The liquid range diagrams of the above metals were constructed using the above data (Table 2) together with the law of rectilinear diameter. They are shown in Fig. 3, where the density (in g/cm³) of both liquid and saturated vapour, in equilibrium with it, are plotted against temperature.

A study of this figure shows that for all these metals the density vs. temperature is a straight line function, at least up to the normal boiling point of the metal.

Fig. 3 shows strikingly the wide difference in the liquid state of metals (compare, for example, sodium vs. tin and molybdenum).

The *experimental slope* of the $D_{\text{liq.}}$ vs. temperature line, i.e., dD/dT , immediately establishes the rectilinear diameter with an accuracy corresponding to the error of the density measurement at the highest temperature.

The critical density for any metal can be roughly estimated since it equals one-fourth to one-fifth of the density at the normal boiling point—see Table 2. In conjunction with the estimated critical temperature (see Table 1) one can now deduce, approximately, the liquid density of any metal in the temperature range where its $D_{\text{vap.}}$ can be neglected. It follows directly from the rectilinear diameter law that the liquid density at the absolute temperature, T , or

$$D_T = D_{\text{c.p.}} \frac{(D_{\text{m.p.}}/D_{\text{c.p.}} - 2)}{(T_{\text{c.p.}} - T_{\text{m.p.}})} (T_{\text{c.p.}} - T) + 2 D_{\text{c.p.}}$$

where $T_{\text{c.p.}}$ and $T_{\text{m.p.}}$ are the critical and melting points, respectively in °K, and $D_{\text{c.p.}}$ and $D_{\text{m.p.}}$ the liquid densities at these points.