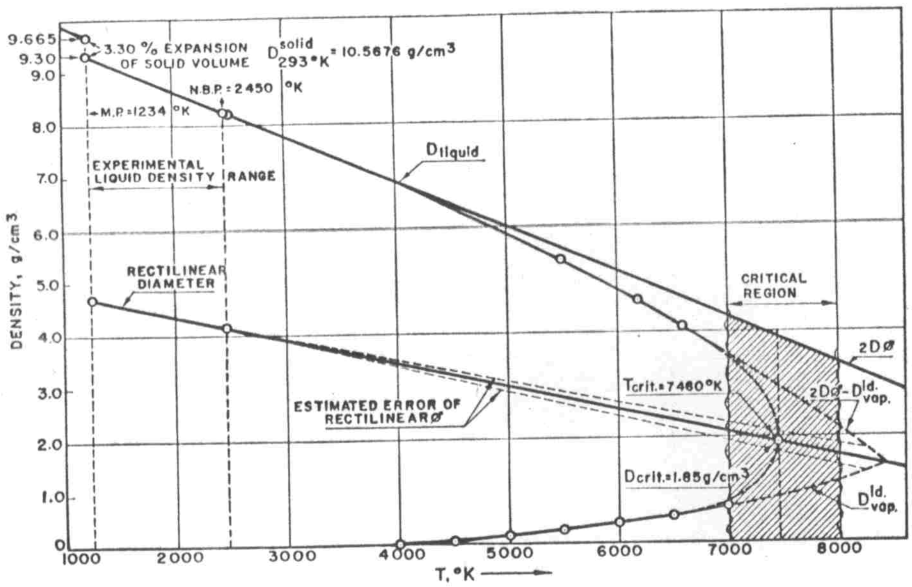

Fig. 3. Temperature-range diagram for liquid silver.

Another problem relates to the nature of chemical substances that can be heated to extremely high temperatures. As I have said, the highest temperature attainable through ordinary chemical reaction is in the range 5000° to 6000°K. This is the limit of existence of chemical compounds. At these temperatures all chemical bonds break and all molecules are dissociated into transient radicals or atoms. Thus, flame temperatures higher than these cannot be produced through chemical reaction.

The temperature above which no known solid can exist has been reached. The metal with the highest melting point is tungsten, which melts at 3643°K, and the oxide with the highest melting point is thorium dioxide, which melts at 3300°K. Tantalum carbide, which melts at 4200°K, has the highest melting point of any known substance. For purposes of containment, in practice at our laboratories, these maxima are attained and used only rarely, because of (i) chemical reaction between the high-melting substance and any other substance being investigated; (ii) the occurrence of eutectic mixtures, which lower the melting point; and (iii) thermal shock. And it is not likely that substances will be found with melting points many hundreds of degrees higher. Thus, we are compelled to find, if possible, thermally stable liquids if we want to contain higher temperatures in some useful way.

Fortunately for the future development of high-temperature research and technology there are substances which will exist as liquids up to very high temperatures—much higher than any at which we had thought liquids could exist. These substances are the refractory metals, which will eventually be useful in our rocket and space technology. Some of them remain as rather dense liquids even up to temperatures of 20,000°K. Since they are *elementary* monatomic liquids they cannot undergo any chemical change (except for ionization), even at extremely high temperatures.

A question which arises in this connection is: What is the liquid-temperature range of a metal—that is, the range from the melting point to the critical point? It had been assumed until very recently that the critical temperature T_c was 1.5 to 1.75 times the normal boiling point T_b, or that (*17*)

$$T_c = 1.4732 \times T_b^{1.0818}$$

where T is expressed in degrees Kelvin. As may be seen later, this is not the case; the critical temperatures of metals are 2.75 to 4 times the normal boiling points. Mercury is the only metal for which the critical constants have been determined. They are as follows: T_c = 1733°K (±50°); P_c = 1587 atm (± 50); D_c = 4.70 g/cm³.

Let us look at the data for mercury in greater detail. Figure 2 shows the temperature-range diagram for liquid mercury. Here the densities of liquid and of saturated vapor (in grams per cubic centimeter) are plotted against absolute temperature; they are based primarily on Julie Bender's determinations made during World War I. All values for the half sum of the densities of liquid and of saturated vapor—that is ½ ($D_{liq} + D_{sat\ vap}$)—fall, within the limits of experimental error, on a straight line, the so-called rectilinear diameter. Thus, mercury follows the law of Cailletet and Mathias, as do all other thermally stable liquids. The value for critical density D_c lies on the rectilinear diameter at the critical point (that is, 1733°K).

Table 3. Critical temperatures, heats of vaporization, and entropies at normal boiling points for various metals.

Metal	Boiling point at 1 atm (deg K)	ΔH_{vap} (cal/g-atom)	ΔS_{vap} (cal/g-atom deg K)	T_{red} from Hg curve, Fig. 3	T_c (deg K)
Cs	958	15,750	16.95	0.445	2,150
Rb	974	16,540	16.99	0.445	2,190
K	1,039	18,530	17.88	0.425	2,440
Na	1,163	21,280	18.40	0.415	2,800
Bi	1,832	36,200	19.75	0.397	4,620
Pb	2,024	42,880	21.15	0.375	5,400
Ga	2,510	61,200	24.40	0.330	7,620
Sn	2,960	69,400	23.42	0.340	8,720
U	4,200	101,000	24.05	0.333	12,500
Mo	5,100	142,000	27.85	0.295	17,000
Re	5,900	169,000	28.63	0.287	20,500
Ta	5,700	180,000	31.60	0.260	22,000
W*	5,800	191,000	32.90	0.250	23,000

Table 4. Critical constants of the alkali metals.

Metal	T_c (deg K)	V_c (cm³/g-atom)	D_c (g/cm³)	P_c (atm)	Compressibility factor Z_c [= $(P_c \times V_c)/(R \times T_c)$]
Na	2,800	130	0.18	~500	0.28
K	2,450	230	0.17	230	0.29
Rb	2,200	265	0.32	210	0.31
Cs	2,150	320	0.42	160	0.29