

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.

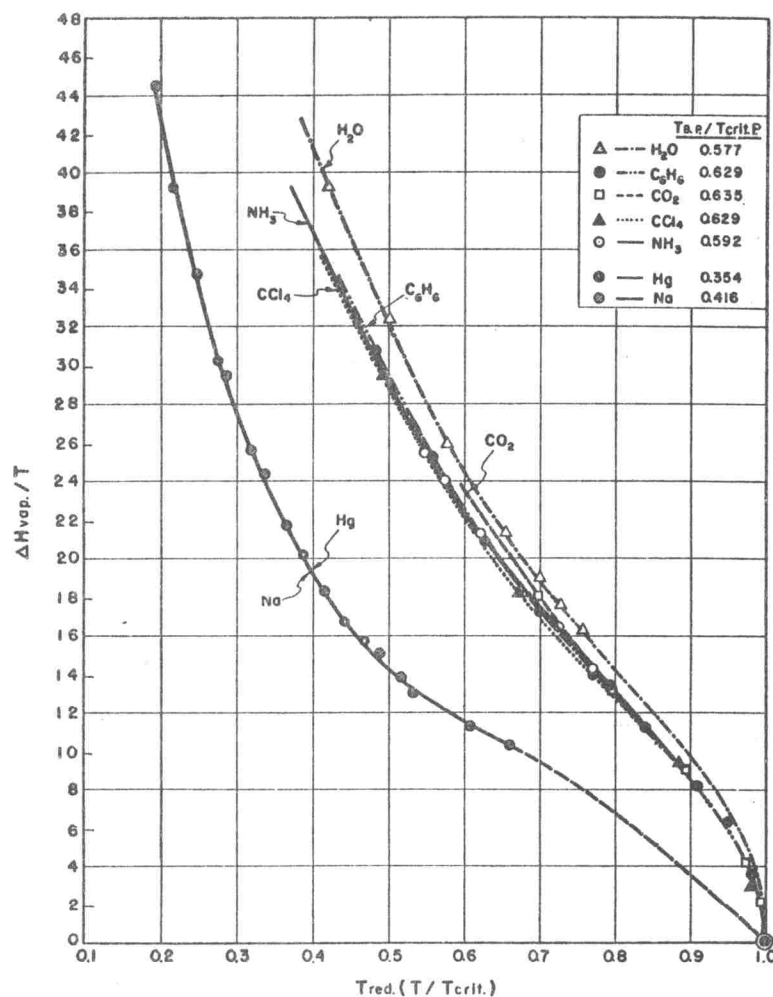


FIG. 2.

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_{red} . from Hg-curve Fig. 2	T_{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).